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Incorporating PET-MIL-101(Fe) within cellulose acetate membrane for thin film microextraction of neonicotinoid insecticides in water

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Herein, cellulose acetate membrane modified with polyethylene terephthalate derived MIL-101(Fe) (PET-MIL-101(Fe)) was used as an extraction phase for the direct immersion-thin film microextraction method (DI-TFME) of neonicotinoid insecticides in water samples. The quantitative analysis of clothianidin, imidacloprid, thiacloprid and thiamethoxam was carried out using high-pressure liquid chromatography (HPLC-DAD). The morphological and structural characteristics of the materials were studied using transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), and energy dispersive X-ray spectrometry (EDX). Under optimum conditions, acceptable analytical performance for the developed DI-TFME/HPLC-DAD method was attained. The linearity of the method ranged from 0.04 to 500 µg/L with R^2 ranging from 0.9981 to 0.9989. The detection limits, quantification limits and relative standard deviation (%RSD) of the DI-TFME/HPLC-DAD method were in the range of 0.013–0.016 µg/L, 0.043–0.053 µg/L and 1.2–3.9%, respectively. The method was applied in the analysis of real water samples, and the spiking recoveries of the target analytes were 95.6–102%, 91.2–98.6% and 79.2–98.7% for river water, effluent and influent samples, respectively, with %RSDs ranging from 1.8 to 4.8%. These findings demonstrated that the developed DI-TFME/HPLC-DAD method had high precision, accuracy, sensitivity and enrichment factor (73–88). The DI-TFME/HPLC-DAD method proved sustainable for the simultaneous quantification of trace neonicotinoid insecticides in real samples.

Keywords Waste utilization, Recycled PET, PET-MIL-101(Fe), Polymer membranes, Neonicotinoid insecticides, Direct immersion-thin film microextraction method

Neonicotinoid insecticides (NIs) are a new class of insecticides that are commonly used to protect crops against insect attack[1,2]. Due to the demand for fighting poverty worldwide and increasing food production, these insecticides are extensively used in various agricultural activities, NIs have been detected across multiple water bodies[3–6]. The high-water solubility, environmental persistence, and frequent detection in soil, groundwater, surface water, and even food products have sparked concerns about their potential ecological and human health hazards[7]. Numerous investigations have detected trace levels of neonicotinoids in rivers, lakes, and drinking water sources near agricultural areas[8], underscoring the need for precise and sensitive analytical techniques for environmental monitoring[9]. Even though NIs have been detected in trace levels in the water matrices, their continuous release to the environment could lead to short and long-term public health[5,6]. Therefore, it is imperative to develop rigorous environmental monitoring campaigns to investigate the occurrence and distribution of these pollutants in the environment. Previous studies have reported that long-term exposure to NIs is linked to harmful human health effects such as declining cognitive development and pulmonary impairment for children and adults, respectively[10,11].

Taking into account NIs' physicochemical features such as thermolability, low volatility, and high polarity, liquid chromatography – tandem mass spectrometry (LC-MS/MS)[12], high performance liquid chromatography-

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diode array detector (HPLC-DAD)[13] and capillary electrophoresis–tandem mass spectrometry[14] are the most widely used techniques for the analysis of NIs in various water systems[15]. Among these, HPLC-DAD has gained widespread use in the analysis of NIs over the years, owing to advantages such as sensitivity, detection, and quantification of trace contaminants, and reliable and robust methods[16,17]. Despite major advancements in analytical instruments, the sample preparation stage is critical before the final analysis. This is due to the complexity of the sample matrices and the presence of analytes at trace levels[18]. Because of their low concentrations (ng/L to μg/L), NIs in water are difficult to assess[5]. In environmental water samples, a range of inorganic and organic materials, such as dissolved ions, suspended particles, and humic compounds, can have matrix effects that impair method accuracy, make quantification difficult, and decrease detection accuracy[19].These factors require the development of more robust, sensitive, and selective analytical techniques to accurately identify and quantify NIs in aquatic matrices[20]. Neonicotinoid insecticides in water samples have been identified using a variety of extraction techniques, including solid-phase extraction (SPE), liquid-liquid extraction (LLE), dispersive liquid-liquid microextraction (DLLME), and solid-phase microextraction (SPME)[21–24]. SPE is widely used due to its superior selectivity, preconcentration capabilities, and compatibility with chromatographic systems; however, it is often time-consuming and solvent intensive[25]. LLE is a traditional method that provides good recovery, even though it frequently uses enormous amounts of hazardous organic solvents and has poor repeatability[22]. Despite being a quick, compact, and solvent-efficient substitute, DLLME is susceptible to matrix effects and might not be as selective as it could be[26]. SPME enables solvent-free extraction and easy automation, but the excessive cost and fibre fragility may cause drawbacks[27]. Thin film microextraction (TFME) is a potential approach for the extraction and preconcentration of NIs compared to other conventional methods, owing to advantages such as surface-to-volume ratio, better sensitivity, less consumption of organic solvents, and significantly shorter extraction times[28,29]. TFME is found to be a suitable method in membrane technology based on the utilisation of a thin film of solid phase in a large supporting area while keeping the sorbent thickness thin[30]. In TFME, the extraction of analytes from the sample can be accomplished simply by directly immersing the membrane in the solution[31]. Metal-organic frameworks (MOFs) are a class of hybrid materials with crystalline structures, high porosity, and various functions, and have been hailed as promising nanomaterials to improve the hydrophilic and antifouling qualities of polymeric membranes[32,33]. MIL-101 is a kind of MOF with great adsorption capabilities, a high specific surface area, and exceptional thermal stability[34]. MIL-101(Fe) is a mesoporous adsorption material made of octahedral chains of Fe(III) as secondary building units (SBUs) and 1,4-benzenedicarboxylic acid (BDC) as a linker. It has a high specific surface area and the necessary mesoporous cages[35]. The main component for the synthesis of MIL-101(Fe) is terephthalic acid; thus, the development of feasible methods whereby terephthalic acid can be extracted in huge amounts from plastic waste is ideal[36,37]. Economically speaking, recycled PET will be far less expensive than commercial terephthalic acid due to the established PET production and recycling infrastructure[38,39]. Consequently, employing terephthalic acid as the organic linker for MIL-101(Fe), derived from the depolymerization process of discarded PET bottles, can effectively address the high costs that hinder the commercial viability of MOFs[37]. This strategy would help ensure that waste PET landfilling is properly eliminated and foster the advancement of innovative green analytical methodologies[40,41].

In this study, we present a unique method for the use of PET-derived MIL-101(Fe) as a functional modifier for cellulose acetate (CA) membranes in direct immersion thin-film microextraction (DI-TFME). This is the first study reporting on the use of a metal-organic framework (MOF) derived from recycled polyethylene terephthalate (PET) waste to improve CA membrane extraction performance. For the detection of neonicotinoid insecticides at the trace level in water, the dual innovation addresses environmental and analytical concerns while enhancing selectivity, adsorption capacity, and sustainability by turning plastic waste into a high-performance MOF and incorporating it into a sustainable membrane. Considering the advantages of TFME as a unique sample preparation tool, this study aimed at establishing a CA-PET-MIL-101(Fe) membrane-based DI-TFME method combined with HPLC-DAD for simultaneous extraction and determination of four neonicotinoid insecticides in water and wastewater samples. The CA-0.6%PET-MIL-101(Fe) membrane exhibited high porous structures, high stability, and high extraction efficiency, thus enabling effective extraction and separation of target analytes from the real water samples. The porous structures of the membrane facilitated rapid mass transfer and acted as a platform for molecular filtration, allowing the neonicotinoid insecticides to enter through the pores and interact with functional groups of the PET-MIL-101(Fe). The factors affecting the DI-TFME procedure were investigated using response surface methodology (RSM) based central composite design (CCD). Under optimum conditions, the resultant CA-0.6%PET-MIL-101(Fe) displayed excellent preconcentration capabilities for neonicotinoid insecticides in real water samples.

Experimental

Reagents and materials

All experiments were conducted using analytical reagent grade chemicals unless otherwise stated. Cellulose acetate, clothianidin (≥ 99%), imidacloprid (≥ 99%), thiacloprid (≥ 99%), thiamethoxam (≥ 99%), methanol (HPLC grade ≥ 99%), formic acid, dimethylformamide, iron (III) oxide (≥ 99%), ethanol, acetonitrile (HPLC grade ≥ 99.9%) and polyvinylpyrrolidone were obtained from Merck (Johannesburg, South Africa).

Instrumentation

The following pieces of equipment were used in this study: An Agilent HPLC 1200 Infinity (Agilent Technologies Inc., Tokyo, Japan), portable pH/EC/TDS meter (HI 9811-5, HANNA Instruments, Woonsocket, RI, USA), Perking-Elmer Fourier transform infrared (FTIR) spectrum 100 spectrometer (Perkin-Elmer, Shelton, CT, USA), scanning electron microscope/dispersive spectroscopy (SEM/EDS) (SEM) (TESCAN VEGA 3 XMU, LMH instrument, Brno, Czech Republic), Scientech Ultrasonic cleaner (Labotec, Midrand, South Africa), and

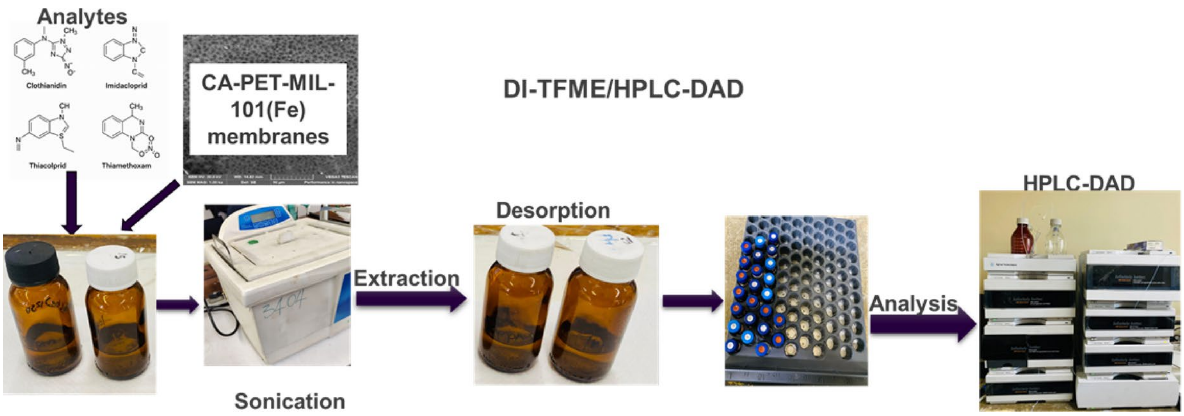

Fig. 1. Schematic diagram of the proposed method.

Parameters	Lower level (−)	Central point (0)	Higher level (+)
pH	2	5.5	9
Eluent volume (µL)	200	700	1200
Elution time (min)	5	12.5	20
Sonication time (min)	5	22.5	40

Table 1. List of parameters, their levels, and experimental domains.

transmission electron microscopic (TEM, JEM-2100, JEOL, Tokyo, Japan). The details of each equipment are presented in the Supplementary Information.

Preparation of PET derived PET-MIL-101 (Fe) and CA-PET-MIL-101(Fe) membrane

Firstly, the terephthalic acid (BDC) was prepared from waste PET plastic bottles following the previous study[42]. Briefly, 10 g of PET flakes, 10 mL of ethylene glycol (EG), and 100 mL of water were combined in a beaker. After that, the mixture was placed in a 250 mL autoclave lined with Teflon, heated to 210 °C, and left there for eight hours. Following the reaction, the product underwent centrifugation, two ethanol washes, and a 24-hour drying process at 100 °C.

PET-MIL-101(Fe) was synthesised according to Duan et al.[43]. The mixture of 0.675 g of $FeCl_3·6H_2O$ and 0.206 g of H_2BDC was added to 25 mL of DMF and agitated for 30 min. The uniform mixture was placed into a 100 mL Teflon autoclave reactor and heated to 110 °C for a day. Centrifugation was used to gather the product. Hot ethanol (60 °C, 3 h) and hot water (60 °C, 1 h) were used to wash the product to eliminate the DMF and excess H_2BDC. After that, the material was dried at 150 °C for 12 h in a vacuum oven. The fabrication of CA-PET-MIL-101(Fe) membranes was carried out according to the method reported elsewhere[28]. Table S1 present different CA-PET-MIL-101(Fe) membrane compositions.

Direct immersion-thin film microextraction (DI-TFME) procedure

The DI-TFME procedure was performed using CA-PET-MIL-101(Fe) membranes, and the detailed procedure was carried out according to Jakavula et al.[28]. The method is summarised in the form of a schematic diagram in Fig. 1. The experimental conditions influencing the performance of the TP-SPME method were optimised using a central composite design. The CCD was selected as it considers parameter interaction, resulting in a precise model for surface curvature. Table 1 shows the levels and associated experimental domains of the investigated variables. Twenty-seven experimental runs for four variables were generated using Statistica Version 14 software, and the investigations were conducted randomly in triplicate.

Method validation

The validity of the DI-TFME/HPLC-DAD method was confirmed in terms of linearity, LOD, LOQ, accuracy, and precision.

Linearity

The linearity was assessed by introducing NIs into ultrapure water at five different concentration levels, ranging from 0.00 to 500 µg/L. Before HPLC-DAD analysis, the optimised method was utilized for extracting and preconcentrating NIs. The analysis procedure was carried out in triplicate.

Limits of detection and LOQs

The LOD and LOQ were determined by analysing ultrapure water injected with the calibration curve's lowest concentration. The values with extraction efficiencies ranging between 80% and 120% with %RSD less than 10%

after the DI-TFME process were repeated eight times, were used. The LOD and LOQ values were estimated by 3 and 10 times the standard deviation of the signal (peak area) of the lowest concentration (0.05 μg/L), divided by the slope of the calibration curve.

Precision and accuracy

The precision (intraday and interday) and accuracy of the DI-TFME/HPLC-DAD procedure were evaluated using real water samples (tap, surface water, and wastewater effluent) spiked at three different concentration levels (0.1, 0.5, and 1.0 μg/L). The assessment was carried out ten times on the same day, while for interday, the evaluation was performed in triplicate for five different successive days.

Application to real samples

Water samples from numerous sources were obtained, including wastewater effluent and influent, as well as river water. Samples were filtered through 0.22 μm PVDF membranes and adjusted to 7.5 pH with 0.01 mol/L acetic acid and NaOH solutions. The DI-TFME method was used to enrich selected NIs from real water samples, and the extraction process was performed in triplicate.

Results and discussion

Characterization of materials

Figure 2a shows the elemental composition of PET-MIL-101(Fe); it can be noted that all the expected elements, such as Fe (16.3%), O (30.3%), and C (53.4%), are present, and confirm the successful synthesis of PET-MIL-101(Fe). Figure 2b,c demonstrate the TEM images of PET-MIL-101(Fe); in both images, the octahedral shape is noted, which further confirms the successful synthesis of PET-MIL-101(Fe) as reported in the literature[35,44].

Figure 3a shows the FTIR spectra of PET-MIL-101(Fe); the characteristic FTIR spectra of PET-MIL-101(Fe) reflected the benzene-carboxylates, which is attributed to the organic ligand (H_2BDC) used. The characteristic peaks of PET-MIL-101-(Fe) were located at 593, 1420, and 1682 cm^{-1}, which indicated the effective synthesis of PET-MIL-101(Fe). The peak at 551 cm^{-1} was assigned to the Fe–O bond. The peak at 3421 cm^{-1} came from -OH in water molecules. The band at 1682 cm^{-1} was attributed to C=O bonding in the carboxylates, and the band at 1420 cm^{-1} was from the aromatic carbon C-C vibrational mode, which was in line with the reported literature[45,46]. Figure 3b shows the X-ray powder diffraction (XRD) patterns of PET-MIL-101(Fe). The diffraction peaks at 2θ 10.13, 17.91, 23.10, 25.32, and 28.17° demonstrate the high quality of crystallinity of PET-MIL-101(Fe). The XRD peaks obtained correspond to previously reported diffraction patterns, confirming that PET-MIL-101(Fe) crystals were well-developed[47,48].

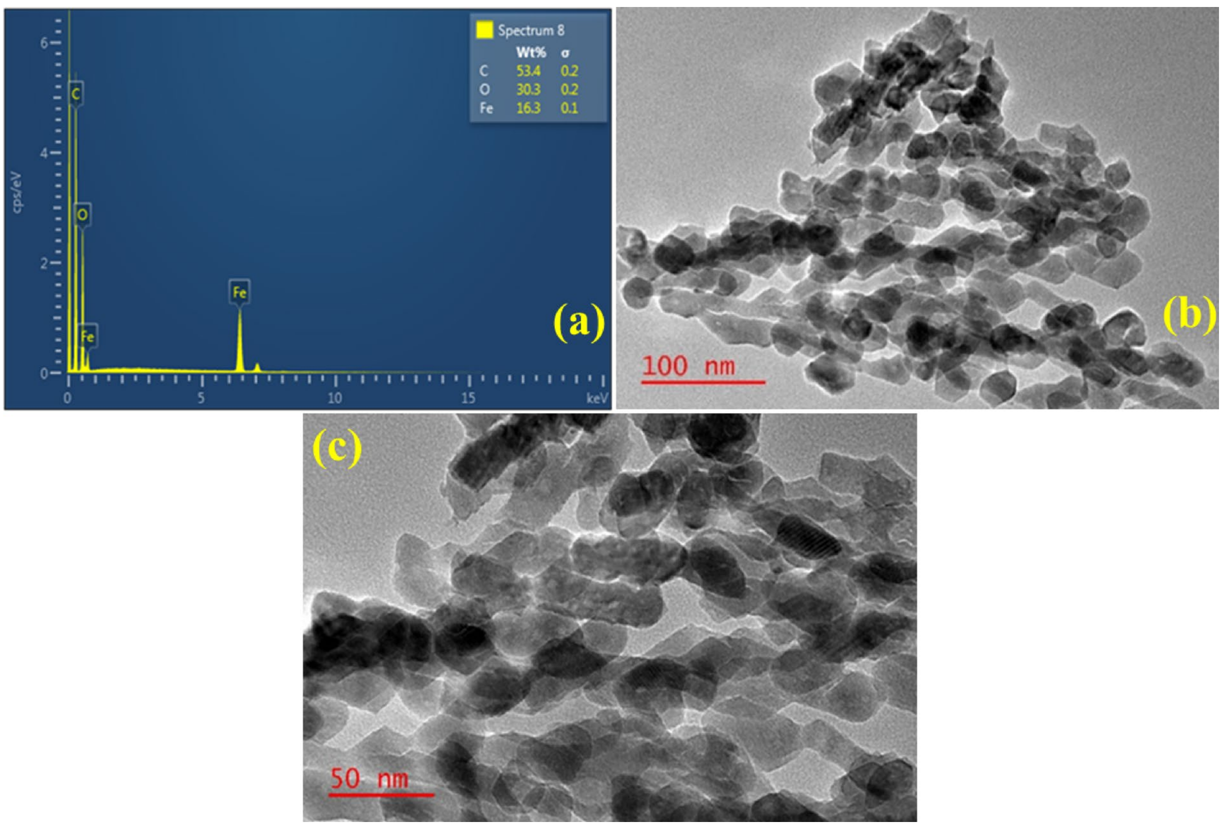

Fig. 2. (**a**) EDS of PET-MIL-101(Fe), (**b**) TEM image of PET-MIL-101(Fe) (100 nm), and (**c**) TEM image of PET-MIL-101(Fe) (50 nm).

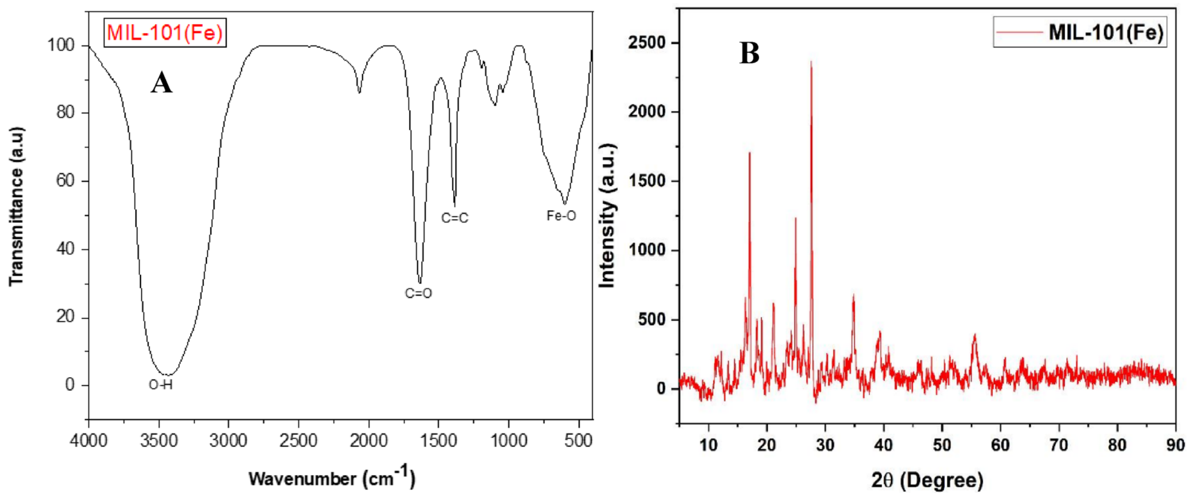

Fig. 3. (**a**) FTIR spectrum and (**b**) X-ray powder diffraction patterns of PET-MIL-101(Fe).

The effect of adding PET-MIL-101(Fe) on CA membranes was studied using SEM. Figure 4 illustrates the SEM images of the surface morphology of the prepared membranes of different compositions. The images in Fig. 4b–d demonstrate how evenly distributed the PET-MIL-101(Fe) was on the membrane surface. The addition of PET-MIL-101 enhanced the porosity of the composite membranes, which improved the efficiency of water remediation. When PET-MIL-101(Fe) was added to the polymeric solution, the penetration of the nonsolvent (DI) in the casting solution was increased, causing additional pores on the surface of the membranes.

The cross-section images in Fig. 5a–d illustrate a dense layer on the membrane's sublayer. Owing to the faster interchange between the water and DMF during the preparation of membranes by phase invasion, the composite membranes exhibit pore channels that are wider than those of pure CA membranes. The inclusion of additional pore channels allows the analytes to be trapped in the pores of the membranes, thus boosting their extraction efficiency. The membrane with 0.6wt.% of PET-MIL-101(Fe) (Fig. 5, M3) showed higher porosity. This was caused by interactions between ingredients present in the prepared casting solution and the fast exchange between water and DMF since PET-MIL-101(Fe) is hydrophilic in nature. The increase in hydrophilicity will thereby result in greater membrane fouling resistance.

Screening of extracting materials

A preliminary study was performed using batch adsorption experiments to select suitable materials for the extraction of NIs from an aqueous solution. The performance of the CA membrane, PET-MIL-101(Fe) and CA-PET-MIL-101(Fe) membrane was investigated (Fig. 6a). As shown in Fig. 6, the CA-PET-MIL-101(Fe) membrane performed better than the pristine CA membrane and the PET-MIL-101(Fe) membrane. The reason for the enhanced performance of the CA-PET-MIL-101(Fe) membrane was attributed to the integration of the PET-MIL-101(Fe) into the CA-membrane. Therefore, due to the notable differences in the performance of the three materials, the CA-PET-MIL-101(Fe) membrane was chosen for further investigations.

Figure 6b demonstrates the comparison of the membranes with different compositions (0, 0.2, 0.4, and 0.6 wt%) of PET-MIL-101(Fe). As seen, M3 (CA-0.6 wt.%PET-MIL-101(Fe) membrane) had superior performance in terms of extraction recoveries compared to other composite membranes. The increase in the PET-MIL-101(Fe) ratio resulted in better extraction efficiency of imidacloprid (ICD), clothianidin (CTN), thiamethoxam (TM) and thiacloprid (TCD); therefore, CA-0.6 wt.%PET-MIL-101(Fe) membrane was then used throughout this study. Since membranes with high PET-MIL-101(Fe) loadings have larger pores, NIs were easily trapped in the pores of the membrane, resulting in higher recoveries for the target analytes.

Optimisation strategy

The CCD was used to assess the importance of independent variables and their interactive effects using a reduced number of experiments. Table S2 presents the analytical results (recoveries as an analytical response) of the analysis randomly performed with the 27 experimental runs of CCD. The analysis of variance (ANOVA), represented as the Pareto charts (Fig. 7), was used to illustrate the input of each factor (pH, ST, EV and ELT) and reveal the influence of their interactive effects on the DI-TFME efficiency. As seen in Fig. 7, the ANOVA results showed a statistically significant influence on eluent volume, while other parameters were not significant at a 95% confidence level for all the analytes. Furthermore, the positive sign corresponding to all investigated independent variables suggested that increasing these parameters towards high levels affected the analytical response positively (Fig. 8).

The 3D response surface plots (Fig. 9) show the interaction of the factors and their effect on the dependent variable (%R). The analysis of the results shows that the %R increased as the values of independent variables increased. Figure 9a depicts the interaction between sample pH and ST, and it can be observed that increasing both parameters resulted in increased analyte recoveries. Figure 9b shows the relationship between sample pH

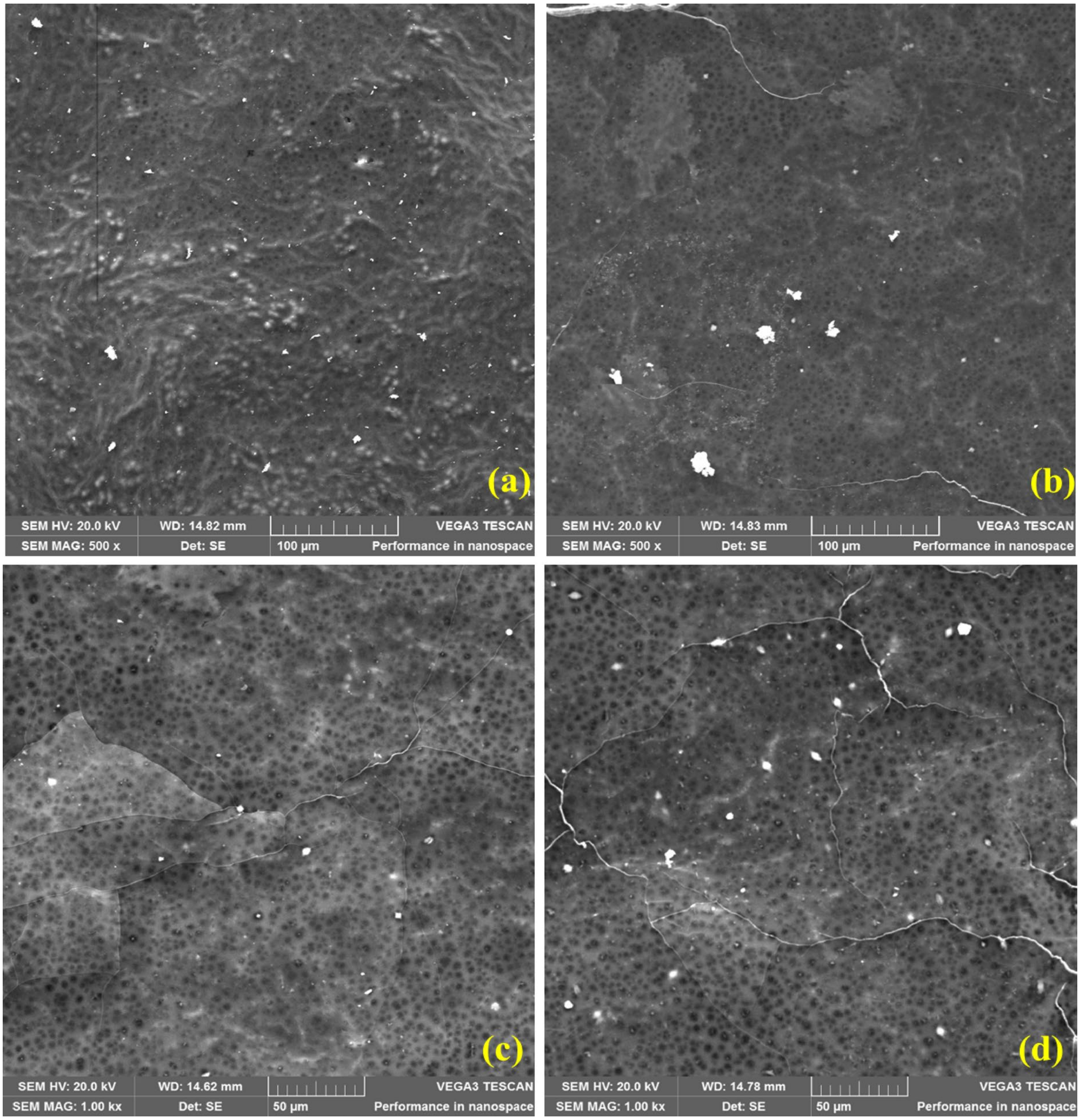

Fig. 4. SEM images for surface morphology of (**a**) CA and CA-PET-MIL-101(Fe) membranes (**b**–**d**).

and EV, indicating that the highest analyte recoveries occur at EC levels above 800 µL. Figure 9c depicts the interaction between ELT and pH, and at ELTs greater than 12 min, maximum recoveries are possible. Figure 9d shows the interaction between ST and EV. ST does not play a significant impact, indicating that maximum recoveries can be obtained at any ST. However, maximum recoveries can be achieved at volumes above 800 µL. The interaction between ELT and ST is shown in Fig. 9e, and for ELT times greater than 12 min, maximum recoveries may be obtained. EV and ST are critical parameters affecting the efficiency of analyte desorption from the sorbent surface. In this study, different elution volumes between 200 and 1200 µL were investigated to determine the minimum solvent volume required for quantitative recovery of NIs. As the EV increased, the extraction efficiency improved due to more complete desorption of the analytes. However, volumes above 1000 µL led to dilution effects, reducing the analyte concentration in the eluate and thereby decreasing sensitivity. Therefore, 1000 µL was selected as the optimal volume, balancing efficient desorption and high preconcentration. However, ST does not have a significant impact, implying that maximum recoveries can be reached at any ST. Figure 9f shows the interaction between ELT and EV. For EV above 800 µL and any ELT, maximum recoveries were obtained. With the presence of PET-MIL-101(Fe) in the CA membrane, the surface charge of MIL-101(Fe) is affected by the pH of the solution. At pH values lower than the pKa values, the NIs become neutral and at pH values greater than the pKa values (Table S3), NIs are negatively charged[2,35].

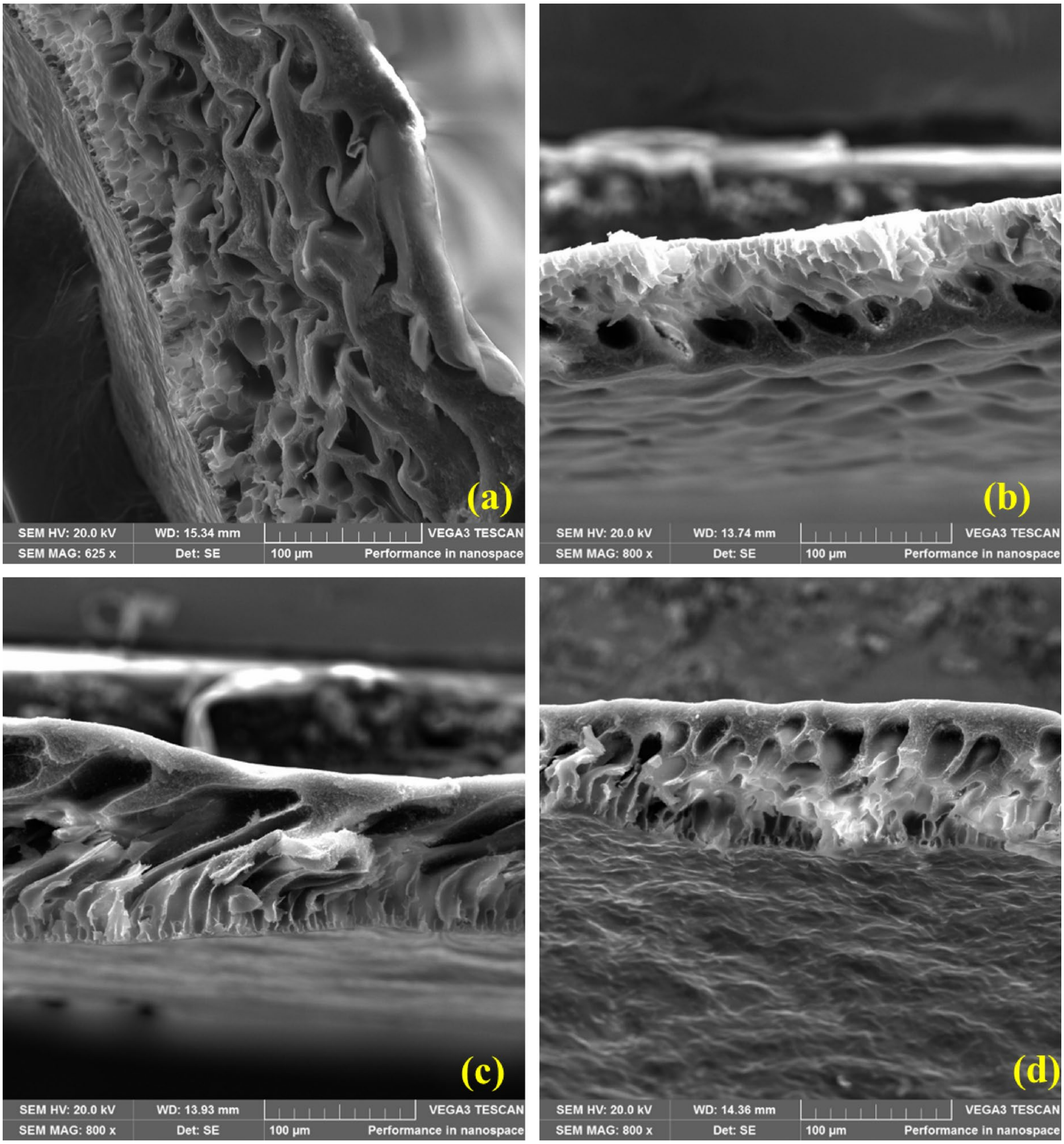

Fig. 5. Cross-section SEM images of (**a**) pristine CA-membrane and CA-PET-MIL-101(Fe) membranes (**b–d**).

PET-MIL-101(Fe) is composed of iron (III) clusters coordinated with terephthalic acid ligands (derived from recycled PET)[49]. The structure has a large surface area, accessible mesoporous cages with aromatic rings, and coordinated hydroxyl/water ligands[50]. Aromatic rings (from terephthalate ligands) allow π-π stacking interactions with the aromatic moieties of neonicotinoids[51]. This improves analyte retention and selective adsorption. Fe (III)-O clusters provide Lewis acidic sites that can interact with electron-donating groups on neonicotinoids (such as nitrogen atoms in nitroguanidine or cyano groups)[52]. Hydrogen bonding occurs with polar functional groups like $-NO_2$, -CN, or heteroatoms (N, O) in neonicotinoids[50]. MIL-101(Fe) has a mesoporous structure (with pentagonal and hexagonal windows) that enables size selective adsorption, boosting interactions through van der Waals forces within constrained pores[51]. The porous PET-MIL-101(Fe) structure promotes neonicotinoid adsorption through π-π stacking, Lewis acid-base interactions, hydrogen bonding, and physical confinement. These interactions (Fig. 7) help to explain the excellent extraction efficiency and selectivity found in this study.

The optimal conditions for the simultaneous DI-TFME of the NIs were estimated using the desirability function (DF), as presented in Fig. 10. The desirability score of 1.0 was used to accomplish the high extraction efficiency of the DI-TFME method. Based on Fig. 10, the optimal conditions attained for pH, EV, ST and ELT were 7.5, 1000 μL, 25 min and 12.5 min, respectively. The optimum conditions obtained using the RSM model

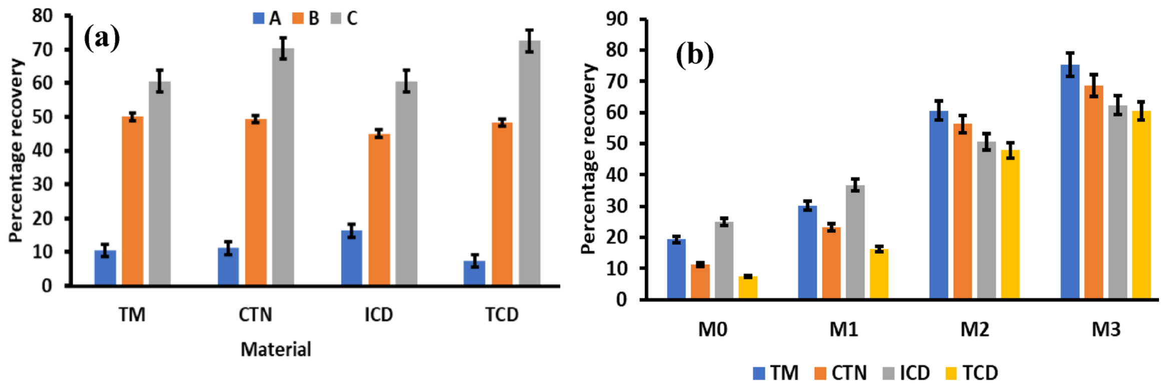

Fig. 6. Selection of suitable (**a**) extracting material (A: pristine CA membrane; B: PET-MIL-101(Fe) and C: CA-PET-MIL-101(Fe) membrane) and (**b**) membrane composition, M0: pristine CA membrane, M1: CA-0.2 wt.%PET-MIL-101(Fe), M2: CA-0.4 wt.%PET-MIL-101(Fe) and M3: CA-0.6 wt.%PET-MIL-101(Fe). Experimental conditions were sample volume (5 mL), sample pH (7), sonication time (30 min), eluent volume (1000 µL) and elution time (10 min).

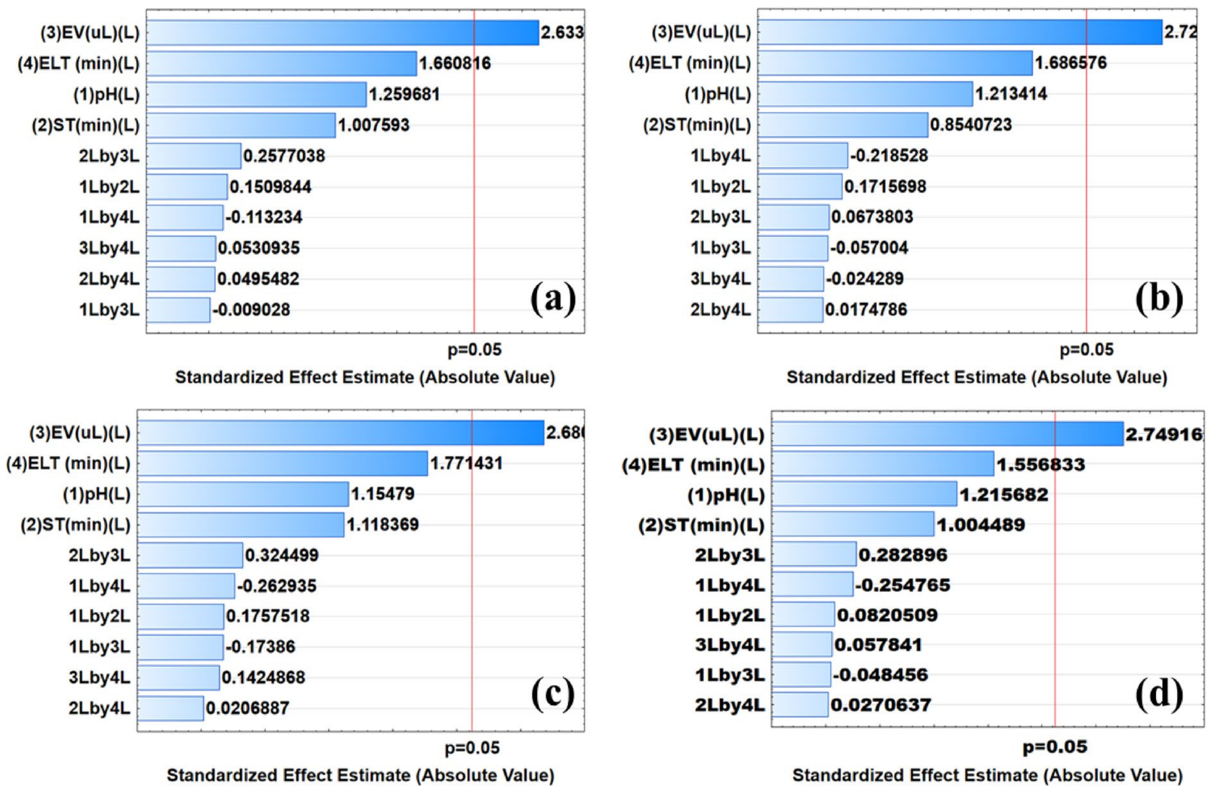

Fig. 7. Pareto chart of the standardised effects for the DI-TFME of (**a**) Imidacloprid, (**b**) clothianidin, (**c**) thiamethoxam and (**d**) thiacloprid. ET = eluent volume; ELT = elution time; ST = sonication time; 1Lby2L, 1Lby3L and 1Lby4L = interactions between pH and ST, EV and ELT; 2Lby3L and 2Lby4L = interactions between ST and ELT and EV; 3Lby4L = Interaction between EV and ELT.

were assessed through an experiment by performing five replicate extraction/desorption experiments. Table 2 shows the expected and experimental percentage R values. According to the Student T-test, the experimental values agreed with the predicted responses at a 95% confidence level because the $t_{calculated}$ (0.065) was less than $t_{critical}$ (3.14, degree of freedom = 3). These results suggested that the RSM model was accurate and valid. The validated optimal conditions were used for subsequent experiments.

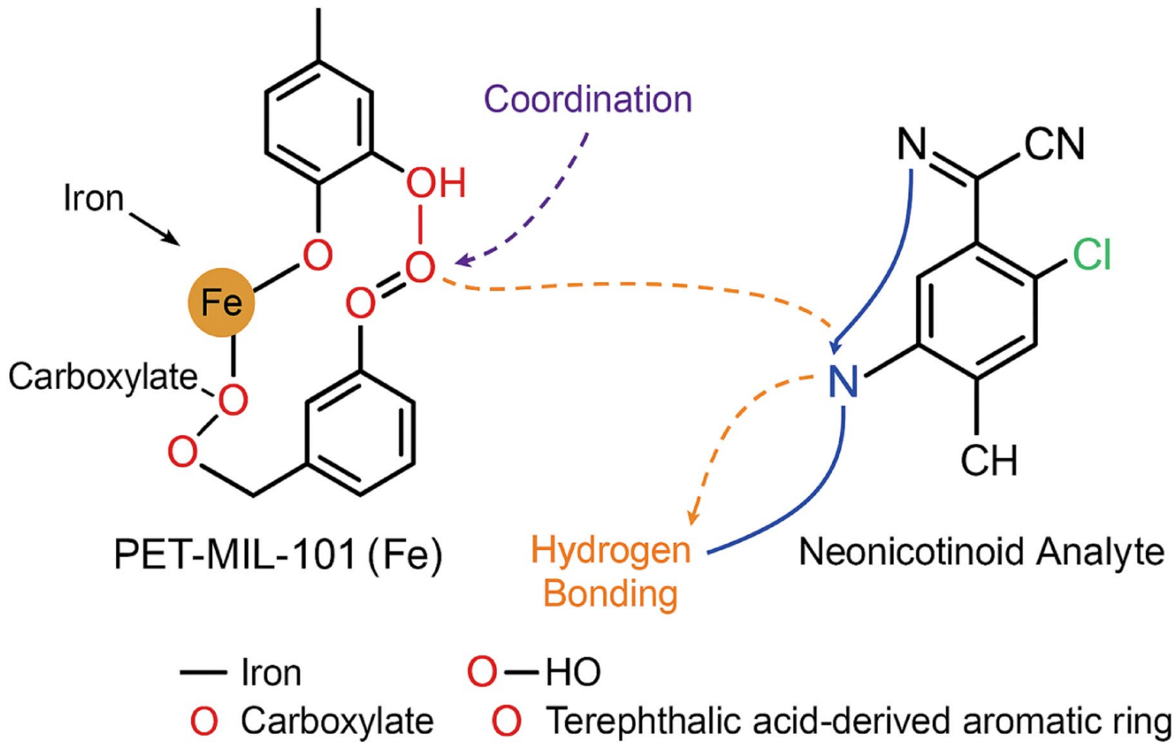

Fig. 8. Schematic diagram illustrating various interactions between the analytes and the PET-MIL-101(Fe) framework.

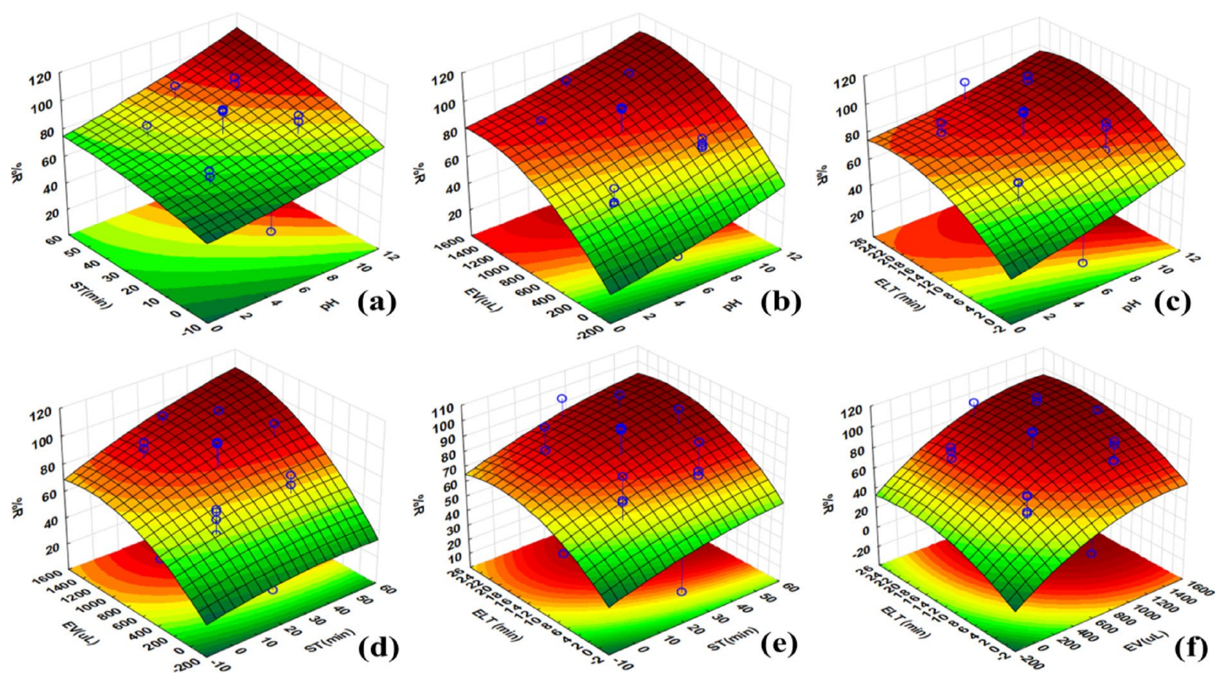

Fig. 9. Response surface methodology for the extraction and preconcentration of Imidacloprid, clothianidin, thiamethoxam and thiacloprid. The individual figures represent the interactions between (**A**) sonication time (ST) and sample pH, (**B**) eluent volume (EV) and sample pH, (**C**) elution time (ET) and, sample pH (**D**) EV and ST, (**E**) ET and ST, (**F**) ET and EV.

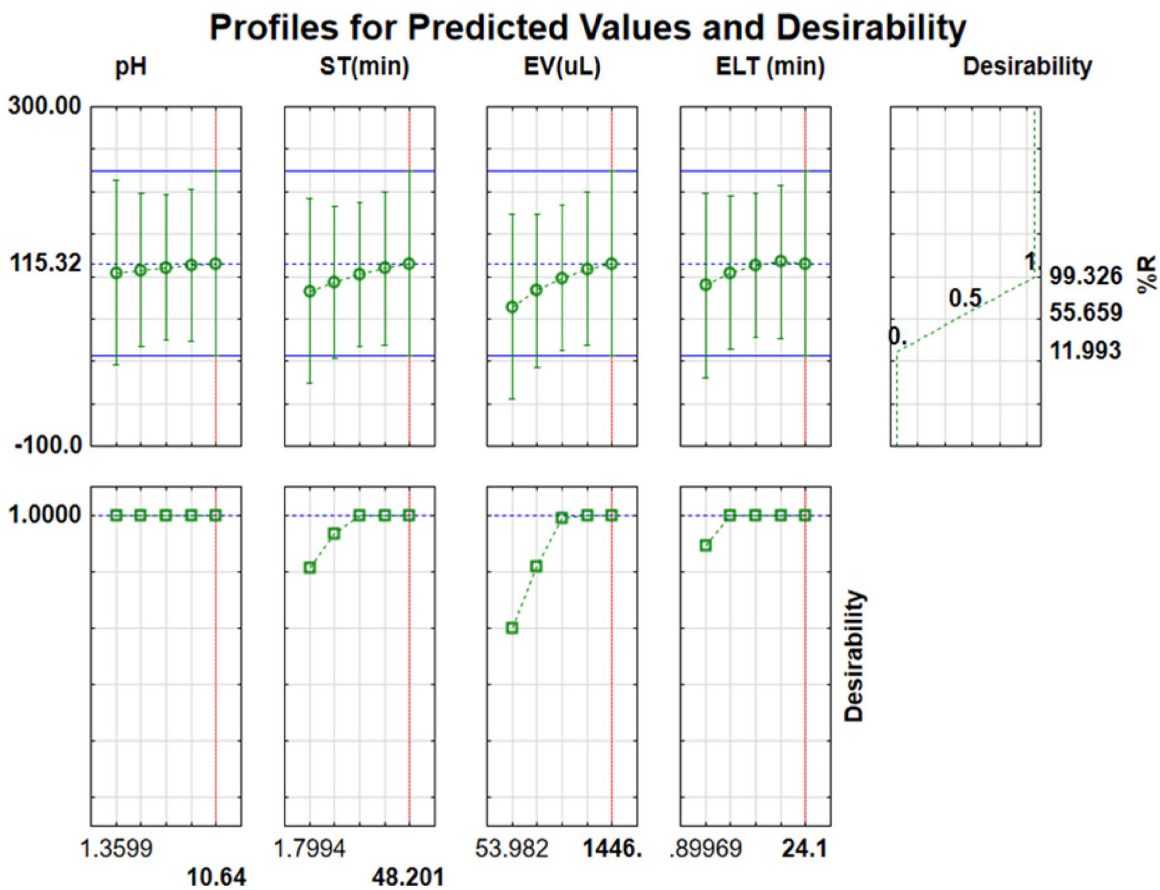

Fig. 10. Profile of predicted values and desirability function for the DI-TFME of imidacloprid, clothianidin, thiamethoxam and thiacloprid; ST: sonication time; ET: elution time; EV: eluent volume.

Analytes	Predicted %*R*	Experimental %*R*
CTN	115	99.5 ± 2.9
ICD	105	99.7 ± 2.8
TCD	101	98.9 ± 3.2
TM	110	98.6 ± 2.1

Table 2. Confirmatory studies: comparison of experimental and predicted %recoveries at optimum conditions.

Stability, reusability and leaching studies

The stability, reusability, and leaching studies are important for real-world applications of the membranes in the sample preparation field and their potential to be prepared on a larger scale. Furthermore, the usability studies are conducted to investigate the possibility of multiple use of CA-0.6%PET-MIL-101(Fe) membrane to confirm sufficient stability. Therefore, this study evaluated the capability of the developed CA-0.6%PET-MIL-101(Fe) membrane coating for consecutive extraction-elution cycles. In addition, the stability of the membrane coating was investigated in terms of leaching studies by analysing the concentration of Fe ions in solution after each extraction-elution cycle. The amount of Fe ions in aqueous samples was below the detection limits of the inductively coupled plasma optical emission spectroscopy in the first seven extraction-elution cycles. However, trace concentrations of Fe (55.8–73.9 µg/L) were detected at concentrations after the eighth to tenth extraction-elution cycles. These observations suggest that the CA polymeric membrane reduces the leaching of Fe from PET-MIL-101(Fe) into the solution, thus indicating the CA-0.6%PET-MIL-101(Fe) membrane is stable and could be used in water treatment because it has no potential toxicity and secondary pollution that might be associated with Fe leaching. The CA-0.6%PET-MIL-101(Fe) membrane was stable until the seventh extraction-elution cycle (Fig. 11). A slight decrease below the recovery of 95% was observed after the seventh cycle, suggesting that the CA-0.6%PET-MIL-101(Fe) membrane could be reused for up to seven extraction-elution cycles without significant changes in extraction efficiency.

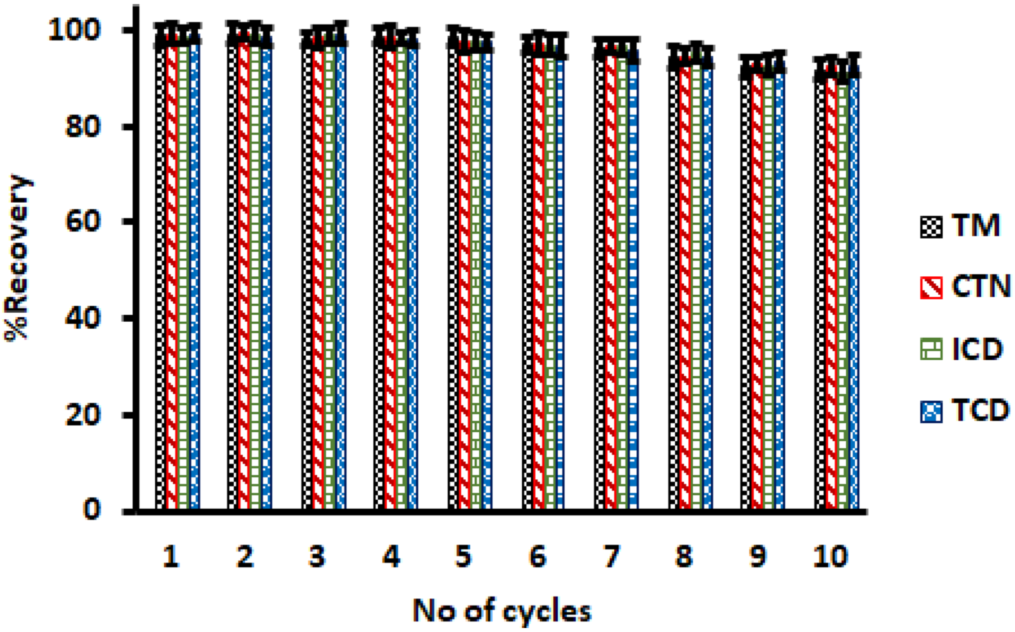

Fig. 11. Reusability and stability of the CA-0.6%PET-MIL-101(Fe) membrane for DI-TFME of imidacloprid, clothianidin, thiamethoxam and thiacloprid from aqueous solution. Sample 5 mL of water with neonicotinoid insecticides (50 µg/L); sample pH 7.5; eluent volume 1000 µL; extraction time 25 min, and elution time 12.5 min.

	CTN	ICD	TCD	TM
Before preconcentration				
Regression equation	y = 0.0131x − 0.0018	y = 0.0137x + 0.0556	y = 0.0137x − 0.0107	y = 0.0155x + 0.009
Linearity (µg/L)	0.2–450	0.2–500	0.2–400	0.2–500
Coefficient of determination	0.9998	0.9997	0.9998	0.9997
Limits of detection (µg/L)	0.067	0.073	0.052	0.071
Limits of quantification (µg/L)	0.22	0.24	0.17	0.22
After preconcentration				
Regression equation	y = 0.9623x + 1.8121	y = 1.018x + 5.35	y = 1.0342x − 0.2848	y = 1.3673x − 9.8226
Linearity (µg/L)	0.04–400	0.04–400	0.05–450	0.05–500
Coefficient of determination	0.9989	0.9982	0.9989	0.9981
Limits of detection (µg/L)	0.013	0.015	0.014	0.016
Limits of quantification (µg/L)	0.043	0.050	0.046	0.053
Intraday precision (%RSD)	2.1	1.2	2.7	1.7
Interday precision (%RSD)	3.3	3.3	3.9	3.6
Enrichment factor	73	74	75	88

Table 3. Analytical figures of merit of DI-TFME/HPLC-DAD for the analysis of selected neonicotinoid insecticides.

Method validation

The analytical performance of developed DI-TFME/HPLC-DAD was assessed using the method described in Sect. 2.5, and the findings are presented in Table 3. The calibration curves of the methods were linear in the range of 0.04–500 µg/L with the correlation of coefficients (R^2) greater than 0.99, respectively. The LODs and LOQs were 0.013–0.016 µg/L and 0.043–0.053 µg/L, respectively. The intraday and interday precision ranged from 1.2 to 2.7% and 3.3–3.9%, respectively. These findings demonstrated that the current method was precise. The enrichment factors of the analytes were determined to be between 73 and 88.

Accuracy and precision of DI-TFME/HPLC-DAD method

The precision, applicability and validity of the developed method were evaluated using spike recovery tests. As seen in Table 4, the concentrations of CTN, ICD, TCD, and TM were higher than the LOQ of the DI-TFME/HPLC-DAD method in the river water effluent and influent wastewater, except for TCD, which was not detected

		TM			CTN			ICD			TCD		
	Added (μg/L)	Found	%R	%RSD	Found	%R	%RSD	Found	%R	%RSD	Found	%R	%RSD
Influent	0	0.95 ± 0.04		4.1	0.50 ± 0.02		4.3	1.23 ± 0.03		2.5	0.67 ± 0.02		3.6
	1	1.86 ± 0.06	90.2	3.4	1.39 ± 0.02	88.9	3.7	2.16 ± 0.05	92.7	2.3	1.46 ± 0.06	79.2	4.1
	2	2.86 ± 0.07	95.2	2.6	2.37 ± 0.09	93.5	3.9	3.18 ± 0.08	97.3	2.4	2.46 ± 0.09	89.6	3.5
	5	5.79 ± 0.13	96.7	2.3	5.27 ± 0.14	95.4	2.7	6.17 ± 0.13	98.7	2.1	5.40 ± 0.18	94.5	3.4
Effluent	0	0.39 ± 0.02		3.8	0.21 ± 0.01		4.7	0.48 ± 0.02		4.3	0.23 ± 0.01		4.4
	1	1.34 ± 0.05	94.5	3.5	1.14 ± 0.04	93.7	3.7	1.43 ± 0.04	95.1	2.7	1.15 ± 0.04	91.2	3.7
	2	2.34 ± 0.06	96.7	2.6	2.12 ± 0.07	95.6	3.3	2.43 ± 0.08	97.4	3.1	2.14 ± 0.06	95.5	2.9
	5	5.31 ± 0.15	98.3	2.9	5.10 ± 0.18	97.8	3.5	5.41 ± 0.14	98.6	2.5	5.10 ± 0.12	97.3	2.4
River water	0	0.13 ± 0.01		4.5	0.11 ± 0.01		4.6	0.24 ± 0.01		4.8	ND		
	1	1.11 ± 0.03	98.5	3.1	1.06 ± 0.04	95.6	3.5	1.20 ± 0.04	96.7	3.2	0.97 ± 0.03	97.3	2.6
	2	2.11 ± 0.05	99.1	2.5	2.08 ± 0.07	98.7	3.2	2.21 ± 0.08	98.4	3.4	1.98 ± 0.04	98.9	1.8
	5	5.23 ± 0.11	102	2.1	5.09 ± 0.13	99.7	2.6	5.21 ± 0.15	99.5	2.9	4.96 ± 0.10	99.1	2.1

Table 4. %RSD of DI-TFME /HPLC-DAD method achieved from the analysis of spiked water samples.

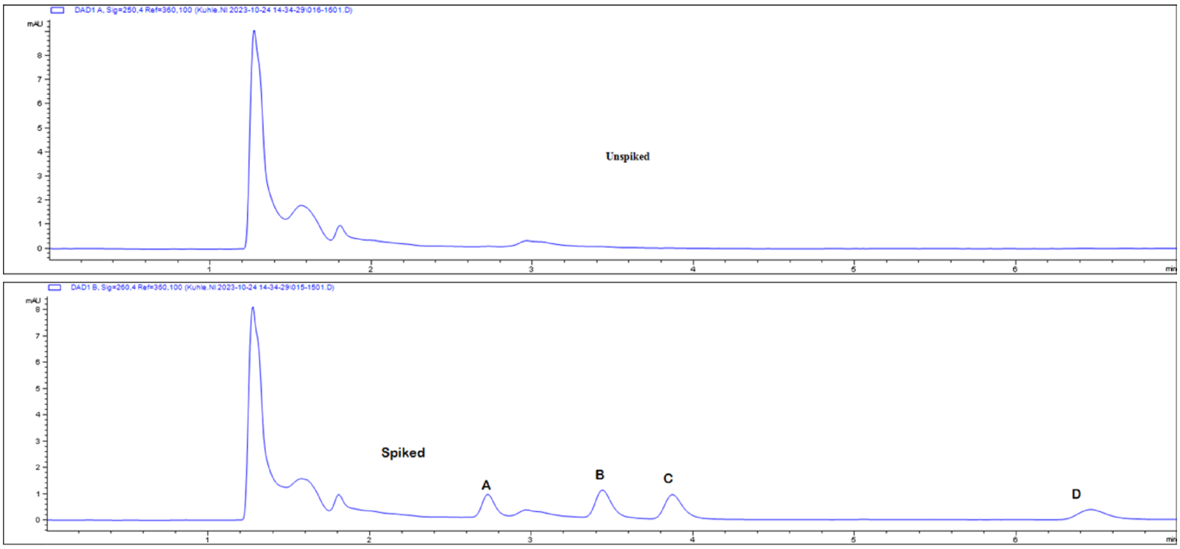

Fig. 12. Unspiked and spiked chromatograms (A = thiamethoxam (TM; 2.7 min); B = imidacloprid (ICD, 3.4 min); C = clothianidin (CTN, 3.8 min) and D = thiacloprid (TCD, 6.4 min)).

in river water. The percentage RSD values for the spiked samples with low, medium, and high concentration levels were 2.3–4.1%, 1.8–3.9%, and 2.1–3.5%, respectively. These results confirm the reproducibility and repeatability of the method. The accuracy of the method for the selected NIs was adequate and acceptable. The %R values for spiked river water, effluent and influent samples were 95.6–102%, 91.2–98.6% and 79.2–98.7%, respectively. Typical chromatographs for the analysis of spiked and spiked water samples are presented in Fig. 12.

Comparison with previously reported studies
For the reconcentration and extraction of selected neonicotinoid insecticides, the proposed DI-TFME/HPLC method was compared to alternative sample preparation methods. Table 5 summarizes the analytical performances of the proposed method in comparison to other reported studies. The sensitivity of this method in terms of LODs and LOQs can be observed, that the developed method showed better sensitivity compared to methods reported by[53–55], whereas methods developed by[56–58] had better sensitivity compared to the developed method. The dynamic linear range of the DI-TFME-HPLC-DAD method was wider than methods developed by[57,58], but methods developed by[53,54] had a wider linear range than the developed method. However, the linear range of the DI-TFME-HPLC-DAD method was comparable to methods developed by[55,56]. The proposed method's accuracy, expressed as %RSD, was found to be lower compared to[53,54] and was comparable with the method reported by[55–58].

Application to real samples
The developed method was used to extract and preconcentrate NIs in real water samples, and the results are shown in Table 6. The results illustrate that the method had a high sensitivity to the target analytes. The findings

Analyte	Detection method	Sample preparation	Linear Range (µg/L)	LOD (µg/L)	LOQ (µg/L)	EF	RSD (%)	Ref
Acetamiprid, clothiandin, thiacloprid and imidacloprid	HPLC-DAD	MSPE	LOQ-600	0.0013–0.0032	0.0043–0.011	–	< 5	[56]
Thiamethoxam, clothianidin, imidacloprid and chiacloprid	HPLC-DAD	CPE	1.0-1000	0.3-1.0	1.0–3.0	–	0.05–8.03	[54]
Acetamiprid, imidacloprid, thiacloprid and clothianidin	HPLC-DAD	d-SPME	1.4–700	0.41–0.82	1.4–2.7	–	0.35–5.5	[55]
Thiamethoxam, acetamiprid, thiacloprid and imidacloprid	HPLC	SPE	0.06–100	0.02–0.08	0.06–0.25	185–220	1.8–5.5	[57]
Thiamethoxam, acetamiprid, thiacloprid and imidacloprid	HPLC	MSPE	0.03–100	0.01–0.08	0.03–0.25	199–302	3.6–5.5	[58]
Acetamiprid and imidacloprid	HPLC-DAD	UA-MSPE	0.064–3500	0.019–0.022	0.064–0.074	–	3.93–8.50	[53]
Imidacloprid, clothianidin, thiamethoxam and thiacloprid	HPLC-DAD	DI-TFME	0.04–500	0.013–0.016	0.043–0.053	73–88	1.8–4.1	This work

Table 5. Comparison of the proposed method with other reported methods for extraction and preconcentration of NIs in water samples. *MSPE* magnetic solid phase extraction, *CPE* could point extraction, *SPE* solid phase extraction, *d-SPME* dispersive solid-phase microextraction, *UA-MSPE* ultrasound assisted-magnetic solid phase extraction, *HPLC-DAD* high-performance liquid chromatography-diode-array detection, *DI-TFME* direct immersion-thin film microextraction.

Samples	CTN	ICD	TCD	TM
River 1	ND	3.12 ± 0.07	ND	ND
River 2	ND	1.93 ± 0.11	ND	1.22 ± 0.02
Outlet	7.27 ± 0.18	6.72 ± 0.12	ND	2.06 ± 0.03
Inlet	ND	15.7 ± 0.9	ND	ND

Table 6. Concentrations (µg/L) of selected NIs in real water samples obtained using the developed method. *ND* not detected.

Country	Matrix	Analyte	Concentration	References
Canada	Surface water	Imidacloprid and thiamethoxam	320 µg/L and 225 µg/L	[59]
China	River water	Imidaclothiz, nitenpyram, thiacloprid	81.92-1022.3 ng/L	[60]
Australia	Wastewater	Imidacloprid	411–4120 ng/L	[61]
USA	Wastewater	Imidacloprid, clothianidin and thiamethoxam	0.12–59.1 ng/L	[4]
South Korea	Watewater, river water and tap water	Acetamiprid, Clothianidin, Dinotefuran, Imidacloprid, Nitenpyram, Thiacloprid and Thiamethoxam	1.11–166 ng/L	[62]
Ireland	Wastewater	Imidacloprid	22–183 ng/L	[63]

Table 7. Global concentrations of neonicotinoids.

demonstrated that the current method could be applied for NIs analysis in real water samples. The presence of ICD in both the river and the wastewater was detected.

Table 7 illustrates the global occurrence of NIs in different water systems. It can be noted that the detected concentration of ICD in South African wastewater (Outlet) reported in Table 6 was comparable to that of most countries (Canada, USA, Ireland, and South Korea). Other NIs, such as CTN, TCD and TM, had higher concentrations in the countries in Table 7 compared to those detected in Table 6.

Conclusion

This work reported an effective, affordable, straightforward and sensitive approach based on DI-TFME/HPLC-DAD for the analysis of acetamiprid, clothianidin, imidacloprid, and thiamethoxam in water samples. CA-PET-MIL-101(Fe) membrane was successfully synthesized, characterized, and used as an extracting media in the DI-TFME/HPLC-DAD method. The incorporation of PET-MIL-101(Fe) into CA led in a more porous CA-PET-MIL-101(Fe), which enhanced the extraction efficiency. In addition, the membrane hydrophilicity was enhanced by the addition of the PET-MIL-101(Fe), resulting in CA-PET-MIL-101(Fe) with a greater membrane fouling resistance. The developed method resulted in enhanced analytical performance. The DI-TFME/HPLC-DAD method was utilised to determine acetamiprid, clothianidin, imidacloprid, and thiamethoxam in spiked real water samples, with comparatively high %R. The developed method was successful in extracting and preconcentrating some of the target analytes from real water samples; however, one analyte was not detected.

Data availability

The datasets used and analyzed in this study are available from the corresponding author upon reasonable request.

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J.S.: conceptualisation; formal analysis; investigation; methodology; validation; visualisation; writing - original draft. N.M.: Visualisation; validation; writing—review & editing. AN.: conceptualisation; supervision; visualisation of the data; methodology; validation, writing—review & editing. J.R.: conceptualisation; supervision; visualisation; validation, writing—review & editing. P.N.N.: Conceptualisation; funding acquisition; methodology; project administration; resources; software; supervision; validation; visualisation; writing - original draft; writing - review & editing. All listed authors have revewed and approved the submission of the manuscript.

Declarations

Competing interests
The authors declare no competing interests.

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