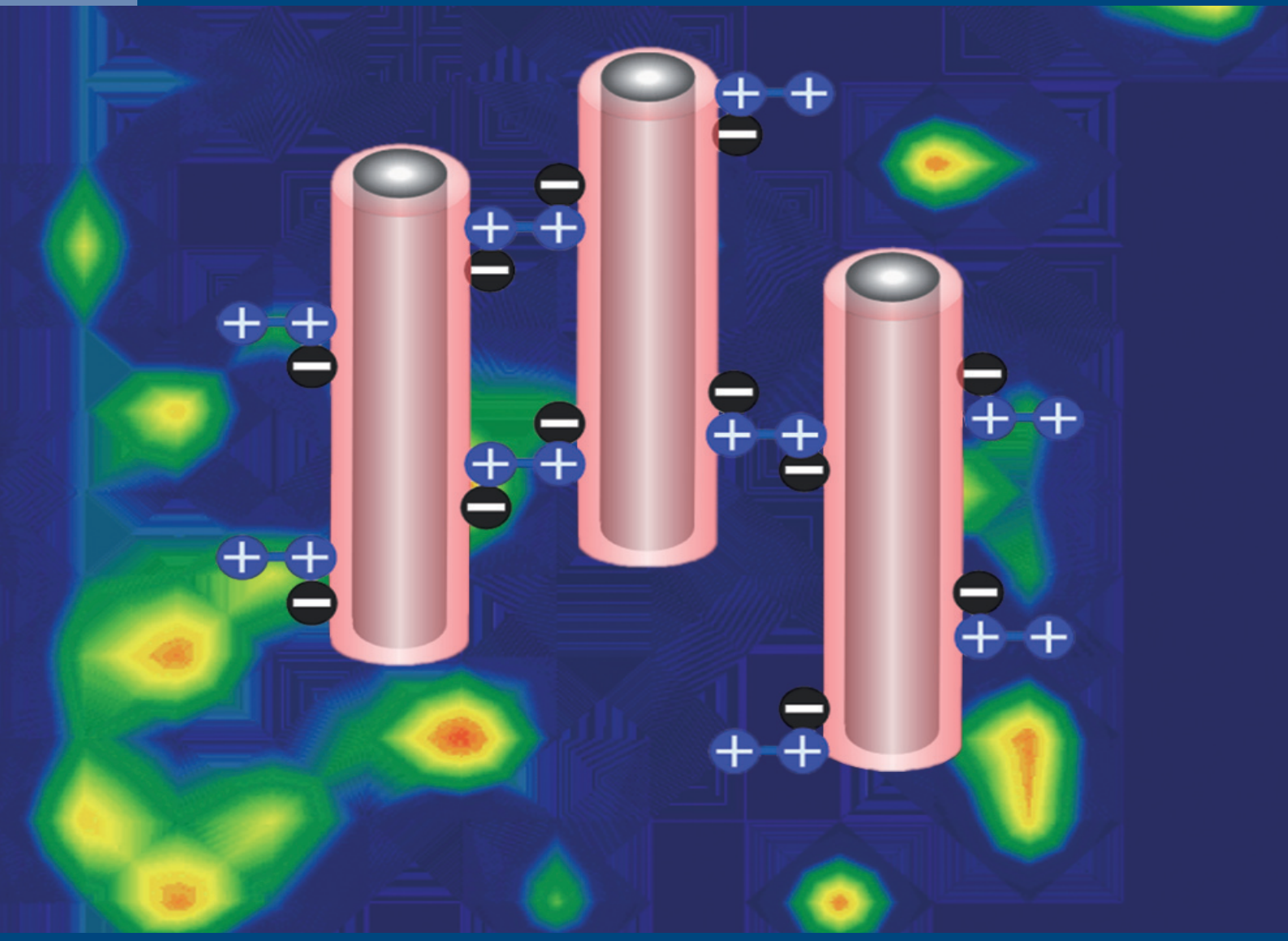
ISSN 1615-9306 · JSSCCJ 41 (2) 417–602 (2018) · Vol. 41 · No. 2 · January 2018 · D 10609

JSS

JOURNAL OF SEPARATION SCIENCE

2|18



Methods
Chromatography · Electroseparation

Applications
Biomedicine · Foods · Environment

www.jss-journal.com

WILEY-VCH

Received: 3 July 2017 | Revised: 27 October 2017 | Accepted: 29 October 2017

DOI: 10.1002/jssc.201700726

RESEARCH ARTICLE

JOURNAL OF SEPARATION SCIENCE

Synthesis and application of a novel solid-phase extraction adsorbent for multiresidue analysis of insecticides in water

Jingjing Xiong[1,2,3] | Huizhen Li[2] | Xue Ma[2] | Jing You[2]

[1]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

[2]School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou, China

[3]University of Chinese Academy of Sciences, Beijing, China

Correspondence
Professor Jing You, School of Environment, Jinan University, Guangzhou, 510632, China.
Email: youjing@jnu.edu.cn

A new solid-phase adsorbent was synthesized for the simultaneous enrichment of multiple classes of trace insecticides (neonicotinoids, organophosphates, fiproles, and organochlorines) in water. The adsorbent was spherical with a diameter, surface area, average pore volume, and pore size of approximately 5 μm, 341 m^2/g, 0.092 m^3/g, and 2.22 nm, respectively. Extraction conditions were optimized, including water pH and the type and volume of the rinsing and eluting solvents. After extraction, target insecticides were analyzed by gas chromatography with mass spectrometry and high-performance liquid chromatography with tandem mass spectrometry. The recovery of neonicotinoids ranged from 63.0 to 124%, except for clothianidin (40.1–52.9%). Recoveries of organophosphates, fiproles, and organochlorines were in the ranges of 37.0–102, 64.0–101, and 42.0–69.3%, respectively. Relative standard deviations were <20% except for profenofos (5.1–30%) and method detection limits were 1.8–12.7 ng/L, suggesting that the precision and accuracy of the developed method were viable. At environmentally relevant concentrations, the new adsorbent achieved comparable recoveries of target insecticides to hydrophilic–lipophilic balance adsorbent while providing an additional advantage by further reducing matrix effects. Field water samples from the Pearl River in Guangzhou, China were analyzed, and the frequent detection of neonicotinoids raises concerns about their aquatic risk.

KEYWORDS
adsorbents, insecticides, matrix effect, polymers, solid-phase extraction

1 | INTRODUCTION

As the world population continues to grow, an evergrowing demand for food supplies has arisen, resulting in large quantities of pesticides being used worldwide [1]. After application, most pesticides enter into surface water through various routes, such as runoff and drift [2]. As a consequence, pesticides, particularly insecticides, have become one of the major threats to global freshwater diversity and ecosystem function [3]. To fully understand aquatic risk caused by insecticides, it is imperative to develop effective methods for monitoring multiple insecticides in water.

To analyze trace insecticide residues in complicated water matrices, intensive sample preparation procedures were required to concentrate and purify the analytes before instrumental analysis. As a replacement of solvent-consuming LLE, SPE has been widely used to extract insecticides from water with the merits of high enrichment capacity, low solvent consumption, and easy operation [4]. Hydrophilic–lipophilic balance (HLB) and C18 are the most often used SPE adsorbents for analyzing insecticide residues in water [5,6]. Compared with C18 absorbent which is limited to nonpolar compounds, HLB adsorbent is preferable for compounds with wide range

Abbreviations: BHC, benzene hexachloride; FIP, fiprole; HLB, hydrophilic–lipophilic balance; MDL, method detection limit; ME, matrix effect; NNI, neonicotinoid insecticide; OC, organochlorine insecticide; OP, organophosphate insecticide

Conflict of interest: The authors have declared no conflict of interest.

of polarity. The cost of HLB adsorbent, however, is higher than C18 [7]. Meanwhile, strong matrix effects (ME) due to coeluting impurities have been noted when the HLB was used as SPE adsorbent [8,9]. The impurities can affect ionization processes of the analytes on MS, leading to enhancement or suppression of chromatographic signals and in turn erroneous quantification [10].

The primary aim of the current study was to develop and validate a novel SPE adsorbent. In comparison with the commercialized adsorbents, the new adsorbent could reduce ME for analyzing multiple classes of insecticides in water without sacrificing extraction efficiency. The adsorbent was synthesized through bulk polymerization using 1-vinyl imidazole and divinyl benzene as monomer and crosslinker, respectively. Four classes of insecticides and their metabolites with a wide range of hydrophobicity (logK_{ow} from –0.13 to 5.11), including neonicotinoids (NNIs), organophosphates (OPs), fiproles (fipronil and its metabolites, FIPs), and organochlorines (OCs) were selected as target analytes. The SPE conditions, including pH of water samples as well as the type and volume of the rinsing and eluting solvents were optimized. After extraction, the insecticides were analyzed using GC–MS and HPLC–MS/MS. Extraction efficiency and ME of the newly developed adsorbent were compared with the commercialized adsorbents. Finally, the SPE method with new adsorbent was validated using field-collected water samples.

2 | MATERIALS AND METHODS

2.1 | Instrumental analysis

A total of 20 insecticides, including eight OPs, three FIPs, four OCs, and five NNIs were analyzed. Physicochemical properties of the insecticides and the respective surrogates and internal standards for analyzing these insecticides are shown in Supporting Information Tables S1 and S2. More details on chemicals and reagents are provided in the Supporting Information.

The OPs and FIPs were analyzed on a QP-2010 plus series GC–MS (Shimadzu, Japan) in negative chemical ionization mode, and OCs were determined on an Agilent 7890A-5975C GC–MS (Agilent Technologies, USA) equipped with an electron impact ion source. More details on GC–MS analysis are discussed in a previous study [11] and the Supporting Information Tables S3 and S4. Alternatively, NNIs were analyzed on a LC-30-AD HPLC (Shimadzu, Japan) coupled with QTRAP 5500 MS/MS (AB Sciex, USA) [12]. Additional information on HPLC–MS/MS conditions is available in the Supporting Information and Supporting Information Table S5. The analytes were all quantified using internal calibration with matrix-matched standards (Supporting Information Tables S3–S5).

2.2 | Synthesis, selection, and characterization of adsorbents

As shown in Supporting Information Table S6, six polymers (A–F) were synthesized by varying the type and composition of monomer and crosslinker. After dissolving approximate amounts of the monomer, crosslinker, and initiator in 5 mL of acetonitrile, the mixture was degassed by purging nitrogen for 10 min, and sealed under nitrogen atmosphere. Polymerization was thermally initiated at 60°C and continued for 24 h. After reaction, the polymer was dried at 60°C for 12 h, ground, and passed through a 58 μm sieve. Finally, the polymer was washed with methanol to remove fine particles and unreacted monomers and then dried at 60°C for 24 h.

The selection of SPE adsorbent was performed by comparing the affinity of the six synthesized adsorbents for target insecticides with HLB adsorbent. Individual adsorbents (20 mg) were packed into 3 mL polypropylene tubes. After preconditioning of the SPE cartridge with 5 mL of acetonitrile and water sequentially, 200 mL of water samples containing OCs, FIPs, and NNIs at 500 ng/L and OPs at 100 μg/L were loaded onto the cartridges. The cartridges were dried for 15 min and the analytes were eluted out of the cartridges with 5 mL of acetonitrile. The effluents were concentrated and redissolved in 0.5 mL of hexane, and OCs, OPs, and FIPs were analyzed by GC–MS after adding 50 μL of 1 μg/mL internal standards. After GC–MS analysis, the solutions were solvent exchanged to 0.5 mL of acetonitrile containing 50 μL of 1 μg/mL internal standards, passed through 0.22 μm filters and analyzed by HPLC–MS/MS for NNIs.

The structure of adsorbent with the highest affinity for target insecticides was characterized. FTIR spectra were obtained using a Vertex 70 FTIR apparatus (Bruker, Germany). The SEM images were recorded using a SU8010 field emission SEM at an accelerating voltage of 1.5 kV (Hitachi, Japan). Nitrogen gas porosimetry measurements were performed on Tristar II 3020 V1.04 surface area and porosity analyzer (Micromeritics, USA) after the polymers were degassed under vacuum at 70°C for 20 min and 120°C for 6 h.

2.3 | Optimization and validation of SPE method using the synthesized adsorbent

2.3.1 | Optimization of SPE method

After selecting the adsorbent, SPE parameters affecting extraction efficiency of the target insecticides were optimized, including water pH (3.0, 4.0, 5.0, and 6.5), rinsing solvent type (water, 10% acetone, 10% methanol, and 10% acetonitrile) and volume (2, 5, and 10 mL), and eluting solvent composition (a mixture of dichloromethane and acetonitrile of 10:0, 7:3, 5:5, 3:7, and 0:10, v/v) and volume (2, 5, and 10 mL). Under individual SPE conditions, 1 L water containing 100 ng/L

of the insecticides and surrogates was extracted with the cartridge packed with 200 mg of the selected adsorbent. Extraction efficiency was compared to optimize SPE conditions.

2.3.2 | Method validation for accuracy, precision, and sensitivity

Accuracy (recovery) and precision (RSD) of the optimized SPE method were evaluated using 1 L of water samples spiked with individual insecticides at concentrations of 20, 200, and 1000 ng/L. In addition, method sensitivity was assessed by the method detection limit (MDL). The MDL means the minimum concentration of a substance that can be quantified with 99% confidence of its concentration being greater than zero. The MDL was estimated from the SD of seven replicates of a water sample that were spiked with 10 ng/L of OPs, FIPs, and OCs and 5 ng/L of NNIs using Eq. (1) [11] and matrix-matched calibration standards were used for quantification.

$$\mathrm{MDLs} = 3.14 \times \mathrm{SD} \quad (1)$$

2.3.3 | Matrix effect

Besides extraction efficiency, the capability of SPE adsorbents to minimize ME during instrumental analysis was compared for the synthesized and HLB adsorbents. The effect of cartridge rinse on the ME was also evaluated. Field-collected water samples were spiked with target insecticides and processed by SPE, resulting in 200 ng/mL analytes in the final extracts. Insecticides in the extracts were analyzed using GC–MS and HPLC–MS/MS, and compared with the insecticides in pure solvents at the same concentration. The ME was calculated under both external and internal standard calibration conditions (Eqs. (2) and (3), respectively) [13].

$$\mathrm{ME_{ex}} = (\mathrm{A} - \mathrm{B})/\mathrm{B} \times 100\%, \quad (2)$$

where, A and B are the peak areas of the quantitative ion of the analyte in the test sample and solvent (hexane or acetonitrile), respectively.

$$\mathrm{ME_{in}} = (\mathrm{C} - \mathrm{D})/\mathrm{D} \times 100\%, \quad (3)$$

where, C and D are the ratios of peak areas of the quantitative ions of the analyte and the internal standard (50 µL of 1 µg/mL) in test samples and matrix-matched standards, respectively.

2.3.4 | Method validation with field samples

The optimized SPE method using the synthesized adsorbent was also used to analyze insecticide residues in field water samples that were collected from the Pearl River in Guangzhou, China (Supporting Information Table S7). Water samples were collected and stored in 4-L brown glass bottles, with 4 mL of 20% NaN_3 and 4 mL of 6 mol/L HCl being added to the water to reduce microbial degradation, the samples were transported back to the laboratory and kept at 4°C before analysis. Before extraction, water samples were adjusted to neutral pH by adding 0.1 mol/L NaOH and filtered through glass fiber filters. All extractions were performed within 3 days after sample collection.

A set of QC samples were analyzed along with the field samples. No target insecticides were detected above their respective MDLs in blank samples. Three surrogates (PCB-67, PCB-209, and acetamiprid-d_3; 100 µL of 1 µg/mL each) were added before extraction to assess the performance of sample preparation procedures. Recoveries of PCB-67, PCB-209, and acetamiprid-d_3 were 52.5–58.1, 55.7–64.7, and 64.4–94.0% with SDs of 6.0–15.2, 1.6–8.7, and 10.3–17.2%, respectively. Statistical comparison among various adsorbents was conducted using a one-way ANOVA test with SPSS version 16.0 software (International Business Machines, USA).

3 | RESULTS AND DISCUSSION

3.1 | Synthesis, selection, and characterization of SPE adsorbents

As shown in Supporting Information Table S6, six polymers were synthesized using the monomers and crosslinkers with different polarity and composition. Figure 1 shows the relative extraction efficiency for individual insecticides by the synthesized adsorbents (A–E) to HLB. Extremely high column

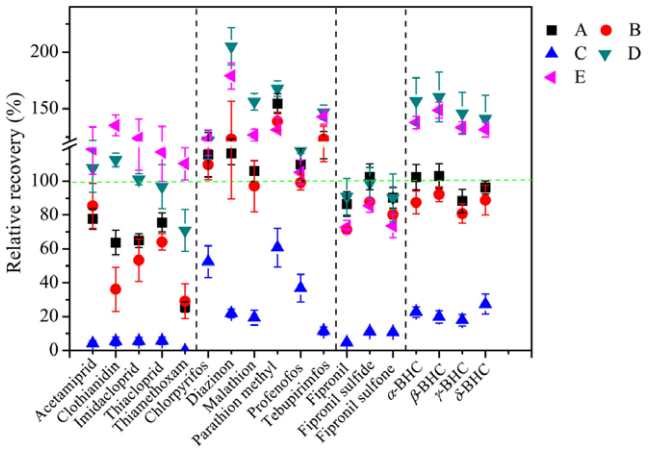


FIGURE 1 Relative recovery of different synthesized adsorbents for individual insecticides to commercial HLB adsorbent. The composition of monomer and cross-linker for the adsorbents were as follows. (A) N-vinyl-2-pyrrolidone/divinyl benzene = 2:1; (B) 1-vinyl imidazole/divinyl benzene = 2:1; (C) acrylamide/divinyl benzene = 2:1; (D) N-vinyl-2-pyrrolidone/divinyl benzene = 5:1; and (E) 1-vinyl imidazole/divinyl benzene = 5:1

pressure prohibited the use of adsorbent F, thus only the other five adsorbents were evaluated. Comparatively, adsorbents D and E, which were made at high monomer to crosslinker ratio (5:1), had higher extraction efficiency than the absorbents with low ratio (2:1). This result is expected as increasing the monomer ratio increased the affinity of the polymers for the analytes. With a relative recovery to HLB greater than 100%, adsorbents D and E also had higher affinity than HLB for most insecticides, except for FIPs (Fig. 1). Adsorbent E was synthesized from a more polar monomer, and had a significantly greater affinity for NNIs than adsorbent D, therefore it was selected as the SPE adsorbent.

Adsorbent E was synthesized from 1-vinyl imidazole monomer and its C–N bond p–π conjugate structure could produce electrostatic force. Meanwhile, the benzene ring in divinyl benzene crosslinker had hydrophobic characteristics. Accordingly, the adsorbent was viable for both polar and nonpolar contaminants. The C–N bond and benzene ring structures were evident in FTIR spectrum of the adsorbent (Supporting Information Fig. S1). The adsorption peaks at 1288, 1110, and 1080 cm^{-1} were related to C–N stretching vibration in 1-vinyl imidazole and peaks at 1602, 1502, 1447, and 1411 cm^{-1} represented benzene ring stretching vibration in divinyl benzene. The UV spectra of individual monomers and polymer showed that the unreacted monomers were thoroughly removed (data are not presented) and FTIR spectrum suggested that 1-vinyl imidazole and divinyl benzene were successfully copolymerized in the synthesized adsorbent.

The SEM image of the adsorbent showed its morphology that was a spherical structure with a diameter of approximately 5 nm (Fig. 2). As plotted in Supporting Information Fig. S2, the nitrogen adsorption/desorption isotherms of the adsorbent showed type IV with an H4 hysteresis loop at P/P_0 between 0.05 and 0.8. These characteristics of the mesoporous material were confirmed by Barret–Joyner–Halenda desorption pore distribution curves. Surface area, pore volume, and average pore size were 341 m^2/g, 0.092 cm^3/g, and 2.22 nm, respectively.

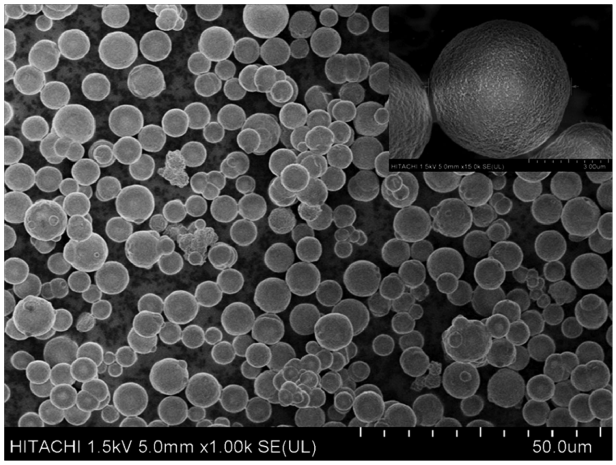


FIGURE 2 The SEM images of the synthesized adsorbent E

3.2 | Optimization of SPE conditions

The selected adsorbent E (200 mg) was used for concentrating insecticides from water samples. To gain good extraction efficiency, SPE conditions were optimized, including pH of water sample and the type and volume of the rinsing and eluting solvents. Water pH may change speciation of polar analytes and affect their interaction with adsorbent [14]. Because insecticides tend to degrade in alkaline conditions [15], the impact of water pH on extraction efficiency was evaluated at following four pH levels: 3.0, 4.0, 5.0, and 6.5. Increasing water acidity caused a higher pressure in the SPE cartridge, most likely due to an altering of polymer structure under acidic condition. It becomes impractical to load the water samples with pH $\leq$ 4.0 onto the cartridges within a reasonable timeframe, thus the recovery of the insecticides was only assessed for samples with pH of 5.0 and 6.5 (Supporting Information Fig. S3). Recoveries of most insecticides were slightly higher at pH of 6.5, particularly for the polar OPs and NNIs. Therefore, water samples with pH close to neutral were used thereafter.

To reduce the matrix interference in field water samples that may bias the quantification, a rinsing step was added before eluting the analytes out of SPE cartridge. Four solutions (water, 10% acetone, 10% methanol, and 10% acetonitrile) with a volume of 2, 5, or 10 mL were assessed as the rinsing solution (Supporting Information Fig. S4). Although the type of rinsing solution had little effect on nonpolar insecticides, rinsing the cartridge with 10% methanol and 10% acetonitrile caused significant loss of NNIs and OPs. Compared with water, 10% acetone was more effective to remove interferences than water while both solutions caused no change of insecticide recovery with rinsing volumes <5 mL. As a result, 5 mL of 10% acetone was chosen as rinsing solution.

Optimizing the composition and volume of elution solution were also imperative to reduce interfering substance while maximizing the recovery of target insecticides. The impacts of the composition of eluting solutions (a mixture of dichloromethane and acetonitrile at 10:0, 7:3, 5:5, 3:7, and 0:10, v/v) and their volume (2, 5, and 10 mL) on recovering the insecticides were evaluated. Results showed that 5 mL of acetonitrile provided the highest recovery for most analytes (Fig. 3).

In summary, the optimum SPE conditions were as follows. After SPE cartridge (200 mg) was preconditioned with 5 mL of methanol and water, sequentially, 1 L water sample at neutral pH was loaded onto the cartridge at a flow rate of 2–3 mL/min. After rinsing the column with 5 mL of 10% acetone, the analytes were eluted out of the cartridge with 5 mL of acetonitrile.

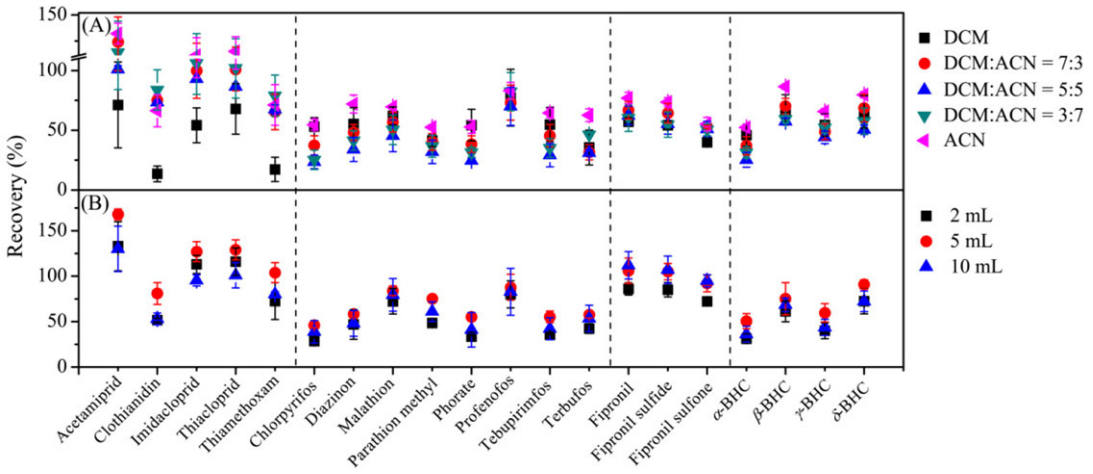


FIGURE 3 The influence of the type (A) and volume (B) of eluting solvents on extraction efficiency of SPE cartridge packed with 200 mg of synthesized adsorbent

3.3 | Method validation

The optimized SPE method was validated by water samples spiked with target insecticides at environmentally relevant concentrations (20, 200, and 1000 ng/L) (Table 1). The recovery of NNIs was in a range of 63.0–124% with RSDs of 3.8–18%, except for clothianidin, which had a relatively low recovery (40.1–52.9%). The recovery of most OPs ranged from 46.8 to 102% and the RSDs were 1.0–20% (profenofos 5.1–30%), expect for malathion, parathion methyl, and phorate. The high tendency of degradation of these three OPs may be the reason for their low recoveries (37.0–63.9%). The recoveries of FIPs and OCs were 64.0–101 and 42.0–69.3% with RSDs of 4.7–17 and 7.2–18%, respectively. Glassware binding partially explained the low recovery of OCs which was also noted for other hydrophobic compounds [6]. A total of

TABLE 1 Recovery (mean ± SD, $n = 3$) of target insecticides in water spiked at concentrations of 20, 200, and 1000 ng/L. The method detection limits (MDLs) are also presented

	Recovery (%)			
Compound	**20 ng/L**	**200 ng/L**	**1000 ng/L**	**MDLs (ng/L)**
Acetamiprid	122 ± 5	113 ± 12	124 ± 18	4.2
Clothianidin	40.1 ± 3.3	48.4 ± 6.2	52.9 ± 9.8	2.1
Imidacloprid	78.8 ± 5.9	77.0 ± 8.7	83.6 ± 14.4	2.2
Thiacloprid	84.7 ± 3.3	90.5 ± 9.5	97.5 ± 13.1	2.7
Thiamethoxam	63.0 ± 2.9	74.9 ± 7.9	81.3 ± 13.8	2.3
Chlorpyrifos	52.8 ± 3.7	53.6 ± 5.0	51.8 ± 4.4	5.6
Diazinon	46.9 ± 1.6	61.2 ± 7.7	60.9 ± 6.7	1.9
Malathion	46.6 ± 2.1	63.9 ± 6.8	46.3 ± 8.3	1.9
Parathion methyl	47.4 ± 2.2	52.5 ± 4.9	37.0 ± 7.1	2.3
Phorate	45.1 ± 1.3	58.8 ± 6.4	39.4 ± 3.7	2.1
Profenofos	61.2 ± 3.1	102 ± 8	75.0 ± 22.2	8.9
Tebupirimfos	56.2 ± 1.3	63.3 ± 5.8	53.0 ± 6.9	3.4
Terbufos	54.0 ± 0.5	51.7 ± 3.7	46.8 ± 9.2	2.3
Fipronil	64.0 ± 3.8	80.5 ± 13.9	73.9 ± 11.0	4.1
Fipronil sulfide	71.2 ± 3.4	82.1 ± 11.9	101 ± 15	9.6
Fipronil sulfone	69.7 ± 3.8	79.5 ± 11.1	91.2 ± 10.5	12.7
α-BHC	45.1 ± 4.2	49.7 ± 4.8	45.9 ± 3.3	1.8
β-BHC	54.7 ± 5.4	52.6 ± 7.0	57.2 ± 9.2	4.4
γ-BHC	44.5 ± 4.0	42.8 ± 5.1	42.0 ± 7.6	2.9
δ-BHC	69.3 ± 5.8	58.3 ± 5.6	56.9 ± 9.4	2.6

10–40% pyrethroids and methoprene found in water were lost due to the sorption of these compounds to glassware. Furthermore, insecticide recoveries changed little though their water concentrations varied across two orders of magnitudes (20–1000 ng/L), indicating the applicability of the SPE method across a wide concentration range.

Method sensitivity was expressed as MDLs and they were in ranges of 2.1–4.2, 1.9–8.9, 4.1–12.7, and 1.8–4.4 ng/L for NNIs, OPs, FIPs, and OCs, respectively (Table 1). The MDLs were compared with previous studies using different analytical methods (Supporting Information Table S8). In general, the use of GC–MS and HPLC–MS/MS made the current method to be more sensitive for most compounds than previous methods.

Sorption capability of the synthesized adsorbent was compared with two commercialized adsorbents which were commonly used for pesticide analysis (HLB and C18) using the optimized SPE method with 1 L of water containing 100 ng/L of target compounds (Fig. 4). Extraction efficiency of C18 was significantly lower than the synthesized adsorbent and HLB for NNIs and most OPs that were relatively polar ($p < 0.05$), yet the later two adsorbents had similar affinity for most insecticides. Moreover, high matrix-enhanced responses with a recovery close to 140% were observed for three OPs (malathion, parathion-methyl, and profenofos) when HLB was used. Comparatively, their recovery was more reasonable (71.3–89.3%) when the synthesized adsorbent was applied.

Overall, extraction efficiency of the synthesized adsorbent for most insecticides was better than C18 adsorbent, particularly for polar compounds. The synthesized adsorbent had similar sorption capacity as HLB adsorbent, but it showed better potential than HLB for improving quantitative accuracy by minimizing ME, which strengthens its practical use for water analysis.

3.4 | Matrix effects

MEs refer to the change of chromatographic responses (enhancement or suppression) in the presence of interfering substances and influence the accuracy and reliability of instrumental qualification [16]. Therefore, it is preferable to minimize ME as much as possible during method development. As shown in Supporting Information Fig. S5, inclusion of a rinsing step in SPE before elution made the GC–MS chromatograms clearer with less interfering peaks in both electron impact ion and negative chemical ionization modes, as a result of removing some matrix components through rinsing SPE cartridges. In addition, a comparison of chromatograms of the same sample processed by the synthesized and HLB adsorbents showed the synthesized adsorbent was more effective in removing matrix components than HLB as indicated by lower peak intensity (Supporting Information Fig. S5).

Quantitative evaluation of ME was performed by comparing chromatographic responses of the insecticides in pure solvent and field water samples. Two calibration approaches were used for the calculations, namely external and internal standard calibrations (Eqs. (2) and (3)), and the results are shown in Fig. 5 and Supporting Information S6, respectively. The lowest ME equals 0, and enhancement and suppression of chromatographic responses lead to a deviation of ME from 0 (ME > and < 0, respectively). As shown in Fig. 5, ME affects quantifying OPs the most, while OCs are the least impacted insecticides.

As shown in Fig. 5, adding a rinsing step in SPE using the synthesized adsorbent reduced ME for most insecticides, except for fipronil sulfone (10.6–24%) and δ-benzene hexachloride (BHC) (3.2–8.1%). Rinsing the cartridge reduced ME_{ex} from −93.0 to −38.5, 170–752, 47.5–139, and 13.2–26.1% to −89.6 to −27.3, 13.4–256, 18.9–76.9, and 5.8–9.6%

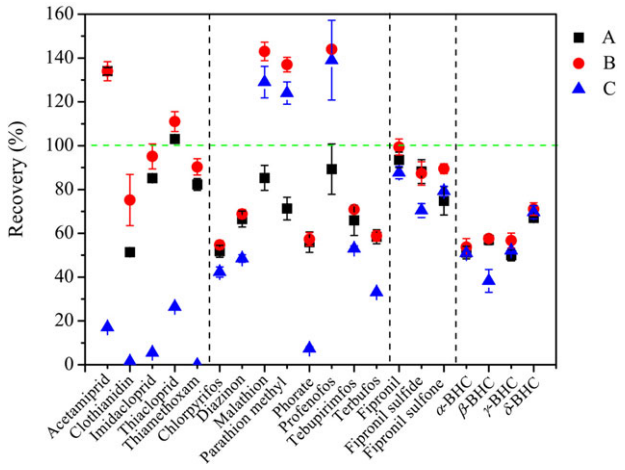


FIGURE 4 Comparison of extraction efficiency of the synthesized adsorbent (A) with the commercialized HLB (B) and C18 adsorbents (C)

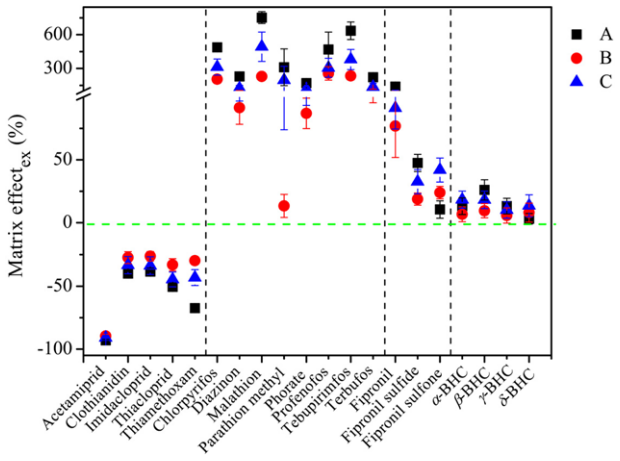


FIGURE 5 The calculated matrix effects (ME_{ex}) of individual insecticides when using the synthesized adsorbent without (A) and with (B) rinsing and the use of the commercialized HLB adsorbent with rinsing (C). External standard calibration method was used

for NNIs, OPs, FIPs, and OCs, respectively. Furthermore, the absolute values of ME_{ex} for the synthesized adsorbent (from 5.8 to 256%) were lower than HLB (from 10.2 to 493%) for all insecticides. The lower ME was supported by clearer full-scan chromatograms (Supporting Information Fig. S5), suggesting that the synthesized adsorbent was more effective in reducing interfering substances than HLB.

Internal calibration with matrix-matched standards was recommended for GC–MS and HPLC–MS analyses to reduce ME [17]. To prepare matrix-matched standards, clean water was processed with SPE and concentrated to 0.5 mL of hexane or acetonitrile solution before adding appropriate amounts of the insecticides, surrogates, and internal standards. Due to the use of internal calibration with matrix-matched standards, ME_{in} were significantly smaller than ME_{ex} for most insecticides (Fig. 5 and Supporting Information S6). For example, ME_{in} for imidacloprid and acetamiprid (8.5 and 18.4%, respectively) were times and five times less than their respective ME_{in} values of −26.2 and −89.6%. The ME_{in} values were also lower than those reported in a previous study using HLB (49 and −20% for imidacloprid and acetamiprid, respectively) [18]. When the synthesized adsorbent was used, ME_{in} values were all less than 40% for target insecticides except for parathion methyl, phorate, tebupirimfos, and FIPs (Supporting Information Fig. S6). The greatest improvement was noted for OPs which were strongly affected by ME (excluding malathion and parathion methyl) when the synthesized adsorbent was used instead of HLB (from −45.4 to −18.0% and from −57.7 to −28.8%, respectively). Overall, the adsorbent developed in the current study had similar affinity for most insecticides as HLB, but it had additional advantages of reducing interfering substances and improving ME.

3.5 | Analysis of field samples

The newly synthesized adsorbent was successfully used as SPE adsorbent to analyze insecticide residues in field-collected water samples from the Pearl River in Guangzhou, China (Table 2 and Supporting Information Table S9). Polar NNIs and OPs were detected at higher concentrations in the water samples than other insecticides (Table 2). The total concentrations of NNIs were from 51.8 ± 19.4 to 111 ± 35.4 ng/L across sites. Acetamiprid and imidacloprid were the dominated NNIs with concentrations ranging from 20.8 ± 9.4 to 45.4 ± 8.1 and 27.9 ± 7.2 to 52.4 ± 19.4 ng/L, respectively. Chlorpyrifos and diazinon were the only OPs detected at concentrations being <MDL and approximately 20 ng/L, respectively. Chlorpyifos had generally higher sediment concentrations in the Pearl River than diazinon [19], yet its water concentrations were lower than diazinon, which is understandable considering chlorpyifos is much more hydrophobic than diazinon (Supporting Information Table S1). FIPs have been detected in freshwater environment [20,21] and fipronil exceeded its aquatic life benchmark in 70% of urban streams in the U. S. from 1992 to 2011 [22]. Although FIPs were detected in the current study, none were above their MDLs. This is similar to previous report on sediment-bound FIPs in the study area. While FIPs were frequently detected, their sediment concentrations in the Pearl River were relatively low [19]. The BHCs were also detected in all sites with concentrations of 13.6 ± 2.88 to 21.0 ± 2.83 ng/L (Table 2). These concentrations were slightly higher than previous data in the Pearl River (0.21–5.12 ng/L) [23,24], but in the similar range of BHC concentrations in other rivers in China (1.10–290 ng/L) [25–27].

The benchmark values of the insecticides for aquatic risk are also presented in Supporting Information Table S9. Although the four classes of insecticides were all detectable in the Pearl River, NNIs were the only insecticides whose concentrations were greater than their chronic ecological threshold of 35 ng/L [28]. Although NNIs have been extensively used worldwide, few studies reported their occurrence in aquatic environment [29]. The presence of NNIs in freshwater ecosystem is ubiquitous with reported concentrations of 3.29–40.0 μg/L in the United States [30,31], 0.26–43.6 μg/L in Australia [32,33], and approximately 10 ng/L in Osaka, Japan [34]. To date, little information is available on water concentrations of NNIs in China. Zhang et al. [12] analyzed NNIs in an urban tributary of the Pearl River and higher

TABLE 2 The total concentrations of neonicotinoids (NNIs), organophosphates (OPs), fiproles (FIPs), and organochlorines (OCs) in surface water collected from the Pearl River in Guangzhou, China. The results are shown as mean ± SD ($n = 3$)

	Concentration of insecticides in field water (ng/L)				
Insecticide class	**S 1**	**S 2**	**S 3**	**S 4**	**S 5**
ΣNNI[a]	75.6 ± 17.6	92.0 ± 7.1	77.0 ± 24.1	51.8 ± 19.4	111 ± 35
ΣOP[b]	20.6 ± 1.4	20.2 ± 0.3	18.2 ± 1.6	22.2 ± 1.4	18.7 ± 1.9
ΣFIP[c]	<MDL[d]	<MDL	<MDL	<MDL	<MDL
ΣOC[e]	16.1 ± 2.6	21.0 ± 2.8	15.9 ± 2.9	14.3 ± 1.6	13.6 ± 2.9

[a]ΣNNI: the sum of acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam.
[b]ΣOP: the sum of chlorpyrifos, diazinon, malathion, parathion methyl, phorate, profenofos, tebupirimfos, and terbufos.
[c]ΣFIP: the sum of fipronil, fipronil sulfide, and fipronil sulfone.
[d]< MDL: lower than the MDLs.
[e]ΣOC: the sum of α-BHC, β-BHC, γ-BHC, and δ-BHC.

concentrations of imidacloprid were found (32–193 ng/L). Although dilution reduced NNI concentrations in large river (the present study) compared with small streams [12], they still exceeded the benchmarks, calling for more studies on their distribution and risk in aquatic ecosystem.

4 | CONCLUDING REMARKS

A novel SPE adsorbent was synthesized using 1-vinyl imidazole and divinyl benzene copolymerization. The applicability of using this adsorbent for simultaneously extracting insecticides with a wide range of polarity, like NNIs, OPs, FIPs, and OCs were evaluated. The accuracy, precision, and sensitivity of the method were acceptable with good recoveries, RSDs, and MDLs for most insecticides. At environmentally relevant concentrations, recoveries of target insecticides were comparable to the commercialized adsorbent but with less ME. Water samples collected from the Pearl River in Guangzhou, China were analyzed and the frequent detection of NNIs calls for concern on their aquatic risk.

ACKNOWLEDGMENTS

We thank W. Tyler Mehler for editing the manuscript. This research was supported by the National Science Foundation of China (41473106 and 41503091), the Ministry of Science and Technology of China (2017ZX07301005) and Guangdong Provincial Department of Science and Technology (2017A020216002, 2015TX01Z168 and 2016A030312009). This is contribution No. IS-2468 from GIGCAS.

ORCID

Jing You http://orcid.org/0000-0002-4006-8339

REFERENCES

1. Verger, P. J. P., Boobis, A. R., Reevaluate pesticides for food security and safety. *Science* 2013, *341*, 717–718.
2. Konstantinou, I. K., Hela, D. G., Albanis, T. A., The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. *Environ. Pollut.* 2006, *141*, 555–570.
3. Stehle, S., Schulz, R., Agricultural insecticides threaten surface waters at the global scale. *Proc. Natl. Acad. Sci. U. S. A.* 2015, *112*, 5750–5755.
4. Soutoudehnia, K. Z., Wan, I. W.A., Rashidi, N. H., Aboul-Enein, H. Y., Sanagi, M. M., Simultaneous preconcentration of polar and non-polar organophosphorus pesticides from water samples by using a new sorbent based on mesoporous silica. *J. Sep. Sci.* 2016, *39*, 1144–1151.
5. Hadjmohammadi, M. R., Peyrovi, M., Biparva, P., Comparison of C18 silica and multi-walled carbon nanotubes as the adsorbents for the solid-phase extraction of chlorpyrifos and phosalone in water samples using HPLC. *J. Sep. Sci.* 2010, *33*, 1044–1051.
6. Hladik, M. L., Smalling, K. L., Kuivila, K. M., A multi-residue method for the analysis of pesticides and pesticide degradates in water using HLB solid-phase extraction and gas chromatography-ion trap mass spectrometry. *Bull. Environ. Contam. Toxicol.* 2008, *80*, 139–144.
7. Visnevschi-Necrasov, T., Cunha, S. C., Nunes, E., Oliveira, M. B. P. P., Optimization of matrix solid-phase dispersion extraction method for the analysis of isoflavones in trifolium pratense. *J. Chromatogr. A* 2009, *1216*, 3720–3724.
8. Marín, J. M., Gracia-Lor, E., Sancho, J. V., López, F. J., Hernández, F., Application of ultra-high-pressure liquid chromatography–tandem mass spectrometry to the determination of multi-class pesticides in environmental and wastewater samples: Study of matrix effects. *J. Chromatogr. A* 2009, *1216*, 1410–1420.
9. Trufelli, H., Palma, P., Famiglini, G., Cappiello, A., An overview of matrix effects in liquid chromatography–mass spectrometry. *Mass Spectrom. Rev.* 2011, *30*, 491–509.
10. Hernández, F., Sancho, J. V., Pozo, O. J., Critical review of the application of liquid chromatography-mass spectrometry to the determination of pesticide residues in biological samples. *Anal. Bioanal. Chem.* 2005, *382*, 934–946.
11. Li, H., Wei, Y., You, J., Lydy, M. J., Analysis of sediment-associated insecticides using ultrasound assisted microwave extraction and gas chromatography–mass spectrometry. *Talanta* 2010, *83*, 171–177.
12. Zhang, J., Wei, Y., Li, H., Zeng, E. Y., You, J., Application of Box-Behnken design to optimize multi-sorbent solid phase extraction for trace neonicotinoids in water containing high level of matrix substances. *Talanta* 2017, *170*, 392–398.
13. Huo, F., Tang, H., Wu, X., Chen, D., Zhao, T., Liu, P., Li, L., Utilizing a novel sorbent in the solid phase extraction for simultaneous determination of 15 pesticide residues in green tea by GC-MS. *J. Chromatogr. B Analyt. Technol. Biomed. Life Sci.* 2016, *1023–1024*, 44–54.
14. Zhang, M., Chen, H., Zhu, L., Wang, C., Ma, G., Liu, X., Solid-phase purification and extraction for the determination of trace neonicotinoid pesticides in tea infusion. *J. Sep. Sci.* 2016, *39*, 910–917.
15. Liu, L., Hao, Y., Zhou, X., Wang, C., Wu, Q., Wang, Z., Magnetic porous carbon based solid-phase extraction coupled with high performance liquid chromatography for the determination of neonicotinoid insecticides in environmental water and peanut milk samples. *Anal. Methods* 2015, *7*, 2762–2769.
16. Kanrar, B., Mandal, S., Bhattacharyya, A., Validation and uncertainty analysis of a multiresidue method for 42 pesticides in made tea, tea infusion and spent leaves using ethyl acetate extraction and liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A* 2010, *1217*, 1926–1933.
17. Wang, D., You, J., Lydy, M. J., Sediment matrix effects in analysis of pyrethroid insecticides using gas chromatography-mass spectrometry. *Arch. Environ. Contam. Toxicol.* 2010, *59*, 382–392.
18. Dujaković, N., Grujić, S., Radišić, M., Vasiljević, T., Laušević, M., Determination of pesticides in surface and ground waters by liquid chromatography-electrospray-tandem mass spectrometry. *Anal. Chim. Acta* 2010, *678*, 63–72.

19. Yi, X., Li, H., Ma, P., You, J., Identifying the causes of sediment-associated toxicity in urban waterways in South China: incorporating bioavailabillity-based measurements into whole-sediment toxicity identification evaluation. *Environ. Toxicol. Chem.* 2015, *34*, 1744–1750.
20. Gan, J., Bondarenko, S., Oki, L., Haver, D., Li, J. X., Occurrence of fipronil and its biologically active derivatives in urban residential runoff. *Environ. Sci. Technol.* 2012, *46*, 1489–1495.
21. Weston, D. P., Lydy, M. J., Toxicity of the insecticide fipronil and its degradates to benthic macroinvertebrates of urban streams. *Environ. Sci. Technol.* 2014, *48*, 1290–1297.
22. Stone, W. W., Gilliom, R. J., Ryberg, K. R., Pesticides in U.S. streams and rivers: Occurrence and trends during 1992–2011. *Environ. Sci. Technol.* 2014, *48*, 11025–11030.
23. Yu, M., Luo, X., Chen, S., Mai, B., Zeng, E. Y., Organochlorine pesticides in the surface water and sediments of the Pearl River Estuary, South China. *Environ. Toxicol. Chem.* 2008, *27*, 10–17.
24. Guan, Y. F., Wang, J. Z., Ni, H. G., Zeng, E. Y., Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: assessment of mass loading, input source and environmental fate. *Environ. Pollut.* 2009, *157*, 618–624.
25. Feng, J., Hu, P., Zhang, F., Sun, J., HCHs and DDTs in Yellow River of Henan section–a typical agricultural area in China: Levels, distributions and risks. *Environ. Geochem. Health* 2016, *38*, 1241–1253.
26. Wang, B., Yu, G., Huang, J., Yu, Y., Hu, H., Wang, L., Tiered aquatic ecological risk assessment of organochlorine pesticides and their mixture in Jiangsu reach of Huaihe River, China. *Environ. Monit. Assess.* 2009, *157*, 29–42.
27. Wang, D., Yang, S., Wang, G., Gao, L., Wang, Y., Jiang, Q., Chen, Y., Residues and distributions of organochlorine pesticides in China's Weihe River. *Pol. J. Environ. Stud.* 2016, *25*, 1285–1292.
28. Morrissey, C. A., Mineau, P., Devries, J. H., Sanchez-Bayo, F., Liess, M., Cavallaro, M. C., Liber, K., Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review. *Environ. Int.* 2015, *74*, 291–303.
29. Bass, C., Denholm, I., Williamson, M. S., Nauen, R., The global status of insect resistance to neonicotinoid insecticides. *Pestic. Biochem. Phys.* 2015, *121*, 78–87.
30. Starner, K., Goh, K. S., Detections of the neonicotinoid insecticide imidacloprid in surface waters of three agricultural regions of California, USA, 2010–2011. *Bull. Environ. Contam. Toxicol.* 2012, *88*, 316–321.
31. Ensminger, M. P., Budd, R., Kelley, K. C., Goh, K. S., Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. *Environ. Monit. Assess.* 2013, *185*, 3697–3710.
32. Schaafsma, A., Limay-Rios, V., Baute, T., Smith, J., Xue, Y., Neonicotinoid insecticide residues in surface water and soil associated with commercial maize (corn) fields in southwestern Ontario. *PLoS One* 2015, *10*, 1–21.
33. Main, A. R., Headley, J. V., Peru, K. M., Michel, N. L., Cessna, A. J., Morrissey, C. A., Widespread use and frequent detection of neonicotinoid insecticides in wetlands of Canada's Prairie Pothole region. *PLoS One* 2014, *9*, 1–12.
34. Yamamoto, A., Terao, T., Hisatomi, H., Kawasaki, H., Arakawa, R., Evaluation of river pollution of neonicotinoids in Osaka City (Japan) by LC–MS with dopant-assisted photoionisation. *J. Environ. Monitor.* 2012, *14*, 2189–2194.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Xiong J, Li H, Ma X, You J. Synthesis and application of a novel solid-phase extraction adsorbent for the multiresidue analysis of insecticides in water. *J Sep Sci*. 2018;41:525–533. https://doi.org/10.1002/jssc.201700726