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Quantification and risk assessment of pyrethroid residues in seafood based on nanoparticle-extraction approach

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ABSTRACT

Seafood is a good source of essential nutrients, but the presence of pyrethroid contaminants may pose risks to consumers' health and its intricate matrices obstruct chemical hazard detection. In this study, a method for detecting residues of four pyrethroids (cypermethrin, deltamethrin, permethrin, and bifenthrin) in fish and finfish was optimized and validated. The proposed method performed with low-temperature cleanup (−20 °C) followed by nanoparticle-extraction and HPLC-PDA. The critical parameters of the method's performance were studied to demonstrate the optimum conditions. The method was verified using mackerel fillet, and its application was extended to determine pyrethroid residues in commonly consumed seafood (salmon, sea bass, threadfin fish, tiger prawn, vannamei prawn, shrimp, squid, grand jackknife clam, and oyster) obtained from local supermarkets in Singapore. The proposed method provided satisfactory recoveries of 75.95–96.81% and achieved LOQs of 0.54–0.85 ng/g, presenting the accomplishment for pyrethroid determination in seafood. Among tested seafood samples, at least one of the target pyrethroids was monitored (0.28–11.28 ng/g); however, the residue was below the level with safety concern. Estimated hazard indexes (≤0.12%) from risk assessment indicate a negligible risk of exposure to four target pyrethroids via consumption of seafood in Singapore.

1. Introduction

Pyrethroid pesticides are a type of synthetic compounds, and their structures are analogous to insecticidal pyrethrins found in *Chrysanthemum* flowers. As a result of their widespread usage, pyrethroid residues (cypermethrin, deltamethrin, permethrin, and bifenthrin) are more frequently detected in the global environment as well as food products (Tang et al., 2018). In an aquatic environment, the contamination of pyrethroids is influenced by the transportation of pesticides through groundwater, drainage channel, soil percolation, rain scouring (Mimbs et al., 2016), and intentional treatment in seafood farms (Aznar-Alemany et al., 2017; Langford et al., 2014). The detected pyrethroid concentrations in aquatic bodies on a global scale ranged from ND to 13 mg/L (Tang et al., 2018). This contamination, assisted by the hydrophobicity of pyrethroid compounds, consequently enriches their levels in fish and other aquatic organisms. Pyrethroid levels in aquatic organisms such as fish, shrimp, and crab worldwide were reported between ND and 9.90 μg/g (Rawn et al., 2010; Tang et al., 2018). The contamination of these hazard residues in aquaculture and seafood raises public health concerns about pyrethroid exposure because their major contact route for the general public is the consumption of contaminated food.

Seafood, both wild and farmed, is widely consumed and acknowledged as a high-quality animal protein and essential nutrient (FAO, 2018); however, they may pose risks to human health because of their chemical contaminants such as pyrethroid residues (Rascón et al., 2019; Xu et al., 2019). Pyrethroid contaminants can potentially increase the risk of respiratory irritation, paresthesia, sperm DNA damage, cancer, and coronary heart disease (Saillenfait et al., 2015). In considerations of consumers' health, the Maximum Residue Levels (MRLs) of pyrethroids in food have been limited by authorities. The Secretary of Animal and Plant Health of the Ministry of Agriculture, Livestock and Food Supply, Brazil regulated the MRLs of cypermethrin (10 ng/g), permethrin (10 ng/g), bifenthrin (10 ng/g), and deltamethrin (30 ng/g) for farmed fish in 2018 (Oliveira et al., 2019). In addition, the EU MRLs of cypermethrin and deltamethrin in fish are defined at 50 and 10 ng/g, respectively (EU European Commission, 2010). The criteria for pyrethroid safety levels may vary among different regions, but the MRLs are normally expressed

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as a trace amount of part per million or part per billion to prevent excessive exposure and consumption of contaminated foods. Although the Singapore Food Agency (SFA) has imposed the MRLs of pyrethroids in meat and fat meat, to date, there is no explicit MRLs for seafood products (SFA, 2020). To encourage the consideration of regulating MRLs of pyrethroids in seafood in Singapore, evidence of pyrethroid contamination is needed. Therefore, it is essential to develop and validate a method to quantify trace amounts of pyrethroids in seafood products.

Over the last decades, diverse analytical methods have been applied to measure pyrethroid contamination in worldwide seafood such as tilapia, tainha, trahira, trout, barbell, carp, salmon, oyster, shellfish, and shrimp (Aznar-Alemany et al., 2017; Corcellas et al., 2015; Gadelha et al., 2019; Oliveira et al., 2019; Rawn et al., 2010). One of the efficient assistance methods is low-temperature cleanup, which was used to remove interferences in matrices of food samples, for instance, fat in vegetable oils (Yu et al., 2017) and lipids, proteins, and water in seafood (Oliveira et al., 2019). Among the current detection methods, the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method has been extensively modified and employed. However, partial modifications of the QuEChERS methods use hazardous organic solvents, and all sorbents are non-recyclable materials that may cause environmental and cost considerations.

To mitigate the concerns mentioned above, magnetic nanoparticles coated with various materials have been developed and applied to quantify analytes in bulk sample matrices because of their reusability and high selectivity (Chen et al., 2016; Liu et al., 2018). Previously, our group has proved that the magnetic nanoparticles coated with polystyrene (reusable nano-adsorbents) have a desirable selectivity to capture pyrethroid residues in matrices of fruit peels, fruit fleshes, vegetables, vegetable oils as well as environmental matrices of soil and water (Wongmaneepratip & Yang, 2021; Yu et al., 2017, 2018; Yu & Yang, 2017). Therefore, in the current study, we would like to enlarge the application of nano-adsorbents for monitoring pyrethroid residues in complex matrices of seafood products. In doing so, the optimization and validation of the analytical method are needed to appraise the method's performance.

Therefore, the aims of this research were to identify and validate the optimum conditions of the method based on nanoparticle-extraction coupled with simple low-temperature (freezing) cleanup and HPLC-PDA for pyrethroid quantification in mackerel fillet, and to apply the proposed method for PY detection and risk assessment on seafood samples purchased from local supermarkets in Singapore.

2. Materials and methods

2.1. Raw seafood samples

Seafood samples, including Spanish mackerel (*Scomberomorus commerson*), salmon (*Salmo salar*), sea bass (*Lates calcarifer*), threadfin fish (Polynemidae), tiger prawn (*Penaeus monodon*), vannamei prawn (Litopenaeus vannamei), shrimp (Litopenaeus setiferus), squid (Sepioteuthis sepioidea), grand jackknife clam (Ensis leei), and oyster (*Crassostrea iredalei*) were purchased from local supermarkets in Singapore. In this study, mackerel (meat and skin with a natural ratio) was used as a sample to investigate the optimization of the analytical method. After the validation, the final condition was applied to quantify pyrethroid residues in other seafood samples mentioned above for an extension of the scope.

2.2. Standards and reagents

Pyrethroid standards with a solid form of bifenthrin (>98.0%), cypermethrin (98.4%), deltamethrin (≥98.0%) and permethrin (98.3%) were purchased from Sigma Aldrich (St. Louis, MO, USA). The different concentrations of mix-standards were prepared by dissolving the powder in acetonitrile (HPLC-grade) obtained from Macron Fine Chemicals, USA.

The major parts of the analytical grade chemicals used for nano-adsorbent synthesis, including hydrated iron (II) chloride ($FeCl_2.4H_2O$), hydrated iron (III) chloride ($FeCl_3.6H_2O$), concentrated hydrochloric acid (HCl), methacrylic acid, oleic acid, potassium persulfate (KPS), sodium dodecylbenzenesulfonate (SDBS), and styrene, were obtained from Sigma Aldrich (St. Louis, MO, USA), while sodium hydroxide (NaOH) peal was acquired from Dickson Instrument & Reagent Store in Singapore. Acetic acid and methanol were procured from Macron Fine Chemicals, USA. Deionized (DI) water was generated using a Milli-Q purification system from Sartorius Stedim Biotech (Goettingen, Germany).

2.3. Preparation of nano-adsorbents and characterizations

Nano-adsorbents were synthesized based on the adapted method from Yu et al. (2018). A four-necked round bottom flask was set in a water bath at 70 °C and connected with a paddle stirrer, a condenser, a dropping funnel and a line of nitrogen gas which generated an N_2 atmosphere during the synthesis. A sodium hydroxide solution (1.5 mol/L) of 200 mL was loaded into the round bottom flask to heat up. Then, the mixed solution containing $FeCl_2{\cdot}4H_2O$ (1.76 g), $FeCl_3{\cdot}6H_2O$ (4.32 g), DI water (20 mL) and concentrated HCl (0.68 mL) was filled in the dropping funnel and added dropwise into the alkaline solution under vigorous stirring for 2 h to contribute Fe_3O_4. The synthesized Fe_3O_4 was cleaned thrice with water and dispersed into 200 mL of DI water in a new round bottom flask. Under the same conditions, 4 mL of oleic acid was added and mixed for 0.5 h. Subsequently, the solution was cooled down to room temperature before adding the SDBS solution (1.08 g of SDBS in 4 mL of DI water) and continuously stirred for 0.5 h to produce a colloidal solution. To initiate an emulsion polymerization of styrene, 50 mL of the colloidal solution was combined with 325 mL of DI water before mixing with 22.5 mL of styrene, 2.25 mL of methacrylic acid and 0.37 g of KPS dissolved in 6.25 mL of DI water. The mixture was vigorously stirred at 80 °C under an N_2 atmosphere for 6 h. The final product, nano-adsorbents, was rinsed thrice with water and thrice with methanol, respectively, before drying overnight in a convection oven prior use.

Both particles of the core structure Fe_3O_4 and nano-adsorbents were characterized via different techniques to confirm the successful synthesis and to examine the stability of nanoparticles. The shape of the core structure Fe_3O_4 before and after coating with polystyrene was identified on Cu-Carbon film by using the JEOL 3010 Transmission Electron Microscope (TEM) (JEOL, MA, USA). In addition, the size distribution and the zeta potential of particles were measured in the nanoparticle solutions (~1 mg/mL DI water) by a NanoBrook (Brookhaven Instruments Crop., NY, USA) (Bagwe et al., 2006). Furthermore, a Bruker-AXS D5005 instrument (Billerica, MA, USA) generated the X-Ray diffraction (XRD) patterns to verify the formation and stability of Fe_3O_4 before and after coating with polystyrene. The magnetic property of nanoparticles was also determined by the Lakeshore Vibrating Sample Magnetometer (VSM) under room temperature measurement. The chemical compositions of nano-adsorbents were identified by a PerkinElmer Spectrum One Fourier Transform Infrared (FT-IR) spectrometer (Waltham, MA, USA).

2.4. Variable factors for optimization design

An optimization process of analytical techniques is an important step in improving the method's performance. In the current study, low-temperature cleanup (freezing at −20 °C) was involved to remove interferences such as water, proteins, and lipids that are normally present in seafood samples, and the synthetic nano-adsorbents were applied to capture and pre-concentrate four pyrethroid residues (cypermethrin, deltamethrin, permethrin, and bifenthrin) in mackerel samples. During

magnetic solid-phase extraction, the method was modified based on a single variable optimization (Yu et al., 2017) to investigate the optimum conditions. Several factors, including the amount of nano-adsorbents (10, 30, 50, 70, and 90 mg), extraction time (10, 20, 30, 40, and 50 min), type of desorption solvent (methanol, acidified acetonitrile (3% acetic acid in acetonitrile), 75% acetonitrile in water, and 100% acetonitrile), the volume of desorption solvent (1, 2, 3, 4, 5, and 6 mL), and elution time (10, 30, 50, 70, and 90 s), were varied. There was only one factor changed while other factors were defined. The best conditions, providing the highest recovery, from each tested parameter were summarized and proposed as the optimum conditions for pyrethroid extraction.

2.5. Final extraction method

The final extraction method is clearly illustrated in Fig. 2A. Concisely, the procedures included the liquid-solid extraction of acetonitrile and minced sample, the simple cleanup method via −20 °C incubation for 12 h, the magnetic solid-phase extraction and the desorption process with the optimum conditions. The extracted solutions were dried at 35 °C with nitrogen gas and kept at −20 °C before HPLC analysis.

2.6. Method evaluation

Analytical performance of the proposed method using nano-adsorbents coupled with low-temperature cleanup was evaluated by assessing recoveries. Recovery measurements were studied by determining pyrethroid concentrations in mackerel samples spiked with the mix-standard solutions before (pre-extraction spike) and after (post-extraction spike) extraction at 0.5, 5.0, and 50 ng/g, with six replicates each. The recoveries were calculated as an area ratio of a sample spiked pre-extraction to a sample spiked post-extraction multiplied by 100. In addition, the repeatability (within-laboratory) was operated with three batches of mackerel samples by a researcher, and the reproducibility (within-laboratory) was performed by two researchers to evaluate the variation and precision of the proposed method.

In addition, the matrix effect was validated by injecting triplicates of solution standards in parallel with matrix-matched standards at concentrations ranging from 5 to 50 μg/L (5, 10, 15, 20, 25, 37.5, and 50 μg/L). The solution standards were prepared in acetonitrile while the matrix-matched standards were manipulated by spiked standard solutions into the blank sample at the end of sample preparation (post-extraction spike). The correlation coefficient (R^2) and root mean square error (RMSE) of the obtained equations were evaluated. Moreover, the slopes of contributed solution calibration curves and matrix-matched calibration curves were used to assess the matrix effect in percentage (%ME) by using the equation as follows (Pano-Farias et al., 2017):

$$\%ME = \left[1 - \left(\frac{Slope_{solution}}{Slope_{matrix-matched}}\right)\right] \times 100\%$$

2.7. Scope extension for other seafood samples

After the method evaluation was accomplished for mackerel samples, the application of the proposed method was extended to determine pyrethroid residues in other seafood samples obtained from local supermarkets in Singapore. Which included salmon, sea bass, threadfin fish, tiger prawn, vannamei prawn, shrimp, squid, grand jackknife clam, and oyster. Recoveries and contamination levels of four target pyrethroids with triplicates were measured in edible parts of the samples. The pre- and post-extraction spikes were performed at 5 ng/g.

2.8. HPLC analysis

The Water 2695 Alliance system of the high-performance liquid chromatography (HPLC) instrument equipped with an auto-sampler, a quaternary pump, and a photodiode array (PDA) detector was used to analyze the obtained extract. The separation of four target pyrethroids was carried out on a Luna 5 μ C18 column of 150 mm length, 4.6 mm internal diameter, and 100 Å pore size (Phenomenex, CA, USA) at 30 °C during the injection. The gradient system of DI water (A) and acetonitrile (B) was developed as follows: 0–30 min, 32% A; 31–40 min, 25% A; 41–50 min, 15% A (Wongmaneepratip & Yang, 2021). The flow rate and injection volume were adjusted to 1 mL/min and 20 μL, respectively. The extracted samples were reconstituted with 100 μL of acetonitrile assisted by sonication and then filtrated through a 0.22 μm membrane filter before injection.

2.9. Risk assessment

Risk assessment of pyrethroid exposure from seafood samples was calculated based on the detected pyrethroid levels, the accepted daily intake (ADI), and the estimated daily intake (EDI). The ADI values for cypermethrin, deltamethrin, permethrin, and bifenthrin were derived from database of the Joint FAO/WHO Meeting on Pesticide Residues or JMPR (http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticides/en/). The EDI values and hazard index (HI) in percentage were determined as follows (Liu et al., 2016; Seo et al., 2013):

$$EDI = (Average\ or\ highest\ detected\ pesticide\ level) \times \frac{Mean\ daily\ intake\ of\ seafood}{Average\ adult\ body\ weight}$$

$$HI\ (\%) = (EDI\ /\ ADI) \times 100$$

The mean daily intake of seafood among adult Singapore residents is 78.4 g, based on data from the Singapore government organization, the Health Promotion Board (https://www.hpb.gov.sg/), and the average body weight is 60 kg.

2.10. Statistical analysis

To obtain reliable and accurate results, the optimization study as well as the commercial samples' analysis was contributed in triplicates independently while the method evaluation was performed in six replicates independently. The results of the optimization and matrix effect study were presented in bar charts and line graphs, respectively, for simplification. Other results were displayed as mean values and the standard deviation (SD). The significant differences of data were assessed by a one-way ANOVA test (Analysis of Variance) at a confidence level of $P < 0.05$ using IBM SPSS statistics software.

3. Results and discussion

3.1. Nano-adsorbent characterizations

The core structure Fe_3O_4 and synthetic nano-adsorbents were

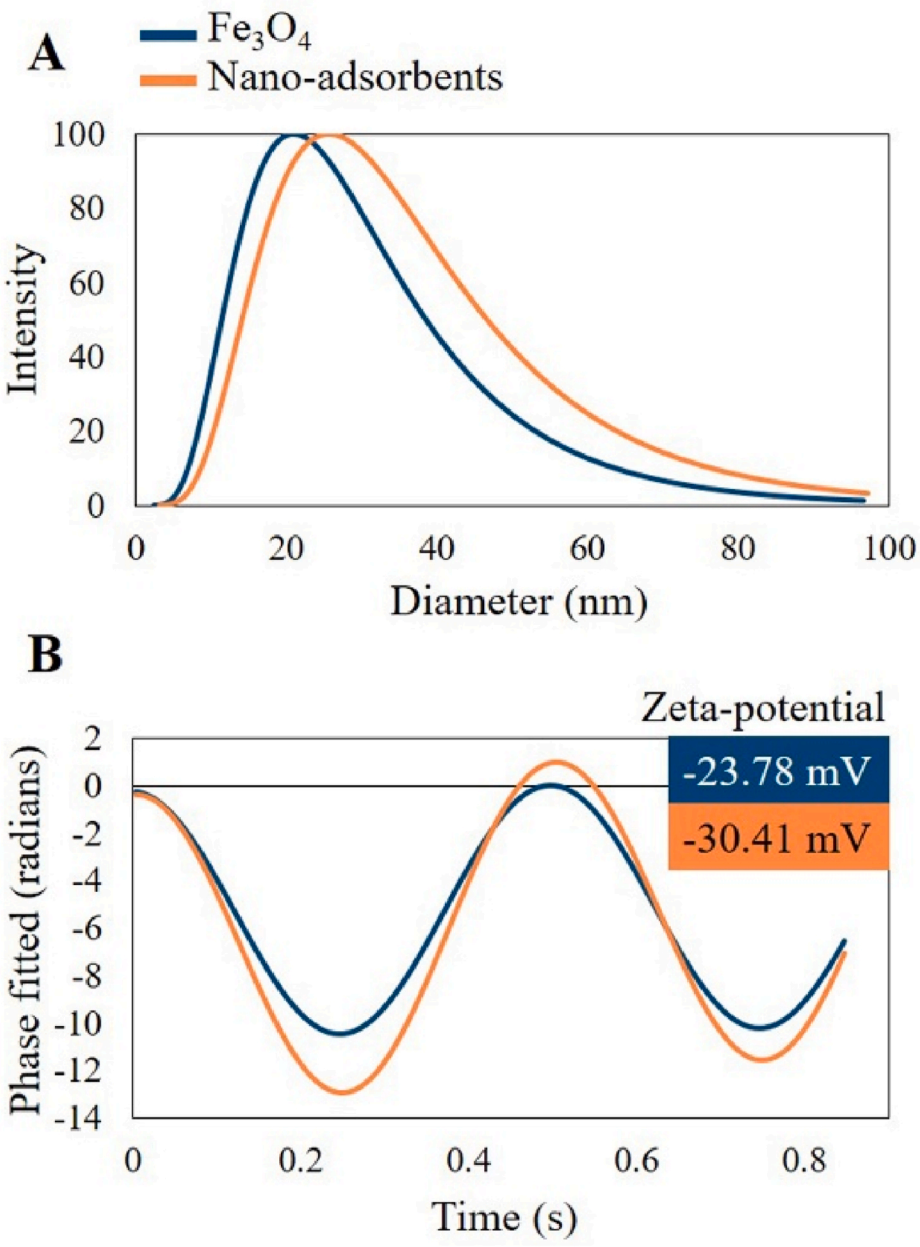


Fig. 1. Characterizations of the core structure Fe_3O_4 and synthetic nano-adsorbents: (A) Particle size distributions; and (B) Phase fitted of the Zeta-potential.

characterized with respect to particle shape, particle size, magnetic property, the structure of crystalline nanoparticles, the functional group of chemical compositions, and degree of stability. According to TEM images (Fig. S1A), both groups of nanoparticles were illustrated as a round shape with an estimated size of 15–25 nm. In addition, the particle size distributions of Fe_3O_4 nanoparticles and nano-adsorbents presented in Fig. 1A confirmed the effective diameters at 21.0 nm and 25.5 nm, respectively. Nano-adsorbents showed a bigger size owing to the coating layer of polystyrene compared with the uncoated Fe_3O_4. The larger particle size (25–60 nm) observed in the distribution graph and the coagulation remarked in TEM images demonstrate their magnetic property, which was evaluated by VSM. The VSM results, shown in Fig. S1B, indicate that the core structure Fe_3O_4 had magnetic saturation of 4.72×10^{-2} emu/mg Fe_3O_4. After coating with polystyrene, the magnetic saturation was lower to 2.40×10^{-2} emu/mg nano-adsorbents; however, this value was high enough for magnetic separation by a magnet during the extraction process (Wang et al., 2014).

Besides the characteristics mentioned above, the structure of Fe_3O_4 crystals was identified in accordance with the XRD spectra shown in Fig. S1C. The obtained peaks of 30.06°, 35.61°, 43.05°, 53.14°, 56.51°, and 62.47° in XRD spectra corresponded to the 220, 311, 400, 422, 511, and 440 crystal planes of Fe_3O_4 (Shagholani et al., 2015). This result verifies that Fe_3O_4 nanoparticles were successfully synthesized and retained their structure after coating with polystyrene. To assert the coating step of polystyrene onto Fe_3O_4 nanoparticles, the FT-TR analysis was used for identifying the functional groups of chemical compositions. The FT-IR spectrums (Fig. S1D) presented an absorption peak at approximately 580 cm^{-1} which attributed to the stretching vibration of Fe–O within the Fe_3O_4 lattice. Besides this peak, the additional peaks around 700 cm^{-1}, 1450 to 1600 cm^{-1}, and 3000 to 3100 cm^{-1} were also clearly visible. These peaks indicate the mono-substitution of the benzene rings, the bending vibration of –C═C– on benzene rings, and the stretching vibration of C–H on aromatic rings, respectively. Moreover, the absorption peaks of 2800–3000 cm^{-1} corresponded to the C–H symmetrical and asymmetrical stretching vibration (Hermán et al., 2015). The appearance of these absorption peaks supported the

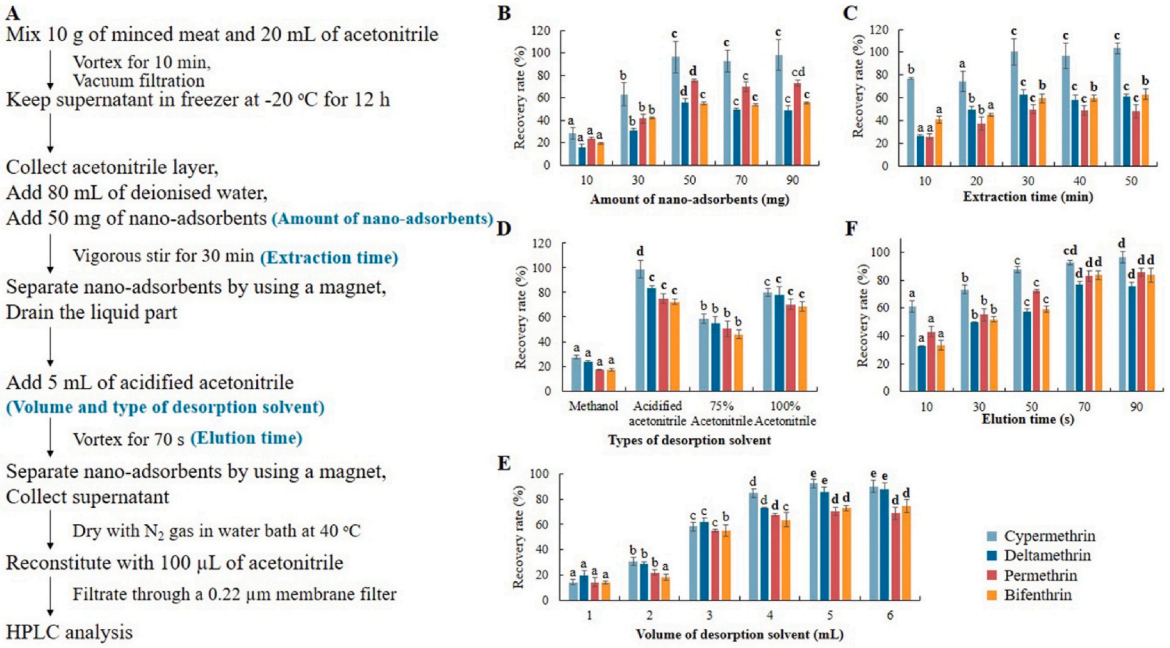


Fig. 2. (A) Process of pyrethroid extraction (low-temperature cleanup and magnetic solid phase extraction) with optimum conditions for seafood samples followed by HPLC-PDA analysis, and optimization results of variable factors affecting extraction performance; (B) Amount of nano-adsorbents; (C) Extraction time; (D) Type of desorption solvent; (E) Volume of desorption solvent; and (F) Elution time.

successful coating of polystyrene onto Fe_3O_4 nanoparticles. Finally yet importantly, the Zeta potential, which is a key parameter to determine the stability of nanoparticles, was measured based on phase analysis light scattering (PALS) measurements displayed in Fig. 1B. The absolute zeta potential of nano-adsorbents (30.41 mV) was higher than the Fe_3O_4 nanoparticles, indicating the greater stability of nano-adsorbents (Singh et al., 2014). The coating layer of polystyrene plays an important role in increasing the stability of Fe_3O_4 nanoparticles by reducing the aggregation rate. Based on different aspects of characterizations, the nano-adsorbents were efficiently synthesized with decent stability.

3.2. Optimization of magnetic solid-phase extraction

In this study, the four pyrethroids (cypermethrin, deltamethrin, permethrin, and bifenthrin) were set as the target compounds because of their detection frequency in the environment and food (Tang et al., 2018). Moreover, mackerel fillet (meat and skin with a natural ratio) was selected for the optimization and validation studies since it is cheap and highly consumed in both Europe and Asia (Cropotova et al., 2019).

In an analytical technique, variable factors can influence the quality of the method and, consequently, the significance of obtained results. In this study, nano-adsorbents coated with polystyrene were used to extract target pyrethroids from the intricate matric of mackerel fillets.

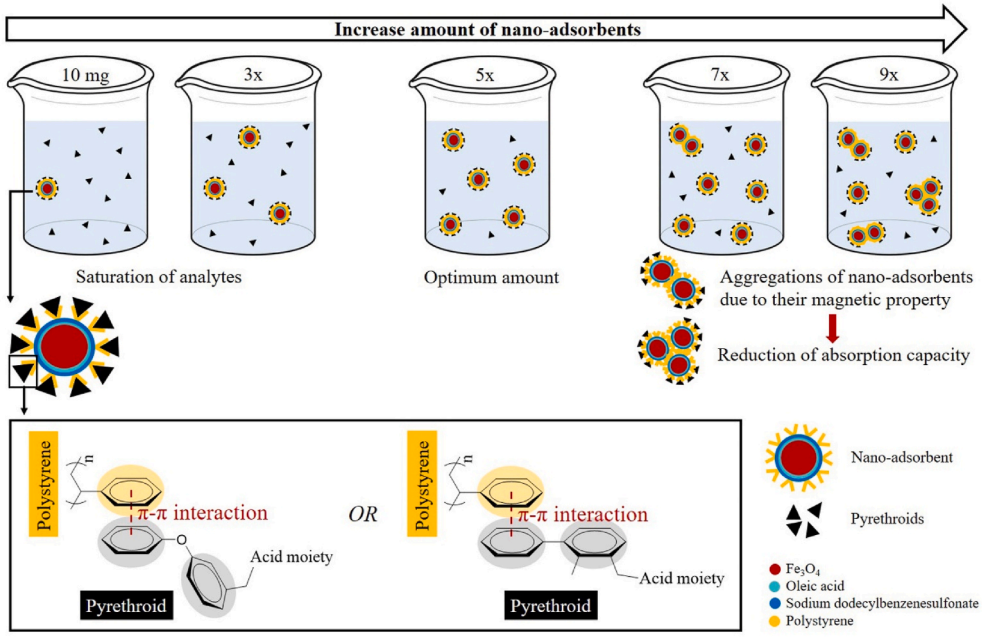


Fig. 3. Schematic of pyrethroid adsorption on the nano-adsorbents and the effect of adsorbent amount on the method's performance.

The schematic of pyrethroids adsorption on the nano-adsorbents is presented in Fig. 3. Polystyrene on the surface of nanoparticles can adsorb pyrethroid compounds via the possible interaction called π- π stacking (Aliakbar et al., 2016). This interaction is an attractive non-covalent interaction, which emerges via the π electronic cloud of two aromatic compounds. Therefore, the surface area of nano-adsorbent related to the amount of sorbent is one of the key factors affecting the efficiency of the extraction method.

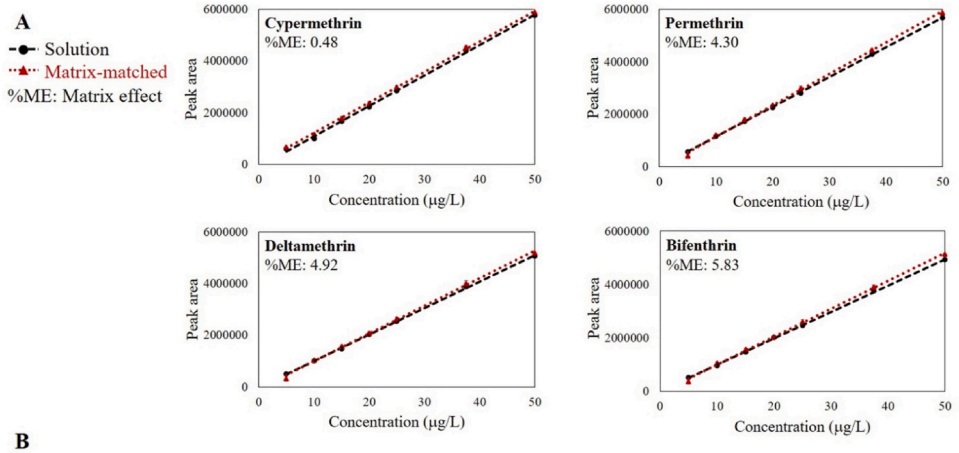
Apart from the quantity of sorbent, the other four parameters (extraction time, type of desorption solvent, the volume of desorption solvent, and elution time) also play an important role in method performance. The optimization results of all impacted factors are demonstrated in Fig. 2B–F as bar graphs. The amount of nano-adsorbents showed a significant effect on extraction efficiency. According to Fig. 2B, the recoveries of four target pyrethroids increased with increasing of nano-adsorbents until 50 mg, and then, the recoveries of deltamethrin and permethrin decreased after adding 70 and 90 mg of nano-adsorbents to the extracted system. The possible reason for decreasing absorption capacity is an excessive amount of nano-adsorbents and their magnetic property. Overabundant sorbents in the system reduced the distance between each nanoparticle and, with the assistance of their magnetic property, resulted in a convenient aggregation of particles (Fig. 3). This aggregation process lessened the surface area of each particle used to capture analytes and subsequently, negatively affected the recovery rate. Besides this reason, Yu and Yang (2017) proposed that the reduction of absorption capacity was caused by the saturation of analytes on the sorbents' surface. Hence, 50 mg of nano-adsorbents was the optimum amount in this study. In addition, this optimum amount of nano-adsorbents suggests that the suitable mass ratio of cypermethrin, deltamethrin, permethrin, and bifenthrin to the quantity of adsorbents were 0.19 ± 0.03, 0.11 ± 0.01, 0.15 ± 0.01, and 0.11 ± 0.01 ng/mg nano-adsorbent, respectively. The second parameter was the extraction time using 10 min intervals and its impact is illustrated in Fig. 2C. The recoveries of pyrethroids after 30, 40, and 50 min extraction processes did not show significant differences. Hence, using 30 min for solid-phase extraction was enough to complete pyrethroid adsorption from the extract solution.

After adsorption of analytes onto the surface of nano-adsorbents, the type of desorption solvent is one of the most critical factors, which impels a method ability. As presented in Fig. 2D, acidified acetonitrile (3% of acetic acid in acetonitrile, v/v) and 100% of acetonitrile were the potent solvents that could efficiently desorb deltamethrin, permethrin, and bifenthrin from the surface of nano-adsorbents. Due to the hydrophobic property of pyrethroids, they are able to dissolve well in acetonitrile rather than other tested polar solvents. However, the acidified acetonitrile was more effective to desorb cypermethrin; hence, it was used as an appropriate desorption solvent in this study. A similar result was reported by Yu et al. (2017), who recommended that the solution of acetonitrile fortified with acid was the most robust eluting solvent for pyrethroids measured in vegetable oils. The small amount of acetic acid may influence the strength of the π- π interaction between nano-adsorbents and analytes, resulting in the detaching of pyrethroids into the desorption solvent (Aliakbar et al., 2016). The volume of desorption solvent was also variable and the obtained results indicate that either 5 mL or 6 mL of acidified acetonitrile provided high recoveries with no significant difference. In terms of economic resources, the optimal volume to elute four pyrethroid species was 5 mL (Fig. 2E). This recommends that the optimum volume ratio of desorption solvents ranged from 1.85 ± 0.07, 1.72 ± 0.07, 1.41 ± 0.06, and 1.46 ± 0.05 ng/mL desorption solvent for cypermethrin, deltamethrin, permethrin, and bifenthrin, respectively.

The last optimized parameter was the elution time involved in the desorption process. According to Fig. 2F, the vigorous stirring of 70 and 90 s provided the highest recovery of analytes in comparison to the shorter time of 10, 30, and 50 s. Under similar conditions of physical force by vortex stirring, the longer time could provide a significant effect on completing the desorption process. Therefore, the optimal elution time required for this study was 70 s. Finally, the optimum conditions of various parameters for solid-phase extraction using nano-adsorbents coupled with low-temperature cleanup were summarized in Fig. 2A.

3.3. Method evaluation

The proposed method's performance was evaluated through various parameters. The solution and matrix-matched calibration curves as well as % ME of four target pyrethroids were validated and the results are



B

Analytes	LOD (µg/L)	LOQ (µg/L)	Solution curve	R^2	RMSE	Matrix-matched curve	R^2	RMSE
Cypermethrin	0.2428	0.8493	y = 117759x - 87292	0.9986	0.5422	y = 118328x + 19040	0.9993	0.2940
Deltamethrin	0.2311	0.7961	y = 102590x - 19657	0.9997	0.2522	y = 107199x - 83940	0.9977	0.5102
Permethrin	0.1474	0.5402	y = 113752x - 3360.9	0.9998	0.1956	y = 119717x - 59014	0.9986	0.3574
Bifenthrin	0.1516	0.5599	y = 98800x + 11369	0.9996	0.2777	y = 104920x - 57744	0.9984	0.3796

Fig. 4. (A) Comparison of standard solution and matrix-matched calibration curves and the matrix effect (%ME) for cypermethrin, deltamethrin, permethrin, and bifenthrin; (B) limit of detection (LOD), limit of quantification (LOQ), equation curves, correlation analysis (R^2) and root mean square error (RMSE) of four pyrethroids.

presented in Fig. 4A. The calibration curves of both solutions were almost the same line and the %ME of four pyrethroids ranged from 0.48 to 5.83%, indicating that there was a minor difference between the slopes of solution curves and matrix-matched calibrations (Pano-Farias et al., 2017). The small values of %ME also indicate the inconsiderable effect of sample matrices on the analytical method. Therefore, it can be considered that the solution calibration curves could be used to quantify four target pyrethroids in this study. Moreover, the details of R^2, RMSE, LOD, and LOQ for both types of calibration curves are presented in Fig. 4B. The good linearity of the calibration curves was observed through the R^2 values higher than 0.9977 and the prediction errors of the curves in terms of RMSE values were smaller than 0.5422. The LOD and LOQ performed by signal-to-noise ratios (S/N = 3 and S/N = 10, respectively) ranged from 0.15–0.24 and 0.54–0.85 ng/g, respectively. Furthermore, HPLC chromatograms of pyrethroid standards and mackerel extracts are displayed in Fig. 5. The HPLC chromatograms clearly showed the separation of four pyrethroid compounds without interference peaks presented at the similar retention times.

Apart from the evaluated parameters mentioned above, recovery results for four target pyrethroids at three different levels (0.5, 5.0, and 50 ng/g) are shown in Table 1. The results revealed sufficient recoveries of target pyrethroids ranged from 87.50–96.34% for cypermethrin; 87.27–92.64% for deltamethrin; 82.88–90.22% for permethrin; and 80.44–83.42% for bifenthrin. In addition, the repeatability contributed from different batches of samples ranged from 79.01 to 92.76% for four pyrethroids, and the reproducibility within the laboratory ranged from 78.84 to 88.38% with a standard deviation (SD) of 4.91 to 13.69%. These validation parameters represent a good performance of the proposed method that provided an acceptable recovery within the range of 70–120% (Kaczynski et al., 2017). In addition, the percent recoveries obtained from the three studies of recovery, repeatability, and reproducibility showed no significant difference ($P < 0.05$) for all target pyrethroids at different concentrations. This indicates that the performance of the proposed method was not influenced by different sample batches and individual personal errors of analysts. It could be concluded that combining low-temperature cleanup and nanoparticle-extraction using nano-adsorbents with the optimum conditions was the achieved method for quantifying pyrethroid residues in the complex matrix of mackerel fillets.

Table 1
The recoveries, repeatability (within-laboratory), and reproducibility (within-laboratory) of the proposed extraction method for pyrethroid quantification in mackerel samples.

Target compound	Spiked concentration (ng/g)	Recovery	Repeatability	Reproducibility
		Recovery ± SD (%)	Recovery ± SD (%)	Recovery ± SD (%)
Cypermethrin	0.5	87.50 ± 5.61	85.67 ± 7.31	80.93 ± 8.95
	5	96.34 ± 4.87	92.76 ± 5.90	87.38 ± 9.34
	50	88.54 ± 9.14	89.23 ± 10.89	81.47 ± 8.38
Deltamethrin	0.5	87.81 ± 3.35	84.67 ± 5.36	84.46 ± 11.16
	5	92.64 ± 10.79	88.14 ± 12.38	86.30 ± 5.23
	50	87.27 ± 7.35	87.98 ± 9.12	82.95 ± 5.98
Permethrin	0.5	82.88 ± 8.80	80.09 ± 10.32	85.29 ± 10.37
	5	90.22 ± 11.52	87.91 ± 9.16	88.38 ± 13.69
	50	85.81 ± 2.01	83.65 ± 6.75	83.10 ± 4.91
Bifenthrin	0.5	80.89 ± 3.38	81.06 ± 8.11	78.84 ± 10.78
	5	83.42 ± 9.72	80.72 ± 12.50	87.28 ± 6.43
	50	80.44 ± 5.96	79.01 ± 7.44	82.41 ± 8.66

3.4. Method's application for other seafood samples

Not only fish, but also other seafood products, are highly consumed food commodities (Watson et al., 2016). To extend an application of the proposed detection method, it was used to quantify pyrethroid residues in other seafood samples (salmon, sea bass, threadfin fish, tiger prawn, vannamei prawn, shrimp, squid, grand jackknife clam, and oyster) purchased from local supermarkets in Singapore. Pyrethroid concentrations in the tested seafood samples with recoveries are presented in Table 2. The proposed analytical method provided satisfied recoveries of four target pyrethroids in seafood samples, ranging from 75.95 to 96.81% with an SD lower than 12.89%. The range of recovery in this study is an acceptable range for a general analytical method (Chatterjee et al., 2016). Overall, pyrethroid contaminations in seafood samples (n = 30) were between N.D. to 11.28 ng/g edible part (Table 2). Among tested seafood samples in this study, residues of cypermethrin, permethrin, and bifenthrin were found in 90% of samples while deltamethrin was detected in 80% of samples. This finding relates to the frequency detection of pyrethroid compounds reported by Tang et al. (2018). The researchers described that cypermethrin was the most frequently detected pyrethroid in aquatic organisms and aquatic environment worldwide, while additional bifenthrin and deltamethrin were

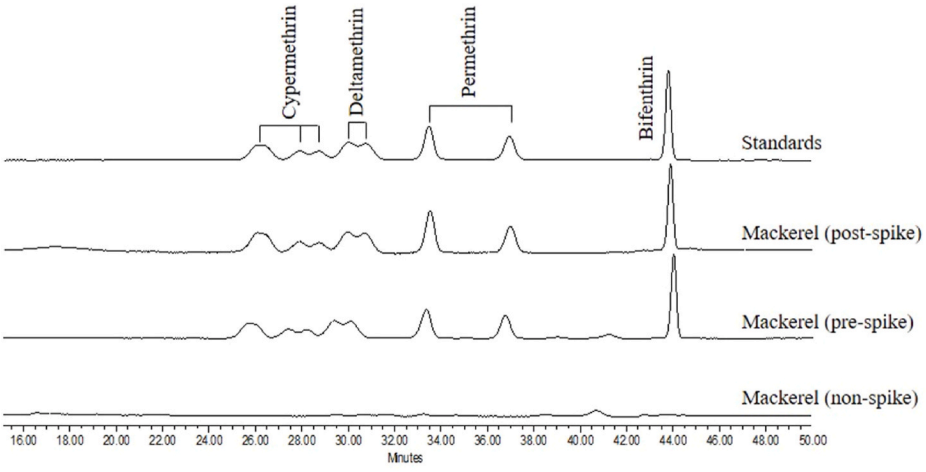


Fig. 5. HPLC chromatograms of pyrethroid standards and mackerel extracts (post-spike, pre-spike, and non-spike samples).

Table 2
Pyrethroid analysis in commercial seafood samples.

Analyte	Spanish mackerel		Sea bass	
	Detected ± SD (ng/g)	Recovery ± SD (%)	Detected ± SD (ng/g)	Recovery ± SD (%)
Cypermethrin	ND	86.71 ± 4.80	2.86 ± 0.14	87.71 ± 10.42
Deltamethrin	ND	87.69 ± 8.79	1.81 ± 0.18	89.82 ± 8.05
Permethrin	1.69 ± 0.17	80.29 ± 7.91	4.04 ± 0.48	84.77 ± 6.26
Bifenthrin	ND	77.01 ± 5.72	0.69 ± 0.14	79.30 ± 5.19
Total	1.69 ± 0.17		9.40 ± 0.94	
Analyte	**Salmon**		**Threadfin fish**	
	Detected ± SD (ng/g)	Recovery ± SD (%)	Detected ± SD (ng/g)	Recovery ± SD (%)
Cypermethrin	2.31 ± 0.13	82.66 ± 6.03	4.56 ± 0.55	87.28 ± 7.60
Deltamethrin	1.08 ± 0.17	80.89 ± 2.39	0.29 ± 0.12	90.14 ± 4.06
Permethrin	1.44 ± 0.16	77.18 ± 5.46	1.69 ± 0.41	85.07 ± 6.78
Bifenthrin	0.49 ± 0.17	75.95 ± 3.91	0.16 ± 0.07	81.62 ± 4.90
Total	5.32 ± 0.63		6.70 ± 1.15	
Analyte	**Tiger prawn**		**Vannamei prawn**	
	Detected ± SD (ng/g)	Recovery ± SD (%)	Detected ± SD (ng/g)	Recovery ± SD (%)
Cypermethrin	2.41 ± 0.61	90.30 ± 11.54	2.50 ± 0.18	90.76 ± 8.83
Deltamethrin	1.25 ± 0.11	90.10 ± 12.89	1.12 ± 0.21	92.31 ± 5.46
Permethrin	2.33 ± 0.17	87.89 ± 9.95	1.83 ± 0.19	90.41 ± 9.57
Bifenthrin	0.48 ± 0.07	81.11 ± 8.15	2.41 ± 0.21	84.04 ± 4.78
Total	6.47 ± 0.96		7.86 ± 0.79	
Analyte	**Shrimp**		**Squid**	
	Detected ± SD (ng/g)	Recovery ± SD (%)	Detected ± SD (ng/g)	Recovery ± SD (%)
Cypermethrin	6.69 ± 0.52	92.00 ± 9.78	11.28 ± 1.04	96.81 ± 12.16
Deltamethrin	ND	93.23 ± 11.74	7.79 ± 1.17	93.70 ± 6.91
Permethrin	1.11 ± 0.19	90.68 ± 8.59	0.65 ± 0.07	90.97 ± 7.66
Bifenthrin	3.61 ± 0.17	85.51 ± 7.55	0.66 ± 0.09	89.61 ± 8.30
Total	11.41 ± 0.88		20.38 ± 2.37	
Analyte	**Jackknife clam**		**Oyster**	
	Detected ± SD (ng/g)	Recovery ± SD (%)	Detected ± SD (ng/g)	Recovery ± SD (%)
Cypermethrin	2.86 ± 0.15	92.97 ± 6.44	3.50 ± 0.29	89.91 ± 5.68
Deltamethrin	4.41 ± 0.27	95.04 ± 8.57	1.87 ± 0.12	92.27 ± 5.19
Permethrin	ND	92.00 ± 5.69	1.08 ± 0.29	87.55 ± 7.81
Bifenthrin	0.28 ± 0.10	88.27 ± 7.47	0.39 ± 0.03	81.87 ± 4.82
Total	7.55 ± 0.52		6.84 ± 0.73	

highly reported in China.

As shown in Table 2, at least one of the target pyrethroids was detected in seafood samples (0.28–11.28 ng/g). The results depict that most of the fish samples (salmon, sea bass, and threadfin fish) contained a high level of cypermethrin (2.31–4.56 ng/g) or permethrin (1.69–4.04 ng/g) followed by deltamethrin (0.29–1.81 ng/g) and bifenthrin (0.16–0.69 ng/g), respectively, excepting the Spanish mackerel which found only permethrin (1.69 ± 0.17 ng/g). Likewise, high levels of cypermethrin (0.03–4.42 ng/g) and low levels of bifenthrin (N.D.–0.28 ng/g) in fish samples were revealed by Aznar-Alemany et al. (2017). The high level of cypermethrin (2.41–6.69 ng/g) was also detected in tiger prawns, vannamei prawns, and shrimp. In addition, squid, grand jackknife clam, and oyster were contaminated with high levels of cypermethrin (2.86–11.28 ng/g) and deltamethrin (1.87–7.79 ng/g) rather than permethrin (N.D.–1.08 ng/g) and bifenthrin (0.28–0.66 ng/g). Conversely, oyster samples collected in Spain found only permethrin (<0.02 ng/g) and bifenthrin (0.03 ng/g), but not cypermethrin nor deltamethrin (Gadelha et al., 2019). Pyrethroid residues in aquatic organisms are impacted by the contamination levels of their habitats. Cypermethrin and permethrin were the most frequently detected pyrethroids in water and sediment media worldwide (Tang et al., 2018); therefore, they have a higher potential to accumulate in aquatic organisms than deltamethrin and bifenthrin.

Other factors influencing contamination levels of pyrethroids in seafood are chemical properties of pesticide compounds, and sample characteristics. The octanol-water partition coefficient is a relative indicator describing the tendency of a pesticide to adsorb to living organisms and it is defined as the ratio of a pesticide in *n*-octanol and water. Among the target pyrethroids in this study, cypermethrin has the highest octanol-water partition coefficient at 6.54 (Laskowski, 2002), which indicates its higher potential for bioaccumulation in aquatic organisms. Moreover, in terms of specimen characteristics, the total fat content of samples is another noticeable reason for the accumulation of pesticides (Tsygankov et al., 2018). Generally, higher levels of hydrophobic pesticides tend to accumulate and persist in samples containing a high ratio of fat. However, the levels of bioaccumulation are heavily influenced by the type and concentration of pyrethroids in the surrounding environment. The seafood samples used in this study were randomly purchased from local supermarkets in Singapore, and they may come from different farms and areas of habitats where the dose and type of pyrethroid usage or contamination level are unknown. This demonstrates the limitation of comparing pyrethroid contamination levels among individual or groups of samples. Therefore, the comparison among uncontrolled samples was not taken into account in this study.

3.5. Safety and risk assessment

Regarding food safety, the levels of pyrethroids and other chemical contaminants in food are always restricted by the maximum residue limits (MRLs). However, the MRLs of pyrethroids for seafood products in Singapore and the international standard of FAO-WHO Codex Alimentarius (http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticides/en/) are still not defined or regulated. Therefore, in this study, the evaluation of pyrethroid residues in seafood samples was compared to the current MRLs (10 ng/g for individual cypermethrin, permethrin, and bifenthrin and 30 ng/g for deltamethrin) published by the Ministry of Agriculture, Livestock, and Food Supply, Brazil (Oliveira et al., 2019) and the EU Commission (50 ng/g for cypermethrin and 10 ng/g for deltamethrin) (EU European Commission, 2010). According to Table 2, the target pyrethroids in tested samples were lower than the MRLs regulated in Brazil, excepting cypermethrin residue (11.28 ± 1.04 ng/g) in squid which slightly exceeded the safety limit (10 ng/g). However, pyrethroid levels in all seafood samples were below the limit set by the EU Commission (EU European Commission, 2010). Hence, it may be deduced that the consumption of seafood samples obtained from local supermarkets in Singapore has a low risk in terms of pyrethroid contamination.

To support the conclusion above, the long-term consumer health risk

Table 3
Risk assessment of pyrethroid residues in tested seafood samples.

Compound	Detected residue level (ng/g sample)		EDI (× 10^{-6} mg/kg BW/day)	ADI (mg/kg BW/day)	HI (%)
Cypermethrin	Average	3.89	5.08	0.02	0.03
	Maximum	12.32	16.10	0.02	0.08
Deltamethrin	Average	1.96	2.56	0.01	0.03
	Maximum	8.96	11.71	0.01	0.12
Permethrin	Average	1.59	2.07	0.05	<0.01
	Maximum	4.52	5.91	0.05	0.01
Bifenthrin	Average	0.93	1.21	0.01	0.01
	Maximum	3.78	4.94	0.01	0.05

EDI: The estimated daily intake.
ADI: The acceptable daily intake (JMPR database).
HI: Hazard index.

was assessed based on the detected pyrethroid levels in this study and the results are displayed in Table 3. The results elaborated that EDIs ranged from 1.21 × 10^{-6} to 5.08 × 10^{-6} mg/kg BW/day and 4.94 × 10^{-6} to 16.10 × 10^{-6} mg/kg BW/day for the average and highest levels of the detected pyrethroids, respectively. The obtained EDIs caused the small values of HI (%), which were less than or equal to 0.12%. These estimated HIs (≤0.12%) indicate a negligible risk of exposure to four target pyrethroids via seafood consumption, presenting that the detected levels are not harmful to humans (Seo et al., 2013). Although the results demonstrate a negligible risk of seafood consumption, monitoring and precaution of total exposure to these pesticides from various foods should be considered. Apart from tested seafood samples in this research, pyrethroid residues have been detected in fruits and vegetables obtained from local supermarkets in Singapore (Yu et al., 2018; Yu & Yang, 2017). The consumption of various foods may exceed AIDs and increase the long-term health risk of consumers. Therefore, the monitoring study should be continuously performed and the MRLs should be regulated to ensure food safety and respond to public health concerns.

3.6. Comparison to preceding methods

Besides an extension of the method's application to various seafood samples, the proposed method was evaluated by comparing it to several existing methods for pesticide analysis in seafood products. The key parameters, including the type of sample, amount of adsorbent, adsorbent reusability, LOD, LOQ, matric effect, and recovery, were taken into account and the information is presented in Table S1.

The proposed method was applicable to different matrices of seafood samples without an extra preparation step of freeze-drying, which was needed in some preceding methods (Gadelha et al., 2019; Li et al., 2018; Oliveira et al., 2019). In addition, the adsorbent used in this study was a reusable material and its amount was at least 10 times lower than the sorbents applied in modified QuECHERS methods (Gadelha et al., 2019; Kaczynski et al., 2017; Li et al., 2018; Munaretto et al., 2013; Oliveira et al., 2019). This suggests that the current method is an economical method. Furthermore, the obtained LODs and LOQs of the proposed method were lower than or comparable to the majority of published methods presented in Table S1 (Gadelha et al., 2019; Jabeen et al., 2015; Kaczynski et al., 2017; Li et al., 2018; Munaretto et al., 2013; Riaz et al., 2018). Meanwhile, the acceptable range of recovery in various sample matrices was achieved. These methods' performances demonstrate the good sensitivity and accuracy of the proposed method. Moreover, the matric effect of the present method was fully studied and the data revealed the good ability (0.5–5.8 %ME) on the extraction of target compounds compared to the previous published methods (10.0–29.0 % ME) (Kaczynski et al., 2017; Oliveira et al., 2019). Therefore, the current method was an efficient analytical method for pyrethroid detection in various seafood samples.

4. Conclusions

The proposed method based on nanoparticle-extraction with optimum conditions achieved desirable recoveries ranged from 75.95 to 96.81% in different matrices of seafood samples (mackerel, salmon, sea bass, threadfin fish, tiger prawn, vannamei prawn, shrimp, squid, grand jackknife clam, and oyster). This demonstrates the promising feature of the method for monitoring pyrethroid residues in intricate samples that consist of different composition ratios of lipids and proteins. In view of the method application, further considerations can be organized to determine other pyrethroid compounds or toxic contaminants presented in seafood.

Despite the fact that pyrethroid levels detected in the tested seafood samples showed a negligible risk to human health, the monitoring study should be continuously performed and extended to other foods to minimize the risk and possible health effects of total pyrethroid exposure. Furthermore, the findings of this research can be used as evidence to advocate consideration for regulating the pyrethroids' MRLs of seafood in Singapore to ensure better safety of seafood consumption.

CRediT authorship contribution statement

Wanwisa Wongmaneepratip: Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing – original draft. **Melody Leong:** Formal analysis, Investigation. **Hongshun Yang:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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