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A simple co-precipitation sorbent-based preconcentration method for the analysis of fungicides in water and juice samples by high-performance liquid chromatography coupled with photodiode array detection

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Abstract

A magnesium hydroxide co-precipitation sorbent-based method in the presence of an anionic surfactant (e.g., sodium dodecylbenzenesulfonate) and high-performance liquid chromatography were used to preconcentrate and analyze fungicides in water and apple juice samples. The preconcentration procedure can be accomplished in a single step based on the co-precipitation of target fungicides and magnesium chloride in the presence of surfactant in a sodium hydroxide solution (pH 11) and a white precipitate gel was simply obtained after centrifugation. The property of precipitate phase was subsequently characterized using Fourier-transform infrared spectroscopy, scanning electron microscopy, and X-ray diffractometry. Under the optimum conditions, the developed method exhibited good sensitivity, with an enrichment factor of 11–18 and limits of detection of approximately 1–5 µg/L for water samples and 7–10 µg/L for apple juices. High reproducibility was achieved with a relative standard deviation of less than 11%, and a good recovery range of 72% to 120% was also obtained. The proposed method was shown to be a simple preconcentration procedure for concentrating fungicides in the samples investigated.

Keywords: Carbendazim, Thiabendazole, Fuberidazole, Sodium dodecylbenzenesulfonate, Metal hydroxide, HPLC

Introduction

Benzimidazole fungicides are a group of pesticides used to protect plants in agricultural areas from fungal infection. They can be sprayed directly on the crop or applied directly to it prior to and after harvest to avoid spoiling (Monzón et al. 2007; Zamora et al. 2009; Cacho et al. 2009). Among the active substances, carbendazim (CBZ) and thiabendazole (TBZ) are the most extensively used systematic fungicides (Zheng et al. 2020; Farooq et al. 2020; Su et al. 2020; Zhao et al. 2020; Yu et al. 2017; Deng et al. 2013). As a result, these fungicides may contaminate food (for example, fruits and vegetables) and environmental samples (e.g., water and soil). Teratogenicity, congenital abnormalities, polyploidy, diarrhea, anemia, pulmonary edema, and necrotic lymphadenopathy have all been linked to fungicide residues in humans (Danaher et al. 2007). The European Community established maximum residual limits (MRLs) of 0.1 and 0.5 µg/L for individual and total pesticides in drinking water samples (Wen et al. 2013; Zamora et al. 2000). The European

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Union (EU) has also defined MRLs for CBZ, TBZ, and fuberidazole (FuBZ) in apple samples of 0.2, 4, and 0.01 mg/kg (EU Pesticide database). It is desirable to monitor samples for fungicide contamination using a straightforward, quick, effective, and reliable method that involves proper sample preparation and instrumental analytical procedures for food and environmental safety.

Gas chromatography (GC) for the determination of benzimidazole fungicides has been limited and found in some application (Lesueur et al. 2008). Meanwhile, high-performance liquid chromatography (HPLC) and ultra-performance liquid chromatography (UPLC) have been widely demonstrated to be effective for single and simultaneous fungicide analysis when combined with several sample preconcentration strategies, including solid-phase extraction (SPE) (Yu et al. 2017), dispersive solid-phase extraction (dSPE) (Xu et al. 2016), matrix solid-phase dispersion combined with dispersive liquid–liquid microextraction (MSPD-DLLME) (Liang et al. 2021), and molecularly imprinted polymers (MIPs) (Farooq et al. 2020), molecularly imprinted SPE (MISPE) (Liang et al. 2019), and magnetic SPE (MSPE) (Zheng et al. 2020; Zhao et al. 2020; Deng et al. 2013; Li et al. 2020). Meanwhile, solvent-based extraction methods such as standard DLLME (Wu et al. 2009), salting-out assisted liquid–liquid extraction (SALLE) (Wen et al. 2013), and liquid–liquid microextraction using methyl benzoate, methyl salicylate, ethyl benzoate, and ethyl salicylate as alternative extractants (Santaladchaiyakit and Srijaranai 2014; Santaladchaiyakit et al. 2015, 2017, 2019, 2021a) have also been accepted as promising preconcentration strategies for fungicides in various sample matrices (e.g., food and environmental samples). Although each of these methods has distinct advantages, some limitations have been found, including a long process and tedious procedure, the use of toxic organic solvents, and relatively high solvent consumption. To overcome these problems, the alternative design based on simple and environmentally friendly preconcentration methods such as metal hydroxides are of interest for further development and applications.

Metal hydroxides using co-precipitation of a single M^{2+} (e.g., Mg^{2+}) or M^{3+} (e.g., Al^{3+}) ion under alkaline conditions have been highlighted for their ability to modify and become attractive as green adsorbents due to their nontoxicity, simplicity, rapidity, and in situ formation process. A $Mg(OH)_2$ co-precipitate form is the most frequently used for preconcentration or removal of various inorganic species (Zhu 2020; Moreira et al. 2020; Tsuchiya et al. 2020), and organic compound (Tsai et al. 2010). Meanwhile, $Al(OH)_3$ co-precipitation strategies were initially developed for the purpose of determining organic compounds, such

as organophosphorus pesticides (Mammana et al. 2017), estrogen (Xiao et al. 2013), and tetracyclines (Li et al. 2013). Surprisingly, the addition of an anionic surfactant [e.g., sodium dodecyl sulfate (SDS)] can enhance the extraction performance of $Al(OH)_3$ co-precipitate for target organic analytes (Xiao et al. 2013; Mammana et al. 2017), due to its hydrophobic and hydrophilic property. These techniques appeared to be effective in preconcentrating nonpolar compounds. To the best of our knowledge, the development of metal hydroxide-based co-precipitation as an extraction and preconcentration method for organic compounds, particularly fungicides, has not been reported. Additionally, the comparison of $Mg(OH)_2$ and $Al(OH)_3$ in the presence of anionic surfactants [e.g., SDS and sodium dodecylbenzenesulfonate (SDBS)] for increasing target fungicide extraction efficiency is also required to evaluate.

The proposed work aimed to develop and evaluate preconcentration strategies based on metal hydroxides via co-precipitation as a sorbent for the studied fungicides (e.g., CBZ, TBZ, and FuBZ) in environmental water samples and commercial apple juices, followed by HPLC analysis. SDS and SDBS were used as anionic surfactants to improve the extraction performance of metal hydroxides. Optimizations of extraction condition have been investigated, and the characterization of the precipitate phase and the possibility of extraction method were also discussed.

Experimental

Chemicals and solutions

All reagents used in this study are analytical reagent grade or higher. CBZ ($\geq 97\%$ purity), TBZ ($\geq 99\%$ purity), and FuBZ (99.5% purity) were purchased from Aldrich (China), Sigma (Italy), and Sigma-Aldrich (Germany), respectively. The stock solutions of fungicides (1000 mg/L) were prepared by dissolving in formic acid (500 μL) and then diluted with methanol (MeOH). The working solutions were daily made by diluting the stock solutions with deionized water. MeOH, acetonitrile (ACN), and formic acid were purchased from Merck (Germany). Ajax Finechem supplied magnesium chloride ($MgCl_2 \cdot 6H_2O$) and aluminum chloride ($AlCl_3 \cdot 6H_2O$) (Australia). BDH Prolabo® (Belgium) provided sodium dodecyl sulfate (SDS), while Sigma-Aldrich provided sodium dodecylbenzenesulfonate (SDBS) (France). NaOH was purchased from Kemaus (Australia). The solutions of magnesium chloride (300 mmol/L), aluminum chloride (300 mmol/L), SDS (10 mmol/L), SDBS (10 mmol/L), and 0.5 mol/L NaOH were prepared separately in deionized water. Unless otherwise specified, all

aqueous solutions were prepared in deionized water (RCI Labscan Ltd., Thailand).

Instrumentations

The HPLC system (Shimadzu, Japan) consists of an LC 20AD pump with an in-line degasser unit (DGU-20As), a photodiode array detector (PDA), and a system controller (LCsolution software). Separation of the target fungicides was accomplished using an Inertsil C8 column (4.6 mm × 150 mm, 5.0 μm) in conjunction with a guard C8 column (4.0 mm × 10 mm, 5.0 μm) (GL Science, Japan). The solution mixing and phase separation procedures were carried out using a vortex mixer Genie-2 model (Scientific Industries Inc., USA) and a centrifugation NF200 model (Nüve Inc., Turkey). For the characterization of the functional groups and morphology of precipitate phases, Fourier-transform infrared (FTIR) spectra were recorded using a PerkinElmer Spectrum Two® spectrometer (UK), and focused ion beam scanning electron microscopy (FIB-SEM) (Helios NanoLab G3 CX, FEI, USA) were used. Additionally, the X-ray diffraction (XRD) patterns were recorded using the Empyrean X-ray diffractometer (PAN-analytical, the Netherlands). The zeta potentials of the various precipitate phases were determined using a Zetasizer (Nano ZS, Malvern, UK) at a temperature of 25 °C and a dispersant of deionized water.

Chromatographic conditions

The gradient elution profile of mobile phases containing ACN and 0.1% (v/v) formic acid was used to separate target fungicides (Santaladchaiyakit and Srijaranai 2014; Santaladchaiyakit et al. 2015, 2019, 2021a) as shown in Additional file 1: Table S1. The flow rate was maintained at 1.0 mL/min, and the separation temperature was set to 25 °C. The sample loop with a volume of 20 μL was used. CBZ, TBZ, and FuBZ detections were measured at 281 nm, 302 nm, and 313 nm, respectively.

Co-precipitation Mg(OH)$_2$-SDBS extraction method

The solutions of 0.5 mol/L NaOH (200 μL), 300 mmol/L MgCl$_2$ (150 μL), and 10 mmol/L SDBS (350 μL) were subsequently added into the 10-mL standard (or sample) solution. The suspension (and/or cloudy) solution was observed (Additional file 1: Fig S1a). After being manually shaken for 10 s, the solution was vortexed at 1800 rpm for 30 s and subjecting it to centrifugation at 3000 rpm for 5 min. Consequently, the obtained precipitate phase of Mg(OH)$_2$-SDBS was observed at the bottom of solution (Additional file 1: Fig S1b). After decanting the aqueous phase, the precipitate was

dissolved in formic acid (200 μL) and subjected to a vortex mixer for 5 s to achieve complete dissolution. A total volume of the solution was about 380 μL (on an average). An aliquot of homogenized solution (20 μL) was analyzed by HPLC–PDA.

Characterization of precipitate Mg(OH)$_2$-SDBS phases

The precipitate phases were obtained after drying at room temperature (Additional file 1: Fig S2) before being subjected to phase property characterization. FTIR spectra, SEM images, and XRD patterns were studied. The Universal Attenuated Total Reflectance (UATR) mode was used to record FTIR spectra in the range of 400–4000 cm^{-1}. For SEM analysis, the samples were placed on aluminum stubs and coated with a gold-thin layer prior to measurements. An X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) was used to investigate XRD patterns covering the 2θ in the range of 5°–80°.
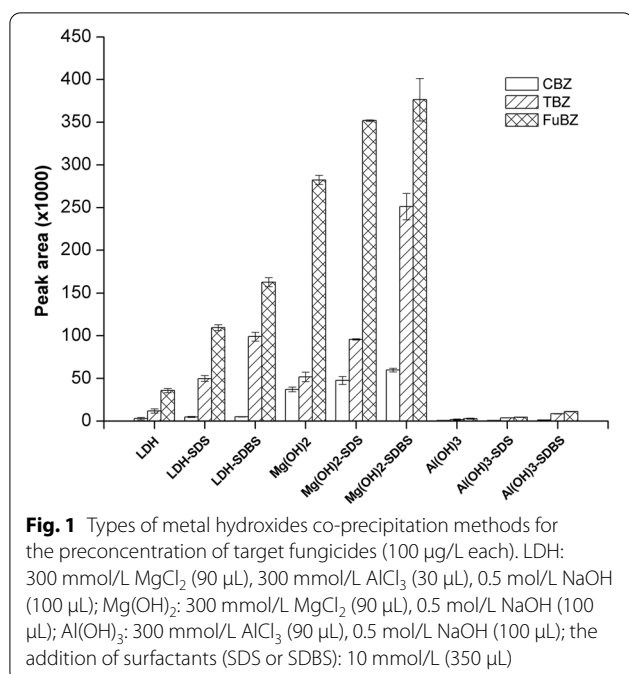
Sample preparation

A variety of water sample matrices, including drinking, pond, and lake water, were analyzed. A sample of drinking water was purchased from a local market in Khon Kaen province (Thailand). Pond and lake water samples were collected from agricultural area in Khon Kaen province. The water samples were kept at a constant temperature of 5 °C until analysis. Water samples were firstly filtered through filter papers (Whatman No. 1) and nylon membranes (0.45 μm, Whatman). Extraction and HPLC analysis were performed on aliquots of 10 mL samples.

Apple juice samples (red apple, green apple, and white grape-mixed green apple) were purchased from a supermarket in Khon Kaen (Thailand). The juice samples were stored at a temperature of 5 °C until analysis. All apple juice samples were filtered through 0.45 μm nylon membranes and diluted 10 times with deionized water. The 10-mL diluted juice samples were then extracted by the proposed preconcentration procedure and followed analyzed by the HPLC technique.

Result and discussion

Selection of metal-hydroxide co-precipitation systems

The various co-precipitation conditions of metal hydroxides, including Mg(OH)$_2$, and Al(OH)$_3$ compared with Mg/Al layered double hydroxide (LDH), were explored for preconcentrating target fungicides, as shown in Fig. 1. Without surfactants, the order of extraction efficiency was Mg(OH)$_2$ >>> LDH > Al(OH)$_3$. When surfactants are introduced to extraction systems, the efficiency of those three methods, particularly SDBS, can be increased. Additionally, it was found that SDBS was significantly more efficient than SDS. This could be because SDBS has a higher degree of hydrophobicity than SDS (i.e., longer

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Fig. 1 Types of metal hydroxides co-precipitation methods for the preconcentration of target fungicides (100 μg/L each). LDH: 300 mmol/L MgCl$_2$ (90 μL), 300 mmol/L AlCl$_3$ (30 μL), 0.5 mol/L NaOH (100 μL); Mg(OH)$_2$: 300 mmol/L MgCl$_2$ (90 μL), 0.5 mol/L NaOH (100 μL); Al(OH)$_3$: 300 mmol/L AlCl$_3$ (90 μL), 0.5 mol/L NaOH (100 μL); the addition of surfactants (SDS or SDBS): 10 mmol/L (350 μL)

Fig. 2 Effect of NaOH volume on the extraction recovery of target fungicides (100 μg/L each). Conditions: 300 mmol/L MgCl$_2$ (90 μL), 0.5 mol/L NaOH, and 10 mmol/L SDBS (350 μL)

carbon chain length and benzene ring in the structure), allowing for greater penetration of target analytes into precipitate Mg(OH)$_2$-SDBS phases. Notably, the formation of metal hydroxides in the absence of surfactants, particularly for Al(OH)$_3$, was less efficient and the phase was more difficult to collect following centrifugation. According to the zeta potentials listed in Additional file 1: Table S2 (systems #1–3), it was observed that the positive zeta potentials of metal hydroxides were in the following order: Al(OH)$_3$ > LDH > Mg(OH)$_2$. In the presence of anionic surfactants, the zeta potentials decreased, particularly for SDBS in system #2 (i.e., Mg(OH)$_2$ precipitate phase). The positive zeta potentials were confirmed the positive charges of metal hydroxides. For the decrease in positive zeta potentials, it can be believed that anionic surfactants were adsorbed onto metal hydroxide precipitate phases. Based on the results above, the co-precipitation of Mg(OH)$_2$-SDBS was chosen as the best efficient condition for further experiments in this work.

Optimization of Mg(OH)$_2$-SDBS co-precipitation method
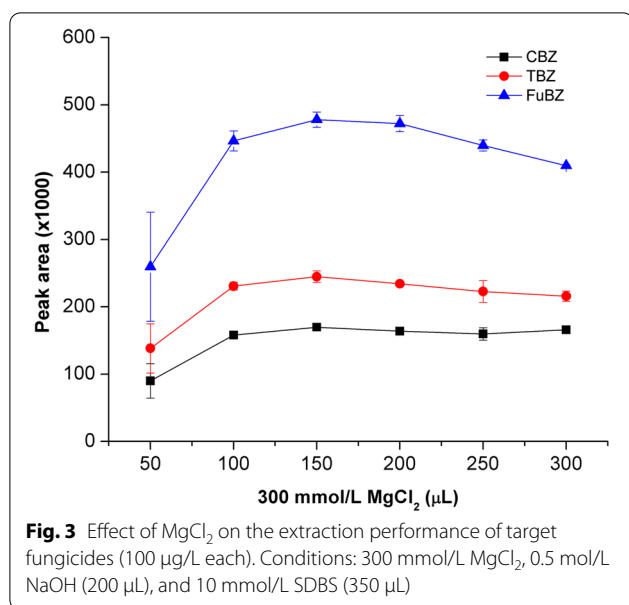### Effect of volume of NaOH solution
The pH of aqueous sample solutions has an effect on the co-precipitation of Mg(OH)$_2$, which forms completely in the basic media and thus has an effect on the extraction efficiency of target fungicides. When the pH of the solution is less than 12.4, it has been observed that the Mg(OH)$_2$ surface has a positive charge (Tsuchiya et al. 2020). The positive zeta potentials of Mg(OH)$_2$ precipitate phases (see Additional file 1: Table S2, systems 2.1
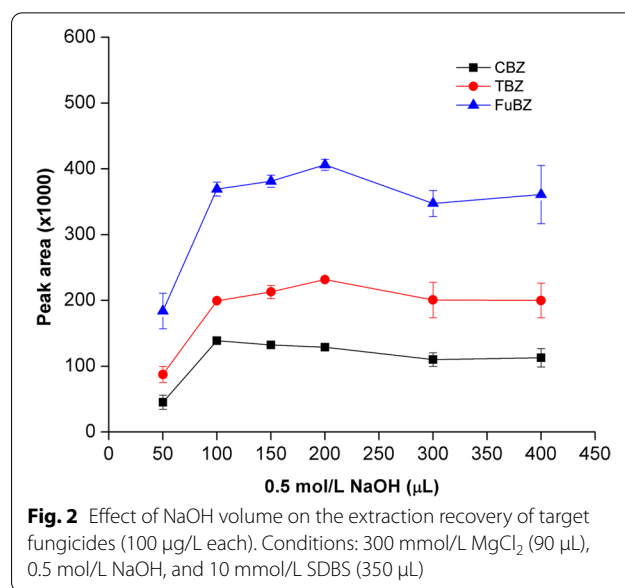
and 4.1) of about + 12.4 and + 17.5 mV depending on the specific co-precipitation conditions confirm this assumption. Volumes of 0.5 mol/L NaOH in the range of 50–400 μL, corresponding to solution pHs of 9–12, were studied in this work. It is worth noting that the original standard solution had a pH of around 5–6. As illustrated in Fig. 2, increasing the volume of NaOH improved the extraction performance of target compounds, particularly when the volume was increased from 50 to 100 μL and the pH was increased from 9 to 10. At increased NaOH volumes up to 200 μL (pH 11), only TBZ and FuBZ exhibited an increase in extraction efficiency, whereas CBZ exhibited a decrease in extraction performance. After that, the extraction performance of all the analytes was seen to degrade. The drop in positive zeta potentials was also observed (data not shown) when the NaOH volume was increased to 200 μL and then decreased less dramatically. This phenomenon may be due to the deprotonation of target fungicides in strong basic solutions (particularly pHs > 12) (Danaher et al. 2007), resulting in repulsion between the negative charges of target fungicides and the SDBS in the excess OH$^-$ medium. Thus, a volume of 0.5 mol/L NaOH of 200 μL (ca. 10 mmol/L) was chosen as the optimal value for the further experiments.

Effect of volume of magnesium chloride solution
The concentration of Mg^{2+} in the basic solution has an effect on the precipitation of Mg(OH)$_2$. Inadequate Mg^{2+} and OH$^-$ cannot form the white precipitate metal hydroxide phase entirely. The extraction efficiency of target fungicides was investigated using MgCl$_2$ volumes

Fig. 3 Effect of MgCl$_2$ on the extraction performance of target fungicides (100 µg/L each). Conditions: 300 mmol/L MgCl$_2$, 0.5 mol/L NaOH (200 µL), and 10 mmol/L SDBS (350 µL)

Fig. 4 Effect of SDBS concentration on the extraction performance of target fungicides (100 µg/L each). Conditions: 300 mmol/L MgCl$_2$ (150 µL), 0.5 mol/L NaOH (200 µL), and 10 mmol/L SDBS

ranging from 50 to 300 µL (about 1.5–9 mmol/L) (Fig. 3). It was clearly noted that the extraction efficiency of the examined analytes increased significantly when the volume was increased to 100 µL and then to 150 µL. After that, a trend for efficiency to become constant over the volume ranges studied was noticed, especially for CBZ and TBZ. This may be because of the formation of a complete complex between positively charged Mg(OH)$_2$ species and negatively charged SDBS, which results in the highest adsorption capacity. As a result, 150 µL MgCl$_2$ (ca. 4.5 mmol/L) was chosen for subsequent experiments.

Effect of concentration of SDBS

Anionic surfactants, such as SDBS, contain both hydrophobic and hydrophilic moieties, and their negative charges can interact with the positive charges of magnesium hydroxide to form surfactant-magnesium hydroxide. As a result, they can increase the efficiency of nonpolar analytes' extraction by promoting their incorporation into a hydrophobic medium. Additionally, surfactants can facilitate the precipitation and formation of metal hydroxide precipitate phases. The separation of two phases (i.e., precipitate and aqueous) can easily be performed by decanting the tube, while it was difficult to separate the phases in the absence of surfactant due to its suspension in bulk solution. As illustrated in Fig. 4, SDBS was investigated in this study at concentrations ranging from 0 to 0.4 mmol/L. The peak areas of the studied fungicides increased significantly in comparison with those without surfactant, where SDBS concentrations increased up to 0.35 mmol/L. The positive zeta potential decreased with the addition of SDBS and target
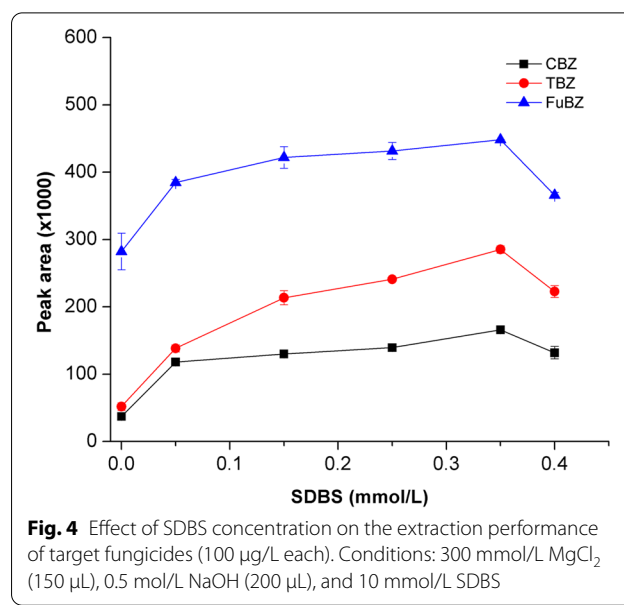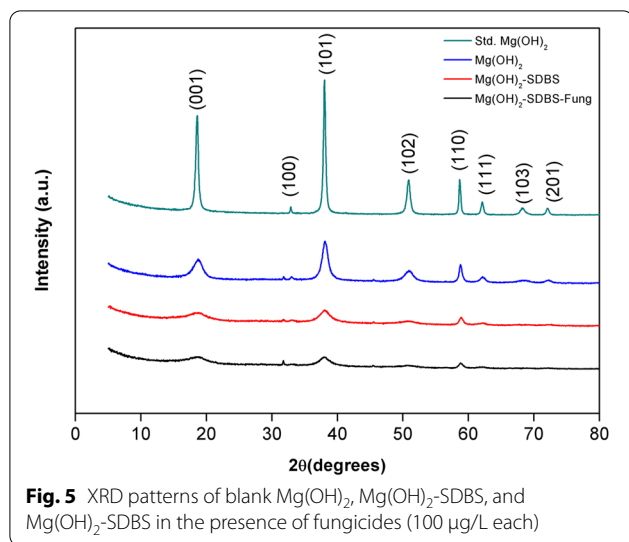
fungicides in this condition (Additional file 1: Table S2, system #4). A higher SDBS concentration may interfere with the mass transfer of target analytes (via self-competition), resulting in decreased extraction efficiency. Thus, for subsequent experiments, an SDBS concentration of 0.35 mmol/L was chosen.

Effect of vortex agitation and centrifugation

Vortex agitation and centrifugation were investigated at speeds ranging from 0 to 3000 rpm for 0 to 60 s and 1000 to 5000 rpm for 1 to 10 min, respectively. As illustrated in Figures S3 and S4, increasing the vortex speed (Additional file 1: Fig S3a) and time of the vortex (Additional file 1: Fig S3b) significantly improved the extraction efficiencies of target fungicides when compared to those of without vortex agitation. Because higher agitation had no effect on extraction performance, the optimal vortex agitation rate was 1800 rpm for 30 s. Meanwhile, from 1000 to 2000 rpm, centrifugation speed appeared to have a significant effect on extraction performance (Additional file 1: Fig S4a). After 3000 rpm, the increase was less significant and remained constant throughout the range of studies. Centrifugation time (Additional file 1: Fig S4b) was found to be most effective at 5 min and decreased thereafter. Thus, 3000 rpm for 5 min was chosen as the optimal centrifugation speed.

Characterization of metal-hydroxide-SDBS phases

The XRD patterns of the samples are shown in Fig. 5, including commercial Mg(OH)$_2$ (as a reference material), precipitate Mg(OH)$_2$ without and with SDBS, and Mg(OH)$_2$-SDBS-Fungicides. The precipitate Mg(OH)$_2$

Fig. 5 XRD patterns of blank $Mg(OH)_2$, $Mg(OH)_2$-SDBS, and $Mg(OH)_2$-SDBS in the presence of fungicides (100 μg/L each)

Fig. 6 FTIR spectra of **a** commercial $Mg(OH)_2$, **b** synthesized $Mg(OH)_2$, **c** SDBS, **d** $Mg(OH)_2$-SDBS, and **e** $Mg(OH)_2$-SDBS in the presence of fungicides (100 μg/L each)

sample's peaks for (001), (100), (101), (102), (110), (111), (103), and (201) planes can be confirmed to be $Mg(OH)_2$ (Shen and Liu 2016). The presence of organic substances (e.g., SDBS and fungicides) changed the intensity and shape of all $Mg(OH)_2$ planes, resulting in lower intensity and broader peaks, indicating that $Mg(OH)_2$-SDBS has a lower crystallinity. This trend was obvious for the $Mg(OH)_2$-SDBS-Fungicides. The d-spacing values for the phases under conditions were calculated as shown in Additional file 1: Table S3. The d-spacing values of (001) for $Mg(OH)_2$ were found to be around 0.47–0.48 nm, whereas the layer structures (i.e., the LDHs) had a d-spacing value of around 0.7–0.8 nm (Santaladchaiyakit et al. 2021b; Molefe et al. 2015).

Figure 6 shows the FTIR spectra of commercial $Mg(OH)_2$, precipitate $Mg(OH)_2$, SDBS, precipitate $Mg(OH)_2$-SDBS, and precipitate $Mg(OH)_2$-SDBS after fungicide extraction. Sharp absorption peaks near 3700 cm^{-1} were attributed to Mg-OH stretching vibrations (Shen and Liu 2016; Wu et al. 2020; Ansari et al. 2018), while broad peaks near 3360–3370 cm^{-1} were identified to OH bond stretching vibrations, and OH bending vibrations have been observed at around 1500 cm^{-1} (Shen and Liu 2016). The peaks between 2800 and 3000 cm^{-1} and 1000 and 1200 cm^{-1} were used to confirm the surfactant's asymmetric and symmetric CH_2 stretching and S=O modes. Based on these findings, it is reasonable to assume that co-precipitation of $Mg(OH)_2$ and SDBS could form under the conditions investigated. Notably, the presence of target fungicides had a much smaller effect on the FTIR spectrum of the precipitate $Mg(OH)_2$-SDBS.
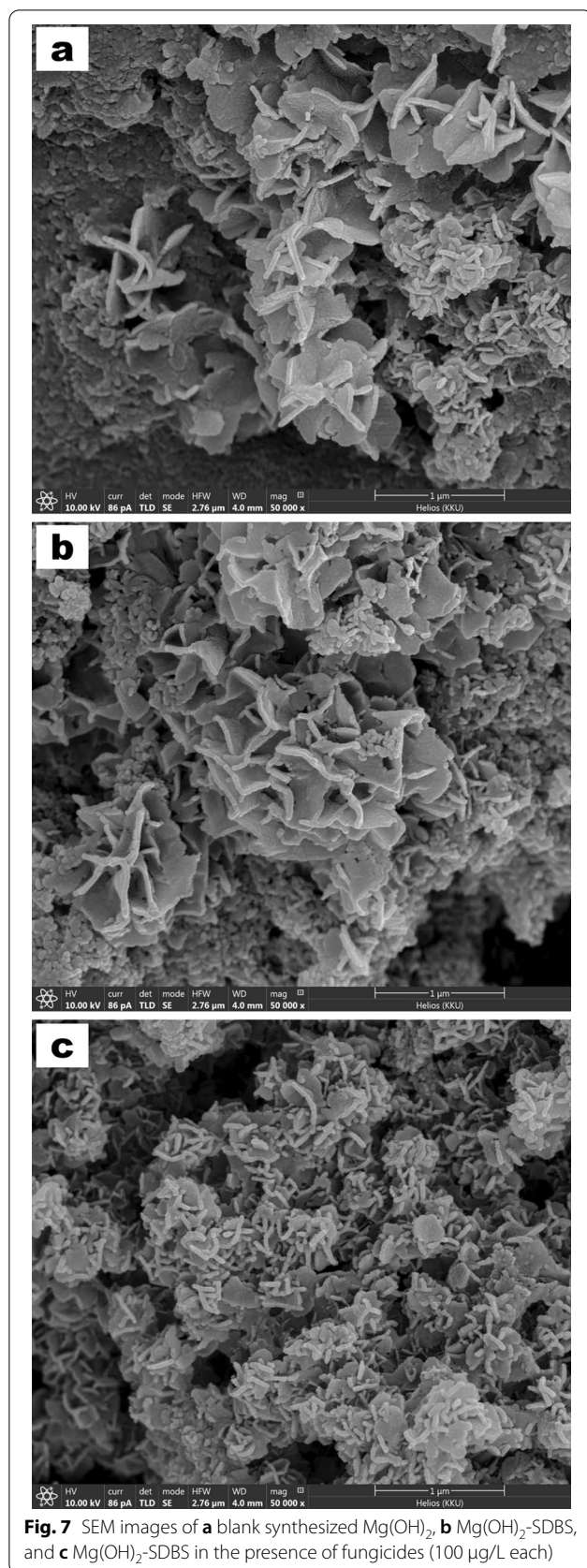
The surface morphology of precipitate $Mg(OH)_2$ in the presence of SDBS and target fungicides is depicted
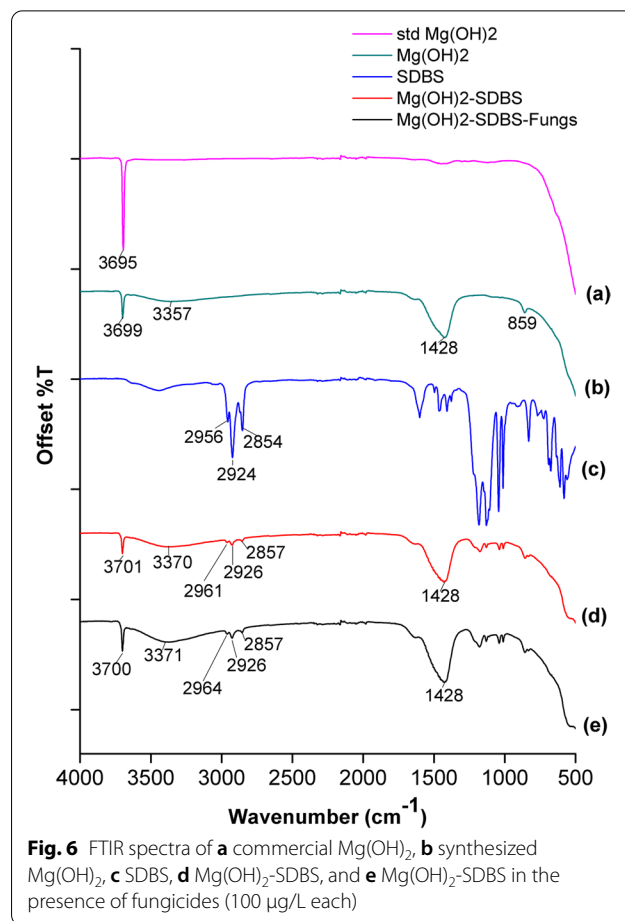
in Fig. 7. It was observed that unmodified or blank precipitate $Mg(OH)_2$ particles produced fewer platelets, whereas SDBS produced numerous flower-like forms. It is reasonable to assume that the surfactant enhanced the particle structure for adsorption of the target analytes. The extraction and preconcentration of target fungicides resulted in the formation of a significant amount of flower-like aggregates of the $Mg(OH)_2$-SDBS-Fungicides. It is possible that target fungicides are adsorbed to or being included in $Mg(OH)_2$-SDBS aggregates.

Analytical characteristics and validation of the method

The analytical performances of the proposed method were also evaluated, including linearity with the determination coefficient (R^2), limits of detection (LODs), and limits of quantitation (LOQs), as well as precisions (i.e., intra-day and inter-day). The analytical characteristics of the proposed method for standard fungicides under optimum conditions are summarized in Table 1. Linearities were obtained between 0.1 and 200 μg/L with an R^2 greater than 0.995. Additionally, the LODs and LOQs were achieved in the concentration ranges

Fig. 7 SEM images of **a** blank synthesized Mg(OH)$_2$, **b** Mg(OH)$_2$-SDBS, and **c** Mg(OH)$_2$-SDBS in the presence of fungicides (100 µg/L each)

of 0.1–0.3 and 0.3–1.0 µg/L, respectively. Meanwhile, without preconcentration (direct analysis), LODs and LOQs in the ranges of 3–10 and 30–100 µg/L were obtained. The intra-day and inter-day precisions were investigated using relative standard deviations (RSD, %) of 50 and 20 µg/L. The results indicated that high precision with an RSD of less than 10.2% was obtained.

The enrichment factor (EF) for the extraction performance of the target fungicides was calculated based on a slope ratio of the calibration curves obtained with preconcentration (S_{ex}) and without preconcentration (S_o), as shown in Table 1. When compared to direct analysis (without preconcentration), the proposed method improves sensitivity with the EF for approximately 11–18. Additional file 1: Fig S5 demonstrates the overlaid chromatograms of target fungicides obtained from without and with preconcentration using Mg(OH)$_2$-SDBS. The extraction recovery (ER) of the proposed preconcentration method was also evaluated for the target analytes at 50 µg/L. At the optimum preconcentration condition, the calculated ER was obtained in the range of 42–68% (see Table 1).

The robustness of the developed method was investigated by making minor adjustments (i.e., upper and lower) to method parameters such as mobile phase composition [i.e., formic acid (%)], flow rate, and detection wavelengths. The standard deviation (SD) and %RSD of peak area and retention time were determined. The data obtained from each parameter ($n = 9$) were also analyzed using a one-way ANOVA test at a confidence level of 95% ($p < 0.05$). The results obtained for each fungicide are displayed in Additional file 1: Tables S4–S6. Peak area and retention time with the %RSDs below 5.2 and 1.1, respectively, were obtained and considered acceptable. Except for carbendazim, the variations in formic acid (%) content, flow rate, and detection wavelength had no statistically significant effect on peak area ($p > 0.05$). Meanwhile, the concentration of formic acid and the flow rate of mobile phase significantly altered ($p < 0.05$) the retention time, particularly the flow rate. Note that the wavelength used for detection had no significant effect ($p > 0.05$) on the retention time shifts of the investigated compounds. Changes in the investigated parameters of the proposed method had no effect on the resolution of the target fungicides (data not shown). Therefore, the proposed method was robust.

The accuracy in terms of recovery of the spiked analytes (50 µg/L) in pure water samples ($n = 6$) was investigated. Additional file 1: Table S7 summarizes the accuracy evaluation of the proposed method. It was found that good recovery was obtained in the range

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Table 1 Analytical performance of the proposed preconcentration method for standard fungicides in pure water

Analyte	Linearity (µg/L)	Linear equation	R^2	LOD (µg/L)	LOQ (µg/L)	Intra-day precision[a] ($n = 4$)		Inter-day precision[a] ($n = 4 \times 3$ days)		EF[b]	ER[c] (%)
						Peak area	t_R	Peak area	t_R		
CBZ	0.3–200	$y = 949.3x - 2516.2$	0.9953	0.3	1.0	1.8 (3.8)	0.6 (2.7)	3.3 (9.3)	2.7 (3.6)	11	42
TBZ	0.1–200	$y = 2576.2x - 7813.2$	0.9968	0.1	0.3	1.7 (2.2)	1.4 (2.8)	5.5 (9.9)	2.7 (3.6)	18	68
FuBZ	0.1–200	$y = 3849.3x - 10{,}437.0$	0.9978	0.1	0.3	0.2 (2.5)	1.3 (2.6)	4.8 (10.2)	2.6 (3.2)	12	46

[a] Precisions were evaluated and expressed as the %RSD of peak area and retention time (t_R) for the concentration of 50 and 20 µg/L (in the parentheses)

[b] Enrichment factor (EF): ratio of the slopes of the calibration curves obtained with preconcentration (S_{ex}) and without preconcentration (S_o)

[c] Extraction recovery: $[EF \times \frac{V_{ex}}{V_o}] \times 100$; where V_{ex} and V_o are volumes of extraction phase (~0.380 mL) and original sample phase (10.00 mL), respectively

of 81.5–87.6% and an RSD of less than 6.1% was also observed.

Sample analysis

The proposed method was then applied to determine fungicides in water samples (e.g., drinking, pond, and lake) and apple juices (e.g., red apple, green apple, and white grape mixed with green apple). For complex sample analyses, the matrix effect (ME, %) should be calculated based on the ratio of the calibration slopes obtained in the sample and solvent (Bazmandegan-Shamili et al. 2018). The matrix effect level can be indicated by the ME (%) as follows: 80–120 (no effect); $50 \leq ME(\%) < 80$, and $120 < ME(\%) \leq 150$ (minor
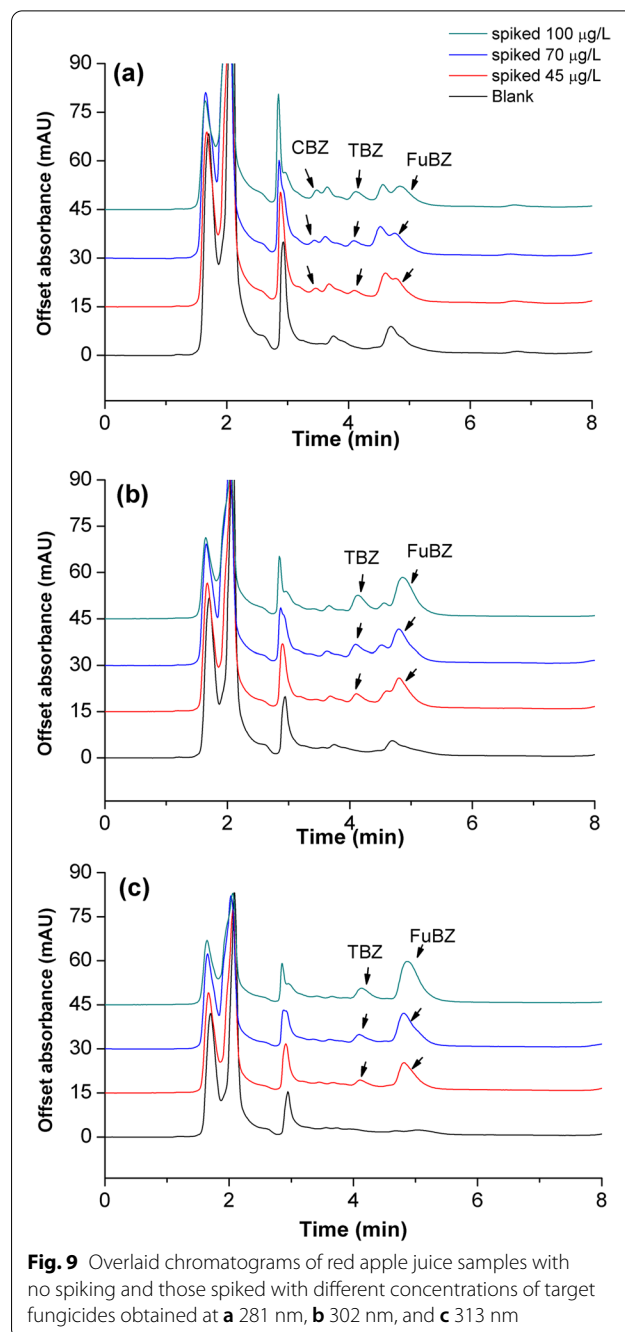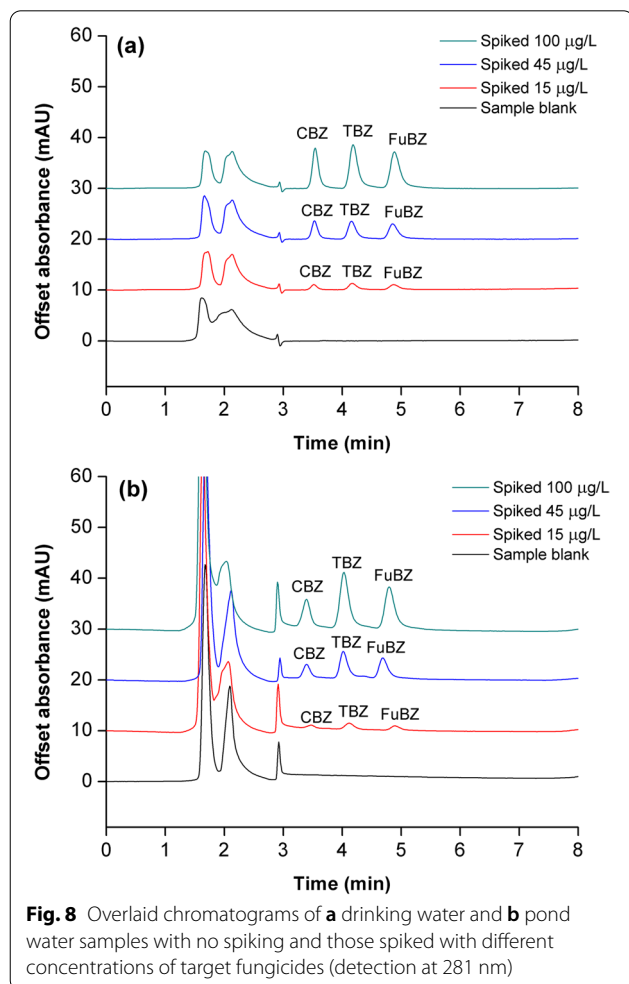
effect); and $ME(\%) < 50$, and $ME(\%) > 150$ (major effect) (Bazmandegan-Shamili et al. 2018; Chen et al. 2015). According to the ME (%) in Additional file 1: Table S8, water samples had a relatively low matrix effect (ME: 59–138%). Meanwhile, significant effects were observed when all apple juice samples examined were analyzed. Furthermore, peak overlap between CBZ and interferences was observed; thus, the calibration graph for CBZ was not evaluated. In this study, matrix-matched calibration methods were used to compensate sample matrices for all real sample analyses. No contamination with the target fungicides was detected in the studied samples, as identified by PDA detection data for each fungicide standard's retention time and absorption

Table 2 Analytical characteristic of the method for the analysis of target fungicides in water and apple juice samples

Analyte	Drinking water	Pond water	Lake water	Red apple juice	Green apple juice	White grape-mixed green apple
CBZ					Not evaluated	Not evaluated
Linear equation	$y = 222.2x - 1239.8$	$y = 542.2x - 1707.8$	$y = 1130.8x - 4665.6$	$y = 171.3x - 1523.6$	–	–
R^2	0.9993	0.9977	0.9947	0.9981	–	–
Linearity (µg/L)	10 – 200	10 – 200	10 – 200	30 – 200	–	–
LOQ (µg/L)	7	10	10	30	–	–
LOD (µg/L)	3	5	5	10	–	–
TBZ						
Linear equation	$y = 1662.3x - 7437.5$	$y = 1815.8x - 9007.0$	$y = 1904.3x - 2003.5$	$y = 737.6x - 10{,}590.0$	$y = 623.4x - 1425.3$	$y = 871.8x - 12{,}904.0$
R^2	0.9975	0.9984	0.9944	0.9961	0.9916	0.9944
Linearity (µg/L)	10 – 200	10 – 200	10 – 200	30 – 200	30 – 200	30 – 200
LOQ (µg/L)	5	10	10	20	30	30
LOD (µg/L)	1	5	5	7	10	10
FuBZ						
Linear equation	$y = 2906.8x - 14{,}576.0$	$y = 3420.7x - 17{,}058.0$	$y = 3577.9x - 6984.6$	$y = 2594.5x - 38{,}724.0$	$y = 3579.3x - 12{,}131.0$	$y = 3404.0x - 16{,}670.0$
R^2	0.9980	0.9983	0.9944	0.9952	0.9946	0.9945
Linearity (µg/L)	10 – 200	10 – 200	10 – 200	30 – 200	30 – 200	30 – 200
LOQ (µg/L)	5	10	10	20	30	30
LOD (µg/L)	1	5	5	7	10	10

spectrum. Peak purity index was also used to evaluate the analyte peaks without interfering impurities in the studied samples. Table 2 summarizes the analytical characteristics of the proposed method for the analysis of target fungicides in real water and apple juice samples. The target fungicides had LODs of 1–5 µg/L in the studied water (drinking, pond, and lake), and 7–10 µg/L in apple juice samples, respectively. To ensure method reliability and validation (i.e., accuracy) for applications, the samples were fortified with known concentrations of fungicide standards (e.g., 15–100 µg/L for water samples and 45–100 µg/L for apple juice samples) prior to subjecting the samples to the proposed preconcentration method. The chromatograms of water and red apple juice samples are shown in Figs. 8 and 9. The accuracy was expressed as a percentage relative recovery (RR, %) for water and apple juice samples, respectively, as summarized in Tables 3 and 4. Water samples had RR ranging from 72.0 to 120.0%, with RSDs less than 6.1%, whereas apple juices had RR ranging from

Fig. 8 Overlaid chromatograms of **a** drinking water and **b** pond water samples with no spiking and those spiked with different concentrations of target fungicides (detection at 281 nm)

Fig. 9 Overlaid chromatograms of red apple juice samples with no spiking and those spiked with different concentrations of target fungicides obtained at **a** 281 nm, **b** 302 nm, and **c** 313 nm

75.3 to 116.9%, with RSDs less than 11.0%. Notably, the accuracy of CBZ was not evaluated for green apple and white grape juice samples mixed with green apple juice because of the overlapping peaks of interferences from other polar species (e.g., pigments) and sugars in the studied samples. According to the RR (%) values above, the accuracy was acceptable and in good agreement with reference values (i.e., RR of 70–120% and RSD of

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Table 3 Recovery of target fungicides in water samples ($n = 3$)

Analyte	Spiked (µg/L)	Drinking water			Pond water			Lake water		
		Detected (µg/L)	RR[b] (%)	RSD (%)	Detected (µg/L)	RR[b] (%)	RSD (%)	Detected (µg/L)	RR[b] (%)	RSD (%)
CBZ	0	ND[a]	–	–	ND[a]	–	–	ND[a]	–	–
	15	10.8	72.0	0.6	18.0	120.0	1.2	15.1	100.7	3.9
	45	46.8	104.0	0.3	47.8	106.2	6.1	43.5	96.7	1.5
	100	105.6	105.6	0.5	95.6	95.6	1.3	99.6	99.6	1.2
TBZ	0	ND[a]	–	–	ND[a]	–	–	ND[a]	–	–
	15	17.4	116.0	1.0	17.7	118.0	2.6	15.2	101.3	0.7
	45	48.2	107.1	0.2	48.5	107.8	4.9	49.0	108.9	0.6
	100	110.5	110.5	0.4	103.8	103.8	3.9	100.8	100.8	3.2
FuBZ	0	ND[a]	–	–	ND[a]	–	–	ND[a]	–	–
	15	17.4	116.0	0.9	15.8	105.3	2.6	15.3	102.0	1.3
	45	50.4	112.0	0.5	44.3	98.4	5.5	47.9	106.4	1.5
	100	108.5	108.5	0.8	102.5	102.5	3.2	100.9	100.9	2.1

[a] ND: Not detected

[b] RR: Relative recovery

Table 4 Recovery of target fungicides in different brands of apple juice samples ($n = 3$)

Analyte	Spiked (µg/L)	Red apple			Green apple			White grape-mixed green apple		
		Detected (µg/L)	RR[b] (%)	RSD (%)	Detected (µg/L)	RR[b] (%)	RSD (%)	Detected (µg/L)	RR[b] (%)	RSD (%)
CBZ	0	ND[a]	–	–	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]
	45	46.4	103.1	7.0	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]
	70	55.5	79.3	3.7	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]
	100	102.0	102.0	6.0	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]	NE[c]
TBZ	0	ND[a]	–	–	ND[a]	–	–	ND[a]	–	–
	45	45.6	101.3	7.2	33.9	75.3	5.8	36.4	80.9	2.9
	70	69.1	98.7	7.1	55.2	78.9	6.0	55.3	79.0	7.4
	100	88.9	88.9	6.8	101.1	101.1	4.7	87.1	87.1	11.0
FuBZ	0	ND[a]	–	–	ND[a]	–	–	ND[a]	–	–
	45	52.6	116.9	1.5	41.8	92.9	6.1	50.0	111.1	4.2
	70	74.0	105.7	4.6	70.3	100.4	8.1	68.5	97.9	0.7
	100	102.8	102.8	4.2	88.1	88.1	4.4	94.1	94.1	5.0

[a] ND: Not detected

[b] RR: Relative recovery

[c] NE: Not evaluated

less than 20%) for the fortification range of 10–100 µg/L (SANTE/11312/2021).

Comparison of various preconcentration methods and HPLC for analysis of fungicides

The comparison of different sorbent-based and solvent-based preconcentration strategies with HPLC for determining fungicides in water, honey, and juice samples is summarized and discussed (Table 5). The proposed method produced LOD values that were comparable to those obtained from the other methods (e.g., micellar extraction (Halko et al. 2004), solid-phase microextraction (SPME) (Monzón et al. 2007), and conventional DLLME (Wu et al. 2009)). As an alternative strategy, a quick and simple procedure without synthesis (in situ procedure) of the proposed method was demonstrated. The sorbent-based methods, such as SPME and magnetic-imprinted solid-phase extraction (MISPE) (Cacho et al. 2009), necessitate the preparation of sorbents prior to use, as well as the use of some specific conditions (e.g., prolonged heating). Meanwhile, solvent-based extraction strategies such as micellar extraction, salting-out assisted liquid–liquid extraction (SALLE) (Wen et al. 2013), and conventional DLLME using

Table 5 The different preconcentration methods coupled with HPLC technique for the determination of benzimidazole fungicides in various sample matrices

Extraction	Extraction solvent/sorbent	Other extraction conditions	Sample	LOD (µg/L)	EF	Refs.
Micellar extraction	Nonionic surfactants (e.g., Genapol X-080 and POLE)	High temperature (90 °C) and incubation time (20 min)	Water	0.008–6.4 (Genapol X-080), 0.004–5.9 (POLE)	NR[a]	Halko et al. (2004)
SPME	Carboxen–polydimethylsiloxane 75 µm fiber	Heating and stirring during extraction process (40 min)	Water	0.03–1.30	NR[a]	Monzón et al. (2007)
MISPE	Molecularly imprinted polymer-divinylbenzene	MeOH/acetic acid (50/50) as an eluent	Water	0.002–0.012	NR[a]	Cacho et al. (2009)
SALLE	Acetonitrile (2 mL)	High salty solution and required buffer	Water	0.14–0.38	NR[a]	Wen et al. (2013)
DLLME	Chloroform (80 µL)	Tetrahydrofuran (as a disperser solvent)	Water	0.5–1.0	150–200	Wu et al. (2009)
MeSA-DLLME	Methyl salicylate (250 µL)	Requires CH_3COONa, without pH adjustment, and not required a disperser solvent	Water	0.03–0.05	24–38	Santaladchaiyakit et al. (2015)
MeSA-VASEME	Methyl salicylate (100 µL)	2 mmol/L SDS (as an emulsifier)	Honey	0.5	32–40	Santaladchaiyakit et al. (2017)
MeBZ-VA-DLLME	Methyl benzoate (250 µL)	EtOH (as a disperser solvent) and 1% (w/v) CH_3COONa	Water	0.01–0.05	14.5–39.0	Santaladchaiyakit and Srijaranai (2014)
MeBZ-VASEME	Methyl benzoate (50 µL)	0.2 mmol/L SDS (as an emulsifier)	Juice	0.01–0.5	15–38	Santaladchaiyakit et al. (2019)
EtSA and EtBZ—VASEME	Ethyl salicylate (200 µL), ethyl benzoate (200 µL),	1.5 mmol/L SDS (as an emulsifier)	Water	0.01 – 0.1	16–28 (18–33)	Santaladchaiyakit et al. (2021a)
$Mg(OH)_2$-SDBS co-precipitation	$Mg(OH)_2$	0.35 mmol/L SDBS (as an agent to improve the extraction efficiency), under basic condition	Water and apple juice	1–5 (water) and 7–10 (apple juice)	11–18	Proposed method

[a] NR: not reported

Abbreviations: MeSA, methyl salicylate; VASEME, vortex-assisted surfactant-enhanced microextraction; VA, vortex-assisted; MeBZ, methyl benzoate; EtSA, ethyl salicylate; and EtBZ, ethyl benzoate

nonionic surfactants, acetonitrile, and chloroform as extraction solvents were found to have some limitations, including a high incubation temperature and long extraction time, the high salty solution required for extraction efficiency, and the use of toxic chlorinated solvent. The previous works using methyl salicylate, methyl benzoate, ethyl salicylate, and ethyl benzoate as extraction solvents (Santaladchaiyakit et al. 2015, 2017, 2019, 2021a; Santaladchaiyakit and Srijaranai 2014) may be beneficial as an alternative for others. However, in some conditions, salt and a dispersive solvent are required.

Conclusions

The proposed preconcentration method based on co-precipitation of anionic surfactant and magnesium hydroxide was successfully demonstrated to be an excellent strategy for monitoring target fungicides in water and apple juice samples. The anionic surfactant used in this study, SDBS, was shown to improve target analyte extraction performance. Excellent sensitivities were obtained with an enrichment factor of 11–18, corresponding to their LODs of 1–5 µg/L for water samples and 7–10 µg/L for apple juices. Additionally, an acceptable accuracy obtained by using a quick and simple preconcentration procedure combined with HPLC-PDA was also advantageous, as it was expected to be an alternative to LDHs and other methods for determining fungicides in samples.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40543-022-00356-z.

Additional file 1 of A simple co-precipitation sorbent-based preconcentration method for the analysis of fungicides in water and juice samples by high-performance liquid chromatography coupled with photodiode array detection. **Table S1**. Gradient elution program of mobile phase (%) for the HPLC separation of target fungicides. **Table S2**. Zeta potential of some precipitate phases obtained under the conditions

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of without target fungicides. **Table S3**. The calculation results of XRD reflections of sorbent forms. **Table S4**. Robustness evaluation of the proposed preconcentration coupled with HPLC method for the determination of carbendazim (50 µg/L) in pure water samples (n=3). **Table S5**. Robustness evaluation of the proposed preconcentration coupled with HPLC method for the determination of thiabendazole (50 µg/L) in pure water samples (n=3). **Table S6**. Robustness evaluation of the proposed preconcentration coupled with HPLC method for the determination of fuberidazole (50 µg/L) in pure water samples (n=3). **Table S7**. Accuracy evaluation of the proposed preconcentration coupled with HPLC method for the determination of target fungicides (50 µg/L) in pure water samples (n=6). **Table S8**. Matrix effect (ME, %) data of the studied fungicides in various samples. **Figure S1**. Photographs of the solutions obtained (a) during extraction and (b) after centrifugation. **Figure S2**. Precipitate phase after drying at ambient temperature. **Figure S3**. Effect of (a) vortex speed and (b) time on the extraction performance. **Figure S4**. Effect of (a) centrifugation speed and (b) time on the extraction performance. **Figure S5**. Overlaid chromatograms of target fungicides obtained from (a) without preconcentration and (b) with preconcentration using Mg(OH)$_2$-SDBS.

Availability of data and materials
Not applicable.

Declarations

Competing interests
The authors declare that they have no competing interests.

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