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Analytical Methods

Magnetic solid phase extraction using ionic liquid-coated core–shell magnetic nanoparticles followed by high-performance liquid chromatography for determination of Rhodamine B in food samples

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ABSTRACT

Three hydrophobic ionic liquids (ILs) (1-butyl-3-methylimidazole hexafluorophosphate ([BMIM]PF_6), 1-hexyl-3-methyl-imidazole hexafluoro-phosphate ([HMIM]PF_6), and 1-octyl-3-methylimidazole hexafluorophosphate ([OMIM]PF_6)) were used to coat Fe_3O_4@SiO_2 nanoparticles (NPs) with core–shell structures to prepare magnetic solid phase extraction (MSPE) agents (Fe_3O_4@SiO_2@IL). A novel method of MSPE coupled with high-performance liquid chromatography for the separation/analysis of Rhodamine B was then established. The results showed that Rhodamine B was adsorbed rapidly on Fe_3O_4@SiO_2@[OMIM]PF_6 and was released using ethanol. Under optimal conditions, the pre-concentration factor for the proposed method was 25. The linear range, limit of detection (LOD), correlation coefficient (R), and relative standard deviation (RSD) were found to be 0.50–150.00 μg L^{-1}, 0.08 μg L^{-1}, 0.9999, and 0.51% ($n = 3$, $c = 10.00$ μg L^{-1}), respectively. The Fe_3O_4@SiO_2 NPs could be re-used up to 10 times. The method was successfully applied to the determination of Rhodamine B in food samples.

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1. Introduction

Rhodamine B (RhB), a red dye, is used as a colorant in textile, plastic, leather, dyeing, paper, and printing industries (Alesso, Bondioli, Talío, Luconi, & Fernández, 2012). However, it is harmful to humans and animals, causing irritation to the skin, eyes, and respiratory tract (Roberts, Fletcher, Moore, & Byers, 2010; Xiao, Gong, & Ledoux, 2007; Xie et al., 2013). The use of RhB as a colorant in foodstuffs was therefore banned. However, owing to its low price and bright color, some traders continue to use RhB as a food additive (Jain, Mathur, Sikarwar, & Mittal, 2007), endangering the health of consumers (Baldev et al., 2013). Thus, the development of a simple method for the determination of RhB in different samples is necessary. Various techniques have been developed, including ultraviolet spectrophotometry (Sun, Li, Mele, Zhang, & Zhang, 2013), fluorescence spectrophotometry (Chauhan et al., 2014), capillary chromatography (Desiderio, Marra, & Fanali, 1998), and high-performance liquid chromatography (HPLC) (Santiago Valverde, Sanchez Perez, Franceschelli, Martinez Galera, & Gil Garcia, 2007). However, direct determination using spectrophotometry is difficult because of the low concentration of RhB in food samples. Therefore, it is necessary to develop a separation/pre-concentration step.

Magnetic solid phase extraction (MSPE) is a technique that uses a magnetic or magnetizable material as a solid absorbent matrix (Ibarra, Miranda, Rodriguez, Nebot, & Cepeda, 2014). In MSPE procedures, magnetic adsorbents can be easily magnetized and

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gathered together in the presence of an external magnetic field and redispersed immediately once the magnetic field is removed, which greatly simplifies the SPE procedure and enhances the extraction efficiency (Jiang, Yang, Wang, Lian, & Hu, 2013). Most MSPE sorbents contain Fe_3O_4 nanoparticles (NPs) with specific chemical functional group modifications on their surface to achieve concentration of the target analytes. Numerous organic and inorganic polymers have been used to modify Fe_3O_4 NPs. Gao et al. used polyaniline-loaded Fe_3O_4 (PANI/Fe_3O_4) as an adsorbent for the magnetic solid-phase extraction of fluoroquinolones in honey samples (Gao, Zheng, Luo, Ding, & Feng, 2012) and Cao et al. used ionic liquid-coated Fe_3O_4@graphene (Fe_3O_4@grapheme/IL) as an adsorbent for the magnetic solid-phase extraction of nitrobenzene compounds in environmental water samples (Cao et al., 2014). Magnetic core-mesoporous shell microspheres with C18-functionalized interior pore-walls (CFe_3O_4@mSiO_2/C18) were used as adsorbents for the analysis of cephalosporin residues in milk (Liu, Yu, et al., 2014). However, this approach has not been reported for the determination of RhB using Fe_3O_4@SiO_2@IL.

In this study, Fe_3O_4@SiO_2@IL were prepared via self-assembly and used as MSPE agents, combining the advantages of the ILs and the magnetic nanoparticles (MNPs). Compared with previous reports (Cao et al., 2014; Gao et al., 2012), the MSPE method reported herein provided a rapid and efficient sample preparation process, which enabled the treatment of a large volume of samples in a short period of time. A novel MSPE method coupled with HPLC was therefore established for the separation/analysis of RhB in food samples.

2. Experimental

2.1. Equipment and reagents

FT-IR spectra were measured on a Bruker Tensor 27 spectrometer (Bruker Company, Germany). Samples were pressed into KBr pellets and spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. A Tecnai 12 transmission electron microscope (Philips, Netherlands) was used to obtain micrographs of the MNPs. Chromatographic separation of the analytes was achieved using an Agilent 1200 HPLC system (Agilent Corporation, Japan).

All chemicals and reagents were at least of analytical grade unless otherwise stated. RhB standards were all obtained from Shanghai, Chemical Reagent Co., Ltd, China. A standard stock solution was prepared by dissolving 10.0 mg RhB in 100.0 mL ethanol. This was then stored in the dark at 4 °C. *N*-Methylimidazole (Darui Fine Chemicals, Shanghai, China), *N*-butyl bromide, 1-bromohexane, 1-bromooctane, tetraethyl orthosilicate (TEOS), KPF_6, $FeCl_3$, $(NH_4)_2Fe(SO_4)_2$, methanol, ethanol, acetone, and methylene chloride were all obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Preparation of Fe_3O_4@SiO_2@IL MNPs

A series of ionic liquids (1-alkyl-3-methylimidazolium hexafluorophosphate) were synthesized using a two-step method described in previous reports (Chun, Dzyuba, & Bartsch, 2001; Dzyuba & Bartsch, 2001; Holbrey & Seddon, 1999; Tokuda, Hayamizu, Ishii, Abu Bin Hasan Susan, & Watanabe, 2004).

Fe_3O_4 NPs were prepared by chemical coprecipitation (Hong et al., 2006; Huang, Fang, Yan, & Cheng, 2012).

For the preparation of Fe_3O_4@SiO_2, a previously reported process was followed (Hou et al., 2013; Hu et al., 2014).

Fe_3O_4@SiO_2@IL MNPs (Fe_3O_4@SiO_2@[BMIM]PF_6, Fe_3O_4@SiO_2@[HMIM]PF_6, and Fe_3O_4@SiO_2@[OMIM]PF_6) were also synthesized using a procedure previously described in the literature (Dang, Ma, & Zhou, 2012).

2.3. MSPE procedure

The MSPE procedure is shown in Fig. 1. First, 0.10 g Fe_3O_4@SiO_2@IL MNPs were added to 100 mL sample solution (pH 3.0), and the mixture was placed on a slow-moving platform shaker and allowed to equilibrate for 10 min at 30 °C. Then, the RhB-adsorbed Fe_3O_4@SiO_2@IL MNPs were separated from the solution using an external magnetic field. Once the suspension became limpid, the supernatant was decanted and the isolated MNPs were eluted with 4.0 mL ethanol to desorb the pre-concentrated target analytes. The eluted solution was collected and then dried under a mild nitrogen stream. Finally, the residue was re-dissolved in 150 μL ethanol, of which 20.0 μL was injected into the HPLC system for detection of the target analytes.

2.4. Sample preparation

Chili powder/hot pepper (5.0 g) was accurately weighed out, poured into a beaker, and dissolved in 80.0 mL ethanol. The resultant clear solution was evaporated to dryness at 60 °C. The residue was diluted with distilled water to 100 mL and stored in the dark for future analysis.

2.5. Chromatographic conditions

Separations were performed on a C_{18} reversed-phase column (250 mm × 4.6 mm I.D., 5 μm, Shimadzu Corporation, Japan) at 35 °C. The injections were carried out through a 10.0 μL loop. The detection was at 554.0 nm. The mobile phase was methanol–water (75:25). The flow rate was 1.0 mL min^{-1}.

3. Results and discussion

3.1. Characterization of the Fe_3O_4@SiO_2@IL MNPs

The Fe_3O_4@SiO_2@IL MNPs were characterized using FT-IR spectroscopy, thermogravimetric analysis (TGA), and magnetic characterization.

Fig. 2A shows the FT-IR spectra of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@[BMIM]PF_6, Fe_3O_4@SiO_2@[HMIM]PF_6, and Fe_3O_4@SiO_2@[OMIM]PF_6 (curves a–e, respectively). Comparing curves a and b,

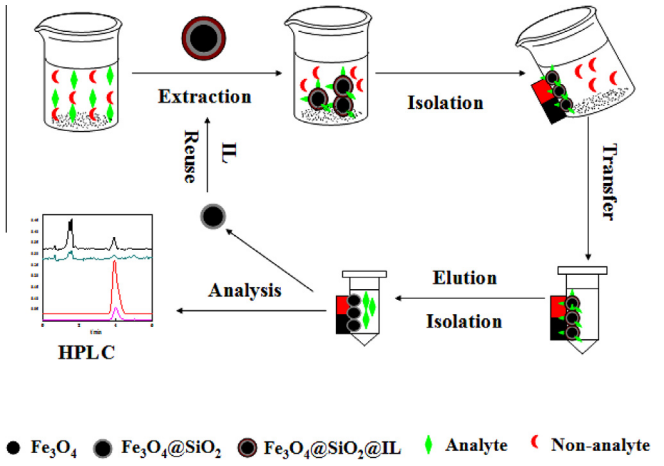

Fig. 1. Schematic of the MSPE method. Procedure for the MSPE of RhB using Fe_3O_4@SiO_2@IL MNPs.

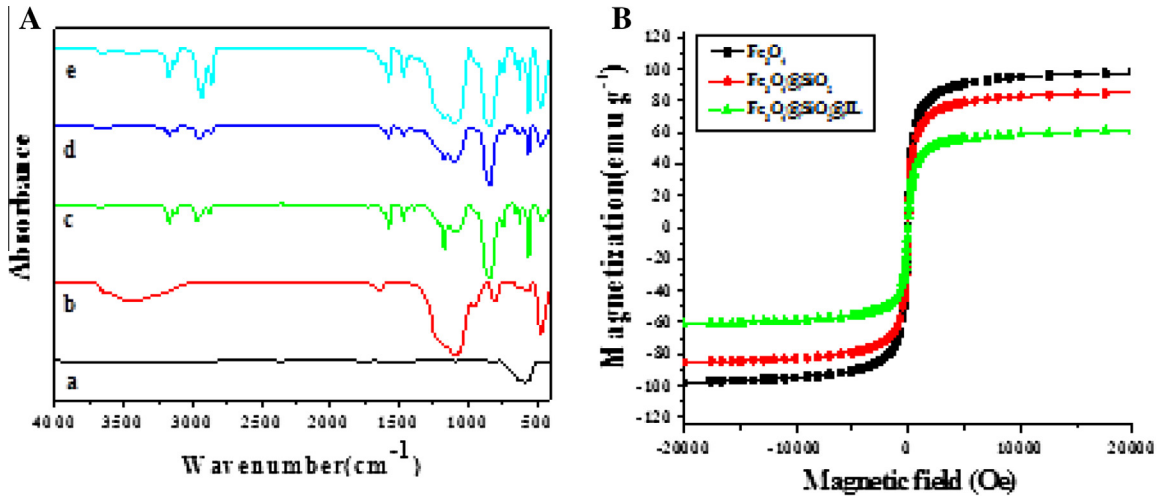

Fig. 2. FT-IR spectra and magnetic hysteresis loops. (A) FT-IR spectra of Fe_3O_4 (a), Fe_3O_4@SiO_2 (b), Fe_3O_4@SiO_2@[BMIM]PF_6 (c), Fe_3O_4@SiO_2@[HMIM]PF_6 (d), and Fe_3O_4@SiO_2@[OMIM]PF_6 (e); (B) magnetic hysteresis loops of Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2@IL.

the peak at 580 cm^{-1} in curve a was assigned to Fe–O–Fe stretching vibrations and the strong peaks at 1200–1000 cm^{-1} in curve b correspond to Si–O–H and Si–O–Si stretching vibrations, which indicated that SiO_2 had been successfully loaded onto the surface of Fe_3O_4. In curves c, d, and e, the peaks at 2920 cm^{-1} and 2850 cm^{-1} correspond to C–H stretching vibrations, and the peaks at 1575 cm^{-1} correspond to the characteristic absorption of imidazole groups in Fe_3O_4@SiO_2@IL. In addition, the peaks at 840 cm^{-1} were attributed to P–F stretching vibrations (Galan-Cano, Alcudia-Leon, Lucena, Cardenas, & Valcarcel, 2013), which indicated that the ILs had been successfully immobilized on the surface of Fe_3O_4@SiO_2 to form Fe_3O_4@SiO_2@IL.

TGA revealed the weight loss of the materials, which demonstrated differences between Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2@[OMIM]PF_6. In this study, TGA was conducted in a nitrogen atmosphere, and the heating rate employed was 5 °C min^{-1} in all cases from 25 to 1000 °C. From the experimental results, it can be concluded that: (1) Fe_3O_4@SiO_2 showed a mass loss of approximately 1.7% after heating to 200 °C, corresponding to water content; and (2) for Fe_3O_4@SiO_2@[OMIM]PF_6, an additional weight loss of 5.6% was observed from 200 to 650 °C due to the decomposition of the ILs. This observation suggests that [OMIM]PF_6 was located on the surface of Fe_3O_4@SiO_2.

Fig. 2B shows the magnetic hysteresis loops of the three types of MNPs. It is apparent that all of the NPs showed superparamagnetic properties due to the core magnetite particles. Magnetic characterization using a magnetometer at 27 °C indicated that the maximal saturation magnetizations of the Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2@[OMIM]PF_6 MNPs were 97.0, 85.3, and 61.1 emu g^{-1}, respectively. The lower maximal saturation magnetization of the Fe_3O_4@SiO_2@[OMIM]PF_6 MNPs resulted from the non-magnetic IL shell. Fe_3O_4@SiO_2@[OMIM]PF_6 MNPs could be rapidly separated from the solution using a magnet on account of their superparamagnetism and large saturation magnetization.

3.2. Extraction efficiency of different MNPs

In this work, the extraction efficiencies of Fe_3O_4, SiO_2, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@[BMIM]PF_6, Fe_3O_4@SiO_2@[HMIM]PF_6, and Fe_3O_4@SiO_2@ [OMIM]PF_6 for RhB (E_{RhB}%) were evaluated. The results were as follows: (1) the order of E_{RhB}% was Fe_3O_4 < SiO_2 < Fe_3O_4@SiO_2 < Fe_3O_4@SiO_2@[BMIM]PF_6 < Fe_3O_4@SiO_2@[HMIM]PF_6 < Fe_3O_4@SiO_2@[OMIM]PF_6 under the same experimental conditions; (2) E_{RhB}% on Fe_3O_4@SiO_2 was far less than that of the three kinds of Fe_3O_4@SiO_2@IL, which revealed that E_{RhB}% largely depended on the hydrophobicity of the ILs; (3) E_{RhB}% gradually increased with increasing length of the loaded IL cationic alkyl chain; and (4) E_{RhB}% on Fe_3O_4@SiO_2@[OMIM]PF_6 showed the highest extraction efficiency, perhaps because the hydrophobicity of the ILs increased with increasing cationic alkyl chain length (Deng et al., 2011). Therefore, Fe_3O_4@SiO_2@[OMIM]PF_6 was employed in subsequent experiments.

3.3. Optimization of extraction

The factors affecting the extraction process of RhB: pH, temperature, ionic strength, solution volume, and extraction time, are discussed (Fig. 3).

3.3.1. Effect of pH

pH is a crucial factor in the extraction process because it affects the form of RhB. In this work, the effect of pH was investigated over the pH range 2.0–13.0. As shown in Fig. 3A, E_{RhB}% increased over pH 2.0–3.0, reached a maximum value at a pH of 3.0, and subsequently decreased. It may be that RhB was mainly present as the neutral molecule at a pH of 3.0 (pKa = 3.2) and in the ionic form at pH > 3.2. The hydrophobicity of the neutral molecule was stronger than that of the ionic form, which was favorable for RhB adsorption by Fe_3O_4@SiO_2@[OMIM]PF_6 MNPs (Ping, Zhu, & Wang, 2014). Therefore, pH 3.0 was selected for the subsequent assays.

3.3.2. Effect of extraction temperature

The effect of extraction temperature was studied by varying the temperature from 20 to 60 °C (Fig. 3B). E_{RhB}% increased with temperature up to 30 °C, after which it decreased. It could be elucidated that increasing the temperature increased the transition of the analytes to the solid phase extraction sorbent (adsorbent), but the analytes may also be desorbed from the adsorbent at higher temperature due to an exothermic extraction process (Liu, Lu, Huang, Liu, & Zhao, 2014). The maximum extraction efficiency for RhB was obtained at 30 °C. Hence, all adsorption experiments were carried out at 30 °C.

3.3.3. Effect of ionic strength

The effect of ionic strength was evaluated using NaCl as a model electrolyte within a concentration interval of 0–30% (w/v) (Fig. 3C). E_{RhB}% increased with NaCl concentration up to 20% for two reasons: (1) the extraction efficiency increased due to the salting

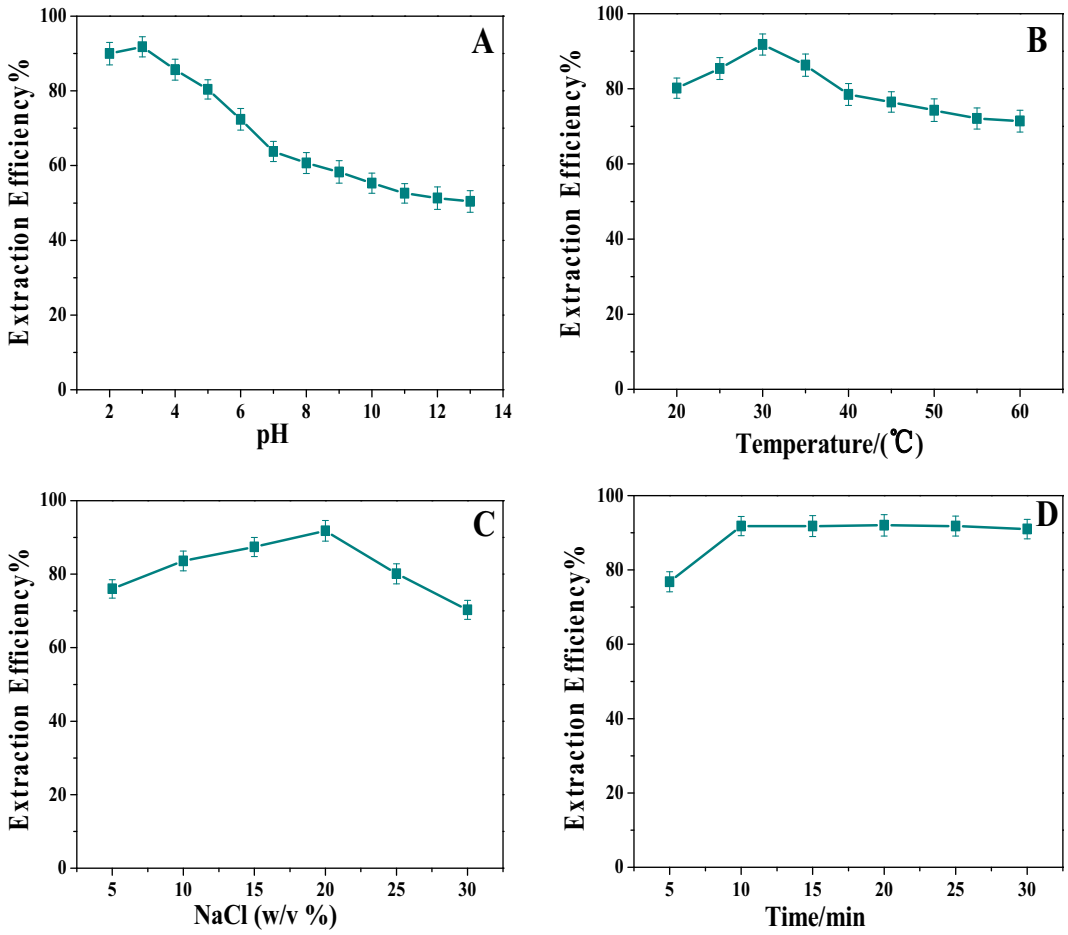

Fig. 3. Factors affecting the extraction efficiency. Effect of pH (A), temperature (B), ionic strength (C), and adsorption time (D) on extraction efficiency.

out effect; (2) electrostatic attractions increased with increasing ionic strength, also increasing the extraction efficiency (Hu et al., 2013). The extraction efficiency decreased when the concentration of NaCl was above 20%. The reason for this phenomenon was that higher ionic strength induced an increase in sample viscosity, making it difficult for the analytes to transfer from the bulk samples to the adsorbent (Ho, Cole, Augusto, & Anderson, 2013). Based on this, 20% (w/v) NaCl was used for subsequent experiments.

3.3.4. Effect of sample volume

The effect of sample volume was studied using different volumes of sample solution (20.0–120.0 mL) for a fixed amount of RhB. The experimental results show that E_{RhB}% decreased when the sample volume was greater than 100.0 mL. Therefore, the sample volume was set as 100.0 mL.

3.3.5. Effect of extraction time

To evaluate the effect of extraction time on E_{RhB}%, different extraction times ranging from 5 to 25 min were tested (Fig. 3D). E_{RhB}% gradually increased up to 10 min, after which it remained almost constant. Thus, 10 min was selected as the optimal extraction time.

3.4. Adsorption capacity

Adsorption capacity is defined as the maximum amount of RhB adsorbed per gram of Fe_3O_4@SiO_2@[OMIM]PF_6. In this work, the adsorption capacity of Fe_3O_4@SiO_2@[OMIM]PF_6 for RhB was studied by varying the concentration of RhB in aqueous samples before the MSPE procedure. The maximum E_{RhB}% was obtained when the concentration of RhB was 70.0 μg mL^{-1}. The adsorption capacity of Fe_3O_4@SiO_2@[OMIM]PF_6 for RhB was calculated as 6.71 mg g^{-1}.

3.5. Optimization of desorption

3.5.1. Selection of eluent and its volume

In this study, different eluents were investigated. The order of elution efficiency of RhB was ethanol > methanol > cetyltrimethyl ammonium bromide (CTAB) > sodium dodecyl sulfonate (SDS) > NaOH (0.1 M) > HCl (0.1 M). Ethanol was therefore adopted as the eluent.

The effect of the volume of ethanol on the elution efficiency of RhB was evaluated in detail. The results show that quantitative elution (above 98.0%) was observed when the volume of ethanol was higher than 4.0 mL. The pre-concentration factor was 25 (the quotient of volume before absorption and after elution). The optimum volume of ethanol was therefore 4.0 mL.

3.5.2. Elution time

The experimental results show that the elution efficiency of RhB increased up to 98.0% after 5.0 min stripping time. Thus, 5.0 min was selected as the optimal elution time.

3.5.3. Reusability of the Fe_3O_4@SiO_2 MNPs

Fe_3O_4@SiO_2 MNPs were washed twice with 2.0 mL ethanol after the MSPE procedure and subsequently assembled with the ILs.

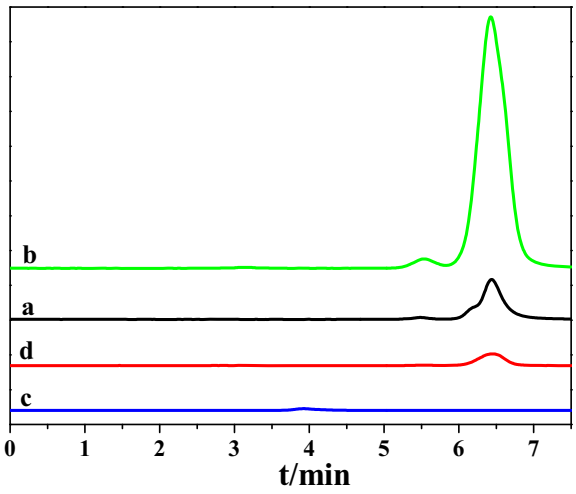

Fig. 4. HPLC results. Chromatograms of RhB: (a) RhB standard solution (10.00 μg L^{-1}); (b) RhB standard solution after separation (60.00 μg L^{-1}); (c) chili powder sample; (d) chili powder after separation.

Table 1
Determination results of the samples (n = 3).

Sample	Added (μg kg^{-1})	Found (μg kg^{-1})	Recovery (%)
Chili powder	0	5.46 ± 0.01	–
	5.00	10.47 ± 0.02	100.2 ± 0.6
	50.00	54.96 ± 0.04	99.0 ± 0.1
	100.00	106.36 ± 0.02	100.9 ± 0.3
Chinese prickly ash	0	ND[a]	–
	5.00	5.02 ± 0.02	100.4 ± 0.4
	50.00	50.4 ± 0.04	100.8 ± 0.3
	100.00	101.2 ± 0.03	101.2 ± 0.6

[a] Not determined.

Each re-prepared adsorbent was used for MSPE. The extraction efficiency of the newly prepared Fe_3O_4@SiO_2@[OMIM]PF_6 MNPs for RhB was greater than 90.0% after being re-used 10 times. Thus, the Fe_3O_4@SiO_2 MNPs could be used repeatedly 10 times.

3.6. Effect of foreign substances

The effects of different foreign substrates were investigated in the determination of 10.00 μg L^{-1} RhB. With a relative error of less than ±5%, the tolerance limits for various foreign ions were as follows (tolerance ratio in mass): SO_4^{2-}, Br^- (500); citrate, glucose (250); NO_3^- (100); Zn^{2+}, Cu^{2+}, phenol, safranin, bright yellow, sunset yellow (20); allura red, congo red (10); rhodamine 6G (2). The results indicate that the majority of these substances showed no remarkable interference in the determination of RhB.

3.7. Analytical performance of the method

Under the optimum conditions, a linear calibration curve was obtained in the concentration range 0.50–150.00 μg L^{-1}. The equation of the calibration graph is I (peak area) = 11.97c + 12.11 (μg L^{-1}), with a correlation coefficient of 0.9993. The limit of detection (LOD), defined as LOD = 3σ/k (where σ is the standard deviation of the blank sample and k is the slope of the calibration graph), was 0.08 μg L^{-1}. The relative standard deviation was 0.51% (n = 3, c = 10.00 μg L^{-1}). The pre-concentration factor, defined as the quotient of volume before absorption and after elution, is 25-fold.

3.8. Sample analysis

Fig. 4 shows the chromatographic peak of RhB standard solution/chili powder before and after separation. It can be seen that: (1) the retention time of RhB was 6.4 min (curve a); (2) the concentration of RhB increased significantly after pre-concentration (curves a and b); and (3) RhB could only be determined in chili powder after separation/concentration (curves c and d).

The proposed method was applied to determine the content of RhB in chili powder and Chinese prickly ash. The results show that the amount and recovery rate of RhB in chili powder were 5.46 μg kg^{-1} and 99.0–100.9%, respectively. RhB was not detected in Chinese prickly ash with a sample added recovery rate of 100.4–101.2% (see Table 1).

3.9. Comparison with other methods

Comparison of the presented method with some other procedures for the determination of RhB (Table 2) revealed that the method described herein had higher sensitivity, a wider linear range, and easier operation.

4. Conclusion

In summary, Fe_3O_4@SiO_2@IL were successfully prepared and applied as magnetic adsorbents to pre-concentrate and separate RhB. MSPE was coupled with HPLC for the analysis of RhB. This MSPE method based on Fe_3O_4@SiO_2@IL MNPs was faster than traditional SPE, thus saving time, and the adsorbent could be easily separated from the sample solution. The hydrocarbon chains of the ILs on the surface of Fe_3O_4@SiO_2@IL provided good adsorption sites for RhB (higher extraction capacity and larger enrichment factors). The proposed method was satisfactory for the analysis of RhB in food samples.

Acknowledgments

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Table 2
Comparison of the results with those from the literature.

Method	LR[a] (μg L^{-1})	LOD[b] (μg L^{-1})	RSD[c] (%)	Refs.
MSPE-fluorescence	0.35–5.00	0.10	2.10–8.20	Bagheri, Daliri, and Roostaie (2013)
SPE-UV	–	3.14	5.0	Soylak, Unsal, Yilmaz, and Tuzen (2011)
SPE-HPLC	1.0×10^3–1.0×10^4	250	2.87	Li, Zhang, and Lu (2011)
HPLC-CL	1.5–82.1	1.50	4.0	Zhang, Cui, Myint, Lian, and Liu (2005)
MSPE-HPLC	0.50–150.00	0.08	0.51 (n = 3)	This method

[a] Linear range.
[b] Limit of detection.
[c] Relative standard deviation.

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