Determination of Rhodamine B Pigment in Food Samples by Ionic Liquid Coated Magnetic Core/Shell Fe$_3$O$_4$@SiO$_2$ Nanoparticles Coupled with Fluorescence Spectrophotometry

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Abstract: The Ionic liquids (IL) 1-octyl-3-methylimidazole hexafluorophosphate ([OMIM]PF$_6$) was selected from three ILs along with (1-butyl-3-methylimidazole hexafluorophosphate ([BMIM]PF6), 1-hexyl-3-methyl-imidazole hexafluoro-phosphate ([HMIM]PF6), were coated by Fe$_3$O$_4$@SiO$_2$ nanoparticles with core-shell structure to prepare magnetic solid phase extraction agent (Fe$_3$O$_4$@SiO$_2$@IL) and establish a new method of magnetic solid phase extraction (MSPE) coupled with Fluorescence spectrophotometry for separation/analysis of Rhodamine B. The results showed that Rhodamine B was adsorbed rapidly byFe$_3$O$_4$@SiO$_2$@[OMIM]PF$_6$ and eluted by ethanol. Under the optimal conditions the linear range, detection limit (DL), correlation coefficient (R) and relative standard deviation (RSD) were found to be 0.40-140.00 µg L^{-1}, 0.06µg L^{-1}, 0.9993 and 0.45% (n=3, c=10.00 µg L^{-1}), respectively. The pre-concentration factor of the proposed method was 25-fold. The Fe$_3$O$_4$@SiO$_2$ NPs can be used repeatedly for 10 times. This method has been applied to the determination of Rhodamine B in food samples.

Keywords: Rhodamine B, IL-magnetic Nanoparticles, Magnetic SPE, Fluorescence Spectrophotometry

1. Introduction

Rhodamine B (RhB), a red pigment, is widely used as colorant in textiles, dyeing, paper and printing [1]. RhB is harmful if swallowed by human and animals, and causes irritation to the skin, eyes and respiratory tract "[2], [3], [4]", and has been considered and used as color additive in foodstuffs. Because of the low price and bright color of rhodamine B, some traders use it as a food additive illegally [5], harming the health of consumers [6]. Thus, due to this, it was considered worthwhile to make efforts to develop a simple method for the determination of RhB in different samples. Various techniques have been developed for the determination of RhB to date, including ultraviolet spectrophotometry [7], fluorescence spectrophotometry [8], capillary chromatography [9], high-performance liquid chromatography (HPLC) [10]. However, direct determination with spectrophotometry is difficult owing to low concentration of RhB in natural samples. So that, it is important to develop a new method for determination/separation procedure of RhB.

Magnetic solid phase extraction (MSPE) is a technique that uses a magnetic material as absorbent matrix in solid-phase extraction technique [11]. In MSPE procedures, the magnetic adsorbents are exposed in the sample solution to adsorb the analyte and then collect the analyte by an external magnetic field, which greatly simplifies the SPE procedure and enhances extraction efficiency [12]. To date, MSPE extraction agent is mainly Fe$_3$O$_4$ nanoparticles (NPs) with specific chemical functional group modified on the surface to

achieve concentration of the targeted analyte. Numerous organic polymers and inorganic polymers have been used to modify Fe_3O_4 NPs. Gao et al. used polyaniline loaded Fe_3O_4 (PANIs/Fe_3O_4) as sorbents for magnetic solid-phase extraction fluoroquinolones in honey samples [13]. Cao et al. used ionic liquid coated Fe_3O_4@graphene (IL/Fe_3O_4@graphene) as sorbents for magnetic solid-phase extraction nitrobenzene compounds in environmental water samples extraction [14]. Liu et al. used magnetic core-mesoporous shell microspheres with C_{18}-functionalized interior pore-walls (C_{18}-Fe_3O_4@mSiO_2) as adsorbent measured the residue of cephalosporins in milk [15]. However, it has not been reported for determination of RhB using $Fe_3O_4@SiO_2$@IL.

In the present work, we have prepared magnetic solid phase extraction agents, $Fe_3O_4@SiO_2$@ILsthrough self-assembly. This extraction agent combines the advantages of the ILs and the magnetic nanoparticles (MNPs). Compared with the previously reported works "[16], [17], [18]", this adsorbent based MSPE providing a rapid, and efficient sample preparation process, which enables the treatment of large volume samples in a short period of time. A novel MSPE method coupled with Fluorescence spectrophotometry was therefore established for separation/analysis of RhB from food samples.

2. Experimental

2.1. Equipment and Reagents

FTIR spectra were measured with a Bruker Tensor 27 spectrometer (Bruker Company, Germany). Samples were pressed into KBr pellets and recorded at the frequencies from 4000 to 400 cm^{-1} with resolution of 4 cm^{-1}. A Tecnai 12 TEM (Philips, Netherlands) was used to obtain micrographs of the MNPs. Chromatographic separation of analytes was achieved with Fluorescence spectrophotometry.

All chemicals and reagents were at least of analytical reagent grade, unless otherwise stated. RhB standards were purchased from Shanghai Chemical Reagent Corporation, (China). A standard stock solution was prepared by dissolving 10.0 mg of each standard in 100 mL of ethanol and stored in 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, methylene chloride (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China).

2.2. Synthesis of$Fe_3O_4@SiO_2$@IL

The two-step synthesis A series of ionic liquids 1-alkyl-3-methylimidazolium hexafluorophosphate were synthesized using a two-step method described in previous reports "[19], [20], [21], [22]".

Fe_3O_4MNPswere prepared by chemical co-precipitation "[23], [24]".

For preparation of $Fe_3O_4@SiO_2$ a previously reported

process was followed "[25], [26]".

ILs functionalized 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 synthesized following a procedure described the literature [27].

2.3. MSPE Procedure

The MSPE procedure was done as follows. First, $Fe_3O_4@SiO_2$@[OMIM]PF_6 MNPs were added to a 40 mL water sample containing RhB (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, a strong magnet was applied to the bottom of the beaker, isolating the $Fe_3O_4@SiO_2$@[OMIM]PF_6 MNPs from the suspension. After 5 min, the suspension was decanted and the residual solution of $Fe_3O_4@SiO_2$@[OMIM]PF_6MNPs was transferred to centrifuge tube. The $Fe_3O_4@SiO_2$@[OMIM]PF_6MNPs were aggregated again by positioning a magnet to the outside of the tube wall so that the residual solution could be completely removed by pipette. Finally, the isolated MNPs were mixed with 3 mL of ethanol and sonicated for 5 min to elute the pre-concentrated target analytes. After wards, a magnet was positioned on the outside of the centrifuge tube, and the supernatant solution was collected and F-7000 FL spectrophotometer (Hitachi, Japan) was used for all the fluorescence measurement.

2.4. Determination Method

2.4.1. Extraction

At room temperature, the sample solution after treatment and the pH buffer were added into a tube, and then distilled water was added to 40.0 mL. 0.1 g IL MNPs was added into the tube. The mixture was shaken on the timing multifunctional oscillator for 20.0 min and then centrifuged. ethanol of 3.0 mL as elution was added into the used IL MNPs. The mixture was ultrasonically vibrated at room temperature and then centrifuged to obtain supernatant solution. Supernatant solution was determined with fluorescence spectrophotometer.

2.4.2. Fluorescence Measurements

In a test tube (10.0 mL), 0.05 g 0.01mol/L IL-MNPs, 0.3mL of ethanol, 2.0 mL of buffer solution (pH=3.0) and adequate Rhodamine B standard solution or sample solution were added; the solution was diluted to the mark with distilled water. Then fluorescence spectra were recorded in the range of 300-700 nm upon excitation at 570 nm.

2.5. Sample Preparation

An amount of 5 g of chili powder/hot pepper/ Chinese prickly ash were accurately weighed into the beakers respectively, dissolved in 80.0 mL of ethanol. The resultant clear solution was evaporated to dryness at 60°C The residue was diluted with distilled water into a 100.0 mL flask and stored in darkness for detection.

3. Results and Discussion

3.1. Characterization of the MNPs

The synthesized Fe₃O₄@SiO₂@ILsMNPs were characterized by FT-IR spectroscopy, thermo-gravimetrical analysis and magnetic characterization.

Figure 1. was shown the FTIR spectra of Fe_3O_4 (curve a), $Fe_3O_4@SiO_2$ (curve b), $Fe_3O_4@SiO_2@[BMIM]PF_6$ (curve c), $Fe_3O_4@SiO_2@[HMIM]PF_6$ (curve d) and $Fe_3O_4@SiO_2@[OMIM]PF_6$ (curve e). Compared the curves of a and b, a peak of 580 cm⁻¹ was assigned to Fe-O-Fe stretching vibration; the strong peaks of 1200-1000 cm⁻¹ correspond to the Si-O-H and Si-O-Si stretching vibration; which indicated that SiO_2 had been successfully loaded on the surface of Fe_3O_4. In the curve c, d and e, the peaks at 2920 cm⁻¹ and 2850 cm⁻¹ corresponded to the C-H stretching vibration; the peaks at 1575 cm⁻¹ corresponded to the characteristic absorption of imidazole groups in the $Fe_3O_4@SiO_2@ILs$; in addition, the peak of 840 cm⁻¹ was attributed to the P-F stretching vibration in the $Fe_3O_4@SiO_2@ILs$ [28], which indicated that ILs had been successfully immobilized on the surface of $Fe_3O_4@SiO_2$.

Thermo-gravimetric analysis (TGA) was conducted in a nitrogen atmosphere, and the heating rate employed was 5°C min⁻¹ all cases from 25 to 1000°C. Figure 2 presents the TGA of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@[OMIM]PF_6$. The figure, illustrates a weight loss of 2.7% at 240°C corresponding to

the water content. Compared curve a and b, an additional weight loss of 6.6% is observed from 200 to 650°Cwhich is due to the ILs coating.
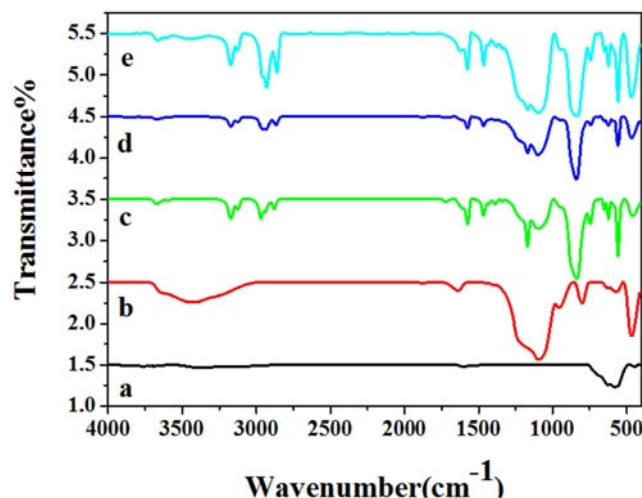

Figure 1. *(a) FTTR spectra of Fe₃O₄ (a), Fe₃O₄@SiO₂ (b), Fe₃O₄@SiO₂@[BMIM]PF₆ (c), Fe₃O₄@SiO₂@[HMIM]PF₆ (d)and Fe₃O₄@SiO₂@[OMIM]PF₆ (e).*

* 1-octyl-3-methylimidazolehexafluorophosphate ([OMIM]PF₆), (1-butyl-3-methylimidazole hexafluorophosphate ([BMIM]PF6),1-hexyl-3-methyl-imidazole hexafluoro-phosphate ([HMIM]PF6)
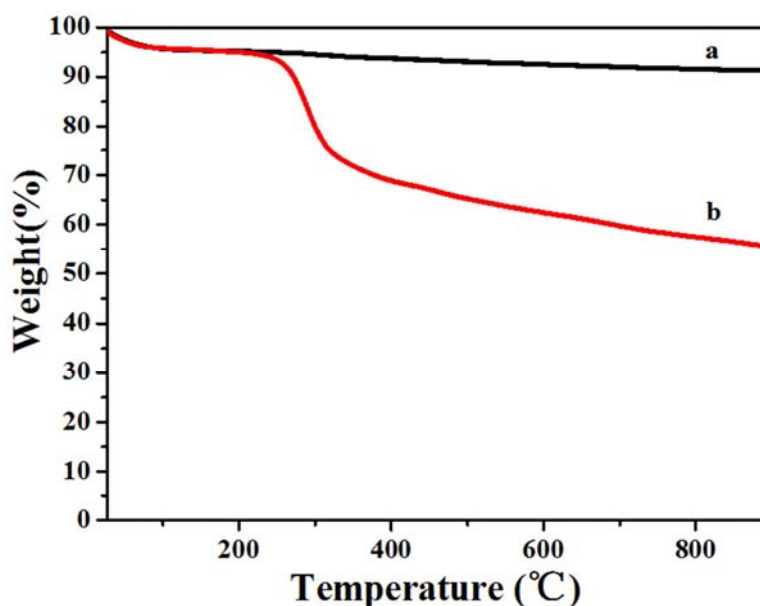

Figure 2. *TGA curves of Fe₃O₄@SiO₂ (a) and Fe₃O₄@SiO₂@IL (b).*

3.2. Optimization of Adsorption

The factors affecting the adsorption process of RhB such as pH, temperature and solution volume were studied and the adsorption behavior of Fe₃O₄@SiO₂@PIL on RhB was compared with that of MNPs.

3.2.1. Effect of pH

As shown in Figure 3, the adsorption efficiency of RhB was varied with the pH, which was between 3.0 to 12. It could be concluded that the adsorption (retention) efficiency of RhB on IL MNPs was above 90.0%. It reached the highest value 94.44% when pH was 3.0. As the dissociation constant (pKa) of RhB is 3.2, the major existence form of RhB was molecule form at pH 3.0, the hydrophobicity of molecule form was stronger than its ionic form, Therefore, pH 3.0 was selected for the subsequent assays.

3.2.2. Effect of Adsorption Temperature and Time

The adsorption efficiency of RhB on IL MNPs and MNPs at different temperatures (5.0-60°C) were studied (Figure 4). The adsorption efficiency of RhB on $Fe_3O_4@SiO_2@IL$ was higher than that on MNPs and was always above 70% from 0.5°C to 15.°C and was above 85% from 0.20°C to 50.°C. The experiment was carried out at room temperature.
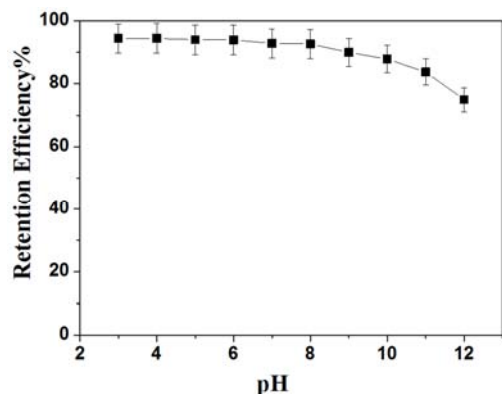

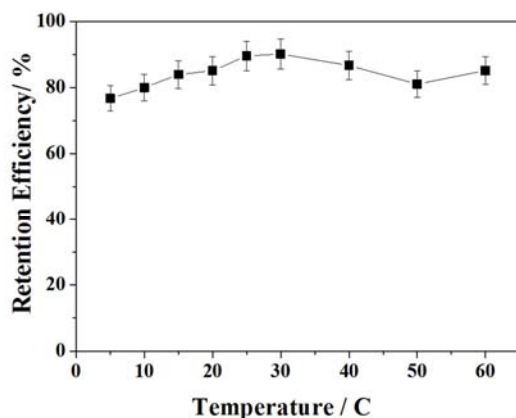**Figure 3.** *Effect of pH on extraction efficiency (c_{c0}=10 µg mL⁻¹).*

Figure 4. *Effect of temperature on extraction efficiency (c_{c0}=10 µg mL⁻¹).*

Effect of adsorption time on extraction efficiency shows the extraction process was completed within 15.0 min, and the adsorption efficiency remained almost stable (86.0%). 15.0 min as the adsorption time for RhB was adopted (Figure 5).
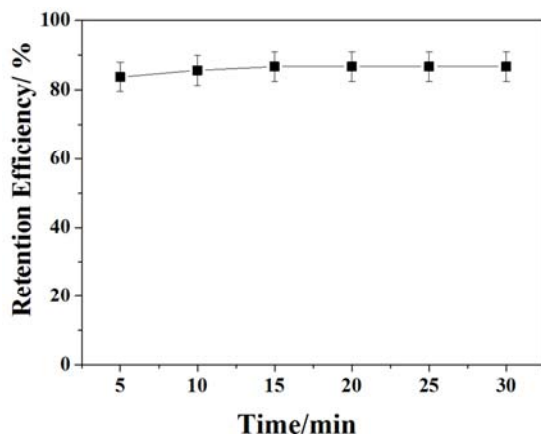

Figure 5. *Effect of adsorption time on extraction efficiency (c_{c0}=10 µg mL⁻¹).*

3.2.3. Effect of the Sample Volume

The adsorption efficiency of RhB varied with the increase of sample volume. The amount of RhB was fixed at 50.0 µg and the volume of the sample solution increased from 10.0 mL to 90.0 mL. The adsorption efficiency of RhB was above 89% from 10.0 to 80.0 mL and remain steady. and 77.85% when sample volume was 90.0 mL. So the largest sample volume allowed was 80.0 mL (Figure 6).
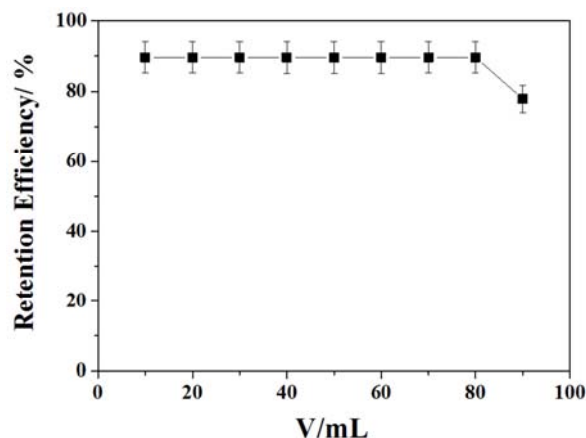

Figure 6. *Effect of Sample volume on extraction efficiency (c_{c0}=10 µg mL⁻¹).*

3.3. Adsorption Capacity

The adsorption capacity is defined as the maximum amount of RhB adsorbed per gram of IL MNPs. The adsorption capacity of RhB on IL MNPs was studied (Figure 7). When the concentration of RhB was 50.0 µg/mL (volume: 50 mL), the adsorption of RhB for 0.0225g IL MNPs reached the maximum. The adsorption capacity for IL MNPs was calculated as 105.80 mg/g.
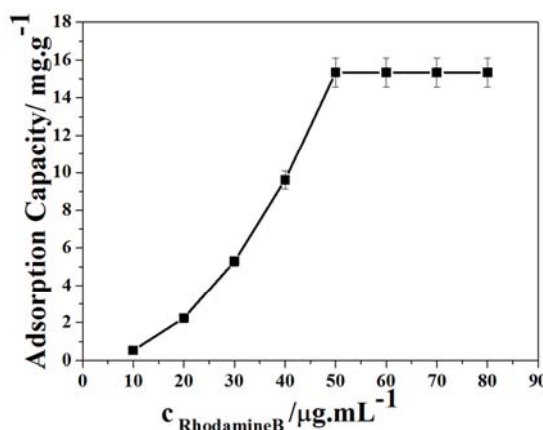

Figure 7. *Adsorption capacity.*

3.4. Optimization of Elution

3.4.1. Selection of Eluent

In this work, different eluents were investigated. The order of elution efficiency was ethanol>methanol> cetyltrimethyl ammonium bromide (CTAB)> sodium dodecyl sulfonate (SDS) > NaOH (0.1 M) > HCl (0.1 M). So ethanol was adopted as the eluent. Figure 8.
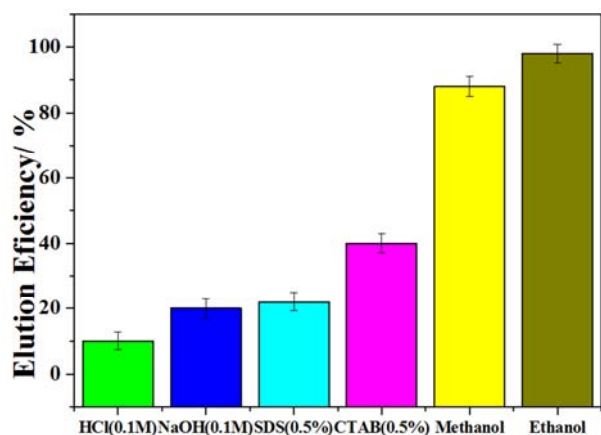
Figure 8. Effect of different dissolvent on elution efficiency.

3.4.2. Eluent Volume

The effect of ethanol volume was evaluated on the elution of RhB. The results in Figure 9 described that quantitative elution (above 90%) was observed as the volume of ethanol was higher than 3.0 mL. The pre-concentration factor is 25-fold. The optimum volume of ethanol was chosen at 3.0 mL.
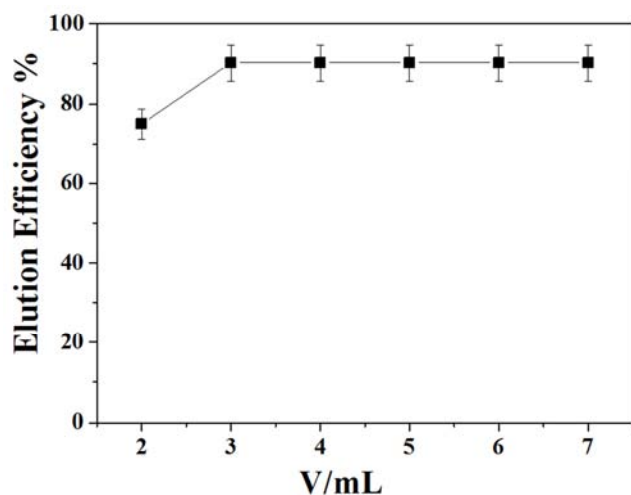

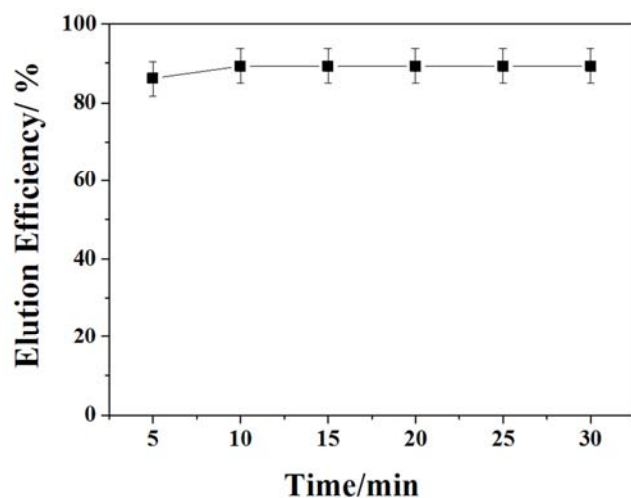*Figure 9. Effect of elution volume on the elution efficiency.*

Figure 10. Effect of elution time on elution efficiency.

3.4.3. Elution Time

The elution process was completed within 10.0 min, and the elution efficiency did not change with a stable elution efficiency of 89.29% thereafter. The elution time of 10.0min for RhB was adopted (Figure 10)

3.5. The Reusability of Fe₃O₄@SiO₂@IL

In order to investigate the recycling of the Fe_3O_4@SiO₂NPs, they were washed with 2mL ethanol for twice after each MSPE run, and subsequently assembled with IL. Each re-prepared adsorbent was used for MSPE. The experimental results are shown in Figure 11. It was clear that no obvious loss of the adsorption capacity occurred after ten times of recycling.
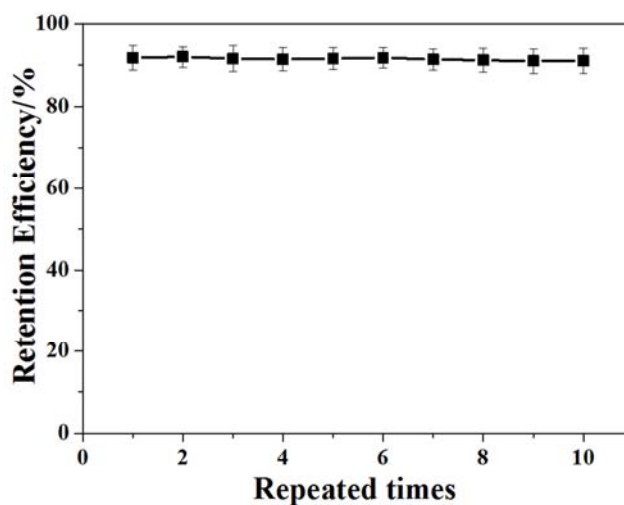
Figure 11. Effect of reuse of IL MNPs in extraction and elution.

3.6. Evaluation of Interferents

With a relative error of less than ±5%, the influence of some interferents that food samples contain on the determination of RhB in the presence of foreign substances was investigated. the tolerance limit for various foreign substances is in table 1. The results indicated that the majority of these substances in samples had no remarkable interference on the (RhB) determination.

Table 1. Tolerance of interfering substances.

Interferent	Tolerance ratio
SO_4^{2-}, Br^-	400
Citrate, glucose	230
NO^-	90
Zn^{2+}, Cu^{2+}, phenol	18
Safranin, Bright yellow, Sunset Yellow	17
Allura Red, Congo red	8
Rhodamine 6G	2

3.7. Analytical Performance of the Method

Under the optimum conditions, the linear calibration curve was obtained in the concentration range of 0.40-140.00 μg L⁻¹. The equations of calibration graph is I (peak area) =

11.97c+12.11 (µg L^{-1}), with a correlation coefficient of 0.9993. The limit of detection (DL) was 0.06 µg L^{-1}. The relative standard deviation was 0.45% (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

The proposed method was applied to determine RhB in chili powder, hot pepper and Chinese prickly ash. RhB is 5.46 µg kg^{-1} in chili powder, with a recovery rate of RhB of 97.0% to 103.5%. and it was 4.53 µg kg^{-1} in hot powder with a recovery rate of RhB of 98.0%.

No RhB is detected in Chinese prickly ash, the recovery rate of RhB was from 100.7% to 100.1%.

Table 2. *Determination results of the samples.*

Sample	Added (µg kg^{-1})	Found (µg kg^{-1})	Recovery (%)
	0	5.46	—
Chili powder	6.00	5.01	103.5
	60.00	49.50	97.0
	102.00	100.9	101.8
	0	4.53	—
Hot pepper	50.00	4.03	98.0
	102.0	100.5	100.7
	0	ND	—
Chinese prickly ash	6.00	5.02	100.7
	60.00	50.4	100.8
	103.00	101.2	100.1

3.9. Comparison of the Proposed Method with Relevant Literature

The comparison of current work with some other methods on the determination of RhB (Table 2) reveals that this method is either comparable or has rather pronounced advantages over them. Moreover, it is obvious that the present work has high sensitivity, wide linear range, and easy operation.

Table 3 listed the linear range and the limit of detection for the analysis of RhB in real samples obtained by the reported methods, such as solid phase extraction coupled with UV spectrophotometry, solid phase extraction coupled with high performance liquid chromatography, and HPLC–CL method. Compared with other reported methods, the method adopted in the present work obviously had a satisfactory linear range and limit of detection.

Table 3. *Comparison with the results in other literatures.*

Method	LR (µg/L)	LOD (µg/L)	RSD (%)	Ref
SPE-UV	_	3.14	5.0	[30]
SPE–HPLC	1000-10,000	250	2.87	[31]
HPLC–CL	1.5-82.1	1.50	4.0	[32]
MSPE-Fluorescence	0.40-140.00	0.06	0.45	This method

4. Conclusion

In this work, IL MNPs was synthesized as magnetic solid phase extraction adsorbent to pre-concentrate/separate RhB from real samples. In summary, we have prepared Fe$_3$O$_4$@SiO$_2$@IL as adsorbent, for MSPE of. The magnetic nano-adsorbent is prepared by a self-assembly technique, which is very simple and mild. Compared with traditional SPE, this MSPE based on the Fe$_3$O$_4$@SiO$_2$@IL MNPs as an SPE adsorbent is fast, and the adsorbent can be easily separated from the sample solution. Moreover, this adsorbent has a high extraction capacity and high enrichment factors and is able to treat large-volume samples in a short period of time. The hydrocarbon chains of ILs on the surface of the adsorbent can provide adsorption sites for Rhodamine B other organic pollutants through π–π and hydrophobic interactions. The proposed method for the analysis of Rhodamine B is satisfactory. Thus, this adsorbent may also find potential application in the extraction and analysis of other analytes.

References

[1]   Alesso, M., Bondioli, G., Talio, M. C., Luconi, M. O.,& Fernandez, L. P. (2012). Micelles mediated separation fluorimetric methodology for Rhodamine B determination in condiments, snacks and candies. Food Chemistry, 134, 513–517.

[2]   Roberts, A. L. K., Fletcher, J. M., Moore, L., & Byers, S. (2010). Trans-generational exposure to low levels of rhodamine B does not adversely affect litter size or liver function in murine mucopolysaccharidosis type IIIA. Molecular Genetics and Metabolism, 101, 208–213.

[3]   Xie, C., Chang, J., Hao, X. D., Yu, J. M., Liu, H. R., & Sun, X. (2013). Mitochondrial-targeted prodrug cancer therapy using a rhodamine B labeled fluorinated docetaxel. European Journal of Pharmaceutics and Biopharmaceutics, 85, 541–549.

[4]   Xiao, J., Gong, S., & Ledoux, M. S. (2007). Caytaxin deficiency disrupts signaling pathways in cerebellar cortex. Journal of Neuroscience, 144, 439–461.

[5]   Jain, R., Mathur, M., Sikarwar, S., & Mittal, A. (2007). Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments. Journal of Environmental Management, 85, 956–964.

[6]   Baldev, E., MubarakAli, D., Ilavarasi, A., Pandiaraj, D., Sheik Syed Ishack, K. A., & Thajuddin, N. (2013). Degradation of synthetic dye, Rhodamine B to environmentally non-toxic products using microalgae. Colloids and Surfaces B: Biointerfaces, 105, 207–214.

[7]   Sun, W. J., Li, J., Mele, G., Zhang, Z. Q., & Zhang, F. X. (2013). Enhanced photocatalytic degradation of rhodamine B by surface modification of ZnO with copper (II) porphyrin under both UV–vis and visible light irradiation. Journal of Molecular Catalysis A: Chemical, 366, 84–91.

[8]   Chauhan, V. M., Hopper, R. H., Ali, S. Z., King, E. M., Udrea, F., Oxley, C. H., & Aylott, J. W. (2014). Thermo-optical characterization of fluorescent rhodamine B based temperature-sensitive nanosensors using a CMOS MEMS micro-hotplate. Sensors and Actuators B, 192, 126–133.

[9]   Desiderio, C., Marra, C., & Fanali, D. S. (1998). Quantitative analysis of synthetic dyes in lipstick by micellar electrokinetic capillary chromatography. Electrophoresis, 19, 1478–1483.

[10] Valverde, R. S., Perez, I. S., Franceschelli, F., Galera, M. M., & Gil Garcia, M. D. (2007). Determination of photoirradiated tetracyclines in water by high-performance liquid chromatography with chemiluminescence detection based reaction of Rhodamine B with cerium (IV). Journal of Chromatography A, 1167, 85–94.

[11] Ibarra, I. S., Miranda, J. M., Rodriguez, J. A., Nebot, C., & Cepeda, A. (2014). Magnetic solid phase extraction followed by high-performance liquid chromatography for the determination of sulphonamides in milk samples. Food Chemistry, 157, 511–517.

[12] Jiang, H. M., Yang, T., Wang, Y. H., Lian, H. Z., & Hu, X. (2013). Magnetic solid-phase extraction combined with graphite furnace atomic absorption spectrometry for speciation of Cr (III) and Cr (VI) in environmental waters. Talanta, 116, 361–367.

[13] Gao, Q., Zheng, H. B., Luo, D., Ding, J., & Feng, Y. Q. (2012). Facile synthesis of magnetic one-dimensional polyaniline and its application in magnetic solid phase extraction for fluoroquinolones in honey samples. Analytica Chimica Acta, 720, 57–62.

[14] Cao, X. J., Shen, L. X., Ye, X. M., Zhang, F. F., Chen, J. Y., & Mo, W. M. (2014). Ultrasound-assisted magnetic solid-phase extraction based ionic liquid-coated Fe_3O_4@graphene for the determination of nitrobenzene compounds in environmental water samples. Analyst, 10, 1–8.

[15] Liu, X. D., Yu, Y. J., Zhao, M. Y., Zhang, H. Y., Li, Y., & Duan, G. L. (2014). Solid phase extraction using magnetic core mesoporous shell microspheres with C_{18}-modified interior pore-walls for residue analysis of cephalosporins in milk by LC–MS/MS. Food Chemistry, 150, 206–212.

[16] Dzyuba, S. V., & Bartsch, R. A. (2001). Efficient synthesis of 1-alkyl (aralkyl)-3-methyl (ethyl) imidazolium halids: precursors for room-temperature ionic liquids. Journal of Heterocyclic Chemistry, 38, 265–268.

[17] Chun, S., Dzyuba, S. V., & Bartsch, R. A. (2001). Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkai metal salt extraction by a crown ether. Analytical Chemistry, 73, 3737–3741.

[18] Holbrey, J. D., & Seddon, K. R. (1999). The phase behaviour of 1-alky-l 3-methylimidazolium tetrafluoroborates; ionic liquid and ionic liquid crystals. Jurnal of the Chemical Society-Dalton Transactions, 13, 2133–2139.

[19] Tokuda, H., Hayamizu, K., Ishii, K., Susan, M. A. B. H., Tsuzuki, S., Hayamizu, K., & Watanabe, M. (2004). Physicochemical properties and structures of room temperature ionic liquids. 1. variation of anionic species. The Journal of Physical Chemistry B, 108, 16593–16600.

[20] Huang, R. X., Fang, Z. Q., Yan, X. M., & Cheng, W. (2012). Heterogeneous sono-Fenton catalytic degradation of bisphenol A by Fe_3O_4 magnetic nanoparticles under neutral condition. Chemical Engineering Journal, 197, 242–249.

[21] Hong, R. Y., Zhang, S. Z., Han, Y. P., Li, H. Z., Ding, J., & Zheng, Y. (2006). Preparation, characterization and application of bilayer surfactant-stabilized ferrofluids. Powder Technology, 170, 1–11.

[22] Hou, Y. H., Han, X. Y., Chen, J., Li, Z. L., Chen, X. C., & Gai, L. G. (2013). Isolation of PCR-ready genomic DNA from Aspergillus niger cells with Fe_3O_4/SiO_2 microspheres. Separation and Purification Technology, 116, 101–106.

[23] Hu, C. H., Deng, J., Wang, J., Zhao, Y. B., Xia, L. S., Huang, K. H., Ju, S. Q., & Xiao, N. (2014). A novel core-shell magnetic nano-sorbent with surface molecularly imprinted polymer coating for the selective solid phase extraction of dimetridazole. Food Chemistry, 158, 366–373.

[24] Dang, G. F., Ma, X. G., & Zhou, J. P. (2012). Preparation of Silica-coated Magnetic Nanomaterials Modified with ionic liquid and its application in detection of trace cadmium ion in water. China Journal of Instrumental Analysis, 7, 823–827.

[25] Cano, F. G., Alcudia-Leon, M. C., Lucena, R., Cardenas, S., & Valcarcel, M. (2013). Ionic liquid coated magnetic nanoparticles for the gaschromatography/mass spectrometric determination of polycyclicaromatic hydrocarbons in waters. Journal of Chromatography A, 1300, 134–140.

[26] Deng, N., Li, M., Zhao, L. J., Lu, C. F., Rooy, S. L., & Warner, I. M. (2011). Highly efficient extraction of phenolic compounds by use of magnetic room temperature ionic liquids for environmental remediation. Journal of Hazardous Materials, 192, 1350–1357.

[27] Liu, X. F., Lu, X., Huang, Y., Liu, C. W., & Zhao, S. L. (2014). Fe_3O_4@ionic liquid@methyl orange nanoparticles as a novel nano-adsorbent for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples. Talanta, 119, 341–347.

[28] Hu, Y. Q., Guo, T., Ye, X. S., Li, Q., Guo, M., Liu, H. N., & Wu, Z. J. (2013). Dye adsorption by resins: Effect of ionic strength on hydrophobic and electrostatic interactions. Chemical Engineering Journal, 228, 392–397.

[29] Ho, T. D., Cole, W. T. S., Augusto, F., & Anderson, J. L. (2013). Insight into the extraction mechanism of polymeric ionic liquid sorbent coatings in solid-phase microextraction. Journal of Chromatography A, 1298, 146–151.

[30] Soylak, M., Unsal, Y. E., Yilmaz, E., & Tuzen, M. (2011). Determination of rhodamine B in soft drink, waste water and lipstick samples after solid phase extraction. Food and Chemical Toxicology, 49, 1796–1799.

[31] Li, X. W., Zhang, J. W., & Lu, T. L. (2011). Comparison of random vibration responses between traditional model and coupled model for a road-rail fire fighting vehicle. International Journal of Vehicle Noise and Vibration, 3, 238–252.

[32] Zhang, Q., Cui, L. H., Myint, A., Lian, M., & Liu, L. J. (2005). Sensitive determination of phenolic compounds using high-performance liquid chromatography with cerium (IV) rhodamine 6G-phenolic compound chemiluminescence detection. Journal of Chromatography A, 1095, 94–101.