

# Determination of Safranin T Pigment in Food Samples by Ionic Liquid Coated Magnetic Core/Shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ Nanoparticles Coupled with Fluorescence Spectrophotometry

Almojtaba Abd Alkhalig Ahmed Bakheet<sup>1, 2</sup>

<sup>1</sup>Department of Family Sciences, Faculty of Education, University of Khartoum, Khartoum, Sudan

<sup>2</sup>College of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou, China

## Email address:

m.bakeet@yahoo.com, moj76@uofk.edu

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**Abstract:** Three hydrophobic ionic liquids (IL) 1-octyl-3-methylimidazole hexafluorophosphate ([OMIM]PF<sub>6</sub>) (1-butyl-3-methylimidazole hexafluorophosphate ([BMIM]PF<sub>6</sub>), 1-hexyl-3-methyl-imidazole hexafluoro-phosphate ([HMIM]PF<sub>6</sub>), were coated by  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoparticles with core-shell structure to prepare magnetic solid phase extraction agent ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{IL}$ ) and establish a new method of magnetic solid phase extraction (MSPE) coupled with Fluorescence spectrophotometry for separation/analysis of safranin T (ST). The results showed that safranin T was adsorbed rapidly by  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  and eluted by ethanol., pre-concentration factor of the proposed method was 20-fold. Under the optimal conditions the linear range, detection limit (DL), correlation coefficient (R) and relative standard deviation (RSD) were found to be 0.30-130.00  $\mu\text{g L}^{-1}$ , 0.05  $\mu\text{g L}^{-1}$ , 0.9998 and 0.35% (n=3, c=10.00  $\mu\text{g L}^{-1}$ ), respectively. The  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  NPs can be used repeatedly for 10 times. This proposed method has been successfully applied to the determination of safranin T in food samples.

**Keywords:** Safranin T, Ionic Liquid Loaded Magnetic Nanoparticles, Magnetic Solid Phase Extraction, Fluorescence Spectrophotometry

## 1. Introduction

Safranin T (ST) is a type of alkali industrial dye or stain (Figure 1), that could be used in different dyeing manufactories [1]. ST was also known as food additives [2], however, in many food manufactories ST was illegally used to improve the properties of food products [3], so introducing a simple and fast method for the separation of ST in dietary products is very important. The well-known techniques for ST separation were performed by using high performance liquid chromatography (HPLC), UV-visible spectrophotometry and the fluorescence method depend on calixarene derivatives. Among these methods, Fluorescence spectrophotometry has many advantages of easy operation and low-cost analysis which should be combined with

separation and enrichment techniques to improve the selectivity and sensitivity of detection..

The definition of magnetic solid phase extraction (MSPE) was that, it is a process depend on using magnetic sorbents for separation of various analytes in different volume of the sample [4]. In MSPE procedures. The magnetic absorbent was mixed with sample and the analyte was absorbed by magnetic sorbents. The analyte- magnetic sorbents were then separated from the sample by using an external magnetic field, after being eluted by a perfect eluent [5]. However, MSPE has been used in widely in many analysis fields such as food, environmental and biological analysis [6, 7]

Nowadays, scientists are focusing on the use of  $\text{Fe}_3\text{O}_4$

nanoparticles (NPs) as MSPE absorbent with special functional groups change to measure the amount of the target analytes. various material were applied in Fe<sub>3</sub>O<sub>4</sub>NPs modification. some scientists selected poly aniline coated Fe<sub>3</sub>O<sub>4</sub> (PANIs/Fe<sub>3</sub>O<sub>4</sub>) as sorbents for MSPE fluoroquinolones in honey samples [8]. Pardasani et al. used multi-walled carbon nano-tube functionalized Fe<sub>2</sub>O<sub>3</sub> (MWCNT/Fe<sub>2</sub>O<sub>3</sub>) as sorbents for dispersive SPE of nerve agents from water [9].

Ionic liquid (IL), are a type of organic salts possess special physicochemical properties, like good stability and hydrophobic properties [10]. Many studies had described the utilization of IL through SPE [11, 12]. Ionic liquids coated MNPs were used as an adsorbent in separation of aromatic hydrocarbons in water [13]. Fe<sub>3</sub>O<sub>4</sub>@IL@methyl orange NPs were used for separation of PAHs in water [14]. However, it has not been reported to separate or extract ST with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub>.

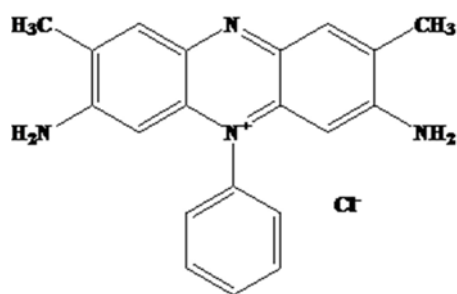


Figure 1. Chemical structure of Safranin T.

In the present work, MSPE sorbents (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub>) were prepared, these sorbents have the property of the ionic liquids and (MNPs). When compared other studies, these MSPE sorbents provides a rapid, and efficient sample preparation process, which enables the treatment of large volume samples in a short period of time [15]., 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 ST 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 potassium bromide KBr pellets and recorded at the frequencies from 4000 to 400 cm<sup>-1</sup> with resolution of 4 cm<sup>-1</sup>. A Tecnai 12 TEM (Philips, Netherlands) was used to obtain micrographs of the MNPs. spectrophotometric separation of analytes was achieved with Fluorescence spectrophotometry.

All chemicals and reagents were at least of analytical reagent grade, unless otherwise stated. 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<sub>6</sub>, FeCl<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, methanol, ethanol, acetone, methylene chloride (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China).

### 2.2. Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IL

The hydrophobic ionic liquid, 1-octyl-3-methylimidazole hexafluoro- phosphate ([OMIM]PF<sub>6</sub>) was prepared according to literature [16, 17].

Fe<sub>3</sub>O<sub>4</sub> MNPs were prepared by conventional co-precipitation method [18, 19]. First, FeCl<sub>3</sub> (3.30 g) was dissolved in deionized water (80 mL) followed by addition of polyethylene glycol (40 mL, 10%, w/w) and of (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> (4.23 g) in water solution under stirring. Then ammonium hydroxide (8 mL, 26.5%, w/w) was added rapidly under vigorous stirring. The resultant solution was stirred (3000 r min<sup>-1</sup>) at 80°C for 60 min. After cooling to room temperature, the obtained Fe<sub>3</sub>O<sub>4</sub> precipitate was collected by an external magnetic field, washed with deionized water five times and dried at 60°C for 12 h in vacuum.

The preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was done according to literature. Fe<sub>3</sub>O<sub>4</sub> (1.0 g) were dissolved in 200 mL of the ethanol and 50 mL of deionized water by sonication for 15 min, and then 4 mL ammonium hydroxide and 6 mL TEOS were added sequentially. The mixture was reacted for 6 h at 60°C under a continuous stirring. The resultant product was collected by an external magnetic field, and rinsed with deionized water and ethanol for six times thoroughly, and then dried in vacuum to obtain Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.

IL functionalized MNPs Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub> (Figure 2) were prepared according to process detailed in literature [20]. A 4.00 g of [OMIM]PF<sub>6</sub> was dissolved in 60.0 mL acetone, and then 3.00 g Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were added. Stir the mixture inside the fume hood until the acetone completely evaporated. The obtained Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub> functionalized material was washed with methylene chloride and dried at 60°C under vacuum for 12 h. The solid was carefully grinded into powders, which were Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub> MNPs [21].

### 2.3. Magnetic Solid Extraction (MSPE) Procedure

The procedure was done as follows. First, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub> MNPs were added to a 90 mL water sample containing ST (pH=7.0), and the mixture was placed on a slow-moving platform shaker and allowed to equilibrate for 15 min at 25°C. Then, a strong magnet was applied to the bottom of the beaker, isolating the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub> MNPs from the suspension. After 15 min, the suspension was decanted and the residual solution of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub> MNPs was transferred to centrifuge tube. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@[OMIM]PF<sub>6</sub> MNPs 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. Extraction Efficiency of Different MNPs

In this work, six types of NPs ( $\text{Fe}_3\text{O}_4$ ,  $\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{BMIM}]\text{PF}_6$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{HMIM}]\text{PF}_6$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$ ) on the extraction efficiency of ST were evaluated (Figure 2). The extraction efficiency of the NPs increased in the order of  $\text{Fe}_3\text{O}_4 < \text{SiO}_2 < \text{Fe}_3\text{O}_4@\text{SiO}_2 < \text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{BMIM}]\text{PF}_6 < \text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{HMIM}]\text{PF}_6 < \text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  under the same experimental conditions. The extraction efficiency of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  is far less than that of three kinds of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@$  ILs, because the extraction of ST largely depends on the hydrophobicity of ILs. Compared  $[\text{BMIM}]\text{PF}_6$ ,  $[\text{HMIM}]\text{PF}_6$  and  $[\text{OMIM}]\text{PF}_6$ , the extraction efficiency extraction was gradually increased with the loaded IL cation alkyl chain growth, this is because the hydrophobicity of ILs as the growth of the cationic alkyl chain and strengthen [22]. Moreover, the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  with longer alkyl chain showed the highest extraction efficiency. Therefore,  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  was employed in this study.

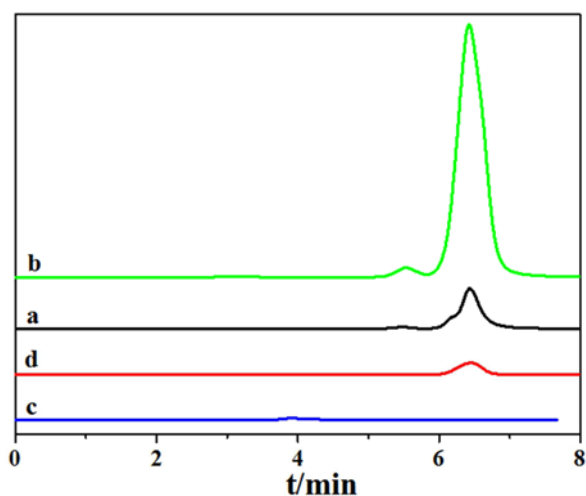


Figure 2. Chromatograms of ST.

ST standard solution(a); ST standard solution after separation(b); Tomato sauce A sample(c); Tomato sauce B after separation(d).

#### 2.5. Fluorescence Measurements

In a 10.0 mL test tube, 0.05 g 0.01 mol/L IL-MNPs, 0.3 mL of ethanol, 2.0 mL of buffer solution (pH=3.0) and adequate safranin T 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.

#### 2.6. Sample Preparation

An amounts of 20.0 g of 2 different manufactured tomato sauce was accurately weighed into the beakers, dissolved in

40.0 mL of ethanol + 1.0 mL of ammonia. Then 0.4 mL of the resultant clear solution was added to 1.5 g of IL  $[\text{OMIM}]\text{PF}_6$  and 2.0 mL of NaCl 15% was added to 10.0 mL test tubes from 3 different types of samples.

### 3. Results and Discussion

#### 3.1. Characterization of the MNPs

The synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2@$ ILs MNPs were characterized by FT-IR spectroscopy, thermogravimetric analysis and magnetic characterization.

Figure 3. A was shown the FTIR spectra of  $\text{Fe}_3\text{O}_4$  (curve a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (curve b),  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{BMIM}]\text{PF}_6$  (curve c),  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{HMIM}]\text{PF}_6$  (curve d) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  (curve e). Compared curves of a and b, the peak at  $1630\text{cm}^{-1}$  was due to the propriety of Si-O-Si, then the peak at  $750\text{cm}^{-1}$  might be at tribute to the silanol groups (Si-OH) of silica, for FTIR spectra of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , the peak at  $550\text{cm}^{-1}$  was significantly reduced. But in the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$ , the peak at wave numbers 750 and  $1360\text{cm}^{-1}$  were due to P-F stretching vibration of imidazole ring in  $[\text{OMIM}]\text{PF}_6$ -MNPs, which showed that Ionic liquid (IL) was well immobilized on the surface of the magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ).

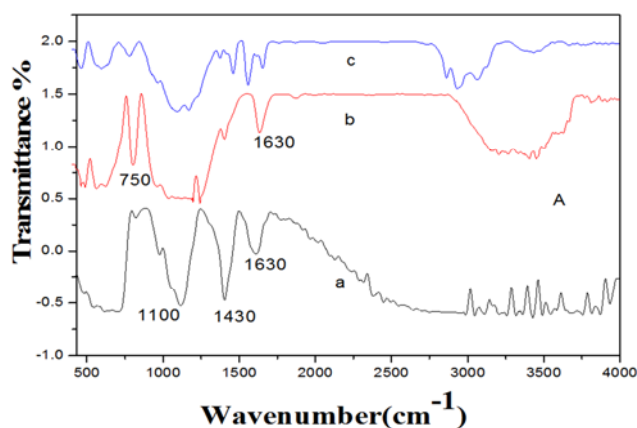


Figure A

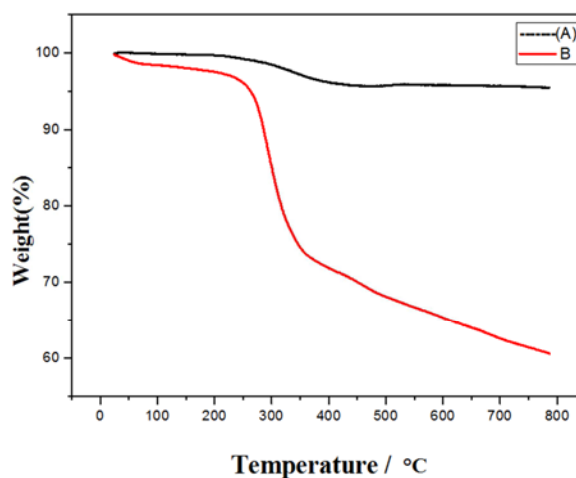


Figure B

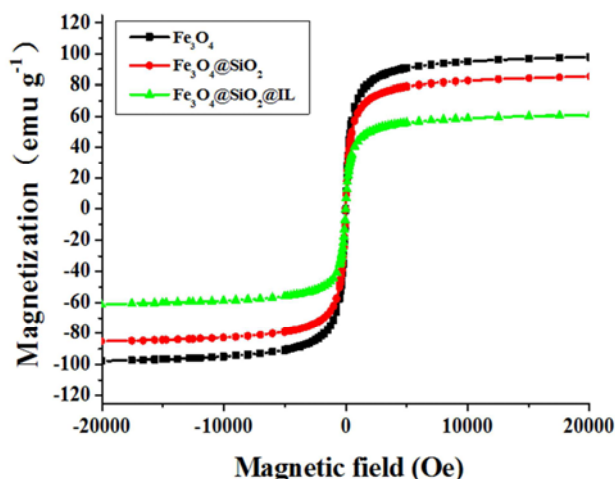


Figure.C

**Figure 3.** (A) FTTR spectra of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b),  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{BMIM}]\text{PF}_6$  (c),  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{HMIM}]\text{PF}_6$  (d) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  (e). (B) TGA curves of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (a) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{IL}]$  (b). (C) Magnetic hysteresis loops of the  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{IL}]$ .

Thermo-gravimetric analysis (TGA) was conducted in a nitrogen atmosphere, and the heating rate employed was  $5^\circ\text{C min}^{-1}$  all cases from 25 to  $800^\circ\text{C}$ . Figure 3. B presents the TGA of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (curve a) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{IL}]$  (curve b). In Figure 3, illustrates a weight loss of 30% at  $250^\circ\text{C}$  corresponding to the water content. Compared curve a and b, an additional weight loss of 4.6% is observed from 300 to  $350^\circ\text{C}$ . which is due to the ILs coating.

Magnetic characterization using a magnetometer at  $27^\circ\text{C}$  indicates that the maximal saturation magnetizations of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  MNPs were 97.0, 85.3 and 61.1  $\text{emu g}^{-1}$ , respectively. The decrease of maximal saturation magnetizations of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  MNPs resulted from the nonmagnetic IL shell. Figure 3.C describes the magnetic hysteresis loops of the three MNPs, and it is apparent that all of the NPs show superparamagnetic properties in the presence of magnetite particles in the core. Therefore, the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{OMIM}]\text{PF}_6$  MNPs prepared here could be rapidly separated from solution with a magnet on account of their superparamagnetism and large saturation magnetization.

### 3.2. Optimization of Adsorption

The factors affecting the adsorption process of safranin T such as pH, temperature and solution volume were studied and the adsorption behavior of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{IL}]$  on ST was compared with that of MNPs.

#### 3.2.1. Effect of pH

As shown in Figure 4, the adsorption efficiency of ST was varied with the pH, which was between 3.0 to 12. It could be concluded that the adsorption (retention) efficiency of ST on IL MNPs was above 80.0%. It reached the highest value 83.28% when pH was 7.0. Therefore, pH 7.0 was selected for the subsequent assays.

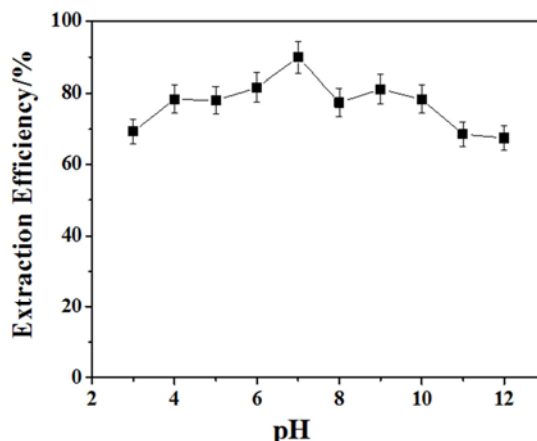


Figure 4. Effect of pH on extraction efficiency ( $c_{c0}=10 \mu\text{g mL}^{-1}$ ).

#### 3.2.2. Effect of Adsorption Temperature and Time

The adsorption efficiency of ST on IL MNPs and MNPs at different temperatures ( $5.0$ – $50^\circ\text{C}$ ) were studied (Figure 5). The adsorption efficiency of AR on  $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{IL}]$  was higher than that on MNPs and was always above 70% from  $10^\circ\text{C}$  to  $15^\circ\text{C}$  and was above 80% from  $0.20^\circ\text{C}$  to  $30^\circ\text{C}$ . The experiment was carried out at room temperature.

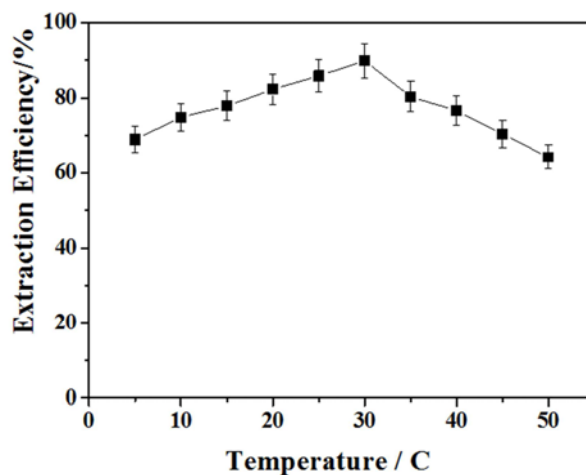


Figure 5. Effect of temperature on extraction efficiency ( $c_{c0}=10 \mu\text{g mL}^{-1}$ ).

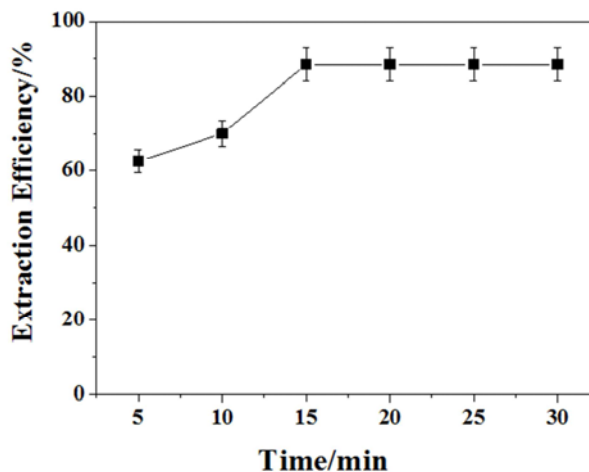


Figure 6. Effect of adsorption time on extraction efficiency ( $c_{c0}=10 \mu\text{g mL}^{-1}$ ).



Effect of adsorption time on extraction efficiency shows the extraction process was completed within 15.0 min, and the adsorption efficiency remained almost stable (88.0%). 15.0 min as the adsorption time for ST was adopted (Figure 6).

### 3.2.3. Effect of the Sample Volume

The adsorption efficiency of ST varied with the increase of sample volume. The amount of ST was fixed at 50.0  $\mu\text{g}$  and the volume of the sample solution increased from 10.0 mL to 90.0 mL. The adsorption efficiency of ST 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 7).

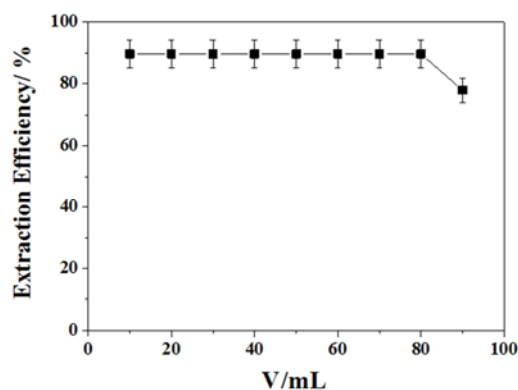


Figure 7. Effect of Sample volume on extraction efficiency ( $c_{\text{ST}}=10 \mu\text{g mL}^{-1}$ ).

### 3.3. Adsorption Capacity

The adsorption capacity is defined as the maximum amount of ST adsorbed per gram of IL MNPs. The adsorption capacity of ST on IL MNPs was studied (Figure 8). When the concentration of ST was 50.0  $\mu\text{g/mL}$  (volume: 50 mL), the adsorption of ST for 0.0225g IL MNPs reached the maximum. The adsorption capacity for IL MNPs was calculated as 105.80 mg/g.

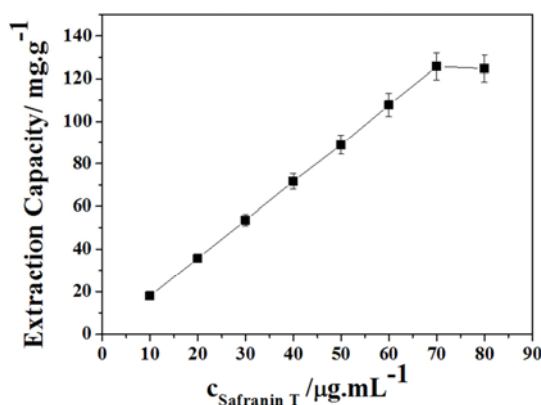


Figure 8. Adsorption capacity.

### 3.4. Optimization of Elution

#### 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 9.

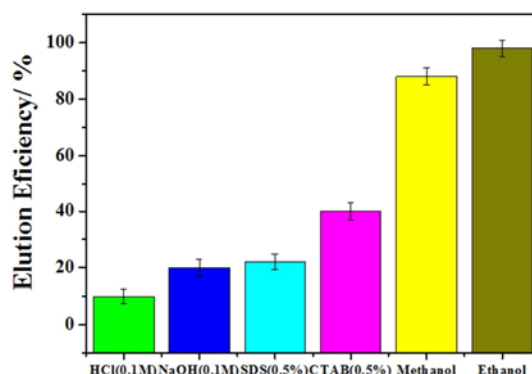


Figure 9. Effect of different eluents on elution efficiency.

The effect of ethanol volume was detailedly evaluated on the elution of ST. The results described that quantitative elution (above 95%) 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.

The elution process was completed within 10.0 min, and the elution efficiency did not change with a stable elution efficiency of 95.% thereafter. The elution time of 10.0min for ST was adopted.

#### Effect of elution temperature

The elution efficiency of ST at different temperatures (5–60°C) was studied. The elution efficiency was increased progressively with an increase of elution temperature from below 40°C. The elution efficiency of ST was greater than 85% and decreased at the elution temperature range from 50 to 60°C. Accordingly, the elution was performed at room temperature.

### 3.5. The Reusability of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{IL}$

In order to investigate the cycling of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  NPs, 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 10. It was clear that no obvious loss of the sorption capacity occurred after ten times of recycling.

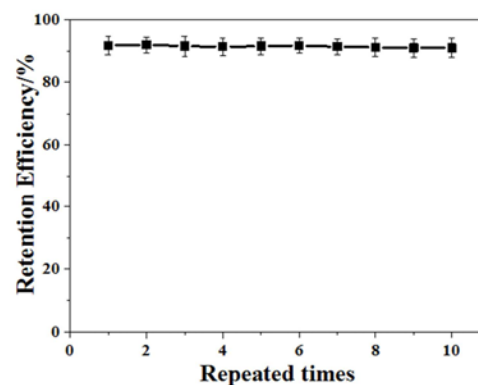


Figure 10. Effect of reuse of IL MNPs in extraction and elution.

### 3.6. Evaluation of Interferents

With a relative error of less than  $\pm 5\%$ , the influence of some interferents that food samples contain on the determination of ST 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 ST determination.

Table 1. Tolerance of interfering substances.

Interferent	Tolerance ratio
SO <sub>4</sub> <sup>2-</sup> , Br <sup>-</sup>	400
Citrate, glucose	230
NO <sup>-</sup>	90
Zn <sup>2+</sup> , Cu <sup>2+</sup> , phenol	18
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 0.30-130.00  $\mu\text{g L}^{-1}$ . The equations of calibration graph is I (peak area) = 11.97c+12.11 ( $\mu\text{g L}^{-1}$ ), with a correlation coefficient of 0.9998. The limit of detection (DL) was 0.05  $\mu\text{g L}^{-1}$ . The relative standard deviation was 0.35% (n=3, c=10.00  $\mu\text{g L}^{-1}$ ). The preconcentration 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 ST in Tomato sauce A, Tomato sauce B. ST is 0.29  $\mu\text{g kg}^{-1}$  in Tomato sauce A, with a recovery rate of ST of 97.4% to 103 %. and it was 0.37  $\mu\text{g kg}^{-1}$  in Tomato sauce B with a recovery rate of ST of 110.0% to 120. 9 %..

Table 2. Determination results of the samples.

	Added ( $\mu\text{g kg}^{-1}$ )	Found ( $\mu\text{g kg}^{-1}$ )	Recovery (%)
Tomato sauce A	0.00	0.23	—
	0.06	0.28	100.1
	0.11	0.35	103.0
	0.16	0.37	97.4
Tomato sauce B	0.00	0.07	—
	0.07	0.16	114.2
	0.13	0.22	110.
	0.18	0.29	120.9

### 3.9. Comparison of the Proposed Method with Relevant Literature

The comparison of current work with some other methods on the determination of ST (Table 3) 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 ST in real samples obtained by the reported methods, 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( $\mu\text{g/L}$ )	LOD( $\mu\text{g/L}$ )	Ref
HPLC fluorescence	1000 - 5.000	4	[23]
UPLC-MS/MS	10 - 500	0.7	[24]
Fluorescence	100 - 4.000	34	[25]
MSPE-Fluorescence	0.30-130.00	0.05	This method

## 4. Conclusion

In this work, IL MNPs was synthesized as magnetic solid phase extraction adsorbent to pre-concentrate/separate ST from real samples. In summary, we have prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@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<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@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 ST other organic pollutants through  $\pi$ - $\pi$  and hydrophobic interactions. The proposed method for the analysis of ST is satisfactory. Thus, this adsorbent may also find potential application in the extraction and analysis of other analytes.

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