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Ionic liquid-based dispersive liquid-liquid microextraction combined with functionalized magnetic nanoparticle solid-phase extraction for determination of industrial dyes in water

Ning Liang¹, Xiaohong Hou¹, Peiting Huang¹, Chao Jiang¹, Lijuan Chen¹ & Longshan Zhao²

N-butyl pyridinium bis((trifluoromethyl)sulfonyl)imide ([Hpy]NTf₂) functionalized core/shell magnetic nanoparticles (MNPs, Fe₃O₄@SiO₂@[Hpy]NTf₂) were prepared and applied as an adsorbent for magnetic solid phase extraction (MSPE) of three commonly used industrial dyes including malachite green, crystal violet and methylene blue. Extraction solution was mixed with 100 mg extraction material of Fe₃O₄@SiO₂@[Hpy]NTf₂, and 1 mL of acetonitrile was used to elute target analytes for further extraction and purification. [Hpy]NTf₂ was used as extraction solution, and 500 μL methanol was selected as dispersive solvent in ionic liquid (IL) dispersive liquid-liquid microextraction (DLLME) method. After sonication for 5 min and centrifugation at 447 g for 10 min, 20 μL of sedimented phase was injected into HPLC-UV system. The limit of detection (LOD) and limit of quantification (LOQ) of current method were 0.03 and 0.16 μg·L⁻¹, respectively, which indicated the sensitivity was comparable or even superior to other reported methods. The relative recoveries of the target analytes ranged from 86.1% to 100.3% with relative standard deviations between 0.3% and 4.5%. The developed method has been successfully applied to determine the level of three industrial dyes in different water samples.

Malachite green (MG), crystal violet (CV) and methylene blue (MB) are three commonly used compounds with a broad range of applications in aquatic product industry as antibiotics and antiparasitics, also in industry as dyes used in the textile process¹⁻³. Those dyes have been known as genotoxic and carcinogenic properties, which can induce hepatic and renal tumors in mice and reproductive abnormalities in fish, along with the risk of human bladder cancer^{4,5}. Widely used MG, CV and MB in diverse aquatic products and textile leads to its presence greater or lesser concentrations in drinking water. Considering of the serious adverse effects on human health, it is important to develop a simple, rapid, and sensitive method for simultaneous trace determination of three dyes in water. However, such dyes are usually present in low concentration in real samples, preconcentration and clean-up steps are necessary for reliable determination of these compounds prior to the analysis.

The most widely used pretreatment methods for isolation and enrichment of MG, CV or MB in aquatic products and water include solid-phase extraction (SPE)^{6,7}, molecularly imprinted solid phase extraction (MISPE)^{8,9}, magnetic solid-phase extraction (MSPE)^{10,11}, dispersive liquid-liquid microextraction (DLLME)^{12,13}, etc. MSPE is a procedure for preconcentration of target analytes from large volumes based on the use of magnetizable sorbents, which can be easily separated from sample solutions by an external magnetic field without additional centrifugation or filtration. Furthermore, the exposed surface between analytes and sorbents is so large that the sorbents can be dispersed in sample solution easily, resulting rapid mass transfer and extraction equilibrium. Ionic liquid (IL) has been used as green solvents instead of traditional organic solvents because of its special chemical and

¹School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang Liaoning Province, 110016, P. R. China. ²School of Pharmacy, Shenyang Pharmaceutical University, Shenyang Liaoning Province, 110016, P. R. China. Correspondence and requests for materials should be addressed to L.Z. (email: longshanzhao@163.com)

physical properties, such as high polarity and thermal stability, low volatility and wonderful miscibility. Recently there are several novel sorbents using ionic liquids coated magnetic nanoparticles have been applied for trace enrichment of drug residues in water samples^{14,15}. DLLME is a microextraction technique applying appropriate extraction solvent and dispersant for the microextraction of analytes in aqueous sample with merits of rapidity, low cost, high recovery and simplicity of operation. However, there are some limitations when using DLLME such as highly toxic extractive and dispersive solvents. To overcome these difficulties, the usage of ILs has been applied as green solvent to replace the conventional organic solvents to extract pollutants which has shown great interests. There are several reports using ionic liquid based DLLME for trace enrichment of organic chemicals in foods, biological, and water samples^{16–18}. In our previous investigations, we developed the method which combined SPE with DLLME (SPE-DLLME) as an efficient hyphenated technique so as to successfully improve the selectivity and sensitivity in pretreatment process^{13,19,20}.

In the present study, a novel kind of MNPs termed as N-butyl pyridinium bis((trifluoromethyl)sulfonyl)imide ([Hpy]NTf₂) functionalized magnetic silica nanoparticles (Fe₃O₄@SiO₂@[Hpy]NTf₂) has been developed to extract MG, CV and MB from water samples. [Hpy]NTf₂ has been applied as extraction solution for further purification in IL-DLLME method. To the best of our knowledge, this is the first report about preparation of ionic liquid based magnetic nanoparticles (MNPs), and their applications of SPE sorbents on simultaneous adsorption of MG, CV and MB in water.

Experimental

Reagents and materials. MG (purity > 98%), CV (purity > 98%) and MB (purity > 98%) were purchased from the National Institute for Food and Drug Control (Beijing, China). N-butyl pyridinium bis((trifluoromethyl)sulfonyl)imide ([Hpy]NTf₂, purity > 99%) was obtained from Shanghai Chengjie Chemical Co., Ltd (Shanghai, China). Iron oxide (100 nm, purity > 98%) was purchased from Aladdin Industrial Co., Ltd (Shanghai, China). Tetrahydroxysilane (TEOs, purity > 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Acetonitrile and formic acid (chromatographic grade) were obtained from Yuwang Industrial Co., Ltd (Shandong, China). All other chemicals and solvents in this experiment including dichloromethane (CH₂Cl₂), dichloroethane (C₂H₄Cl₂), trichloromethane (CHCl₃), carbon tetrachloride (CCl₄), chlorobenzene (C₆H₅Cl) were analytical grade. Deionized water was used throughout the experiments. The cartridges used for solid phase purification were Cleanert Alumina N (1000 mg, 6 mL) which was purchased from Agela Technologies (Tianjin, China).

The drinking water was obtained from bottled water in Shenyang and samples of running water were taken from the tap in the laboratory. River water (RW) samples were collected from the South Canal of Shenyang. Influent (IWW) and effluent (EWW) wastewaters were collected from the urban wastewater treatment plant of Shenyang. All samples were collected in December 2015 and filtered by 0.45 μm nylon membrane and stored in amber glass bottles at −20 °C before analysis.

Instrumentations and analytical conditions. An LC-20AT liquid chromatography equipped with a UV detector (Shimadzu Co., Ltd., Kyoto, Japan) was used for the chromatographic analysis and the detection wavelength was 615 nm. Separations were performed on a Kromasil C₁₈ column (250 mm × 4.6 mm, 5 μm) and the column temperature was maintained at 30 °C. A good chromatographic separation was implemented with a mobile phase consisting of acetonitrile and 0.1% formic acid in water solution (60:40, v/v) at a flow rate of 1 mL·min^{−1}. An X'Pert PRO X-ray diffractometer (PANalytical Co., Netherlands), an HCT-1 TA instruments (Beijing Hengjiu Scientific Instrument Factory, Beijing, China), an SSX-550 SEM instruments (Shimadzu Co., Ltd., Kyoto, Japan) and a Waters 2414 Infrared spectrometer (Waters Corp., Milford, MA, USA) were conducted for characterization of the materials. A KQ5200DE ultrasonic cleaner bath (Kunshan ultrasonic instrument co., Ltd., Kunshan, China) and JJ-1 electric mixer (Jiangsu Ronghua instrument manufacturing co., Ltd., Jiangsu, China) were used for synthesis of the materials. A pH meter (PHS-3CF, Shanghai, China) was employed for pH adjustment. A vortex mixer (XW-80A, Jiangsu, China) was used for thoroughly mixing the solution.

Preparation of Fe₃O₄@SiO₂@[Hpy]NTf₂ MNPs. *Preparation of Fe₃O₄@SiO₂ MNPs.* 1.0 g Fe₃O₄ was added to a round-bottom flask which contained 50 mL ethanol and 15 mL pure water. The mixture was sonicated for 15 min to ensure homogeneous mixture. After adjusting the pH to 9 using ammonia, 2 mL of TEOs was added dropwise to the flask. The mixture was mechanically stirred under nitrogen protection for 24 h to perform the silica coating. The produced Fe₃O₄@SiO₂ was separated and washed with deionized water, to which was added 1 mL HCl solution (1 mol·L^{−1}) and mechanically stirred for 12 h at room temperature. The MNPs were collected by a magnet, washed with water, and vacuum-dried at 60 °C for 12 h.

Synthesis of Fe₃O₄@SiO₂@[Hpy]NTf₂. 1.0 g of [Hpy]NTf₂ was dissolved in 10 mL acetone, followed by addition of 1.0 g Fe₃O₄@SiO₂. The mixture was stirred for 30 min, and the sample was dried under stirring and a stream of nitrogen purge. The resultant was washed with CH₂Cl₂, and dried at 60 °C.

Extraction procedure. One hundred milligram of Fe₃O₄@SiO₂@[Hpy]NTf₂ was added to 100 mL of water sample (pH was adjusted to 4.0 by using HCl) in a conical flask. The mixture was shaken for 20 min and an external magnet was applied to isolate the material from the water. 1 mL of acetonitrile was used to elute target analytes from the material by shaking for 20 min. The elute solvent was transferred to a 10-mL glass conical tube after being separated by a magnet. The elution was evaporated to dry on a rotary vacuum evaporator at 35 °C, and 5 mL of pure water (adjusted pH to 4.0 using HCl) was added to the test tube to reconstitute the residue. A mixture of 70 μL of [Hpy]NTf₂ and 500 μL of methanol was rapidly injected into the aqueous solution to form a cloudy solution, which was sonicated for 5 min to increase the extraction efficiency. The mixture was centrifuged at 447 g for

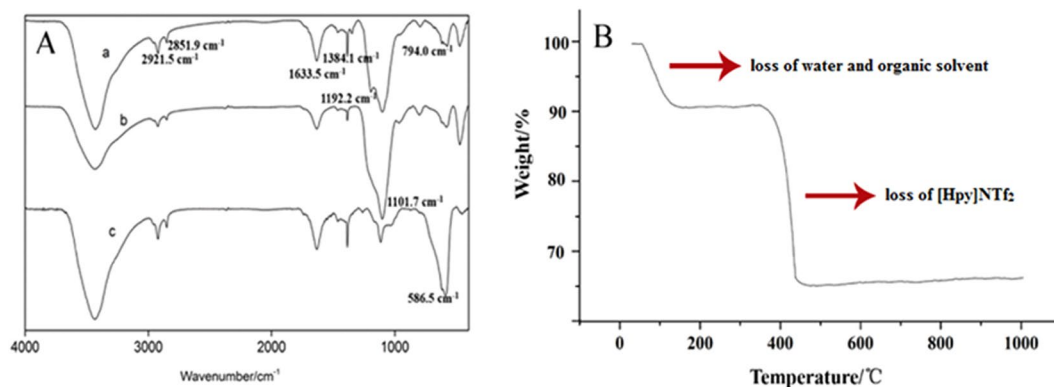


Figure 1. FTIR spectra of (A) $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$ (a), $\text{Fe}_3\text{O}_4@SiO_2$ (b), Fe_3O_4 (c) (B) TGA of $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$.

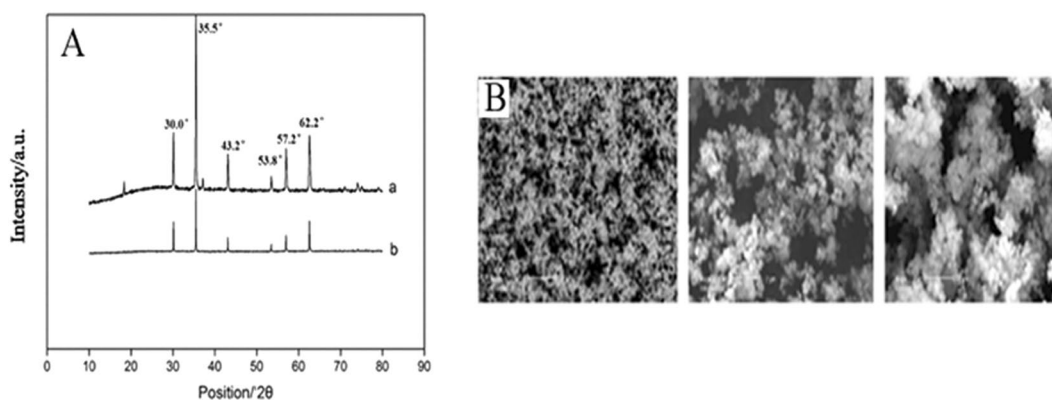


Figure 2. (A) XRD of $\text{Fe}_3\text{O}_4@SiO_2$ (a) and $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$ (b); (B) SEM of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@SiO_2$ (b), $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$ (c).

10 min and the dispersed fine particles of the extraction phase were deposited at the bottom of the test tube. The supernatant was removed using a microsyringe. The remaining sedimented phase was diluted by mobile phase solution (acetonitrile/water, *v/v*, 60/40), 20 μL of which was injected into HPLC system for analysis.

Results and Discussion

Characterization of $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$ MNPs. The prepared $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$ MNPs were characterized with FTIR spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscope (SEM).

As shown in Fig. 1A, the appearance of $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$ (a) characteristic peaks at 2921.5 and 2851.9 cm^{-1} were attributed to the C-H asymmetrical stretching vibration, 1633.5 cm^{-1} for the C=N stretching vibration, 1384.1 cm^{-1} for -CH₃ bending asymmetrical vibration, 1192.2 cm^{-1} for C-H flexural vibration, and 794.0 cm^{-1} for C=C stretching vibration, respectively. Comparing curves between $\text{Fe}_3\text{O}_4@SiO_2$ (b) and Fe_3O_4 (c), prominent peaks at 586.5 cm^{-1} (Fe-O-Fe) disappeared and there was a peak shown at 1101.7 cm^{-1} which was related to Si-O-H and Si-O-Si, all of these results demonstrated the successful surface modification of the MNPs.

In this study, TGA was conducted in a nitrogen atmosphere, and the temperature was increased from 25 to 1000 °C at a rate of 5 °C·min⁻¹. As can be seen in Fig. 1B, an additional weight loss of 8% after heating to 150 °C, corresponded to water and organic solvent content. Besides, an obvious weight loss of 25% was observed from 400 to 600 °C due to the decomposition of the ILs, which was consistent with the decomposition temperature of Bis(trifluoromethane sulfonimide) ILs²¹. This observation indicated that [Hpy]NTf₂ was located on the surface of $\text{Fe}_3\text{O}_4@SiO_2$. There was no significant weight loss when the temperature increasing up to 500 °C, which indicated the yield of final products was about 70%.

Figure 2A showed the XRD of $\text{Fe}_3\text{O}_4@SiO_2$ (a) and $\text{Fe}_3\text{O}_4@SiO_2@[Hpy]NTf_2$ (b). There were 6 characteristic diffraction signals at $2\theta = 30.0^\circ, 35.5^\circ, 43.2^\circ, 53.8^\circ, 57.2^\circ, 62.2^\circ$ which were related to Fe_3O_4 . Furthermore, there was a smooth diffraction peak at $2\theta = 20.0^\circ$ corresponding to the amorphous structure of the SiO₂ nanomaterials. Which illustrated the appearance of $\text{Fe}_3\text{O}_4@SiO_2$. Comparing with curve a, the intensity of all signals was decreased in curve b which was caused of ionic liquid coated on the surface of $\text{Fe}_3\text{O}_4@SiO_2$. The spectrum of XRD indicated that synthesized $\text{Fe}_3\text{O}_4@SiO_2$ nanoparticles contained both Fe_3O_4 and SiO₂ crystal structure, and [Hpy]NTf₂ was successfully coated on $\text{Fe}_3\text{O}_4@SiO_2$.

Scanning electron microscope (SEM) produces microscopic images of sample surface material. As shown in Fig. 2B, these are SEM pictures of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{Hpy}]\text{NTf}_2$. SEM spectrum of Fe_3O_4 shows small particle size, spherical shape, no accumulation, dispersed particles, and 100 nm-pore size, which are consistent with the parameters in label of commercial product. The particle size of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ is about 200 nm, which is larger than that of Fe_3O_4 . Most of the particles are spherical, but the size is large which may be due to poor grinding and dispersion forming during synthesis process. The particle size of $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{Hpy}]\text{NTf}_2$ is between 200–800 nm, but aggregated which affects the particle size. It is due to high viscosity of ionic liquid, which can be further demonstrated that the synthesized material is $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{Hpy}]\text{NTf}_2$.

Optimization of chemical synthesis. *Chemical synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$.* When large amount of TEOs was added to the reaction system, most of the synthesized SiO_2 would disperse into the solution. This was because of limited binding sites on the surface of Fe_3O_4 , whereas extra TEOs would lead to more SiO_2 into the free state. The amount of TEOs was also optimized and results indicated that 2 mL of TEOs was the most suitable volume which was applied in the further investigation. Besides, pH showed great influence on the productivity. When the pH was below 9, the final productivity was extremely low, however when pH was adjusted to 9–10, productivity was improved from 40% to 70%. This indicated the reaction should be proceeded under basic conditions, because hydroxyl group (-OH) group could provide binding sites for SiO_2 . Insufficient basicity could interfere the number of binding sites, whereas the basicity showed no influence on the binding sites when it was saturated.

Chemical synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{Hpy}]\text{NTf}_2$. Acetone was used as the reaction solvent, while volume could directly affect the synthesis efficiency, and therefore, 5, 10, 15, 30 mL of acetone was investigated under the conditions of both $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $[\text{Hpy}]\text{NTf}_2$ applying 1.0 g. The results indicated that the highest synthesis efficiency of 64.96% was achieved with the volume of 10 mL acetone. Therefore, 10 mL acetone was used in the further investigation.

The ratios of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $[\text{Hpy}]\text{NTf}_2$ were selected as 2:10, 3:10, 5:10, 10:10, 15:10, 20:10 (m:m) so as to investigate the best ratio for synthesis. The results indicated that the productivity and availability of $[\text{Hpy}]\text{NTf}_2$ were 64.96% and 30.14% when using the ratio of 10:10, so the final amount of both $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $[\text{Hpy}]\text{NTf}_2$ were 1.0 g.

When the temperature was below 25 °C, ILs could not be efficiently attached on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$. However, productivity will not increase above 30 °C, with the possible reasons of molecular thermal movement; therefore, 25 °C was selected as the reaction temperature.

Optimization of MSPE. The effects of several parameters on extraction efficiency by MSPE were studied, including pH, sorbent amount, extraction time, type of desorptive solvent and volume. The influence of all these parameters was evaluated in terms of peak areas.

Effect of pH. The sample pH is a crucial factor in the extraction process which could affect the existing state of the targets and extraction efficiency. Considering the pKa values of 6.9, 0.8 and 4.5 for MG, CV and MB, respectively, the water samples should be acidic, so as to make the targets to be presented in molecular form in water samples. In this work, the effect of pH was investigated over the pH range of 2.0–7.0. As shown in Fig. 3A, the recoveries of three targets increased and reached a maximum value at a pH of 4.0, and subsequently decreased, which indicated that three targets were successfully extracted to the IL sediment phase. Therefore, pH 4.0 was selected for the subsequent assays.

Effect of amount. The effect of amount of $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{Hpy}]\text{NTf}_2$ MNPs was investigated with the amount varying from 70 to 120 mg. Figure 3B demonstrated that the peak areas of almost all the 3 dyes increased continuously with increasing the sorbent amount from 80 to 100 mg. Further increasing the sorbent amount showed no obvious increasing in the peak area of the targets. These results indicated that 100 mg of sorbent was sufficient to extract dyes in water, and therefore, 100 mg of sorbent was used for the following experiments.

Effect of extraction time. To evaluate the effect of extraction time on the recoveries of targets, different extraction time ranging from 5 to 30 min were tested (Fig. 3C). The recoveries gradually increased up to 20 min, and slightly increased when extraction time was increased to 30 min. Thus, 20 min was selected as the optimal extraction time.

Effect of the type of elution and its volume. An appropriate type of elution solvent is important for perfect extraction efficiency by $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{Hpy}]\text{NTf}_2$ MNPs. Four types of solvents were selected as desorptive solvent, including methanol, ethanol, acetonitrile and acetone. As shown in Fig. 3D, acetonitrile yields higher recovery than that of methanol, ethanol, and acetone. The effect of sample volume on extraction efficiency of targeted dyes was investigated with the volume changing from 700 to 1100 μL . As shown in Fig. 3E, the recoveries of all these three dyes declined with increasing the sample volume from 1000 to 1100 μL . This is because when increasing the sample volume, especially for 700–1000 μL , the magnetic sorbents would be dispersed more widely and sorbents lost as long as volume increased. Then, 1000 μL was selected as sample volume.

Based on the above discussions, the optimal conditions for enrichment of targets were determined as follows: $\text{Fe}_3\text{O}_4@\text{SiO}_2@[\text{Hpy}]\text{NTf}_2$ MNPs, 100 mg; sample pH, 4.0; extraction time, 20 min; desorption solvent and volume, 1000 μL acetonitrile.

Optimization of DLLME. *Effect of extraction solvent volume.* In order to evaluate the influence of extraction solvent volume on extraction efficiencies of targets, different volumes (40, 50, 60, 70, 80, 90 μL) of $[\text{Hpy}]\text{NTf}_2$ were tested using the same MSPE-DLLME procedure. As shown in Fig. 4(A), the recoveries of targets increased

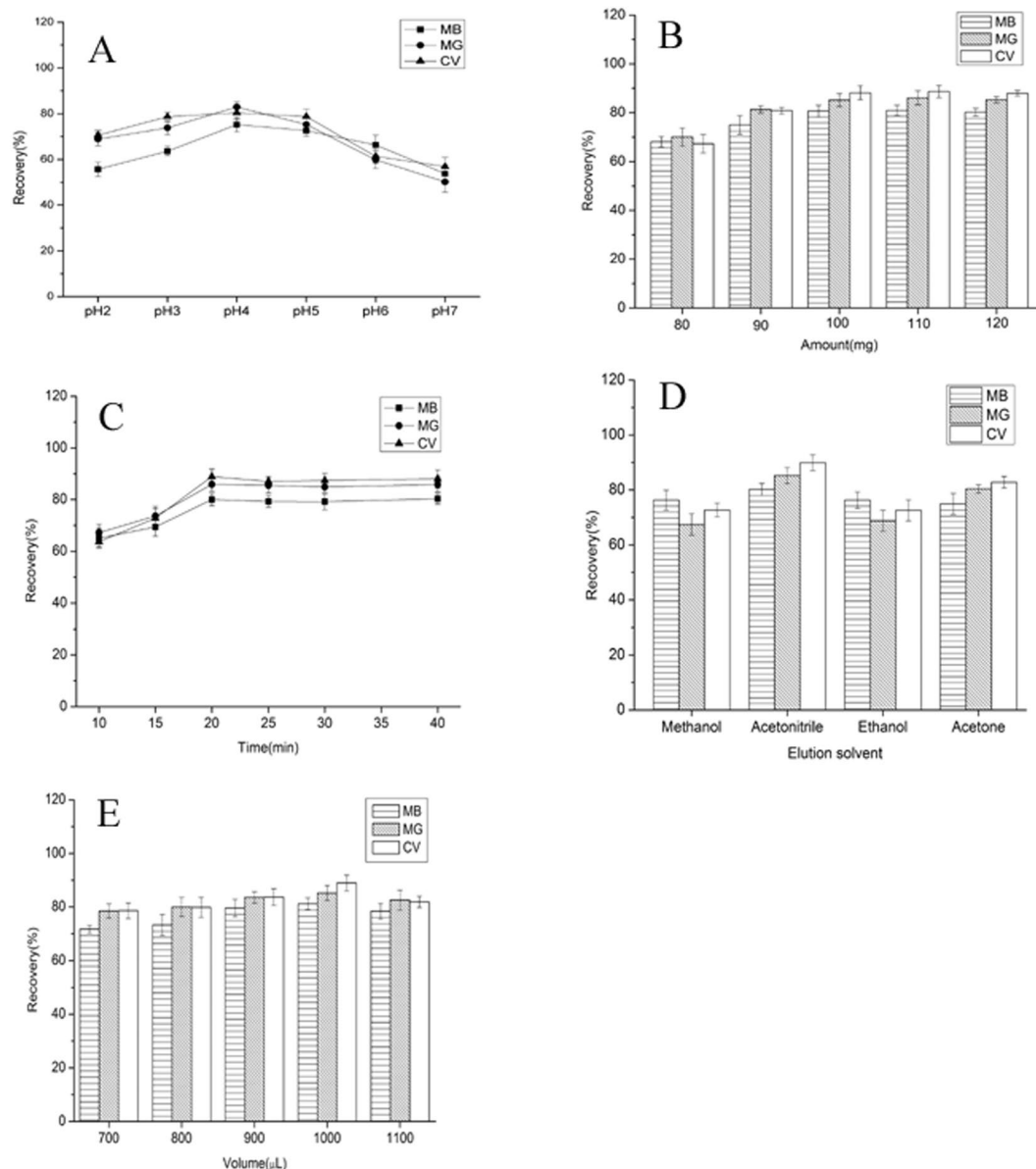


Figure 3. (A) Effect of pH of MSPE on the recoveries of targets; (B) Effect of amount of material on the recoveries of targets; (C) Effect of time of MSPE on the recoveries of targets; (D) Effect of elution solvent on the recoveries of targets; (E) Effect of volume of elution solvent on the recoveries of targets.

with increasing the volume of [Hpy]NTf₂ from 40 to 70 μL, but above 70 μL, the recoveries remained a constant level. Considering the enrichment factor decreased when the IL solvent volume was increased. Thus, 70 μL of [Hpy]NTf₂ was selected in the following studies, since the higher recoveries were obtained and the EFs were acceptable.

Effect of dispersive solvent and its volume. The dispersive solvent should efficiently disperse the extraction solvent into the aqueous sample to increase the contact area. The main point to be considered in selecting dispersive solvent is its miscibility in both organic and aqueous phases. Methanol, ethanol, acetone and acetonitrile were widely used as dispersive solvents. Based on Fig. 4(B) we concluded that methanol gave the highest recoveries among the solvents. Thus, methanol was chosen as the disperser solvent.

In the meanwhile, the volume of disperser solvent affects the dispersion degree of the extraction solvent in aqueous phase, consequently affecting the extraction efficiency. Therefore, the effect of dispersive solvent volume on the extraction recovery was also investigated in the range of 0.4–1.2 mL. The obtained results (Fig. 4C) showed that the extraction recovery increased with the increasing volume of methanol up to 0.5 mL and slightly decreased as the volume increasing. Thus, 0.5 mL of acetonitrile was selected as the optimum volume.

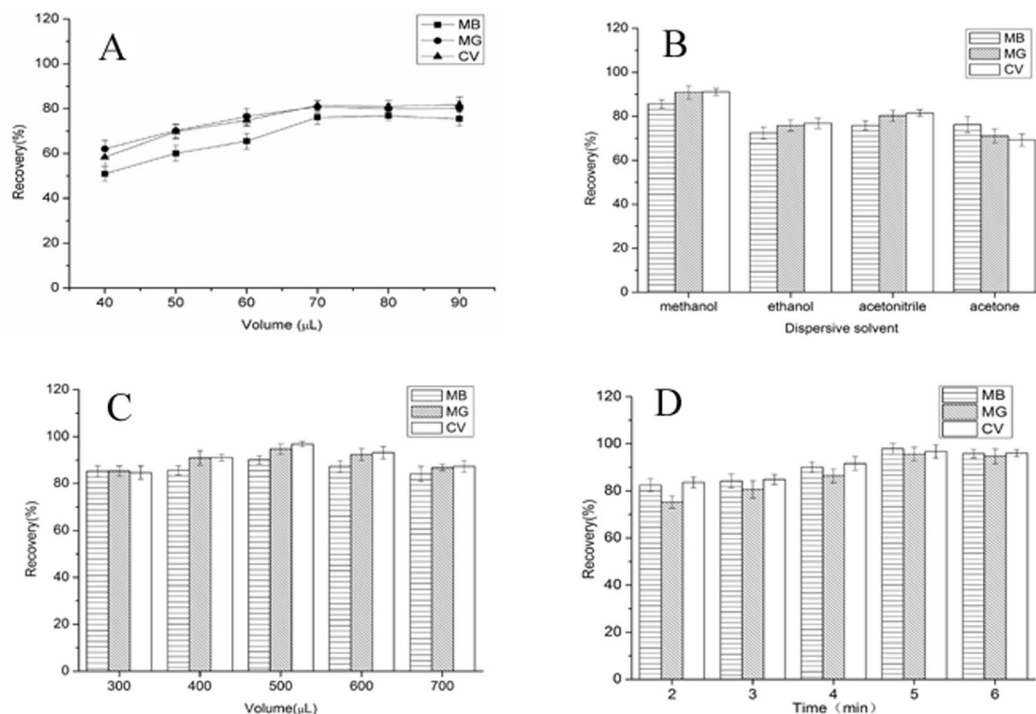


Figure 4. (A) Effect of extraction solvent volume of DLLME on the recoveries of targets; (B) Effect of dispersive solvent of DLLME on the recoveries of targets; (C) Effect of dispersive solvent volume of DLLME on the recoveries of targets; (D) Effect of ultrasound time of DLLME on the recoveries of target.

Analytes	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	r	LOD ($\mu\text{g}\cdot\text{L}^{-1}$)	LOQ ($\mu\text{g}\cdot\text{L}^{-1}$)	Precision RSD% (n = 6)	Repeatability RSD % (n = 6)	Enrichment Factor
MB	0.20–20	0.9993	0.05	0.16	1.2	2.4	502
MG	0.20–20	0.9986	0.03	0.11	2.6	3.8	484
CV	0.20–20	0.9991	0.04	0.13	1.9	3.4	499

Table 1. The performance characteristics of MSPE-DLLME.

Effect of ultrasound time. The effect of ultrasonic time on the extraction efficiency was examined within the range from 2 to 6 min. As shown in Fig. 4(D), ultrasonic time of 5 min was the optimal condition and longer ultrasonic time could not obtain higher extraction efficiency. When the mixture of ionic liquid extraction solvent and dispersive solvent were injected to the aqueous sample, the fine droplets of extraction solvent provided an infinitely large contact surface area between aqueous phase and extraction solvent to speed up the mass-transfer process. It would take a short period of time for the analytes to transfer from aqueous phase to extraction phase and to reach an equilibrium state. However, the volatilization of organic solvent and consequent thermal effect of analytes would lead to the loss of analytes as the reaction time went longer. Hence, 5 min was chosen as the optimum ultrasonic time.

Effect of ionic strength. The effect of ionic strength of the sample solution was evaluated by adding NaCl (0–10%, w/v) under the previous optimum conditions. Generally, addition of moderate salt could decrease the solubility of targets in the aqueous sample, thus increasing the extraction efficiency. However, in the current investigation, we concluded that ionic strength did not have significant effect on the extraction of target dyes. Therefore, the MSPE-IL-DLLME procedure was performed without salt addition to the sample solutions.

Analytical performance of the method. Under the optimized conditions, the method was applied to determination of dyes in water samples. The analytical results can be found in Table 1. The calibration curves were established by plotting peak area against concentration. The regression coefficients were determined to be 0.998. The limit of detection (LOD) and limit of quantification (LOQ) were 0.03–0.05 $\mu\text{g}\cdot\text{L}^{-1}$ and 0.11–0.16 $\mu\text{g}\cdot\text{L}^{-1}$, respectively. The precisions of the method ranged from 1.2% to 2.6% (n = 6) and accuracies varied between 0.3% and 4.5%, indicating that the method showed high sensitivity and reproducibility.

Analysis of real water samples. To further evaluate the method applicability, South Canal river water, tap water, drinking water and waste water samples were analyzed using established method. Accuracy of a method was

Analytes	Spiked ($\mu\text{g}\cdot\text{L}^{-1}$)	R% (RSD %)				
		Drinking water	Running water	River water	Influent wastewater	Effluent wastewater
MB	0.4	96.1(2.8)	91.5(2.4)	94.8(2.2)	91.5(3.1)	91.3(3.5)
	2.0	96.3(2.9)	89.4(3.4)	96.2(4.5)	94.9(2.3)	93.6(2.2)
	10.0	100.3(2.3)	99.8(1.4)	96.1(2.1)	94.6(3.2)	97.6(0.8)
MG	0.4	96.2(1.2)	93.2(0.4)	86.1(1.3)	89.5(1.9)	89.8(1.1)
	2.0	94.4(1.2)	93.4(4.2)	91.3(2.5)	92.3(0.9)	93.1(1.6)
	10.0	96.9(2.5)	99.5(1.9)	92.4(3.3)	98.2(2.4)	94.0(1.1)
CV	0.4	92.4(1.4)	95.4(1.1)	95.3(1.8)	94.4(1.1)	90.9(0.3)
	2.0	91.4(2.4)	96.3(1.8)	98.2(2.2)	90.3(0.4)	93.1(1.2)
	10.0	99.2(1.3)	97.5(0.7)	92.1(0.9)	93.5(1.3)	98.5(2.7)

Table 2. Recoveries of spiked water samples ($n = 3$).

Analytes	Drinking water	Running water	River water	Influent wastewater	Effluent wastewater
MB	—	<LOQ	0.38	<LOQ	—
MG	—	—	0.20	0.13	—
CV	—	—	0.82	1.16	—

Table 3. Determination of MB, MG, and CV in real water samples ($\mu\text{g}\cdot\text{L}^{-1}$). —: Not detected.

Methods	Analytes	Analytes in common	Matrix	Extraction Solvent	Volume (μL)	LOD ($\mu\text{g}\cdot\text{L}^{-1}$)	Precision (RSD%)	EF	Recovery (%)	References
MSPE-HPLC/FLD	Malachite green, Gentian violet, Leuomalachite green, Leucogentian violet	Malachite green	Aquafarm water	—	—	0.09–0.22	2.7–6.5	91–95	87.0–92.8	3
MCPE-UV/Vis	Malachite green, Crystal violet, Rhodamine B	Malachite green, Crystal violet	Tap water; Wastewater	—	—	2.2–5.1	4.5–8.39	29.26–85.47	59.5–115.0	25
S-FF-DSPE-UV/Vis	Methylene blue	Methylene blue	Tap water; River water	—	—	2.5	2.9	135	99.0–109.0	26
DLLME-HPLC/UV	Malachite green, Crystal violet	Malachite green, Crystal violet	Upriver water	$[\text{C}_8\text{MIM}]\text{PF}_6$	80	0.030–0.086	7.6–9.4	254–276	71.7–97.2	27
SM-DLLME-UV/Vis	Malachite green	Malachite green	Textile industry wastewater	Decanoic acid-tetrahydrofuran	45500–500	4	1.8	52	85.3–108.6	28
MSPE-DLLME-HPLC/UV	Malachite green, Crystal violet, Methylene blue	—	Drinking water; Running water; Influent wastewater; Effluent wastewater; River water	$[\text{Hpy}]\text{NTf}_2$	70	0.03–0.05	1.2–2.6	484–502	86.1–100.3	Represented method

Table 4. Comparison of MSPE-DLLME-HPLC/UV with other methods for the determination of industrial dyes.

evaluated as the percentage of deviation from the known added amount of analyte in the sample. It is generally investigated by recovery experiments. Analyte recovery was calculated according to the equation as follows:

$$\text{Rec} = \frac{C - B}{A} \times 100$$

where A is the concentration of analyte standards prepared in mobile phase, B is the concentration of blank (unspiked) sample, C is the concentration of analyte detected from the sample spiked before extraction.

In recovery experiments, the recovery value will not exceed 100% in theory, however the system error, operation error and other errors are inevitable in practice. So, the measured value (C-B) may be greater than the actual amount added (A), resulting in recovery values higher than 100%, which is a common phenomenon in method validation^{22–24}. Generally, the recovery value of range of 85–115% can be acceptable, which means that the analytical error of the method is $\pm 15\%$, and that is in full compliance with the requirements in analysis.

In our study, unspiked water samples and water samples spiked with 3 dyes at three concentration levels (0.4, 2 and $10\mu\text{g}\cdot\text{L}^{-1}$) were analyzed by using proposed method ($n = 3$). The results are listed in Table 2. The relative recoveries of dyes at three concentration levels were in the range of 89.4–100.3%, with RSDs within 3.5%. MG, CV

and MB were detected in river water and influent wastewater samples (Table 3). These results indicated that the established method could be successfully applied to analysis of target dyes at trace level in real samples.

Comparison of MSPE-IL-DLLME method to previous methods. The extraction effects of MG, CV and MB were significantly enhanced by the proposed MSPE-IL-DLLME coupled with HPLC–UV method. Furthermore, the current protocol can be evaluated by comparing with previously reported work from the viewpoints of extraction solvent, LODs, enrichment factor (EF), and recoveries etc. The extraction solvent using in DLLME is [Hpy]NTf₂, which is more environmental and provides new insight in extraction techniques. According to the Table 4, the established method provides relatively more sensitive, higher EF and better recoveries than previous reports^{3,25–28}. These merits make our method as a reliable tool in monitoring MG, CV and MB pollution in water samples.

Conclusions

A novel sorbent based [Hpy]NTf₂ functionalized MNPs was synthesized for the pretreatment through MSPE combined DLLME for the enrichment of 3 dyes in water. The obtained Fe₃O₄@SiO₂@[Hpy]NTf₂ adsorbents were characterized via FTIR, TGA, XRD and SEM. Under the optimized conditions, the method provided suitable analytical characteristics including extraction efficiency up to 86%, enrichment factor over 480, and LOD between 0.03–0.05 µg·L⁻¹. Based on the results, we can conclude that Fe₃O₄@SiO₂@[Hpy]NTf₂ MNPs could be introduced as a novel sorbent for rapid extraction of dyes from aqueous solution.

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Author Contributions

N.L. and L.Z. designed the experiments. X.H., P.H. and C.J. carried out the whole procedure of this experiment. L.C. analyzed the experimental data. L.Z. wrote the manuscript. All authors discussed the experimental results and reviewed the manuscript.

Additional Information

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

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