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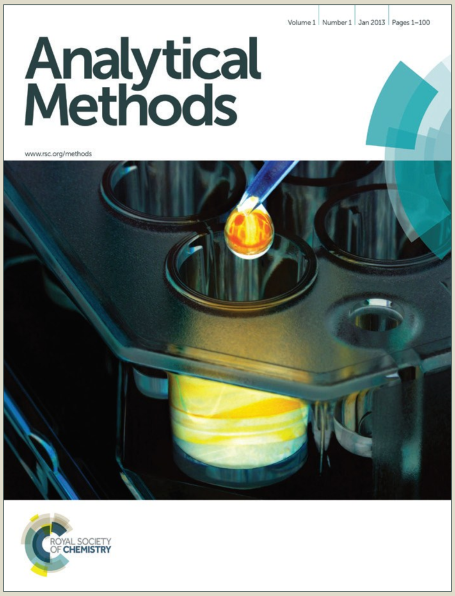

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Magnetic solid-phase extraction based on Fe_3O_4@polyaniline particles followed by ultrafast liquid chromatography for determination of Sudan dyes in environmental water samples

Bo Xu, Yuanpeng Wang, Rui Jin, Xinpei Li, Daqian Song,
Hanqi Zhang and Ying Sun*

College of Chemistry, Jilin University, Qianjin Street 2699,
Changchun 130012,
PR China

*Corresponding author: Ying Sun
Tel.: +86-431-85168399
Fax: +86-431-85168399
E-mail address: yingsun@jlu.edu.cn

Abstract

The magnetic Fe_3O_4@polyaniline (Fe_3O_4@PANI) particles were successfully prepared and used as adsorbent in magnetic solid-phase extraction of Sudan dyes in environmental water samples. The Fe_3O_4@PANI particles adsorbed analytes were isolated from the sample matrix conveniently with an external magnetic field. The analytes were separated and determined by ultrafast liquid chromatography. Some major influencing factors, including amount of Fe_3O_4@PANI particles, pH value, ion strength, extraction time, type of desorption solvent, volume of desorption solvent, desorption time and sample volume were optimized. Satisfactory extraction recoveries were obtained with merely 8 mg Fe_3O_4@PANI particles and the Fe_3O_4@PANI particles can be reused after an easy washing process. The limits of detection for Sudan I, II, III and IV were 0.041, 0.080, 0.147 and 0.151 ng mL^{-1}, respectively. The intra-day and inter-day precision with relative standard deviations were in the range of 1.3-5.4% and 2.6-7.3%, respectively. Recoveries obtained by analyzing spiked environmental water samples were between 92.4 and 106.9%.

Keywords: Magnetic solid-phase extraction / Fe_3O_4@polyaniline particles / Sudan dyes / Environmental water / Ultrafast liquid chromatography

1 Introduction

Sudan dyes are a group of synthetic lipophilic azo dyes and widely used as coloring agents in industry, such as petrol, plastics, fats, waxes, printing inks, shoes spirit varnishing and floor polishing.[1] Due to the dyes and their metabolites may cause liver, spleen and bladder cancer, International Agency for Research on Cancer (IARC) has categorized Sudan dyes as class 3 carcinogen.[2] However, over 15% of the dyes are lost in industrial effluents during dyeing operation.[3] Sudan dyes can easily enter environmental water system from irrigation, laundry, rain and many other ways. Consequently, water sources polluted by Sudan dyes pose an increased risk to public health.[4] Due to the low levels in environmental waters, fast and accurate determination of Sudan dyes becomes particularly necessary to guarantee public safety and health.

Sample preparation before instrumental analysis is one of the most crucial steps. Various extraction methods have been reported for preparing samples, including solid phase extraction (SPE),[5] molecularly imprinted solid-phase extraction (MISPE),[6] subcritical water extraction (SCWE),[7] supercritical fluid extraction (SFE),[8] cloud point extraction (CPE)[9] and dispersive liquid-liquid microextraction (DLLME).[10] Among various pretreatment methods, SPE is considered to be one of the most popular methods for its high enrichment performance, low solvent-cost and ease of use[11-13]. However, traditional SPE still has disadvantage of being time-consuming. The magnetic solid-phase extraction (MSPE), is one of the latest developments in SPE methods, has attracted much attention in sample preparation.[14] In MSPE, magnetic adsorbents are used as new adsorbents to substitute for the routine nonmagnetic adsorbents in SPE because of the magnetism of the particles simplifies the separation process and improves the rate of separation compared with traditional sample preparation sorbents.[15-17] MSPE has the outstanding advantage of convenient phase separation with an external magnetic field. What's more, the extraction performance is greatly improved because of the high surface area-to-volume ratio of the extraction phase,[14] which is particularly necessary for preparing environmental water samples with pollutants at low concentration levels. Moreover, the magnetic adsorbents are very economical and environmental friendly because the adsorbents can be recycled after appropriate washing process. Therefore, MSPE is becoming more and more popular as a promising extraction method in recent decades.

Currently, considerable efforts are paid to the exploitation of various polymer-coated magnetic particles as adsorbents in MSPE, because they tend to possess plentiful functional groups for adsorption, which is very advantageous for effective extraction.[18-20] During the course of preparing of polymer-coated magnetic particles, different magnetic oxides have been used as magnetic cores. And among all magnetic oxides, Fe_3O_4 is most usually used for their unique hollow structure and high specific surface area.[21] Modifications using compounds and functional groups on the surface of magnetic cores to improve their capabilities have aroused interest of the people. Numerous synthetic and natural polymers have been used to modify magnetic cores. Different types of polymer coating endow these particles with a variety of adsorptive selectivity, which makes them excellent candidates for highly selective MSPE. Besides, the polymer coating provides the particles with protection from coagulation and oxidization, which results in no loss of magnetism and dispersibility.[22]

The most obvious disadvantage of MSPE is that the synthesis of these magnetic materials, especially the functional groups or special structures coated on them being used for further fictionalizations, is complex and difficult to operate. Hence, attempts to explore a kind of novel and simple adsorbent with excellent extraction performance will make much practical significance. Polyaniline (PANI) is found to be an attractive polymer for its ease of preparation; low cost monomer, tunable properties, and excellent environmental stability compared to other polymers.[23] The works about the synthesis of Fe_3O_4@PANI have been published. However, relevant reports mainly focused on the surface modification, characterization or the study of Fe_3O_4@PANI for its properties of microwave absorption,[24] electrochemical,[25] electromagnetic wave absorption,[26] catalysis,[27] few attempts were made for its application in MSPE as adsorbent. PANI has exceeding advantages in the separation of various compounds and contains high proportion of π-conjugated groups in structures, which makes it very likely to be proper adsorbent for MSPE.[28, 29]

This paper describes a simple, sensitive and reliable method for the determination of Sudan dyes in environmental waters using MSPE coupled with ultrafast liquid chromatography-ultraviolet (UFLC-UV) spectrometry. In the present method, Fe_3O_4@PANI particles with superparamagnetic properties, high specific surface area and a lot of π-conjugated groups were synthesized successfully. The as-prepared Fe_3O_4@PANI particles have a predominant ability to capture Sudan dyes in water samples. Also, the Fe_3O_4@PANI particles showed operational stability and remained excellent adsorption and magnetic property even after a twenty-cycle run for the adsorption and desorption of Sudan dyes. Fe_3O_4@PANI particles adsorbents are dispersed into the sample matrix in the MSPE, and could be readily separated from solution by applying an external magnetic field after extraction. Thus, a time saving, convenient, low toxic, effective and sensitive method for the determination of Sudan dyes was established. To the best of our knowledge, this is the first study about MSPE using Fe_3O_4@PANI as adsorbent coupled with UFLC-UV for the identification and quantification of Sudan dyes in environmental water samples up to now.

2 Materials and methods

2.1 Chemicals and samples

The standards of Sudan I-IV were obtained from National Institutes for the Control of Pharmaceutical and Biological Products (Beijing, China). The chemical information of the Sudan dyes is shown in Fig. 1. The stock solutions of Sudan dyes (100 μg mL^{-1}) were separately prepared by dissolving appropriate amount of analytes in HPLC-grade acetonitrile and stored at 4℃ in darkness. Mixed working standard solutions at desirable concentration levels were freshly prepared by diluting the stock solutions with HPLC-grade acetonitrile.

HPLC-grade methanol and acetonitrile were obtained from Fisher (New York, USA). Analytical-grade methanol, ether, acetonitrile, acetone, ethanol, dichloromethane, n-hexane, ethyl acetate, hydrochloric acid (HCl, 36-38 wt %), 3-aminopropyltriethoxysilane (APTES), sodium dodecyl benzene sulfonate (SDBS), ammonium peroxodisulfate (APS) were obtained from Beijing Chemical Works (Beijing, China). Aniline was obtained from Beijing Chemical Works (Beijing, China) and distilled at a reduced pressure before use. Ferric chloride ($FeCl_3$•$6H_2O$) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium acetate (NaAc) was purchased from Xilong Chemical Co. Ltd.

(Guangzhou, China). Polyvinylpyrrolidone (PVP-K40) was purchased from Sigma-Aldrich Co. (Shanghai, China). All chemicals were of analytical grade and used without further purification. Deionized water was prepared with a Milli-Q water purication system (Millipore, USA).

Five kinds of environmental water samples, including tap water (sample 1), rain water (sample 2), reservoir water (sample 3), surface water (sample 4) and lake water (sample 5), were acquired for validating the present method. Reservoir water and lake water were collected from Jingyuetan Reservoir and Nanhu Lake in Changchun, China, respectively. Tap water was taken from our own laboratory after continual flow for 10 min. Rain water was obtained from Jilin University in Changchun, China. Surface water was acquired on the ground with many factories nearby. The spiked water samples were prepared by adding the mixed working standard solution in the environmental water samples and stored in glass containers at 4℃ in the dark. All the samples were filtered through 0.45 µm micro-pore membranes before experiment.

2.2 Instruments

A UFLC-UV system (Shimadzu, Kyoto, Japan) equipped with two LC-20AD pumps, an SIL-20A autosampler, a CTO-20A thermostatted column compartment and an SPD-20A UV-vis detector was used. The chromatographic separation of the analytes was carried out on a shim-pack VP-ODS column (150 mm × 4.6 mm, 4.6 μm particle size). Data acquisition and processing were performed with LC-solution software (Shimadzu, Kyoto, Japan).

An electric constant temperature drying oven (DGG-9070BD, Shanghai, China) was used to prepare magnetic particles. A transmission electron microscope (TEM, JEOL JSM-6700F, Japan) was used to obtain transmission electron microscopic images. A magnetic property measurement system (SQUID-VSM, Quantum Design, USA) was used to study the magnetic properties. An ultrasonic wave cleaning machine (KQ-100, 40KHz, 100W, Kunshan China) was used for extraction of the analytes. A vortex agitator (Vortex-6, Kylin-Bell Lab Instruments Corporation, Jiangsu, China) was used for elution of analytes.

2.3 Preparation of Fe_3O_4@PANI composite

2.3.1 Synthesis and chemical modification of Fe_3O_4 particles

The Fe_3O_4 particles were prepared by the modified solvothermal method.[30] $FeCl_3•6H_2O$ (2 g) and NaAc (5.7 g) were dissolved in ethylene glycol (80 ml). The mixture was stirred vigorously for 30 min and then transferred into a Teflon-lined stainless-steel autoclave for heating at 200℃ for 8 h. After the autoclave was cooled to room temperature, the black products were thoroughly washed with ethanol and deionized water several times, and dried at 50℃ overnight. Subsequently, the Fe_3O_4

particles (0.15 g) were chemically modified by dissolving in a mixture of 80 mL anhydrous ethanol and 3 mL APTES. The resulting mixture was stirred continuously and refluxed for 15 h under nitrogen current. The resulting modified Fe_3O_4 particles were separated with the help of a magnet and then washed with ethanol. Finally, the product was dried in vacuum at 60℃ overnight to obtain the functionalized Fe_3O_4 particles.

2.3.2 Preparation of Fe_3O_4@PANI

The Fe_3O_4@PANI particles were prepared by a modified *in situ* surface polymerization method.[31-33] 0.04 g of functionalized Fe_3O_4 particles was ultrasonically dispersed in 150 mL of deionized water. And then PVP (0.15 g) and SDBS (0.25 g) dissolved in 200 mL deionized water were added. Aniline (50 μL) in the presence of concentrated HCl (250 μL) was added into the mixture under vigorous stirring. After 1 h, a 50 mL aqueous solution of APS (0.01 g mL^{-1}) was added into the above mixture instantly to start the oxidative polymerization and the reaction was performed under mechanical stirring for 7 h at room temperature. The resulting precipitates were magnetically separated and washed with deionized water and ethanol several times. Finally, the product was dried in vacuum at 60℃ overnight.

2.4 MSPE procedure

Eight milligram of Fe_3O_4@PANI was added into 100 mL of spiked water sample in a 250 mL conical flask, the pH value of the water sample was adjusted to pH 7.0. The mixture was sonicated for 15 min. Then, the solution was decanted with a strong magnet on the wall of the conical flask. The analytes were eluted from the Fe_3O_4@PANI particles with 2 mL of ethanol by oscillation with a vortex agitator for 4 min and the eluate was decanted with magnet. Two such replicate elutions were carried out for quantitative desorption of the analytes from the Fe_3O_4@ PANI particles. The eluate was evaporated to dryness under mild nitrogen stream at 55℃, and the residue was redissolved in 100 μL acetonitrile. Then the resulting solution was filtered through a 0.22 μm syringe filter before injecting into the UFLC system. All experiments were performed in triplicate. After the MSPE, the Fe_3O_4@PANI particles were dried and recycled after ultrasonic cleaning with deionized water and methanol in turn.

2.5 UFLC-UV analysis

In this study, a convenient isocratic elution was adopted for the chromatographic separation of the Sudan dyes. The mobile phase was acetonitrile/water (99: 1, v/v) at a flow rate of 1.0 mL min^{-1}. The temperature of the column was kept at 30℃. Injection volume was 10 μL. The monitoring wavelength was 478 nm for Sudan I, Sudan II and 520 nm for Sudan III, Sudan IV. The Sudan dyes can be separated from each other absolutely within 10 min.

3 Results and discussion

3.1 Characterization of Fe_3O_4 and Fe_3O_4@PANI particles

The characterization of the Fe_3O_4@PANI was carried out based on TEM images and magnetization curves of both the semi-product (Fe_3O_4) and the Fe_3O_4@PANI particles. Fig. 2 displays the TEM images of Fe_3O_4 and Fe_3O_4@PANI particles. Fig. 2a shows that the particles are almost spherical with diameters about 90 nm. Fig. 2b shows that the gray PANI is coated on the dark core of magnetic Fe_3O_4 and the thickness of the PANI layer is about 15 nm.

Fig. 2c shows a hysteresis loop of typical Fe_3O_4 and Fe_3O_4@PANI particles measured by sweeping the external field between -1 and 1 T at room temperature. The magnetization curve shows no remanence or coercivity at room temperature, suggesting the superparamagnetic character. The saturation magnetization values of Fe_3O_4 and Fe_3O_4@PANI particles are 77.9 and 64.1 emu g^{-1}, respectively. The difference of saturation magnetization values indicates the existence of PANI on Fe_3O_4@PANI. And the Fe_3O_4@PANI particles still shows strongly magnetic properties due to the presence of magnetite particles in the core. Thus, they can be easily dispersed and rapidly separated with a conventional magnet, which is an advantage for their applications in extraction.

3.2 Optimization of conditions for MSPE

In this study, the spiked water sample at analyte concentration of 5 ng mL^{-1} was employed for the optimization. Some major conditions, including amount of Fe_3O_4@PANI particles, pH value, ion strength, extraction time, type of desorption solvent, volume of desorption solvent, desorption time and sample volume were investigated in detail to obtain high extraction recoveries. *PF* was calculated based on the following equation:

$$PF=\frac{C_f}{C_0}$$

Where C_f and C_0 are the analyte concentration in eluate after extraction with MSPE process and the initial analyte concentration in the sample solution, respectively.

3.2.1 Amount of Fe_3O_4@PANI particles

The amounts of Fe_3O_4@PANI particles ranging from 2 mg to 12 mg were subjected to the same MSPE to achieve desirable recovery. As can be obviously seen from Fig. 3A, no significant effect was observed when the amount was more than 8 mg. This can be attributed to a comprehension influence of the total specific surface area of the Fe_3O_4@PANI particles and their dispersibility in the water sample. Thus, 8 mg of Fe_3O_4@PANI particles was adopted in the following studies.

3.2.2 pH value of sample

The pH value of the samples is a significant parameter affecting adsorption and recoveries of the analytes. It always influences the interactions between the analytes and the adsorbent. All four Sudan dyes are neutral molecules and do not undergo noticeable dissociation or protonation in moderately acidic or basic media. Therefore, in the present study, the effect of solution pH was investigated by adjusting the pH value from 5 to 10. As shown in Fig. 3B, the optimal extraction recoveries were obtained at pH 7.0. The pH value of deionized water is about 6.7, which is close to 7.0. Therefore, to simplify the experiment procedures, no extra solution was added to adjust the pH of deionized water employed for the optimization.

3.2.3 Ion strength

To investigate the effect of salinity on the recoveries of target compound, KCl with concentrations of 0-12% (w/v) was added into solution. As shown in Fig. 3C, the effect of ion strength on extraction recoveries was not significant and the change of recoveries with the increasing of ion strength was not regular. The results indicated that ionic strength had no significant effect on the extraction efficiency in the proposed method. Therefore, the effect of ion strength on the extraction efficiencies of target compound in real water sample is negligible. To simplify the experiment procedures, no extra solution was added for ion strength adjustment in this work.

3.2.4 Extraction time

The extraction time was optimized by increasing the ultrasound extraction time from 2 min to 30 min. It can be seen from the experimental results shown in Fig. 3D that the recoveries show an increase with increasing of ultrasound time shorter than 15 min. When the ultrasound time is longer than 15 min, the recoveries of Sudan I, Sudan II decrease with the increasing of ultrasound time oppositely and the recoveries of Sudan III, Sudan IV slightly change. Accordingly, 15 min was the best appropriate extraction time.

3.2.5 Type of desorption solvent

The type of solvent has significant influence on desorption efficiency. Because the Fe_3O_4@PANI particles are hardly dispersed in ethyl acetate, n-hexane, ether and dichloromethane, poor desorption efficiency was obtained when these desorption solvents were used. Acetone, methanol, acetonitrile and ethanol were selected and employed for desorption of analytes from the adsorbent. The experimental results are displayed in Fig. 4A. Under the same conditions, ethanol provides the best desorption efficiency. Hence, ethanol was selected as desorption solvent in subsequent experiments.

3.2.6 Volume of desorption solvent

To achieve good recoveries, the influence of the volume of desorption solvent was studied. Fig. 4B shows the analytical results. Clearly, 4 mL of ethanol is enough to obtain total desorption. Multiple elution can obtain higher recoveries when the total volume of desorption solvent was the same. Therefore, duplicate desorptions with 2 mL of ethanol each time was applied in the following experiments.

3.2.7 Desorption time

The optimization of desorption time was conducted by increasing the vortex oscillating time from 1 min to 10 min. According to the experimental results shown in Fig. 4C, 4 min of desorption time is enough to thoroughly elute the analytes from the adsorbent. Thus, desorption time was fixed at 4 min in this study.

3.2.8 Sample volume

In order to obtain high enrichment factor of this method, the effect of the volume of water samples (40-200 mL) was investigated. As demonstrated in Fig. 4D quantitative recoveries of Sudan dyes were obtained up to 100 mL. When the sample volume exceeded 100 mL, the adsorption rate decreased apparently. Thus, 100 mL was considered to be the maximal enrichment volume for water samples.

3.3 Reusability of the Fe_3O_4@PANI particles

In order to evaluate the reusability of the Fe_3O_4@PANI particles, a certain amount of Fe_3O_4@PANI particles were repeatedly and used in MSPE for 20 times. They were washed with 20 mL of ethanol and 20 mL of deionized water in turn and dried in vacuum at 60℃ each time before reusing. The results shown in Fig. 5 indicate that there is no significant reduction in the recoveries of the Sudan dyes when the Fe_3O_4@PANI particles are reused.

3.4 Evaluation of the present method

3.4.1 Linearity

To evaluate the performances of the present method for quantitative determination of the analytes, the working curves were constructed by plotting the peak areas versus the concentrations of Sudan dyes. Corresponding linear regression equations and correlation coefficients (r) obtained under the optimal experimental conditions are displayed in Table

1. Satisfactory correlation coefficients (0.9973-0.9997) for four Sudan dyes are achieved in their linear range.

3.4.2 Limit of detection and quantification

Limits of detection (LODs) and quantification (LOQs) are considered as the lowest concentration of a certain analyte for its confident identification and quantification, respectively. As shown in Table 1, the LODs and LOQs of analytes are in the range of 0.041-0.151 ng mL^{-1} and 0.136-0.497 ng mL^{-1}, respectively.

3.4.3 Recovery and precision

The intra-day and inter-day precision of the present method were evaluated by analyzing the spiked samples at three concentrations levels (2, 5 and 15 ng mL^{-1}) on the same day and the five consecutive days, respectively. The detailed results are listed in Table 2. The intra-day and inter-day relative standard deviations (RSDs) for all Sudan dyes were in the range of 1.3-5.4% and 2.6-7.3%, respectively.

3.5 Analysis of environmental water samples

Five kinds of environmental water samples, including tap water, rain water, reservoir water, surface water and lake water were analyzed to evaluate the applicability of the present method. As can be seen from the typical chromatograms of the blank and spiked sample 1 shown in Fig. 6, no Sudan dyes were detectable in these samples. The recoveries and RSDs are in the range of 92.4-106.9 % and 1.6-6.8%, respectively. The detailed analytical results are listed in Table 3.

3.6 Comparison of the present method with other methods

In order to evaluate the performances, the present method was compared with the other extraction techniques used for Sudan dyes. It can be seen from Table 4 that the present method was convenient, fast with acceptable recoveries and detection limit and obtained efficient enrichment of trace Sudan dyes from large volume of water samples with low solvent consumption over other methods.

4 Conclusion

The Fe_3O_4@PANI particles were successfully prepared and used as reusable adsorbent for MSPE. A convenient, economical, green and effective method was developed successfully for the determination of Sudan dyes in environmental water samples. The analytical performances are satisfactory. The present method is feasible and should have a promising application to the determination of Sudan dyes in other complex samples by varying the extraction conditions.

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Figure Captions

Fig. 1. Chemical structures of Sudan dyes.

Fig. 2. Characterization of Fe_3O_4 and Fe_3O_4@PANI particles: TEM images of Fe_3O_4 particles (a); Fe_3O_4@PANI particles (b); Hysteresis loops of Fe_3O_4 particles and Fe_3O_4@PANI particles (c).

Fig. 3. (A) The effects of the amount of Fe_3O_4@PANI particles; (B) pH value; (C) ion strength and (D) extraction time on the recoveries of the Sudan dyes.

Fig. 4. (A) The effects of the type of desorption solvent; (B) volume of desorption solvent; (C) desorption time and (D) volume of sample on the recoveries of the Sudan dyes.

Fig. 5. Reusability of the Fe_3O_4@PANI particles. The concentration of each Sudan dye is 5 ng mL^{-1}.

Fig. 6. The chromatograms for the extracts of (A) the blank and (B) the spiked tap water at the analytes concentration of 5 ng mL^{-1} obtained at wavelength 478 nm and 520 nm. 1, Sudan I; 2, Sudan II; 3, Sudan III; 4, Sudan IV.

Tables

Table 1 Analytical performances.

Table 2 The recoveries of the analytes and inter and intra-day precision.

Table 3 Analytical results for environmental water samples.

Table 4 Comparison of the present method with other methods

529 **Table 1** Analytical performances.

Analyte	Linear range (ng mL^{-1})	Regression equation	Correlation coefficient	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	*PF*
Sudan I	0.1 - 25	$A = 7780.2\ C - 502.6$	0.9973	0.041	0.136	950
Sudan II	0.25 - 25	$A = 12372\ C - 1735.7$	0.9988	0.080	0.262	946
Sudan III	0.5 - 25	$A = 14553\ C -5372.8$	0.9993	0.147	0.486	938
Sudan IV	0.5 - 25	$A = 14171\ C -5079.1$	0.9997	0.151	0.497	958

Table 2 The recoveries of the analytes and inter and intra-day precision.

Analyte	Concentration (ng mL^{-1})	Intra-day (n=5)		Inter-day (n=5)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sudan I	2	107.1	5.4	102.5	6.3
	5	104.6	4.1	106.1	5.0
	15	101.6	2.5	103.6	4.7
Sudan II	2	95.3	4.2	96.5	6.3
	5	97.1	3.3	94.8	4.5
	15	98.3	2.0	103.8	3.4
Sudan III	2	100.8	2.6	99.9	3.7
	5	97.0	1.7	101.4	7.3
	15	103.9	1.3	96.5	2.6
Sudan IV	2	100.3	3.1	99.5	6.0
	5	94.9	2.6	93.8	5.3
	15	102.6	2.1	98.9	5.8

Table 3 Analytical results for environmental water samples.

Sample	Spiked (ng mL^{-1})	Sudan I		Sudan II		Sudan III		Sudan IV	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sample 1	3	97.9	2.5	95.6	5.4	99.8	3.6	96.5	5.1
	10	98.6	5.3	102.5	5.6	102.5	5.4	106.3	4.3
Sample 2	3	105.3	4.2	106.3	3.5	96.5	5.7	95.4	2.5
	10	106.9	3.0	105.4	6.8	95.6	2.3	96.5	2.7
Sample 3	3	105.3	4.5	99.8	4.6	99.5	2.9	92.4	4.6
	10	101.2	6.3	100.2	2.9	99.7	1.6	93.5	3.8
Sample 4	3	105.4	2.9	100.4	3.5	100.5	2.3	103.6	3.4
	10	101.5	5.3	106.6	3.6	99.5	1.8	99.5	2.6
Sample 5	3	98.6	5.6	99.8	2.4	103.5	2.6	98.4	4.5
	10	93.6	2.8	96.8	5.6	100.9	5.3	97.5	2.5

Table 4 Comparison of the present method with other methods

Method	Amount of water sample（mL）	Solvent (amount)	Extraction time (min)	LODs (ng mL^{-1})	Recoveries (%)	RSDs (%)	Reference
Dispersive liquid-phase microextraction with solidification of floating organic drop	10	1-dodecanol （100 µL）, ethanol（400 µL）	20	0.03	91.1-108.6	0.2-5.5	34
Magnetic solid-phase extraction	75	Acetonitrile (4 mL)	6	0.082-0.12	87.1-111.4	0.6-7.9	35
SPE based on mixed hemimicelles	500	Acetonitrile (3 mL)	20	0.0029-0.0073	86.9-93.6	2.5-9.3	36
Molecularly imprinted solid-phase extractio	100	Methanol (8 mL)	1.5	0.01-0.05	88.5-101.2	1.9-4.6	37
Solid-phase extraction	750	Methanol (4 mL)	22	0.05-0.2	91.9-98.1	1.1-4.6	38
In situ ionic liquid-dispersive liquid-liquid microextraction	8	$[C_6MIM]Cl$ (0.050 g)	1	0.299-0.655	93.7-109.2	1.0-5.6	39
Magnetic solid-phase extraction	100	Ethanol (4 mL)	15	0.041-0.151	92.4-106.9	1.6-6.8	This work

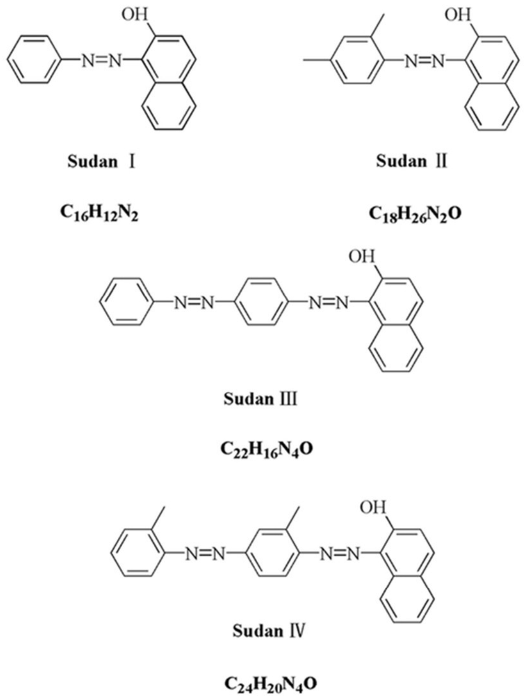

Fig. 1. Chemical structures of Sudan dyes.
77x60mm (300 x 300 DPI)

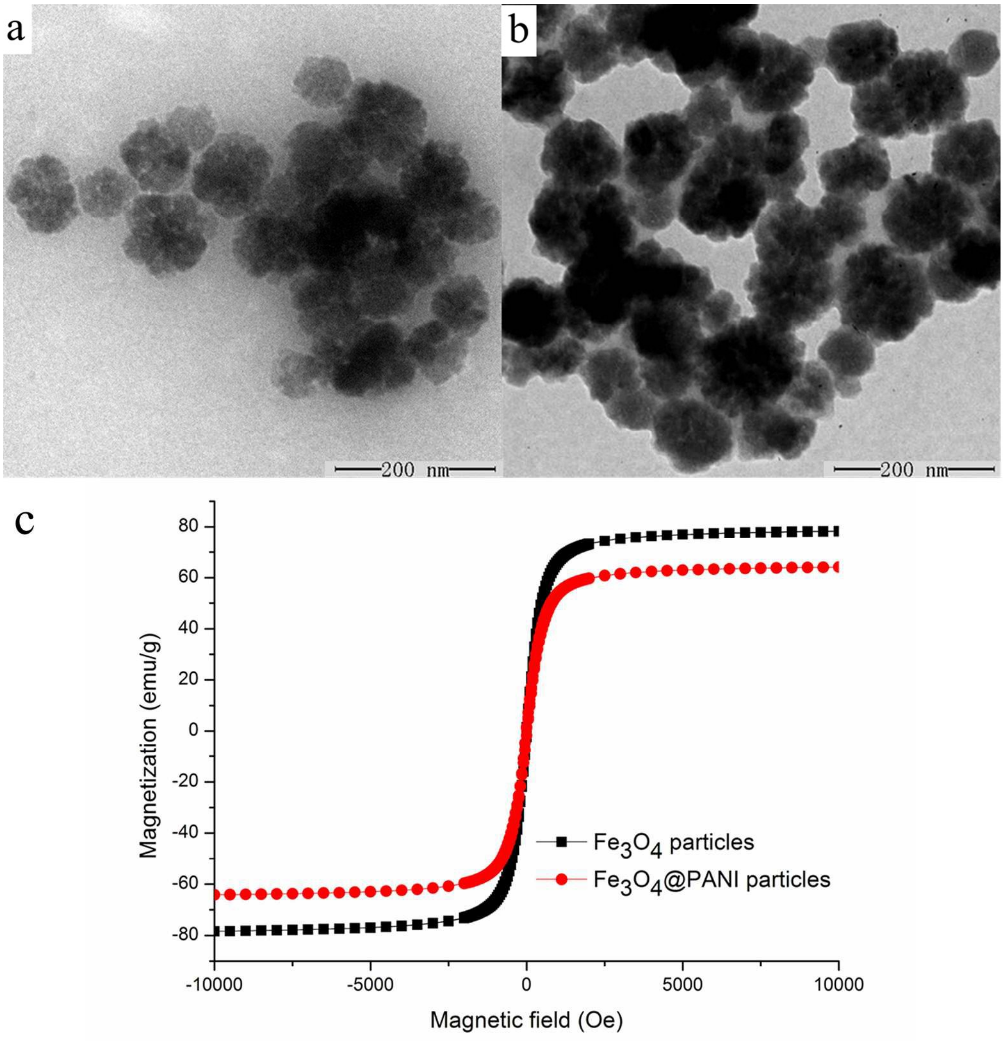

Fig. 2. Characterization of Fe_3O_4 and Fe_3O_4@PANI particles: TEM images of Fe_3O_4 particles (a); Fe_3O_4@PANI particles (b); Hysteresis loops of Fe_3O_4 particles and Fe_3O_4@PANI particles (c).
199x233mm (300 x 300 DPI)

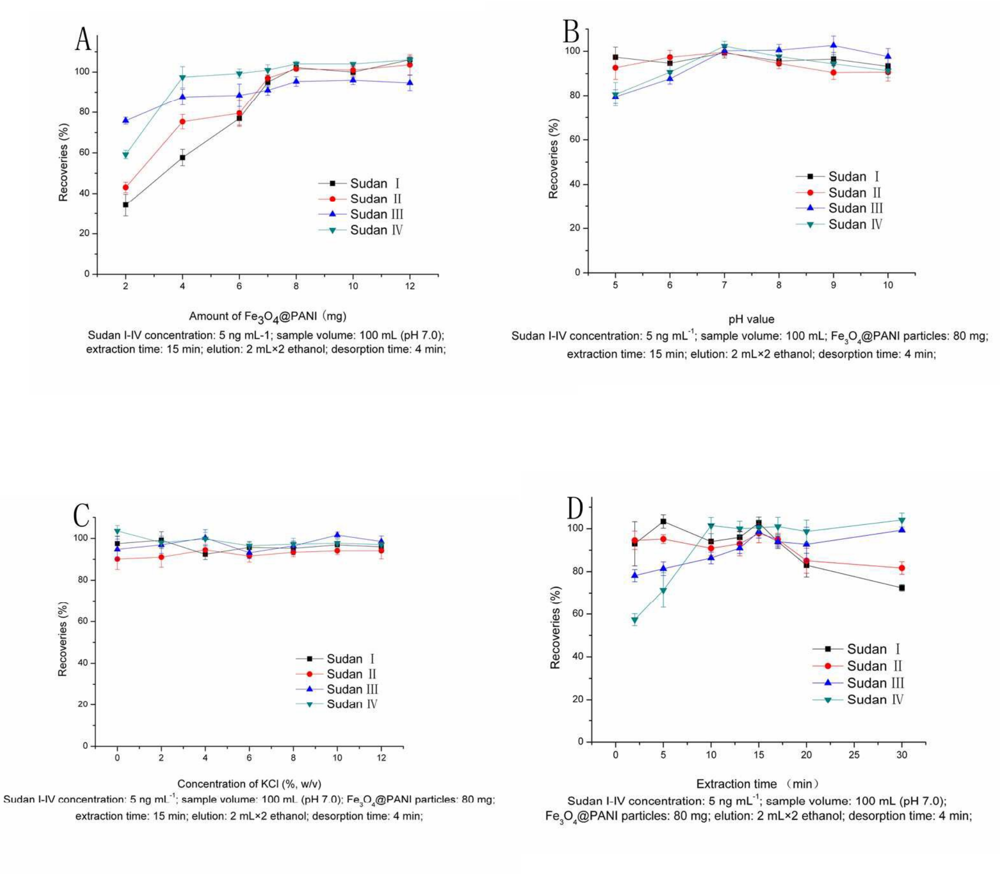

Fig. 3. (A) The effects of the amount of Fe_3O_4@PANI particles; (B) pH value; (C) ion strength and (D) extraction time on the recoveries of the Sudan dyes.
199x199mm (300 x 300 DPI)

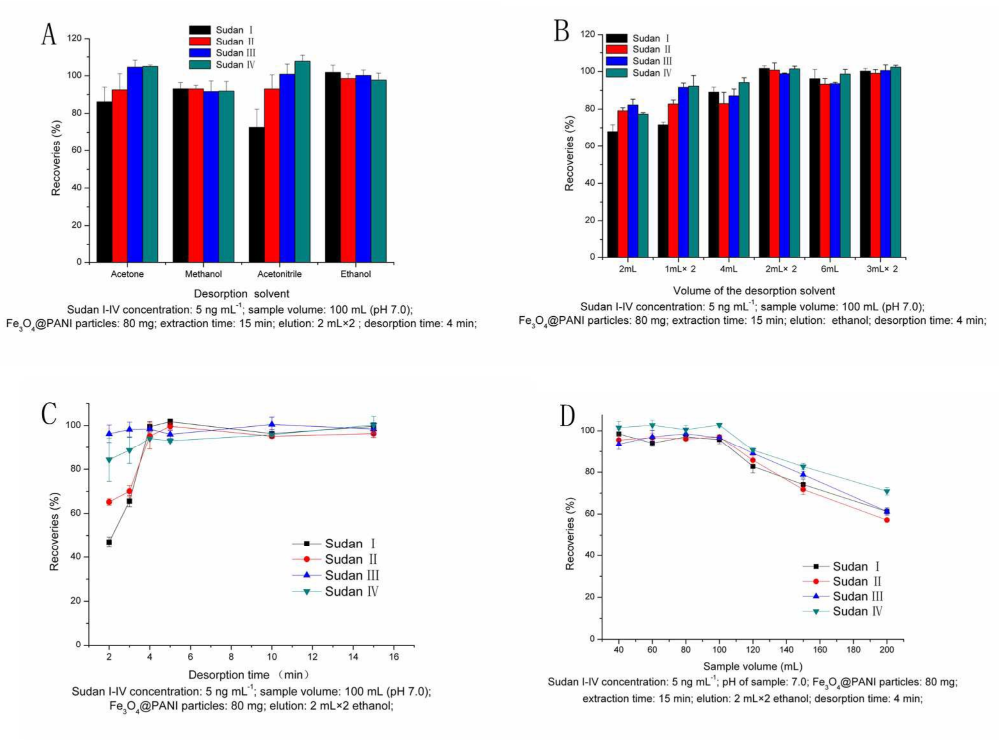

Fig. 4. (A) The effects of the type of desorption solvent; (B) volume of desorption solvent; (C) desorption time and (D) volume of sample on the recoveries of the Sudan dyes.
199x199mm (300 x 300 DPI)

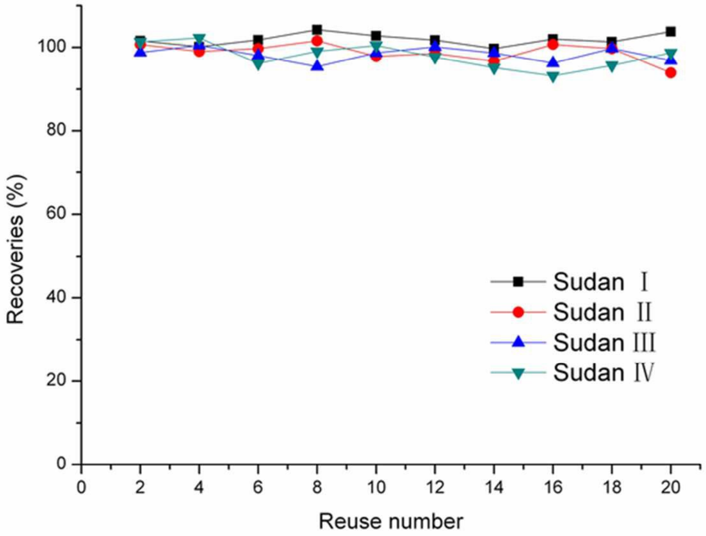

Fig. 5. Reusability of the Fe_3O_4@PANI particles. The concentration of each Sudan dye is 5 ng mL^{-1}.
70x49mm (300 x 300 DPI)

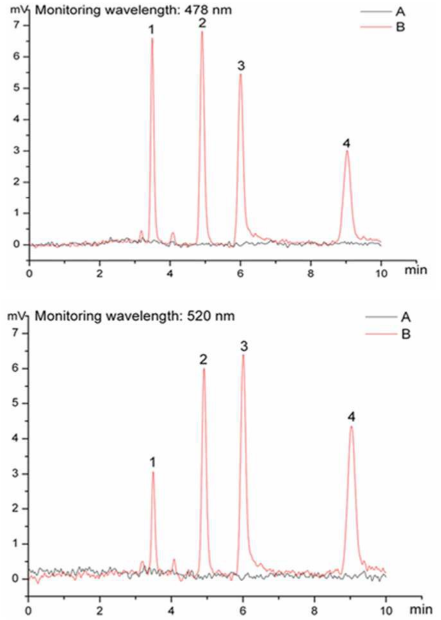

Fig. 6. The chromatograms for the extracts of (A) the blank and (B) the spiked tap water at the analytes concentration of 5 ng mL^{-1} obtained at wavelength 478 nm and 520 nm. 1, Sudan I; 2, Sudan II; 3, Sudan III; 4, Sudan IV.
77x60mm (300 x 300 DPI)