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Removal of sudan dyes from water with C_{18}-functional ultrafine magnetic silica nanoparticles

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ABSTRACT

In this study, the new C_{18}-functionalized ultrafine magnetic silica nanoparticles (C_{18}-UMS NPs) were successfully synthesized and applied for extraction of sudan dyes in water samples based on the magnetic solid-phase extraction (MSPE). The extraction and concentration were carried out in one step by blending C_{18}-UMS NPs and water samples. The sudan dyes adsorbed C_{18}-UMS NPs were isolated from the matrix easily with an external magnetic field. After desorption the quantitation of sudan dyes was done by ultra fast liquid chromatography (UFLC). Satisfactory extraction recovery can be obtained with only 50 mg C_{18}-UMS NPs. The effects of experimental parameters, including the amount of the nanoparticles, extraction time, pH value, desorption solvent, volume of desorption solvent and desorption time were investigated. The limits of detection for sudan I, II, III and IV were 0.066, 0.070, 0.12 and 0.12 ng mL^{-1}, respectively. Recoveries obtained by analyzing the six spiked water samples were between 68% and 103%.

1. Introduction

Sudans dyes are kind of coloring additives in fuels, waxes, plastics, floor and shoe polishes [1]. The dyes are harmful to human health. The International Agency for Research on Cancer (IARC) has classified the sudan dyes as category 3 carcinogens [2]. So it is banned in most countries using sudan dyes as additives in food products destined for human consumption at any level. Because of their low cost and the enhancement of products appearance, sudan dyes are still used in food stuffs unfortunately [3,4]. This illegal use is a severe danger for public health. Liu et al. extracted and separated sudan dyes in chilli powder by cloud point extraction [5]. Chailapakul et al. detected sudan dyes in soft drink with electrochemical detection [6]. Zhao et al. extracted sudan dyes in tomato sauce and sausage with molecularly imprinted polymers [7]. Recently, the biological method is widely applied to treatment of dyes in plant effluent. But it is not very effective to remove dyes. In some textile processing plants, the non-adsorbed dyes combined with the dispersing agents were sent to the treatment system [8]. This process may result in an increase of dyes in wastewater. Although dyes are released into the environment from various sources, there are very few researches about the sudan dyes in environment water.

In view of the low levels of sudan dyes in water samples and the complexity of the matrices, it is difficult to determine these compounds directly, so the pre-concentration and cleaning steps prior to their determination become necessary. At present, solid-phase extraction (SPE) is the most popular sample preparation method for isolating and pre-concentrating desired components from the sample matrix [9,10]. SPE has many obvious advantages compared with other extractions, such as simplicity, low consumption of organic solvent and high enrichment factor. In some cases, however, SPE still has some inherent limitations. Due to the limited rate of diffusion and mass transfer, the extraction time is usually very long when applied in the adsorption and separation of contaminant from large volume of environment samples. So it is necessary to develop new SPE method with short extraction time.

The magnetic separation technique based on small magnetic particles was introduced in 1973 and from then on more and more attentions have been paid to its development and application. Magnetic solid-phase extraction (MSPE) was first introduced by Safariková et al. in 1999 [11]. The new mode of SPE was based on the use of magnetic adsorbents or nanoparticles (NPs). The magnetic adsorbents are not packed into the SPE cartridge, but dispersed into the sample matrix. In MSPE, the target analytes from the complicated matrix are pre-concentrated based on the use of magnetic adsorbents, separated from the matrix under an external magnetic field and then readily dispersed into organic phase after removal of the magnetic field. MSPE has been widely applied in many fields including isolation, catalysis and environmental science based on its advantages, such as high extraction yield, large breakthrough volume and easiness of operation [12]. Fe_3O_4 NPs have been used as the most popular adsorbents in MSPE [13,14]. However, it should be point out that pure magnetic NPs (such as Fe_3O_4 NPs) are prone to form aggregates which may alter their magnetic properties and be oxidized, lost their magnetism easily when the pH is below 4.0.

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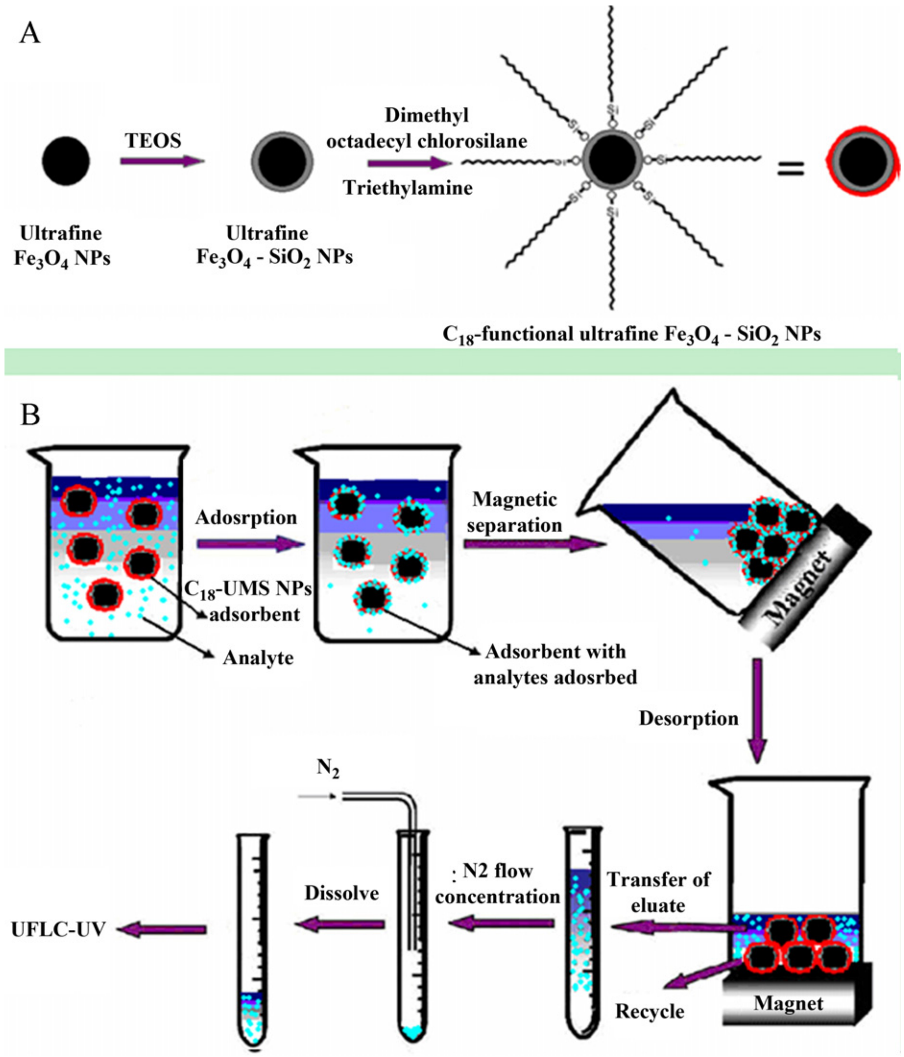


Fig. 1. Synthesis procedure of C_{18}-UMS NPs (A) and enrichment process of sudan dyes (B).

So it is indispensable to coat Fe_3O_4 NPs with a suitable protective coating.

Silica is a kind of the most popular material for protecting Fe_3O_4 NPs because of its stability under acidic condition, high thermal resistance and versatility in surface modification [15]. Furthermore, silica is also abundant and inexpensive. The unique magnetization characteristics of Fe_3O_4 NPs would not sacrificed when Fe_3O_4 NPs were coated with silica [16,17]. Zou et al. reported the extraction of glycopeptides with the superparamagnetic silica particles [18]. Specifically, the inner magnetic Fe_3O_4 NPs core has magnetic property, while the outer silica shows high chemical stability and biocompatibility. Moreover, the surface of magnetic particles coated with SiO_2 can be used to graft various desirable functional groups [19].

In recent years, a few papers have reported on the application of alkoxysilanes modified with magnetic NPs in isolation and purification. C_{18} is most widely used [20,21]. The adsorption ability of magnetic NPs is enhanced after the magnetic NPs are modified with C_{18} group by silylation reaction. C_{18} has been widely used for the pre-concentration of environmental organic pollutants because of its high adsorption ability, excellent stability and long lifetime. Shen et al. reported the application of C_{18} functionalized Fe_3O_4 NPs to the separation of organophosphorous pesticides in cabbage [22]. Ding et al. prepared C_{18} modified Fe_3O_4 NPs and investigated the efficiency of these materials in pre-concentration of polycyclic aromatic hydrocarbons in water samples [23]. These successful studies have intrigued us to prepared C_{18}-functionalized magnetic silica NPs for pre-concentration of sudan dyes from large volume of water samples.

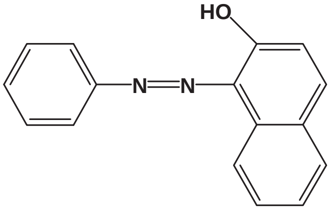
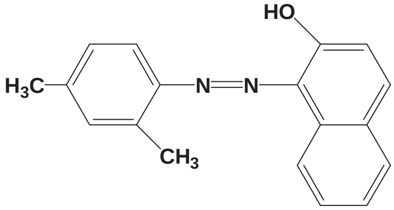
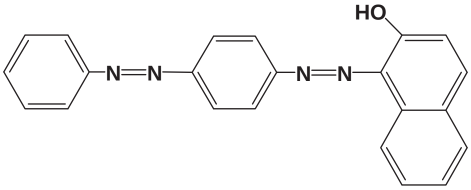
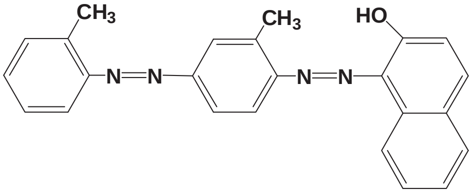
In this study, C_{18}-functionalized ultrafine magnetic silica nanoparticles (C_{18}-UMS NPs) were synthesized by coating ultrafine Fe_3O_4 NPs with silica and subsequently modified with dimethyl octadecyl chlorosilane (OCS). Ultrafine magnetic NPs, Fe_3O_4 NPs, prepared by chemical coprecipitation method in this study have smaller diameter, larger surface area and can be more easily dispersed in aqueous samples compared with those prepared by solvent-thermal method. These magnetic adsorbents were used to extract four kinds of sudan dyes (sudan I, II, III and IV) in water samples based on MSPE. The sudan dyes were analyzed by the ultra fast liquid chromatography (UFLC). To our best knowledge, the application of C_{18}-UMS NPs to separation and concentration of sudan dyes from large volume water samples was reported first time.

2. Experimental

2.1. Chemicals and water samples

The standards of sudan I (content 90%), sudan II (content 88%), sudan III (content 96%) and sudan IV (content 92%), were obtained

Table 1
Chemical information about sudan dyes.

Dye[a]	Purity (%)	Formula	Structure	MW (u)
Sudan I	90	$C_{16}H_{12}N_2$		248.28
Sudan II	88	$C_{18}H_{26}N_2O$		276.33
Sudan III	96	$C_{22}H_{16}N_4O$		456.54
Sudan IV	92	$C_{24}H_{20}N_4O$		380.44

[a] Category 3 carcinogen to humans.

from National Institutes for the Control of Pharmaceutical and Biological Products (Beijing, China). The chemical information of the compounds is shown in Table 1. Appropriate amounts of the compounds were dissolved in methanol to prepare 50 μg mL^{-1} stock standard solutions of each compound. Then the mixed stock solution containing all compounds (10 μg mL^{-1}) were prepared from individual stock standard solution by diluting with methanol and stored under dark condition at 4 °C. Chromatographic-grade methanol and acetonitrile were purchased from Fisher (New Jersey, USA). Dimethyl octadecyl chlorosilane (OCS) (content 95%) was supplied by Alfa Aesar (USA). Iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and sodium hydroxide were supplied by Guangfu Fine Chemical Research Institute (Tianjin, China). Analytical-grade toluene, triethylamine, n-hexane, ethanol, isopropanol, tetraethyl orthosilicate (TEOS), ammonia, hydrochloric acid were obtained from Beijing Chemical Works (Beijing, China). The deionized water was prepared with Milli-Q water purification system (Millipore, Bedford, MA, USA)

The river water samples were taken from Dongliao river (Liaoyuan, China) and Banjie river (Liaoyuan, China). The lake water sample was collected from Nanhu (Changchun, China). The surface water sample was obtained from Mudanyuan (Changchun, China). The industrial water samples were collected from Yitong river (Changchun, China). There are many factories on the banks of Yitong river and some factories discharge the wastewater into the river. All water samples were collected randomly and filtered through 0.22 μm nylon membranes (Shanghai Institute of Pharmaceutical Industry, China) to remove suspended solid. The spiked water samples were prepared by adding standard solution of sudan dyes into the real water samples and stored at 4 °C.

2.2. Preparation of C_{18}-functionalized ultrafine magnetic silica nanoparticles

The route for preparation of C_{18}-UMS NPs is illustrated in Fig. 1A.

2.2.1. Preparation of ultrafine magnetic Fe_3O_4 nanoparticles

The Fe_3O_4 NPs were prepared by chemical coprecipitation method [24]. $FeCl_2{\cdot}4H_2O$ (1.0 g), $FeCl_3{\cdot}6H_2O$ (2.6 g) and HCl (12 mol L^{-1}, 0.425 mL) were dissolved in 12.5 mL deionized water. The mixture was added dropwise into 125 mL NaOH solution (1.5 mol L^{-1}) under vigorous stirring with nitrogen gas passing continuously through the solution during the reaction, as illustrated in Fig. 2. The reactor was placed into an 80 °C water bath and stirred vigorously for 3 h. After the reaction, the obtained Fe_3O_4 NPs precipitate was separated from the reaction medium under the magnetic field and washed with 100 mL deionized water four times.

2.2.2. Preparation of ultrafine magnetic silica nanoparticles

The magnetic silica colloids were synthesized by a modified Stöber method [25]. Typically, new prepared Fe_3O_4 NPs were added into a solution containing deionized water (6 mL), isopropanol (43 mL) and ammonia (25 wt%, 1.25 mL). After stirring for 15 min with nitrogen gas passing through the solution, TEOS (125 μL) was introduced into the solution. The reaction was then allowed to proceed at room temperature under continuous stirring for 4 h.

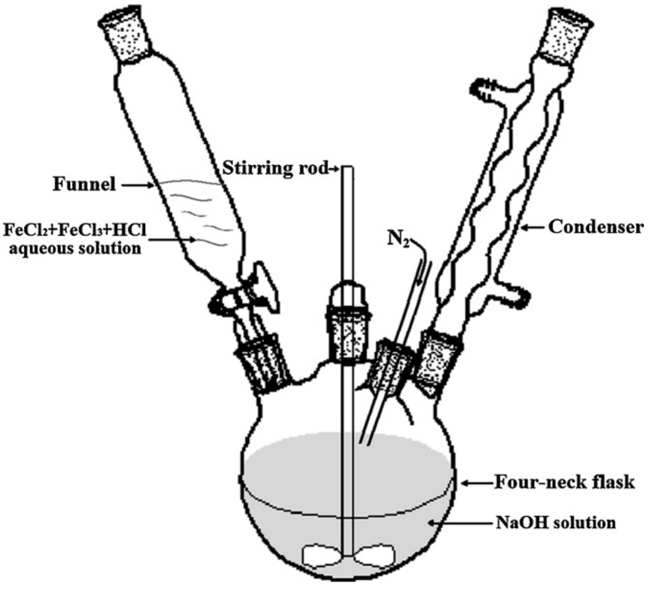


Fig. 2. Reactor for preparating Fe_3O_4 NPs.

Then the magnetic silica nanoparticles were washed with deionized water three times and dried in a vacuum oven at 60 °C.

2.2.3. Preparation of C_{18}-functional ultrafine magnetic silica nanoparticles

OCS was coated on the surface of magnetic silica nanoparticles through alkylation. The dried magnetic silica microspheres (0.6 g) were added into anhydrous toluene (30 mL). The slurry was heated to boiling, and then triethylamine (0.6 mL) and OCS (0.9 g) were added. The mixture was then refluxed for 5 h. The obtained C_{18}-UMS NPs were washed and dried.

2.3. MSPE procedure

Firstly, 50 mg of C_{18}-UMS NPs was added into 100 mL of water sample. The mixture was stirred for 25 min. Subsequently, the C_{18}-UMS NPs were isolated with a strong magnet at the bottom of the beaker and the supernatant was poured away. Then C_{18}-UMS NPs were placed in 4 mL of methanol, stirred for 3 min and the sudan dyes were dispersed in methanol. After magnetic separation, the eluate was dried under a stream of nitrogen at 55 °C and dissolved in 0.5 mL methanol. The highest enrichment factor should be 200. C_{18}-UMS NPs were recycled by washing with methanol for 25 min. The extraction procedure of sudan dyes is shown in Fig. 1B.

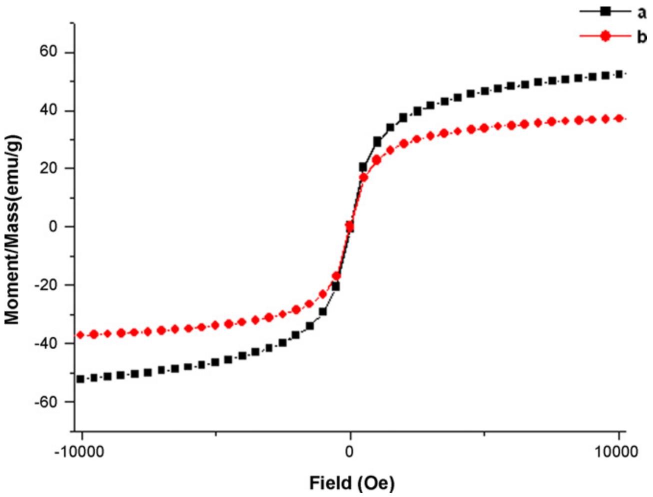


Fig. 3. Room-temperature magnetization curves of (a) Fe_3O_4 NPs and (b) C_{18}-UMS NPs.

2.4. UFLC determination

The sudan dyes were separated and determined using an ultra fast liquid chromatograph-ultraviolet (UFLC-UV) system, which was manufactured by Shimadzu (Shimadzu Corporation, Kyoto, Japan), and equipped with two LC-20AD pumps, a SIL-20A automatic sample injector, a CTO-20A column oven and a SPD-20A UV–vis detector. The separation was performed on a Shimadzu XR-ODS column (75 mm × 2 mm, 2.2 μm particle size) using methanol/water (95:5, v/v) as mobile phase at a flow rate of 0.2 mL min^{-1}. The monitoring wavelength was 478 nm for sudan I and 520 nm for sudan II, III and IV. The temperature of column was controlled at 30 °C. Injection volume was 10 μL.

3. Results and discussion

3.1. Characterization of Fe_3O_4 NPs and C_{18}-UMS NPs

The magnetization curves show that Fe_3O_4 NPs and C_{18}-UMS NPs exhibit typical superparamagnetic behavior due to no hysteresis (Fig. 3). There is no remanence and coercivity, suggesting that

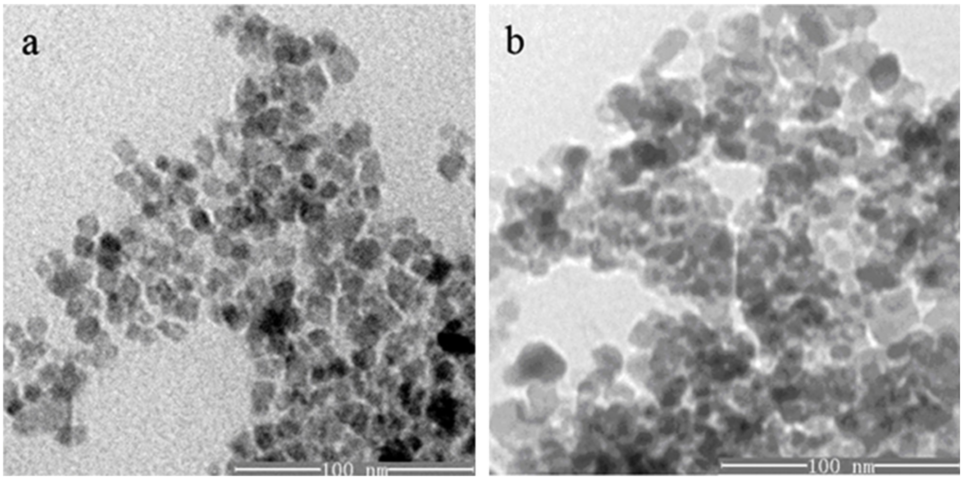


Fig. 4. TEM images of (a) Fe_3O_4 NPs and (b) C_{18}-UMS NPs.

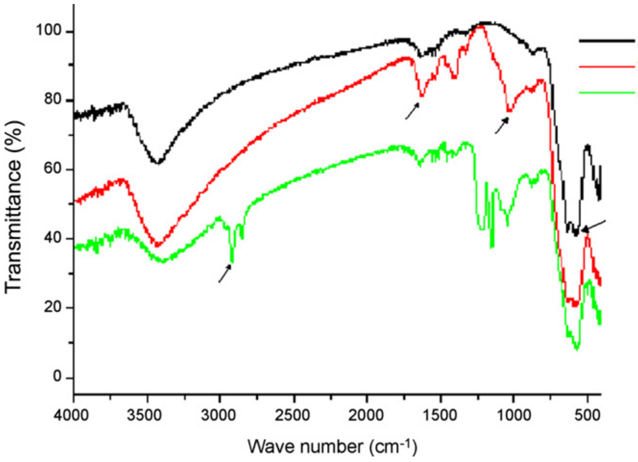


Fig. 5. FT-IR spectra of (a) Fe_3O_4 NPs, (b) Fe_3O_4-SiO_2 NPs, and (c) C_{18}-UMS NPs.

such NPs are superparamagnetic. The saturation intensities of magnetization are 59.49 emu g^{-1} for Fe_3O_4 NPs and 41.31 emu g^{-1} for C_{18}-UMS NPs, which are sufficient for magnetic separation with a conventional magnet. Apparently, the nonmagnetic SiO_2 and C_{18} coating on the Fe_3O_4 NPs result in the decrease of the magnetic strength for C_{18}-UMS NPs. Fig. 4 displays the TEM images of Fe_3O_4 NPs and C_{18}-UMS NPs, which illustrate the uniform size distribution of the nanospheres. Fig. 5 exhibits the FT-IR spectra of Fe_3O_4 NPs, Fe_3O_4-SiO_2 NPs, and C_{18}-UMS NPs. The absorption peak at ~584 cm^{-1} is assigned to Fe–O–Fe vibration of magnetite (Fig. 5a). The absorbing region of 1110–1000 cm^{-1} in the spectrogram of Fig. 5b results from the stretching vibration of Si–O–Si group. The adsorption peak at ~1640 cm^{-1} can be assigned to the adsorbed water on the silica shell or the silanol groups of the silica. After surface modification, the new emergence of absorption peak at ~2960 cm^{-1} is ascribed to CH_2 originated from silane coupling agent, suggesting the alkyl groups have been successfully grafted on the surface of magnetic silica microspheres (Fig. 5c).

3.2. *Optimization of the MSPE conditions*

3.2.1. *Effect of the amount of C_{18}-UMS NPs*

The amount of absorbent is correlated with the amount of analyte adsorbed. Thus, the effect of the amount of C_{18}-UMS NPs was investigated. 20, 30, 40, 50, 60 and 70 mg of C_{18}-UMS NPs were used and the results are shown in Fig. 6. 50 mg of C_{18}-UMS NPs could adsorb the analytes sufficiently and the recoveries of three kinds of sudan dyes are the highest. Therefore, 50 mg of C_{18}-UMS NPs is chosen as the amount of adsorbent in the following studies.

3.2.2. *Effect of the extraction time*

The extraction time had an obvious effect on the recoveries of target analytes. The adsorption process of sudan dyes from water samples must be in equilibrium to obtain satisfactory recoveries. In order to establish adsorption equilibrium, a certain extraction time was required after the C_{18}-UMS NPs were dispersed into the sample solution. As shown in Fig. 7, the recoveries increase with the increase of the extraction time and the highest recoveries of these analytes are obtained when the extraction time is 25 min.

C_{18}-UMS NPs have superparamagnetism property and high saturation intensity of magnetization, and can be completely isolated in a short time (less than 1 min) with an external magnetic field. In a word, extraction time is shortened greatly compared with the traditional time-consuming column passing SPE.

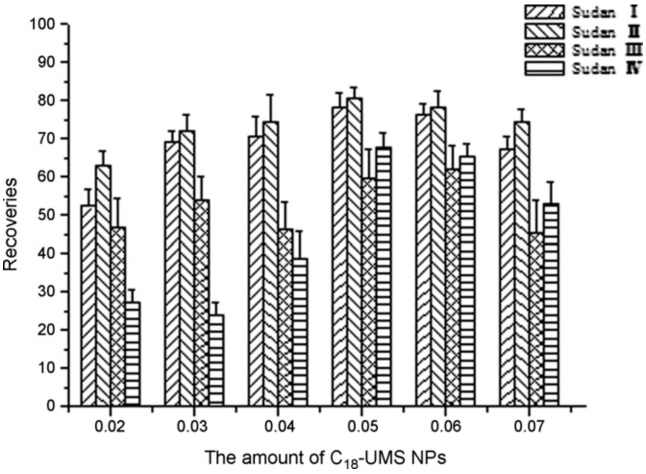


Fig. 6. Effect of the amount of C_{18}-UMS NPs on recoveries of sudan dyes. The extraction time, 30 min; pH value, 7; desorption solvent, methanol; volume of desorption solvent, 3 mL; desorption time, 5 min; sudan dyes concentration, 4 ng mL^{-1}; sample volume, 100 mL.

3.2.3. *Effect of pH values of solution sample*

An appropriate pH value is beneficial for improving of the adsorption efficiency and reducing of interference from the matrix. It was found that pure Fe_3O_4 NPs were oxidized and easily lost their magnetism when pH was below 4.0 [26]. In the present study, the effect of pH was studied by varying the pH in the range of 5–10. The effect of solution pH is shown in Fig. 8. As can be seen from Fig. 8 that the pH does not affect the recoveries of sudan dyes obviously (except sudan III and IV, pH 5). The independence of the recoveries from pH may be due to three reasons: the first one is that the sudan dyes exist in neutral molecules under ordinary conditions; the second one is that the C_{18}-UMS NPs are stable under different conditions; and the third one is that hydrophobic interactions between analytes and C_{18}-UMS NPs play a major role in the adsorption. Because the actual water samples are mostly neutral or slightly acidic, pH 7 is selected for next experiments.

3.2.4. *Effect of the desorption solvent*

The desorption of sudan dyes from C_{18}-UMS NPs was studied with different organic solvents, including acetonitrile, n-hexane, methanol and ethanol. From Fig. 9, we can find that all the four desorption solvents can desorb sudan I and II from C_{18}-UMS NPs

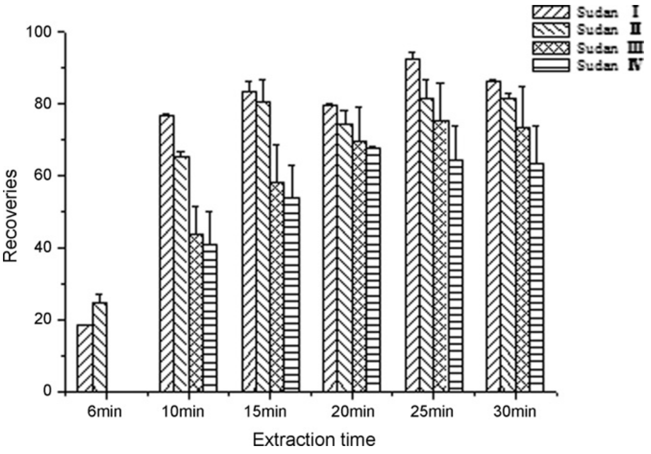


Fig. 7. Effect of the extraction time on recoveries of sudan dyes. The amount of C_{18}-UMS NPs, 50 mg; pH value, 7; desorption solvent, methanol; volume of desorption solvent, 3 mL; desorption time, 5 min; sudan dyes concentration, 4 ng mL^{-1}; sample volume, 100 mL.

Table 2
Experimental results of the orthogonal test ($n = 3$).

Design ID number	Factor			Sudan I	Sudan II	Sudan III	Sudan IV
	(A) Amount of C_{18}-UMS NPs	(B) Extraction time	(C) Desorption time	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)
1	A_1	B_1	C_1	81.76	87.91	46.38	27.62
2	A_1	B_2	C_2	91.09	97.20	84.24	45.70
3	A_1	B_3	C_3	82.17	94.11	79.62	47.63
4	A_2	B_1	C_3	93.15	99.69	91.61	85.45
5	A_2	B_2	C_1	94.63	100.1	94.79	94.26
6	A_2	B_3	C_2	79.81	88.73	89.23	85.24
7	A_3	B_1	C_2	95.49	96.92	91.39	88.58
8	A_3	B_2	C_3	79.18	90.19	92.56	60.04
9	A_3	B_3	C_1	87.34	99.03	88.56	40.75

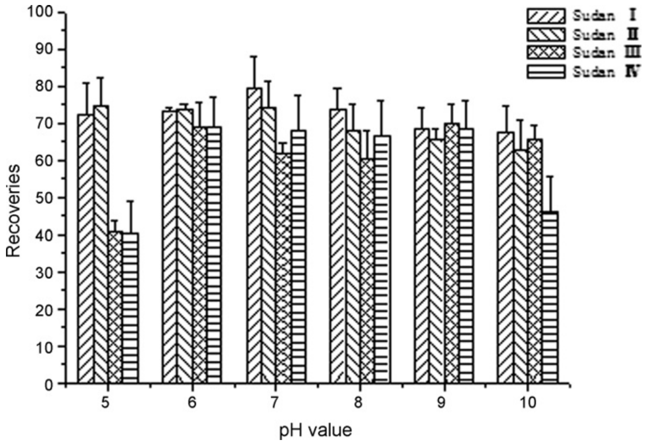


Fig. 8. Effect of pH values of sample solution on recoveries of sudan dyes. The amount of C_{18}-UMS NPs, 50 mg; extraction time, 25 min; desorption solvent, methanol; volume of desorption solvent, 3 mL; desorption time, 5 min; sudan dyes concentration, 4 ng mL^{-1}; sample volume, 100 mL.

effectively. Both acetonitrile and methanol are able to desorb sudan III and IV from the adsorbent completely, whereas the desorption ability of methanol is superior to that of acetonitrile. Furthermore, methanol has lower boiling point and can evaporate more easily than acetonitrile. Therefore, methanol is used as the desorption solvent.

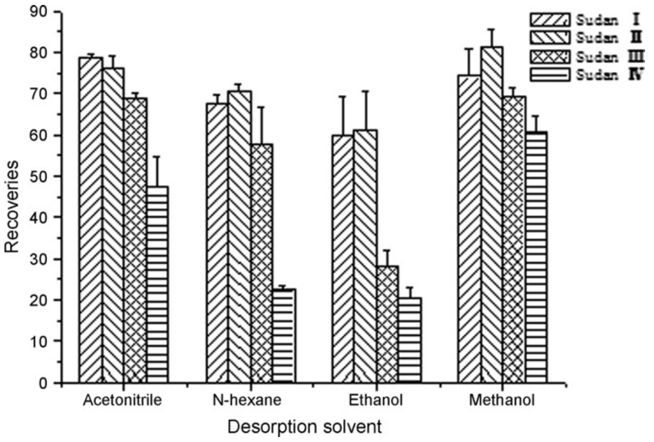


Fig. 9. Effect of the desorption solvent on recoveries of sudan dyes. The amount of C_{18}-UMS NPs, 50 mg; extraction time, 25 min; pH value, 7; volume of desorption solvent, 3 mL; desorption time, 5 min; sudan dyes concentration, 4 ng mL^{-1}; sample volume, 100 mL.

3.2.5. Effect of the volume of desorption solvent

In order to obtain high recoveries of sudan dyes, the effect of the volume of desorption solvent was also investigated. From Fig. 10, it can be seen that only three kinds of sudan dyes are detectable when the volume of methanol is 1 mL. The recoveries of four kinds of sudan dyes increase with the increasing volume of methanol, and do not increase significantly when the volume of methanol is larger than 4 mL. Finally, 4 mL is selected as the volume of methanol.

3.2.6. Effect of the desorption time

For achieving the more efficient desorption condition, the desorption time (0.5, 1, 2, 3, 4 and 5 min) was investigated. The desorption process is an equilibrium process. As shown in Fig. 11, a duration time of 3 min appeared to be sufficient for complete desorption. Finally, 3 min was selected as the optimum desorption time.

3.3. Orthogonal experiment

Based on the previous experimental results obtained by single-factor method, orthogonal experiment (L9 (3^3)) was carried out in order to determine the optimum experimental conditions. The effects of amount of C_{18}-UMS NPs (A_1, 30 mg; A_2, 50 mg; A_3, 70 mg), extraction time (B_1, 20 min; B_2, 25 min; B_3, 30 min) and desorption time (C_1, 1 min; C_2, 3 min; C_3, 5 min) on the recoveries are shown in Table 2. The K and R values are calculated and listed in Table 3. In the table, K_n is the mean effect of each factor at the different levels and R is the range. In this study, the pH value of solution sample was 7 and 4 mL of methanol was used as desorption solvent. From the R

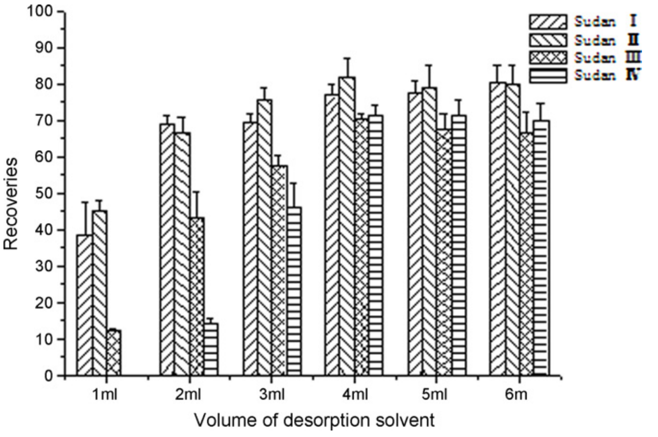


Fig. 10. Effect of the volume of desorption solvent on recoveries of sudan dyes. The amount of C_{18}-UMS NPs, 50 mg; extraction time, 25 min; pH value, 7; desorption solvent, methanol; desorption time, 5 min; sudan dyes concentration, 4 ng mL^{-1}; sample volume, 100 mL.

Table 3
Analysis of orthogonal test results.

Analyte	Factor	K_1[a]	K_2	K_3	R[b]	Optimal level
Sudan I	A	85.00	89.19	87.33	4.19	A_2
	B	90.13	88.30	83.11	7.02	B_1
	C	87.91	88.79	84.83	3.96	C_2
Sudan III	A	93.07	96.20	95.38	3.13	A_2
	B	94.84	95.85	93.95	1.90	B_2
	C	95.70	94.28	94.66	1.42	C_1
Sudan III	A	70.08	91.88	90.83	21.80	A_2
	B	76.46	90.53	85.80	14.07	B_2
	C	76.57	88.28	87.93	11.71	C_2
Sudan IV	A	40.31	88.31	63.12	48.00	A_2
	B	67.21	66.67	57.87	9.34	B_1
	C	54.21	73.17	64.37	18.96	C_2

[a] $K_i^F = (1/3)\sum$ the recoveries of target analytes at F_i.

[b] $R_i^F = \max\left\{K_i^F\right\} - \min\left\{K_i^F\right\}$, here F and i mean factor and setting level, respectively.

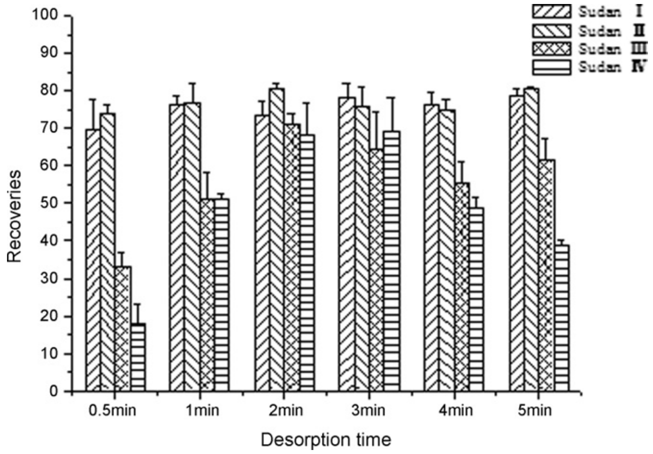


Fig. 11. Effect of the desorption time on recoveries of sudan dyes. The amount of C_{18}-UMS NPs, 50 mg; extraction time, 25 min; pH value, 7; desorption solvent, methanol; volume of desorption solvent, 4 mL; sudan dyes concentration, 4 ng mL^{-1}; sample volume, 100 mL.

values shown in Table 3, it can be seen that the amount of C_{18}-UMS NPs plays an important role in the extraction and the influence of desorption time is less significant compared with that of extraction time (except for sudan IV). Based on the experimental results, the amount of C_{18}-UMS NPs, the extraction time and the desorption time were selected as 50 mg, 25 min and 3 min, respectively.

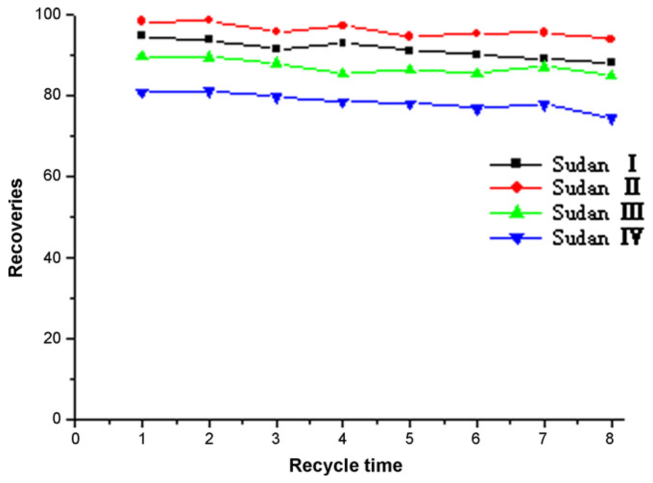


Fig. 12. Effect of recycling times on the recoveries of sudan dyes.

3.4. Reusability of the sorbents

In order to investigate the effectiveness of the nanoparticle sorbents, the C_{18}-UMS NPs were reused in MSPE. The C_{18}-UMS NPs were rinsed with 50 mL of methanol for 25 min before the reuse. The experimental results shown in Fig. 12 indicate that the sorbents are reused 8 times the recoveries of analytes decrease only slightly.

3.5. Analytical performance

Under the optimized conditions, calibration curves are established for sudan dyes at the concentration range of 0.1–50 ng mL^{-1} for sudan I and II, and 0.5–50 ng mL^{-1} for III and IV. The limits of detection (LODs) and quantification (LOQs) of the analytes were estimated as the minimum concentration producing a signal-to-noise ratio of 3 and 10, respectively. The linear ranges, calibration

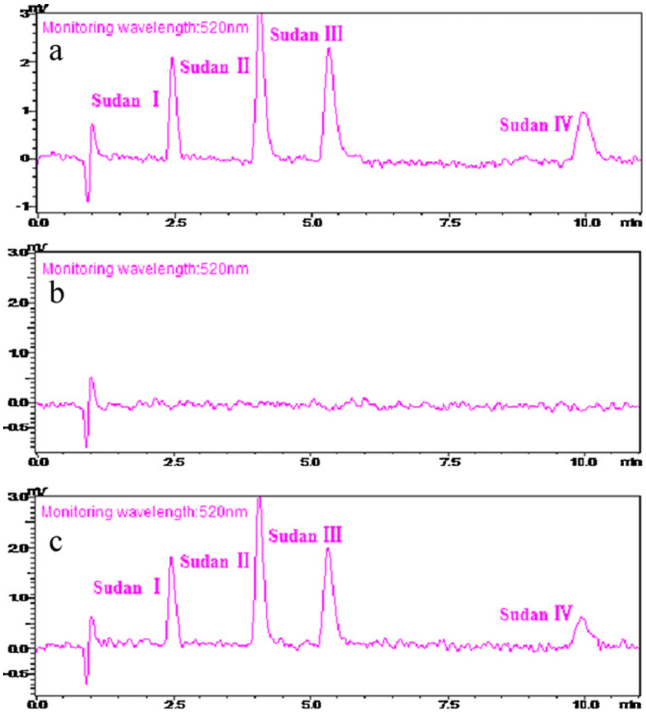


Fig. 13. The chromatograms of standard solution (a), surface water sample (b), and spiked surface water sample (c). The concentration of sudan dyes in standard solution and spiked sample is 2 ng mL^{-1}.

Table 4
Analytical parameters of the proposed method.

Analyte	Linear range ($ng\,mL^{-1}$)	Calibration equations	Correlation coefficient (r)	LOD ($ng\,mL^{-1}$)	LOQ ($ng\,mL^{-1}$)
Sudan I	0.10–50	$y = 15863x + 225.85$	0.9999	0.066	0.22
Sudan II	0.10–50	$y = 16856x + 2406.6$	0.9996	0.070	0.24
Sudan III	0.50–50	$y = 14858x - 2116.7$	0.9998	0.12	0.39
Sudan IV	0.50–50	$y = 8536.4x - 2301.5$	0.9993	0.12	0.41

Table 5
The intra- and inter-day precision and recoveries ($n = 6$).

Analyte	Concentration ($ng\,mL^{-1}$)	Intra-day precision		Inter-day precision	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sudan I	0.5	100	5.7	101	7.3
	2.0	98	3.7	100	4.0
	10.0	99	8.6	93	9.6
Sudan II	0.5	97	2.3	98	2.0
	2.0	98	4.9	97	6.9
	10.0	103	4.3	101	8.5
Sudan III	0.5	102	4.7	104	7.5
	2.0	91	2.4	97	4.5
	10.0	95	5.3	99	8.0
Sudan IV	0.5	98	2.7	102	6.8
	2.0	97	5.5	91	4.7
	10.0	99	8.5	94	10.6

equations, correlation coefficients (r), LODs and LOQs are listed in Table 4. It suggests that the present method has wide linear range, high sensitivity and good precision. Calibration curves of the analytes exhibit good linearity with correlation coefficient $r > 0.9993$. The LODs of the analytes were 0.066–0.12 $ng\,mL^{-1}$. Precision was evaluated by measuring intra- and inter-day relative standard deviations (RSDs). The intra-day precision was performed by analyzing spiked samples six times in one day at three different concentrations of 0.5, 2 and 10 $ng\,mL^{-1}$. The inter-day precision was performed by analyzing spiked samples over 6 days at three different concentration of 0.5, 2 and 10 $ng\,mL^{-1}$. The results obtained are shown in Table 5. The intra- and inter-day precision are in the range of 2.3–8.6% and 2.0–10.6%, respectively.

3.6. *Analysis of water samples*

The proposed method was applied to analyze six kinds of real water samples, including Dongliao river (sample 1), Banjie river (sample 2), Nanhu lake (sample 3), surface (sample 4) and Yitong river (sample 5 and 6) water samples. Sample 5 was collected upstream. Sample 6 was collected downstream. No sudan dyes were found in the real water samples. Then the recoveries of sudan dyes were studied by analyzing the spiked samples. Fig. 13 shows chromatograms of 2 $ng\,mL^{-1}$ standard sudan dyes solution, surface water sample and spiked surface water sample at the analyte concentration of 2 $ng\,mL^{-1}$. The experimental recoveries and standard deviations (SDs) are shown in Table 6. The recoveries of sudan I, II,

Table 6
Recoveries of sudan dyes by analyzing spiked real water samples, mean ± SD (n = 3).

Water sample	Spiked ($ng\,mL^{-1}$)	Recovery (%)			
		Sudan I	Sudan II	Sudan III	Sudan IV
Sample 1	0.5	92 ± 6	89 ± 1	71 ± 2	89 ± 1
	2.0	87 ± 4	87 ± 4	74 ± 4	68 ± 6
	10.0	78 ± 3	85 ± 6	70 ± 1	75 ± 1
Sample 2	0.5	96 ± 2	92 ± 4	89 ± 6	90 ± 1
	2.0	87 ± 6	83 ± 3	87 ± 5	81 ± 7
	10.0	85 ± 3	99 ± 1	97 ± 2	93 ± 6
Sample 3	0.5	94 ± 1	84 ± 2	82 ± 6	87 ± 3
	2.0	82 ± 1	81 ± 6	71 ± 4	69 ± 3
	10.0	81 ± 7	83 ± 4	70 ± 6	74 ± 6
Sample 4	0.5	90 ± 6	83 ± 5	80 ± 1	87 ± 1
	2.0	83 ± 2	93 ± 5	88 ± 7	90 ± 3
	10.0	85 ± 2	95 ± 2	92 ± 3	90 ± 4
Sample 5	0.5	93 ± 3	85 ± 2	93 ± 3	89 ± 6
	2	91 ± 1	89 ± 1	94 ± 2	96 ± 2
	10	98 ± 2	103 ± 2	97 ± 5	97 ± 3
Sample 6	0.5	90 ± 2	88 ± 6	93 ± 2	87 ± 4
	2	90 ± 1	85 ± 3	90 ± 2	92 ± 3
	10	91 ± 5	99 ± 4	97 ± 3	96 ± 1

III and IV are in the range of 78–98%, 81–103%, 70–97% and 68–97%, respectively. The results indicate that the recoveries of the analytes in the spiked water samples are satisfactory.

4. Conclusions

In this study, ultrafine magnetic nanoparticles were successfully coated with silica and then functionalized with C_{18} groups. They were used for convenient, fast and efficient enrichment of trace sudan dyes from large volume of water samples based on MSPE. These new adsorbents were prepared easily and utilized conveniently. Magnetic separation in the method shortened analysis times. A high enrichment factor can be obtained. C_{18} UMS NPs showed great analytical potential in the separation, purification and concentration of analytes in large volumes of real water samples.

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