



Synthesis of magnetic nanoparticles to detect Sudan dye adulteration in chilli powders



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ABSTRACT

Magnetic nanoparticles were synthesised to extract Sudan dyes from chilli powders. The adsorbents used were magnetic ferromagnetic oxide nanoparticles coated with polystyrene. The extraction procedures for Sudan dyes comprised liquid-solid extraction and magnetic solid phase extraction. The conditions were optimised to achieve efficient magnetic solid phase extraction, including extraction and desorption time, type and volume of the desorption solvent, and the mass of the adsorbents. Repeatability tests showed satisfactory recovery rates of 80.2–115.8%, with a relative standard deviation < 3.8%. The results suggested that the proposed extraction method was effective and efficient to extract Sudan dyes from chilli powders. The extraction process was simpler compared with traditional approaches because the adsorbents can be rapidly removed from the sample matrix using a permanent magnet. The use of recyclable adsorbents decreased the cost greatly. Chilli powder samples collected from local markets in Singapore were tested using the proposed method under optimum conditions.

1. Introduction

Chilli powders play an important part in cooking worldwide. Their intense heat and red colour can enhance the flavour and appearance of food (Fan et al., 2009; Gukowsky, Xie, Gao, Qu, & He, 2018; Prabhakaran & Pandian, 2015). Thus, many manufacturers are seeking ways to colour chilli powder to make it more appealing to the market (Chen, Zhou, Qin, Gao, & Peng, 2015).

Illegal food additives, such as melamine in dairy products, clenbuterols in meat, and Sudan dyes in chilli powders, have been increasingly reported because of consumers' growing awareness of food healthy and safety (Ertaş, Özer, & Alasalvar, 2007; Hu, Wang, Wang, & Lu, 2017; Huang et al., 2018; Ma, Nilghaz, Choi, Liu, & Lu, 2018; Rebane, Leito, Yurchenko, & Herodes, 2010). Sudan dyes are synthetic colouring agents employed to colour waxes, hydrocarbon solvents, and shoes (Cornet, Govaert, Moens, Van Loco, & Degroot, 2006). They have an intense red-orange colour and are very cheap, making them an attractive choice for food colouring by illegal merchandisers (Ou et al., 2016). Four types of Sudan dyes of interest in this article, Sudan I to IV, whose chemical structures and colours are shown in Fig. 1. All four Sudan dyes are aromatic, and each has an azo group. The highly conjugated chemical structures account for their intense red-orange colour, making

them suitable for use as colourants (Haughey, Galvin-King, Ho, Bell, & Elliott, 2015; Schummer, Sassel, Bonenberger, & Moris, 2013).

Despite their low cost and intense colour, Sudan dyes are harmful to the human body when ingested (Pei et al., 2015). The azo-group of the dyes releases aniline, which can cause hepatic diseases (Mazzotti et al., 2007). Furthermore, Sudan dyes, especially Sudan I, were proven to cause cancer in rats and may cause cancer in humans (Stiborová, Martínek, Rýdlová, Hodek, & Frei, 2002). Thus, they are classified as class three carcinogens by the International Agency for Research on Cancer (Fan et al., 2009). As a result, in most countries and regions, such as the EU, the use of Sudan dyes in foods is strictly limited and the maximum residue limits (MRLs) for Sudan dyes are set at the mg·kg⁻¹ level (Wang et al., 2013). In the EU, the MRL of Sudan dyes in foods is 0.5 mg·kg⁻¹ (Schummer et al., 2013). To help enforce this ban and keep consumers safe, it is imperative to develop fast and reliable methods to detect overdoses of illegal Sudan dyes in food samples.

Analysis methods for Sudan dyes essentially comprise two steps: extraction and detection. The food matrix is complex; therefore, the extraction step should decrease the interference from non-target compounds and enhance the sensitivity of the analysis protocol (He & Yang, 2018; Hua, Feng, Wang, & Lu, 2018; Song et al., 2014). Thus, the extraction step is crucial to develop an accurate and effective analysis

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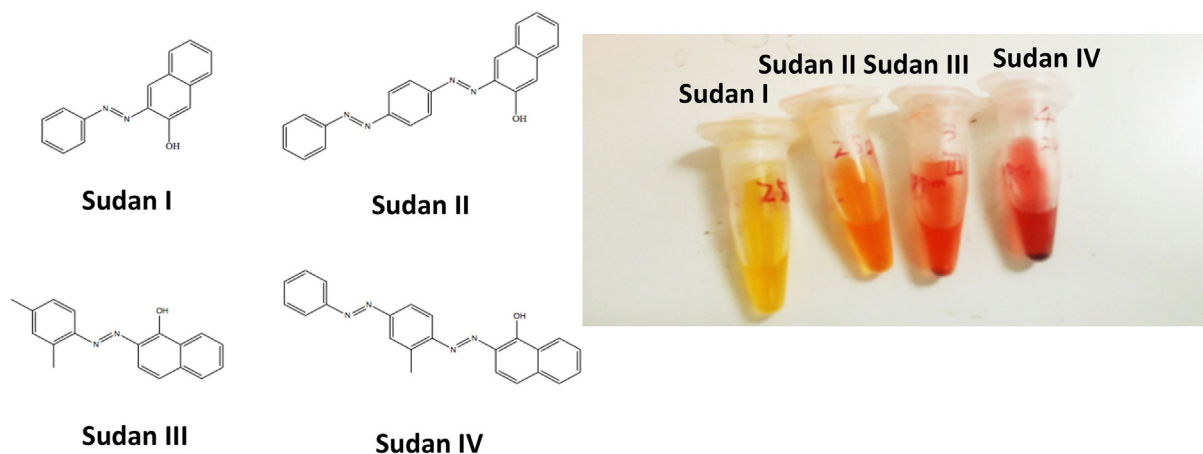


Fig. 1. Chemical structures and colours of Sudan dye I–IV.

method. Many extraction methods have been developed to extract Sudan dyes from chilli products and popular methods are liquid-liquid extraction (LLE), solid phase extraction (SPE), magnetic solid phase extraction (MSPE), solid phase micro extraction (SPME), and molecular imprinted SPE (MISPE) (Baggiani et al., 2009; Kesikünaitė, Linkevičiūtė, Naujalis, & Padaruskas, 2009; Mazzotti et al., 2007; Rajabi, Sabzalian, Barfi, Arghavani-Beydokhti, & Asghari, 2015). LLE uses a large amount of solvent that cannot be recycled, making it harmful to the environment (Zhang, Yu, Li, Mustapha, & Lin, 2015). SPE and SPME require non-recyclable adsorbents that must be synthesised, thereby increasing the costs of these methods (Alsammaraie et al., 2018). MISPE adsorbs the target analyte by making cavities that match the analyte of interest or template. However, this requires tedious and complex extraction and washing protocols (Hua et al., 2018; Tang et al., 2017).

Recently, MSPE has become popular because of the fast development of magnetic nanomaterials. MSPE utilises magnetic nanomaterials to realise the rapid separation of adsorbents and sample matrices (Tolmacheva, Apyari, Furltov, Dmitrienko, & Zolotov, 2016; Yu et al., 2019). However, the application of MSPE techniques is still mostly limited to liquid matrices, which hinder its development (dos Reis, Vidal, & Canals, 2017; Yu, Li, Ng, Yang, & Wang, 2018). Thus, improvements to MSPE methods for use in solid phase samples, which account for majority of food products, are required.

The present study aimed to construct magnetic Fe_3O_4 nanoparticles coated with polystyrene ($\text{PSt@Fe}_3\text{O}_4$) as magnetic solid phase adsorbents. We hypothesised that the nanoparticles could be used to develop a convenient and efficient method to extract and preconcentrate Sudan dyes from the complex sample matrices of chilli powders for accurate quantitative analysis. In the proposed scheme, $\text{PSt@Fe}_3\text{O}_4$ nanoparticles were used as the adsorbents to carry out the extraction. Liquid-solid extraction was carried out before MSPE to adapt the technique to solid food matrices, which greatly expanded the application of MSPE. The principle of extracting Sudan dyes with $\text{PSt@Fe}_3\text{O}_4$ nanoparticles is that the non-polar Sudan dyes would be adsorbed onto the similarly structured non-polar polystyrene coated on the nanoparticles, which would allow their extraction. The Sudan dyes would then be released using a desorption agent, followed by detection and quantification. The advantages of the method are that the nanoparticles are very small, resulting in a large surface ratio and more sites being open for adsorption. In addition, the $\text{PSt@Fe}_3\text{O}_4$ nanoparticles are magnetic and can be easily removed from the matrix after extraction using a permanent magnet, making the extraction process faster and more convenient. Furthermore, the synthesis of $\text{PSt@Fe}_3\text{O}_4$ nanoparticles uses low cost reagents and the nanoparticles can be washed and reused for subsequent extractions.

2. Materials and methods

2.1. Chilli powder samples

Chilli powder samples of different brands were purchased from local markets in Singapore. One specific brand of chilli powder was checked to be free of any Sudan dye residues using traditional liquid-solid extraction coupled with HPLC method (Ertaş et al., 2007). And this brand of chilli powder was used for preliminary trial experiments, optimisation, and method evaluation. The Sudan dye stock solution used to spike the chilli powder samples was prepared by mixing individual standards of Sudan I to IV in acetonitrile at 0.5 mg mL^{-1} . Spiked chilli powder samples were prepared by adding the Sudan dye standard stock solution to the chilli powders and leaving the sample to dry naturally in a fume hood at room temperature. Optimisation experiments were carried out using samples spiked at 0.5 mg kg^{-1} , while the method was evaluated using samples spiked at three different concentrations (0.1, 0.5 and 5 mg kg^{-1}). Real sample analysis was carried out using both blank and samples spiked at 0.5 mg kg^{-1} level to achieve reliable results.

2.2. Chemicals and standards

High performance liquid chromatography (HPLC) grade methanol and acetonitrile were obtained from Fulltime Specialised Solvents and Reagents Co. Ltd (Anqing, Anhui, China). NaOH pellets were bought from Dickson chemical and instrument store, Singapore. Analytical grade ethanol and hexane, tetra-hydrated iron (II) chloride (98%), reagent grade iron (III) chloride (97%), methacrylic acid (99%), potassium persulfate (KPS, 99%), Sudan I–IV standards, technical grade sodium dodecylbenzenesulphonate (SDBS), and styrene (99%) were purchased from Millipore-Sigma Co. Ltd (St Louis, MO, USA). Deionised (DI) water was purified using a Milli-Q purification system purchased from Sigma Aldrich Co. Ltd.

2.3. Synthesis of magnetic adsorbents

Magnetite was synthesised via a co-precipitation reaction by refluxing 5.4 g of FeCl_3 and 2.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in the presence of 1.5 M of NaOH solution (250 mL). The reactants were added into a four necked round bottom flask and stirred mechanically at $80.0 \text{ }^\circ\text{C}$ for 2 h with N_2 protection. After reflux, the solids were removed using a permanent magnet. The supernatant was discarded, and the solids were washed twice by shaking with DI water to remove any NaOH residues before they were used for subsequent synthesis (Wang et al., 2013).

DI water (250 mL) was then added to the magnetite solid. The suspension was stirred mechanically and refluxed together with 5.0 mL

of oleic acid at 80.0 °C for 30 min. The suspension was then cooled gradually to room temperature before adding 1.35 g of SDBS. The suspension was stirred at room temperature for another 30 min before being used for next step. Polystyrene was polymerised and coated on the magnetite using a bilayer surfactant through emulsion polymerisation. DI water (150 mL) and 50 mL of magnetite fluid were added to a four-necked round bottom flask and heated to 70.0 °C. Styrene (18 mL) and 1.8 mL of methacrylic acid were then added to the suspension. Lastly, 0.3 g of KPS freshly dissolved in 50 mL of DI water was added and the suspension was refluxed at 70.0 °C for 6 h, resulting in a brown suspension comprising the PSt@Fe₃O₄ nanoparticles. KPS was added at the last step because it is very unstable, and it was used to initiate the polymerisation of styrene. After 6 h, the suspension was centrifuged, and the solids were collected and washed with DI water twice. The solids were then placed in an oven to dry overnight at 60.0 °C (Yu & Yang, 2017).

2.4. Extraction of Sudan dyes

Chilli powder (1.5 g) was stirred with 9.0 mL of methanol for 20 min. The suspension was then filtered, and the filtrate was then topped up to 100 mL using DI water. PSt@Fe₃O₄ nanoparticles (90 mg) were then added to the sample solution before stirring for 30 min to absorb the Sudan dyes. The hydrophobic and highly conjugated structure of the Sudan dyes meant that they would be attracted to the hydrophobic and aromatic surface of the PSt@Fe₃O₄ nanoparticles, while other interfering compounds would be removed. Thus, the Sudan dyes were purified, and the detection sensitivity was enhanced. The PSt@Fe₃O₄ nanoparticles with Sudan dyes were then retained using a permanent magnet and the supernatant was discarded. After the adsorption was complete, the PSt@Fe₃O₄ nanoparticles were transferred to a 15 mL centrifuge tube, DI water was added with the adsorbents being retained on the wall of the tube, and then the DI water was removed by decantation. Acetonitrile (4 mL) was then added to the PSt@Fe₃O₄ nanoparticles for elution by mixing for 6 min using a vortex machine. Then, the supernatant was transferred to another centrifuge tube while the nanoparticles were retained using a magnetic and the liquid was dried using N₂ gas to further preconcentrate the extracted Sudan dyes to further facilitate their highly sensitive detection. Once dried, the extract was re-constituted using 200 µL of acetonitrile and then sent for detection.

2.5. HPLC analysis

The HPLC apparatus used in this experiment was a Waters 2965 separation module coupled with a Waters 2996 Photodiode Array (PDA) detector (Waters, Milford, MA, USA). A Luna 5 µ C18 column with 4.6 mm internal diameter, 150 mm length, and 100 Å pore size (Phenomenex, Torrance, CA, USA) was used. Isocratic elution was used with a mobile phase comprising 95% HPLC methanol and 5% DI water. The flow rate was set at 1.00 mL·min⁻¹ and the total analysis time was set at 20 min. The sample was injected at room temperature and the injection volume was set at 10.0 µL. The PDA detector wavelength was set at 478 nm for Sudan I and Sudan II, and at 520 nm for Sudan III and Sudan IV (Jiang et al., 2012; Wang et al., 2013).

2.6. Optimisation

Optimisation was performed to determine the optimum parameters to conduct the extraction process to achieve the highest extraction efficiency. Optimisation used single variable optimisation methodology with five parameters being optimised one-by-one. One specific parameter was varied within a certain range while the other parameters were fixed to avoid interaction between the different parameters (Li et al., 2015; Mao, Yan, Wan, Luo, & Yang, 2019; Tolmacheva et al., 2016). The five parameters chosen for optimisation were: the type of

desorption solvent, the desorption time, the mass of the magnetic adsorbents, the volume of the desorption solvent, and the stirring duration for adsorption. The results were plotted as bar charts with the peak area against the changing variable to determine the optimum value for the variable under consideration. Statistical analysis was carried out to help determine the optimum value.

2.7. Statistical analysis

One-way analysis of variance (ANOVA) was carried out using SPSS software (SPSS Statistics 19, IBM Corp., Armonk, NY, USA) to help determine the optimum parameters in the optimisation experiments. Triplicate experiments were performed for each variable and one-way ANOVA analysis was carried out to identify the optimum parameters. In the figures, capital letters were used to show significant differences between the recoveries when using the different parameters.

3. Results and discussion

3.1. Characterisation of the magnetic adsorbents

3.1.1. Fourier-transform infrared spectrometry

The Fourier-transform infrared (FT-IR) spectrum of the PSt@Fe₃O₄ nanoparticles is shown in Fig. 2a. The absorption peaks strongly indicate the presence of polystyrene and Fe₃O₄ magnetite in the solid. The absorption peaks at 3300, 1700, and 1628 cm⁻¹ corresponded to the stretching vibration of polystyrene benzene C–H functional groups, the stretching vibration of methacrylic acid C=O functional groups, and the stretching vibration of polystyrene benzene C=C functional groups, respectively. Meanwhile, another group of fingerprint peaks at 1400–1000 and 700 cm⁻¹ represent the single substitution of polystyrene benzene rings. Finally, the existence of Fe₃O₄ was proven by the presence of the peak at 690 cm⁻¹ representing the Fe–O functional group (Chen, Peng, & Mi, 2007; Tolmacheva et al., 2016). These results suggested the successful coating of polystyrene on magnetite and that the PSt@Fe₃O₄ nanoparticles were synthesised successfully.

3.1.2. Magnetism study

The magnetisation curve obtained using the vibrating sample magnetometer (VSM) (Fig. 2b) shows that the PSt@Fe₃O₄ nanoparticles were influenced by an external magnetic field. The lack of a hysteresis loop means that the particles did not retain magnetic moment after the external field was removed, suggesting that the PSt@Fe₃O₄ nanoparticles were paramagnetic. Furthermore, the saturation point of the PSt@Fe₃O₄ nanoparticles was 0.221 emu, suggesting that the magnetism of the particles was sufficient for extraction (Chen et al., 2007).

3.1.3. Atomic force microscopy

The morphology of the PSt@Fe₃O₄ nanoparticles was obtained using atomic force microscopy (AFM). Two sphere-like objectives were identified in Fig. 2c, with diameters of 0.55 and 0.43 µm, respectively. However, the diameters of the obtained PSt@Fe₃O₄ obtained were slightly larger than those stated in previous works, suggesting possible coagulation (Yu & Yang, 2017).

3.2. Optimisation

Fig. 3a shows that the extract obtained using acetonitrile as the desorption solvent resulted in the highest peak area for all four Sudan dyes compared with that from the other solvents. The reason that Sudan dyes can be desorbed from the PSt@Fe₃O₄ nanoparticles into acetonitrile is that the Sudan dyes are soluble in acetonitrile and the interaction between Sudan dye molecules and acetonitrile is stronger than their interaction with polystyrene (Ertas et al., 2007; Wang et al., 2013). This resulted from acetonitrile's high polarity and elution power (Jiang et al., 2012). Therefore, acetonitrile was chosen as the

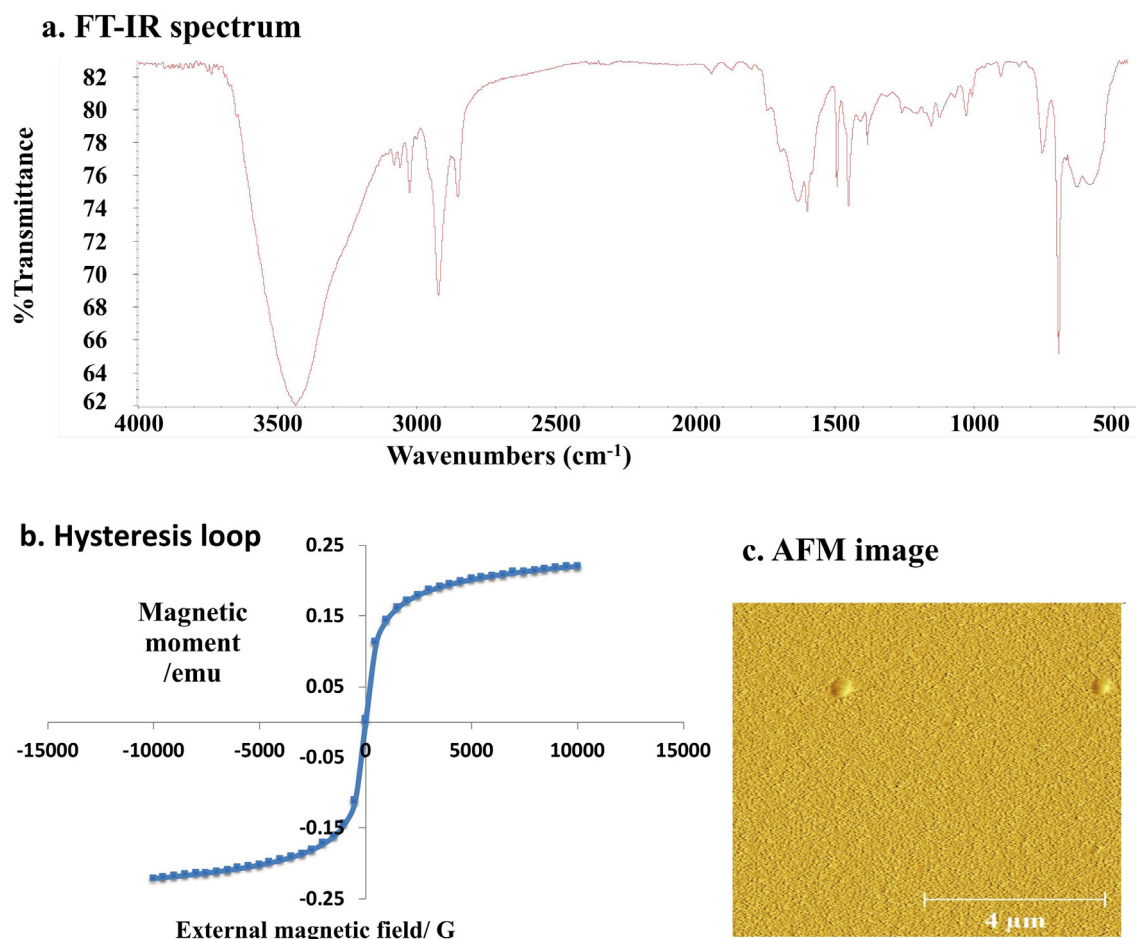


Fig. 2. Characterisation of the polystyrene coated Fe₃O₄: a) Fourier-transform infra-red spectroscopy (FT-IR) spectrum, b) Vibrating sample magnetometer (VSM) curve, c) Atomic force microscopy (AFM) image. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

desorption solvent for subsequent experiments.

Fig. 3b shows that the peak areas of the Sudan I, II, and III increased with longer desorption time (from 2 to 6 min), which was reasonable as the longer desorption time allowed for more desorption to occur and reach equilibrium (dos Reis et al., 2017; Jiang et al., 2012). However, the peak area decreased slightly after 6 min, which could be because a longer vortex time caused scratching on the walls of the centrifuge tubes, which led to adsorption of Sudan dyes onto the walls and thus a lower recovery rate. Thus, the optimised desorption time for vortexing was determined as 6 min.

Fig. 3c shows that the peak areas for the Sudan dyes increased with increased mass of added PSt@Fe₃O₄ nanoparticles (10–110 mg), but reduced when more PSt@Fe₃O₄ nanoparticles were added. An increase of adsorbents from 10 to 90 mg allowed more Sudan dyes to be adsorbed. However, further addition of adsorbents might result in reduced absorption efficiency because of limited space for dispersion (Yu & Yang, 2017; Yu, Ang, Yang, Zheng, & Zhang, 2017). Therefore, 90 mg was chosen as the optimal mass of adsorbents for extraction.

Fig. 3d shows that the peak areas for Sudan I and II were the highest when using 4 mL of acetonitrile, whereas, for Sudan III and IV, 2 mL was equally effective as 4 mL. Our proposed method seeks to analyse Sudan I-IV simultaneously; therefore, 4 mL was selected as the optimum volume of the elution solvent.

Stirring time was varied from 15 to 40 min to determine the optimum time. Fig. 3e shows that the recovery of Sudan dyes generally increased with longer stirring time up to 30 min because a longer stirring time caused more Sudan dyes to be adsorbed to the magnetic adsorbents until equilibrium was reached (Wang et al., 2013). After

30 min, the peak areas reached a plateau. Therefore, the optimum stirring duration was set at 30 min.

3.3. Methods evaluation

3.3.1. Linearity, limit of detection and quantification

A series of samples with different spiked concentrations of Sudan dye, ranging from 0.001 to 500 mg·kg⁻¹, were prepared to obtain a calibration curve for the proposed method of quantifying Sudan dyes in chilli powders. Linear regressions of the peak area for each Sudan dye against the spiked concentration were conducted and the results are summarised in Table 1. All the calibration curves had R² values greater than 0.983, indicating that the method had satisfactory linearity and accuracy, and could be used for quantification, which further proved the reliability of the nanoparticles for use as adsorbents for Sudan dyes in chilli powders. The large capacity for enrichment of the magnetic nano adsorbents, and the removal of the mass interference during the sample pretreatment process, markedly increased the sensitivity of the proposed method compared that of traditional methods (Ma et al., 2018; Rebane et al., 2010). The limit of detection (LOD) and limit of quantification (LOQ) of the four Sudan dyes were determined as the lowest concentration that could be detected with a signal-to-noise ratio above 3 and 10, respectively (Li et al., 2015). To achieve accurate LOD and LOQ values of the proposed method, samples were assayed ten times for each analyte. The LOD and LOQ values of the four Sudan dyes of interested were determined to be within the range of 0.26–2.33 and 0.83–7.69 μg·kg⁻¹, respectively, suggesting good sensitivity of the proposed method (Jiang et al., 2012; Wang et al., 2013).

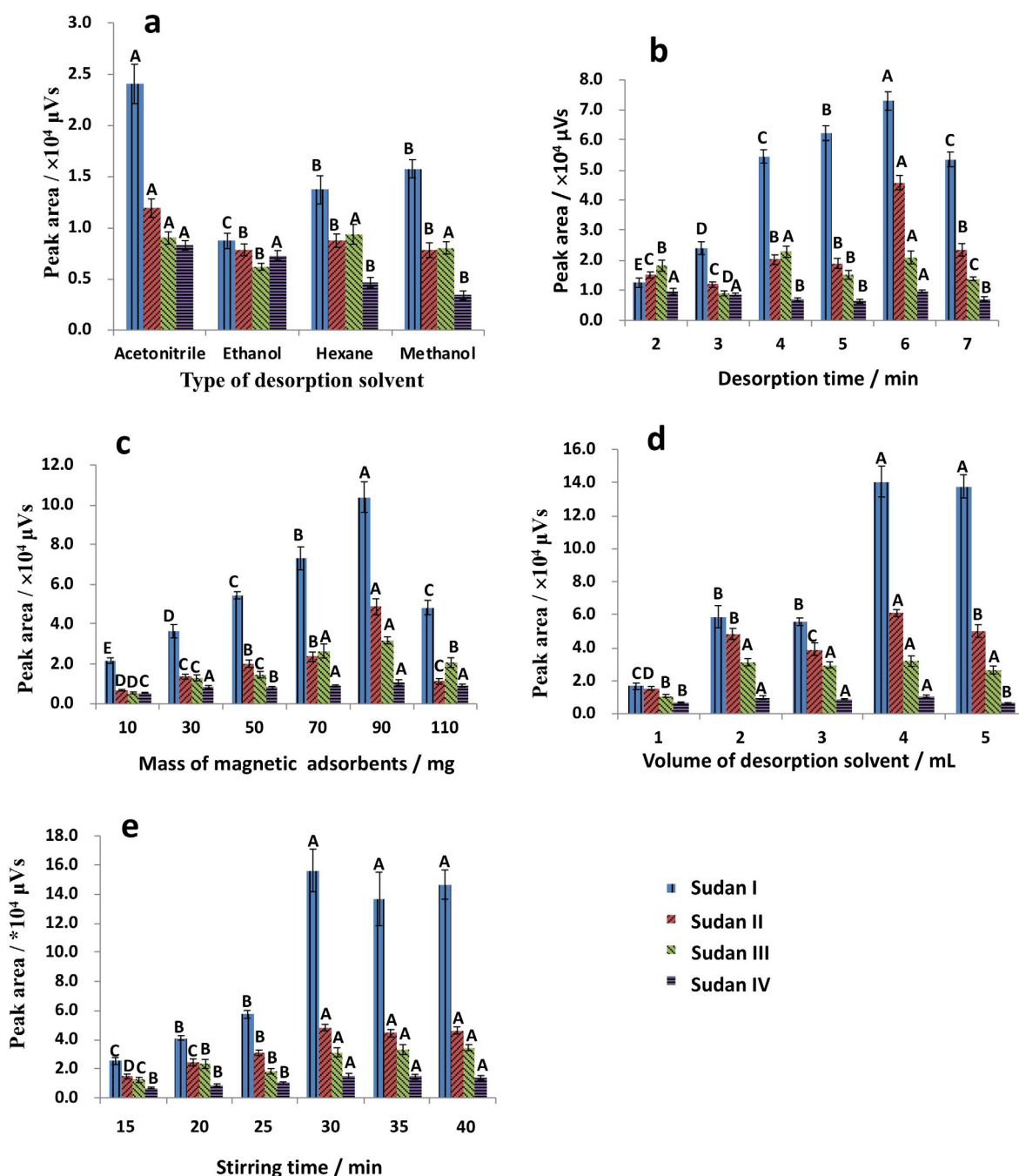


Fig. 3. Optimisation of the extraction parameters: a) Type of desorption solvent, b) Desorption time, c) Mass of the magnetic adsorbents, d) Volume of the desorption solvent, e) Stirring time. Note: Different capital letters between different parameters indicate significant differences.

Table 1

Linearity, limits of detection (LODs), and limits of quantification (LOQs) of the proposed method to determine Sudan dyes in chilli powders.

Analyte	Equation of calibration curve	R ²	LOD mg kg ⁻¹	LOQ mg kg ⁻¹
Sudan I	$y = 3.82 \times 10^8 x + 8793$	0.992	0.00026	0.00083
Sudan II	$y = 2.03 \times 10^8 x + 7204$	0.983	0.00057	0.00164
Sudan III	$y = 1.91 \times 10^8 x + 6273$	0.990	0.00079	0.00207
Sudan IV	$y = 7.76 \times 10^7 x + 6324$	0.987	0.00233	0.00769

3.3.2. Method reproducibility and Reusability of the magnetic adsorbents

The reproducibility test was conducted by repeating the same experiment three times in the same day and three times on three consecutive days, respectively. Chilli powder samples were spiked at three

different concentrations (0.1, 0.5, and 5 mg·kg⁻¹). The purpose of using different spike concentrations was to investigate the reproducibility of the proposed method within a wide concentration range, including below, near, and above the MRLs, so that the results were more reliable, and to evaluate the applicability of the proposed method. Relative standard deviations (RSDs) and percentage recoveries were calculated and compared within one day and between three consecutive days (Xu et al., 2011). The intra-day results and inter-day results are summarised in Table 2. As can be seen from the table, the recovery rates were within the range of 80.2–115.8%. The differences in recovery rates showed no specific regularity or trends for the different Sudan dyes, suggesting that such differences were caused by random errors during the experiments. All the inter-day and intra-day RSDs were less than 13.8%, suggesting that the reproducibility of the proposed method was

Table 2
Reproducibility of the proposed method to determine Sudan dyes in chilli powders.

Analyte	Spiked concentration (mg kg ⁻¹)	Intra-day (n = 3)		Inter-day (n = 3)	
		Average recovery (%)	RSD (%)	Average recovery (%)	RSD (%)
Sudan I	0.1	80.6	5.1	96.3	8.4
	0.5	103.6	5.6	113.9	8.2
	5	95.8	3.2	89.7	5.6
Sudan II	0.1	101.9	4.6	108.7	13.8
	0.5	93.2	7.2	101.2	7.4
	5	87.6	4.1	89.1	11.5
Sudan III	0.1	82.4	6.8	115.8	7.9
	0.5	89.1	3.2	109.3	10.4
	5	102.5	7.5	89.1	9.7
Sudan IV	0.1	98.1	5.4	103.3	7.9
	0.5	112.3	3.6	80.2	12.3
	5	100.2	2.3	92.4	10.4

*Note: RSD: relative standard deviation.

Table 3
Analysis of Sudan dyes in real samples of chilli powders.

Chilli powder sample	Sudan I (mg kg ⁻¹)	Sudan II (mg kg ⁻¹)	Sudan III (mg kg ⁻¹)	Sudan IV (mg kg ⁻¹)
Brand 1	ND	ND	ND	0.41 ± 0.06
Brand 2	ND	ND	ND	ND
Brand 3	ND	ND	ND	ND
Brand 4	0.25 ± 0.04	ND	ND	ND
Brand 5	ND	ND	ND	ND
Brand 6	ND	ND	ND	ND

*Note: ND: not detected.

acceptable. Intra-day reproducibility was better than inter-day (RSDs of below 7.5% and 13.8%, respectively). In summary, the developed extraction method was accurate and had satisfactory reproducibility (Jiang et al., 2012).

Reusability of the magnetic adsorbents was evaluated using the same batch of adsorbents repeatedly for 30 extractions. The adsorbents were washed with methanol thrice each time after use and were dried in oven at 60.0 °C overnight. The dried adsorbents were stored in centrifuge tubes with parafilm seal before being used again. The relationship between the peak area of Sudan I–IV in the extract and number of cycles is displayed in Supplementary Fig. S1. The results showed that the efficacy of the nanoparticles did not decrease after 30 cycles of reuse. The RSDs of the peak area of Sudan I–IV were 1.7%, 3.4%, 7.3%, and 3.2%, respectively, suggesting that the recyclability of the magnetic nanoparticles was good. This recyclability of the nanoparticles would reduce the cost of the method compared with traditional methods using disposable adsorbents and would cause less harm to the environment by producing less nanoparticulate waste (Ma et al., 2018; Rebane et al., 2010).

3.4. Real sample analysis

Real sample analysis was carried out using different brands of chilli powders purchased from local markets in Singapore and using the optimised extraction conditions. According to the results shown in Table 3, two out of six of the tested samples were detected to contain Sudan dyes. Sudan I was detected in one sample and Sudan IV was detected in another sample. None of the samples appeared to contain any Sudan II or III. The detected concentrations were below the MRL set by the Singapore authorities. According to previous reports, low amounts of Sudan dyes below the MRLs set by the authorities were

sometimes detected by sensitive detection methods (Ertaş et al., 2007; Rebane et al., 2010). Therefore, it is generally safe for the public to consume these chilli powder products.

4. Conclusion

In conclusion, PSt@Fe₃O₄ nanoparticles were successfully synthesised via co-precipitation combined with emulsion polymerisation. The obtained PSt@Fe₃O₄ nanoparticles could extract Sudan dyes from spiked chilli powder samples with satisfactory recovery rates using optimised extraction conditions. Reproducibility tests showed that the intra-day and inter-day RSDs were below 13.8%, suggesting that the method was stable and reliable for use. The LODs and LOQs of the four Sudan dyes of interest were within the range of 0.26–2.33 and 0.83–7.69 µg·kg⁻¹, respectively, suggesting that the proposed method has good sensitivity. The PSt@Fe₃O₄ nanoparticles could be easily separated from the sample matrix using a magnet; therefore, the proposed extraction technique is more convenient and rapid compared with traditional techniques. Moreover, the PSt@Fe₃O₄ nanoparticles can be recycled after washing, which will reduce the cost of the extraction method. The proposed method is promising to detect Sudan dye adulteration in chilli powder.

Declaration of Competing Interest

The authors declare no conflict of interest associated with this study.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2019.125144>.

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