



Graphene-coated polystyrene-divinylbenzene dispersive solid-phase extraction coupled with supercritical fluid chromatography for the rapid determination of 10 allergenic disperse dyes in industrial wastewater samples

Chaoyan Lou^a, Can Wu^a, Kai Zhang^a, Dandan Guo^a, Lei Jiang^b, Yang Lu^b, Yan Zhu^{a,*}

^a Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou 310028, China

^b Zhejiang Textile Testing Research Institute, Hangzhou 310013, China

ARTICLE INFO

Article history:

Received 1 February 2018

Received in revised form 15 March 2018

Accepted 20 March 2018

Available online 21 March 2018

Keywords:

Supercritical fluid chromatography

Dispersive solid-phase extraction

Graphene-coated

polystyrene-divinylbenzene

Allergenic disperse dyes

Industrial wastewater

ABSTRACT

Allergenic disperse dyes are a group of environmental contaminants, which are toxic and mutagenic to human beings. In this work, a method of dispersive solid-phase extraction (d-SPE) using graphene-coated polystyrene-divinylbenzene (G@PS-DVB) microspheres coupled with supercritical fluid chromatography (SFC) was proposed for the rapid determination of 10 allergenic disperse dyes in industrial wastewater samples. G@PS-DVB microspheres were synthesized by coating graphene (G) sheets onto polystyrene-divinylbenzene (PS-DVB) polymers. Such novel sorbents were employed in d-SPE for the purification and concentration of allergenic disperse dyes in wastewater samples prior to the determination by SFC with UV detection. To achieve the maximum extraction efficiency for the target dyes, several parameters influencing d-SPE process such as sorbent dosage, extraction time, desorption conditions were investigated. SFC conditions including stationary phase, modifier composition and percentage, column temperature, backpressure and flow rate were optimized to well separate the allergenic disperse dyes. Under the optimum conditions, satisfactory linear relationship ($R \geq 0.9989$) was observed with the concentration of dyes ranging from 0.02 to 10.0 $\mu\text{g/mL}$. The limits of detection (LOD, $S/N = 3$) for the ten dyes were in the range of 1.1–15.6 ng/mL . Recoveries for the spiked samples were between 89.1% and 99.7% with relative standard deviations (RSD) lower than 10.5% in all cases. The proposed method is time-saving, green, precise and repeatable for the analysis of the target dyes. Furthermore, the application of G@PS-DVB based d-SPE process can be potentially expanded to isolate and concentrate other aromatic compounds in various matrices and supercritical fluid chromatography methodology featuring rapidity, accuracy and green will be an ideal candidate for the analysis of these compounds.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Synthetic dyes have various applications in dyeing polyester, nylon, polyacrylonitrile and many new synthetic hydrophobic fibers in textile industry as well as in the leather, printing ink and cosmetic industries [1–3]. However, according to some reports [4–6], approximately 12% of the synthetic dyes have been inevitably discharged into the wastewater because of incomplete exhaustion and washing operations during processing and manufacturing production and about 10–20% of these losses would enter the environment through effluents from wastewater treatment plants. A

major class of the synthetic dyes used is represented by disperse dyes, especially allergenic disperse dyes. Allergenic disperse dyes are a class of low molecular weight synthetic dyes that are derivatives of azo, anthraquinone and other compounds. Such sensitizing disperse dyes can cause allergic reactions in the skin, mucous membrane and respiratory tract, resulting in contact dermatitis and respiratory diseases [7–11]. Furthermore, some of the dyes with azo groups ($-\text{N}=\text{N}-$) in their structure are known as carcinogenic aromatic amines since they can be reduced by azo reductases present in liver enzymes, intestinal bacteria and skin-surface micro-flora [12–14]. Thus, the presence of allergenic disperse dyes in industrial wastewater and effluent has raised great concern because of their contamination to groundwater and drinking water supplies [6]. The increasing awareness of the potential risk of allergenic disperse dyes to human health leads to the introduction of some legislation.

* Corresponding author.

E-mail address: zhuyan@zju.edu.cn (Y. Zhu).

For example, the Oeko-Tex standard 100 (2017 edition) [15] lists 20 allergenic disperse dyes as monitoring standards for ecological textiles and stipulates that the concentration of these dyes should not exceed 0.006%. In order to prevent the environmental water from being polluted by allergenic disperse dyes, it is urgent to develop a rapid, simple, sensitive and environmentally friendly technique for monitoring allergenic disperse dyes in industrial wastewater samples.

In many analytical laboratories, DIN 54231 standard procedure [16] is regarded as a routine process wherein TLC approach is used for the analysis of allergenic disperse dyes. However, its handling is quite complicated which requires plenty of time and organic solvents. In addition, liquid chromatography (LC) with DAD detection [17–19] or more selective and sensitive MS detection [20,21] has been applied to the analysis of allergenic disperse dyes. Regrettably, LC methods cannot meet the requirements of free of organic solvents and rapid analysis. In general, most of the reported methods have drawbacks such as the use of toxic organic solvents, time consuming, poor selectivity or requirement of derivatization. In the present work, supercritical fluid chromatography (SFC), classified as a green analytical technique, is supposed to be a more environmentally friendly and more efficient alternative for the determination of allergenic disperse dyes. Due to the use of supercritical CO₂, SFC possesses obvious advantages in comparison with other chromatographic techniques [22–25]. On the one hand, supercritical CO₂ is considered as a green and non-toxic solvent, which renders the process less hazardous to the environment and mankind. On the other hand, on account of the low viscosity and high diffusivity of supercritical CO₂, a high flow rate can be used, which shortens the analysis time and increases the throughput capacity without deteriorating the separation efficiency. Moreover, with the addition of different modifiers in supercritical CO₂, the polarity of the mobile phase can be varied greatly so the resolution is further improved.

Industrial wastewater is kinds of samples with complicated matrix where the concentrations of allergenic disperse dyes are at trace levels. Hence, a workable sample preparation is highly demanded prior to instrumental analysis. With an appropriate preparation technique, high method precision, accuracy and sensitivity can be obtained. Nowadays, diverse pretreatment techniques have been used for the preparation of target analytes from sample matrices, such as solid-phase extraction (SPE), solid-phase microextraction (SPME), dispersive solid-phase extraction (d-SPE), and dispersive liquid–liquid microextraction (DLLME). Among all the methods, d-SPE is an advantageous method for both matrix removal and preconcentration of analytes due to its merits of low organic solvent consumption, high preconcentration factor, ease of operation and homogenization [26–29]. The core of d-SPE is the adsorbent material which determines the selectivity and accuracy. In recent years, carbonaceous materials such as carbon nanotubes (CNT), graphene (G) and fullerene have attracted growing interest due to their excellent adsorption properties [29–32]. Among these highlighted materials, graphene [33–37], a two-dimensional nanomaterial consisting of a thin honeycomb lattice of sp²-bonded carbon, has received tremendous attention owing to its remarkable thermal and chemical stability, low production cost and high mechanical strength. G has an ultrahigh surface area (theoretical value 2630 m²/g) with a nanosheet morphology, which makes it a promising adsorbent material with good sorption capacity. Besides, due to its large delocalized π -electron system, G has strong affinity for organic compounds (especially aromatic compounds) by π - π stacking interactions with benzene rings. However, the direct use of G as a sorbent often suffers from its irreversible aggregation and water solubility. The aggregation may reduce the extraction capacity of the sorbent, and water solubility of G aggravates the sorbent loss. Moreover, it is difficult to completely isolate the miniscule G

sorbent from a well-dispersed solution during d-SPE process. To overcome these potential problems associated with pristine G, we developed a novel d-SPE sorbent by immobilizing G sheets onto polystyrene-divinylbenzene (PS-DVB) polymers (named as G@PS-DVB). Compared with G sheets, G@PS-DVB microspheres achieve a considerable improvement in properties. G@PS-DVB microspheres are easy to be isolated during d-SPE operation. Meanwhile, the highlighted adsorption properties of G are maintained in G@PS-DVB microspheres.

In this study, d-SPE based on G@PS-DVB sorbent followed by SFC was proposed for the rapid and green analysis of 10 allergenic disperse dyes in industrial wastewater samples. PS-DVB polymers were prepared by seed swelling polymerization according to precious work [38–40] and were used as the virgin polymers for further synthesizing G@PS-DVB microspheres. Graphene oxide (GO), as a precursor to G, was synthesized according to Hummers method [41]. The fabrication of G@PS-DVB microspheres was accomplished after several steps using these two materials. To achieve the maximum efficiency in d-SPE, predominant parameters were investigated such as extraction time, desorption solution, desorption time, etc. SFC variables including stationary phase, modifier composition and percentage, column temperature, backpressure and flow rate were examined to improve the chromatographic separation. Subsequently, the developed green and rapid method was applied to quantify the target compounds in industrial wastewater samples.

2. Experimental

2.1. Reagents and materials

Disperse yellow 1 (82%), disperse yellow 49 (90%), disperse yellow 9 (89%), disperse orange 37/76 (44%), disperse yellow 3 (30%), disperse red 1 (98%), disperse orange 3 (85%), disperse red 17 (83%), disperse orange 1 (80%) and disperse brown 1 (50%) were purchased from Dr. Ehrenstorfer, GmbH (Augsburg, German). Their chemical structures and more information are shown in Fig. S1 and Table S1. All the HPLC-grade organic solvents were purchased from Tedia Company (Fairfield, USA), such as methanol and acetonitrile. Since some of the disperse dyes standards were of low purity, the factor of purity was considered when preparing the standard stock solution in methanol (200 mg/L). The standard solutions were prepared every day by diluting the stock solution with HPLC-grade methanol. The spiked sample solutions used in the work were prepared by spiking allergenic disperse dyes standards into blank real samples at required concentrations. Industrial wastewater samples were collected from different textile factories in Zhejiang, China. They were all stored in a refrigerator at 4 °C.

PS-DVB polymers (15 μ m diameter) were prepared by seed swelling polymerization [38–40] and GO was synthesized according to Hummers method [40]. They were used for further synthesizing G@PS-DVB microspheres.

2.2. Instruments

Separation of 10 allergenic disperse dyes was conducted in a Nexera UC SFC system (Shimadzu, Japan) with UV detection. The SFC system was equipped with a CO₂ delivery pump, an autosampler with a 5 μ L loop for injection, an online degasser, a column oven, a SPD-20A UV detector and a back pressure regulator (BPR). Modifier solvent was delivered by LC-20ADXR pump and mixed with supercritical CO₂ fluid. Lab Solutions Ver5.8 was used for instrument control, data acquisition and handling. During data acquisition, the computer read the UV signals at a sampling rate of 2 Hz which was consistent with the standard responding time

(0.5 s). With this sampling rate, the sensitivity of the UV detection in this work could be lowered to 2×10^{-4} Au.

The final chromatographic conditions in SFC were as follows: 10 allergenic disperse dyes were separated using a WondaCract ODS-2 column (5 μ m, 4.6 mm $\times$ 250 mm) (Shimadzu, Japan) at 38 °C. The binary mobile phase was composed of (A) CO₂ and (B) methanol (93.7/6.3, v/v) at flow rate 2.0 mL/min. The back pressure was maintained at 10.5 MPa. The UV detection wavelength was set at 440.0 nm. The sample volume injected was 5 μ L at a sampling speed of 5 μ L/s.

2.3. Preparation of G@PS-DVB microspheres

2.3.1. Synthesis of PS-DVB polymers

Firstly, 20 g of styrene (St), 0.7 g of azobisisobutyronitrile (AIBN) and 3 g of polyvinylpyrrolidone (PVP) were dispersed in the mixture solvent of ethanol and water (95:5, v/v). The polymerization reaction of the dispersion was conducted at 70 °C under the atmosphere of nitrogen. After 12 h, monodisperse polystyrene (PS) seeds with average size were obtained. Subsequently, 0.56 g of PS seeds as well as an emulsified solution consisting of dibutyl phthalate (DBP) and sodium dodecylsulfonate (SDS) aqueous solution were placed into a 500 mL three neck flask. After stirring overnight, another emulsified mixture and 250 mL of polyvinyl alcohol aqueous solution was poured into the flask for swelling. After 24 h, the temperature of the system was increased to 70 °C and the reaction was maintained for 48 h under the protection of nitrogen. Afterwards, the resulting particles were washed and dried in the oven.

2.3.2. Preparation of pristine graphene oxide

Graphene oxide was synthesized by oxidation of natural graphite flake through Hummers method. 2 g of graphite powder and 2 g of sodium nitrate were mixed with 96 mL of concentrated sulfuric acid (98%) in an ice bath under constant stirring. 12 g of potassium permanganate was then added slowly to the mixture at a temperature lower than 5 °C. After stirred for 1.5 h, the slurry was transferred to a 35 °C bath and was completely stirred for another 1.5 h. 80 mL water was then added to the system drop by drop. After that, 200 mL of hot water and 10 mL of H₂O₂ was added under stirring until the colour of the solution changed to yellow from dark brown. To eliminate metal ions, the suspension was washed with HCl (5%). Afterwards, the solution was washed with large amounts of water until the pH reached 7. Finally, the obtained GO product was fully dried in oven at 70 °C.

2.3.3. Fabrication of G@PS-DVB microspheres

The fabrication of G@PS-DVB microspheres was conducted according to the previous work [40]. To be specific, 2.5 g of PS-DVB polymers was ultrasonically suspended in 50 mL of tetrahydrofuran. Subsequently, 50 mL of GO dispersion (1.0 mg/mL) was added into this suspension. The mixture was interacted for 30 min to obtain the brownish GO@PS-DVB polymers, which were the precursors of G@PS-DVB. Then the GO@PS-DVB particles were suspended in 100 mL of 1:1 (v/v) water/ethanol, and 23 μ L of hydrazine and 1.7 mL of ammonia hydroxide were added into the suspension. The mixture was stirred and heated at 80 °C for 3 h. With this step, the GO@PS-DVB polymers (brown) were reduced to G@PS-DVB (dark). The particles were washed with deionized water for several times to remove exterior contamination. Finally, the dark particles were dried for 1 h under vacuum at 60 °C. A simple schematic diagram of fabricating G@PS-DVB microspheres is depicted in Fig. S2.

2.4. Characterization of G@PS-DVB microspheres

The synthesized G@PS-DVB microspheres were characterized by CHN elemental analysis, X-ray photoelectron spectroscopy

(XPS), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) and thermo gravimetric analysis (TGA).

2.5. d-SPE procedure

Firstly, 20 mg of G@PS-DVB microspheres were dispersed into aqueous sample (10 mL) in a centrifuge tube. Subsequently, the mixture was extracted for 15 min in ultrasonic bath at 30 °C. Afterwards, the sorbents were isolated from the solution by centrifugation and the upper water phase was discarded. Then a desorption solvent (0.5 mL) was added, and the mixture was sonicated for 10 min at 30 °C. Next, the mixture was centrifuged and the supernatant was transferred into a 1.8 mL vial. Finally, 5 μ L of extracts were injected into the SFC system for analysis. An enrichment factor (EF) of 20 was theoretically calculated as the ratio of the initial sample volume to the final desorption volume. The G@PS-DVB microspheres were regenerated by ultrasonic in methanol for recycled use. Fig. 1 describes the whole d-SPE process.

3. Results and discussion

3.1. Characterization of G@PS-DVB microspheres

Since graphene plays an important role in adsorption capacity of G@PS-DVB microspheres, it is necessary to confirm the amount of graphene on G@PS-DVB. In the work, 50 mg of GO was used to modify 2.5 g PS-DVB polymers (as mentioned in Section 2.3.3). After the fabrication procedure, there were no residual graphene sheets in the filtrate during the washing step, which indicated that the graphene was completely coated onto the PS-DVB polymers. Thus the amount of graphene on the G@PS-DVB microspheres was estimated to be approximately 20 mg/g.

Table S2 shows the element contents of G@PS-DVB and PS-DVB measured by CHN elemental analysis. Relative to PS-DVB, an obvious increase of carbon content was observed for G@PS-DVB, indicating that graphene was successfully immobilized onto PS-DVB. Accordingly, the 1.96% increase of carbon content of G@PS-DVB was attributed to the graphene loaded on the G@PS-DVB microspheres. Thus the surface coverage of graphene was calculated to be $\sim$ 20 mg/g, which was in agreement with theoretical result in the previous paragraph. Meanwhile, no content of nitrogen was detected for G@PS-DVB in CHN elemental analysis, which implied that there was barely co-immobilization of hydrazine occurring during the synthesis of G@PS-DVB. In addition to CHN elemental analysis, XPS test was conducted to further confirm the elemental composition of the particles. As we can see in Fig. S3, the peak at 284.5 eV is attributed to carbon-containing species. However, peak of N1s band is not observed in XPS spectrum, which certifies again that there is no hydrazine co-immobilization in G@PS-DVB particles.

The morphology and dispersibility of the self-prepared G@PS-DVB microspheres was characterized by SEM. Fig.S4-b shows the SEM image of G@PS-DVB microspheres, while Fig.S4-a is the SEM image of original PS-DVB polymers at the same magnification. As can be seen in Fig.S4, both polymers are non-agglomerating and evenly distributed with a uniform size of about 15 μ m. In comparison with the unmodified PS-DVB polymers, G@PS-DVB microspheres are encapsulated by corrugated ultrathin G sheets. From the enlarged SEM image in Fig.S4, we can see the corrugated and wrinkled textures on the surface of G@PS-DVB. The results from Fig.S4 confirm the successful synthesis of G@PS-DVB sorbents.

As G@PS-DVB microspheres carried sufficient mesopores, the adsorptive characterization of the material was determined by BET test. The results showed that the specific surface area of G@PS-DVB microspheres was 207 m²/g, pore volume was 0.224 cm³/g and

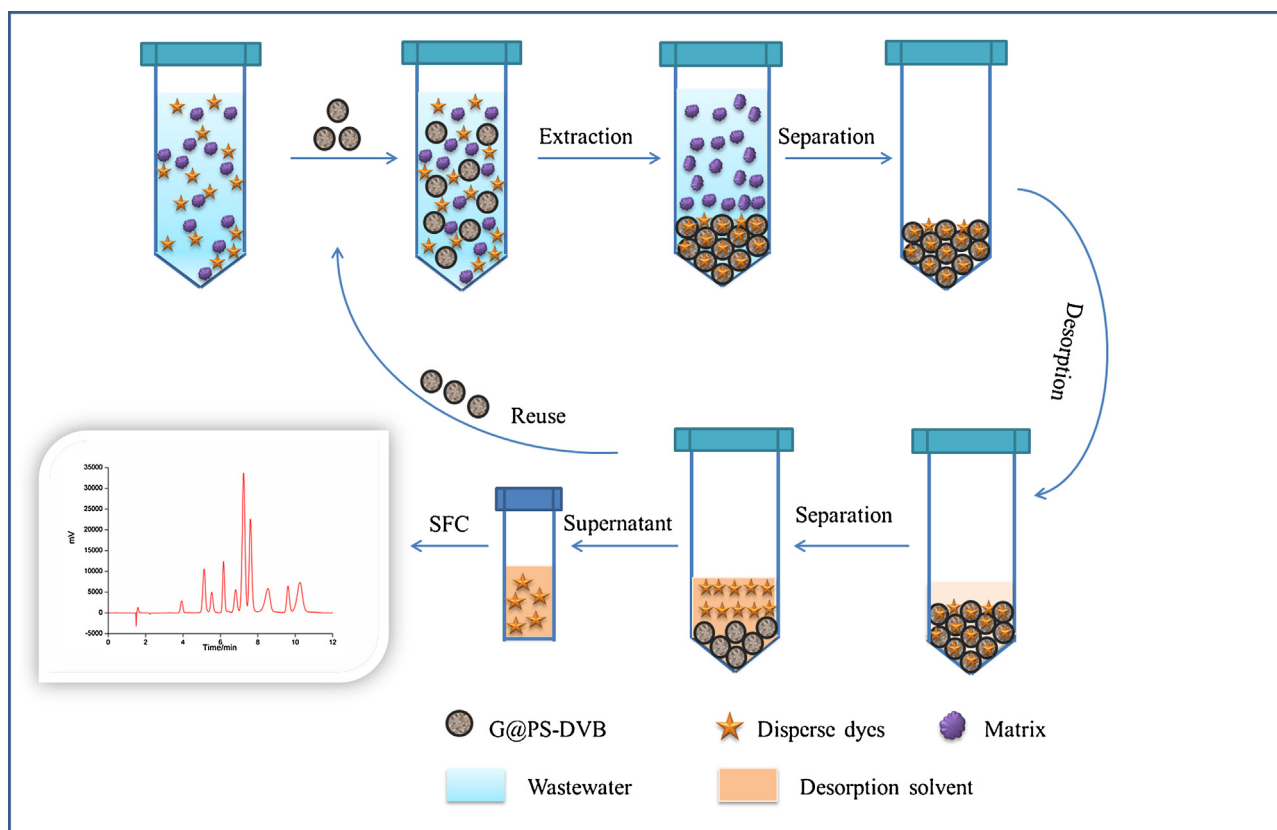


Fig. 1. Schematic of the d-SPE procedure.

average pore size on the surface was about 3.97 nm. According to the BET data, there was sufficient void cavity and acceptable surface area for G@PS-DVB to store a large number of target molecules. Therefore, the G@PS-DVB is a potential sorbent material for extracting and enriching target molecules in real samples.

The thermal stability of the particles was investigated by TGA test. Fig.S5 shows the TG curves of PS-DVB and G@PS-DVB in the temperature range of 10–620 °C (20 °C/min, N₂). The decomposition temperature of the two microspheres is higher than 320 °C, which demonstrates that the sorbents possess excellent thermal stability.

3.2. Optimization of d-SPE conditions

The influences of different parameters including sorbent amount, extraction time, desorption conditions were discussed in detail. The optimization experiments were carried out by using 10 mL real samples spiked with 0.5 µg/mL for each of allergenic disperse dyes. All the experiments were performed in triplicate and the means of the results were used for optimization evaluation.

3.2.1. The amount of G@PS-DVB

The amount of G@PS-DVB sorbents used in d-SPE procedure was investigated so that the sorbents were not only sufficient but also fully utilized. In this experiment, the amount of G@PS-DVB for extracting disperse dyes was estimated in the range of 5–30 mg. As shown in Fig. 2-a, the extraction efficiency of the ten dyes increases as the amount of G@PS-DVB increases from 5 mg to 20 mg. When the amount of the sorbents further increases from 20 mg to 30 mg, there is no substantial increase in the extraction efficiency. Therefore, 20 mg of G@PS-DVB was adopted as the optimized sorbent dosage in the following experiments.

3.2.2. Optimization of extraction time

An appropriate extraction time could be confirmed owing to the equilibrium of the two phases. The effect of extraction time on the extraction efficiency for target dyes was investigated over the range of 5–20 min. As shown in Fig. 2-b, the extraction efficiency increases with the extraction time increasing from 5 to 15 min and then keeps almost constant with further prolongation of extraction time to 20 min. Based on such observation, an extraction time of 15 min was adopted for subsequent experiments.

3.2.3. Selection of desorption solvent

The selection of desorption solvent is of vital importance for d-SPE since it determines the elution ability towards the 10 allergenic disperse dyes. The target dyes may not be easily desorbed if the improper solvent is used. Four solvents (methanol, acetonitrile, ethanol and isopropanol) with varying polarity were selected in this study to break the interactions between the dyes and G@PS-DVB microspheres. Desorption performance of different solvents is compared in Fig. 2-c. As shown in Fig. 2-c, quite different behaviors are observed for the release of dyes from G@PS-DVB microspheres using four different solvents. Among the alcoholic solvents (methanol, ethanol and isopropanol), methanol possesses the best desorption capacity. This is probably because the polarity and hydrogen bonding of methanol are stronger than ethanol or isopropanol. The result also indicates that the desorption yield with methanol is higher than those obtained with acetonitrile. Although acetonitrile has a similar polarity with methanol, it has no capability of hydrogen bond. Comparing with acetonitrile, methanol solvent with hydrogen bond donor character can compete with the sorbent to interact with the dyes by hydrogen bonding, and the hydrogen bonding force enhances the eluting selectivity and desorption yield. Hence, methanol is selected as the optimum desorption solvent for further experiments. In order to confirm the minimum desorption

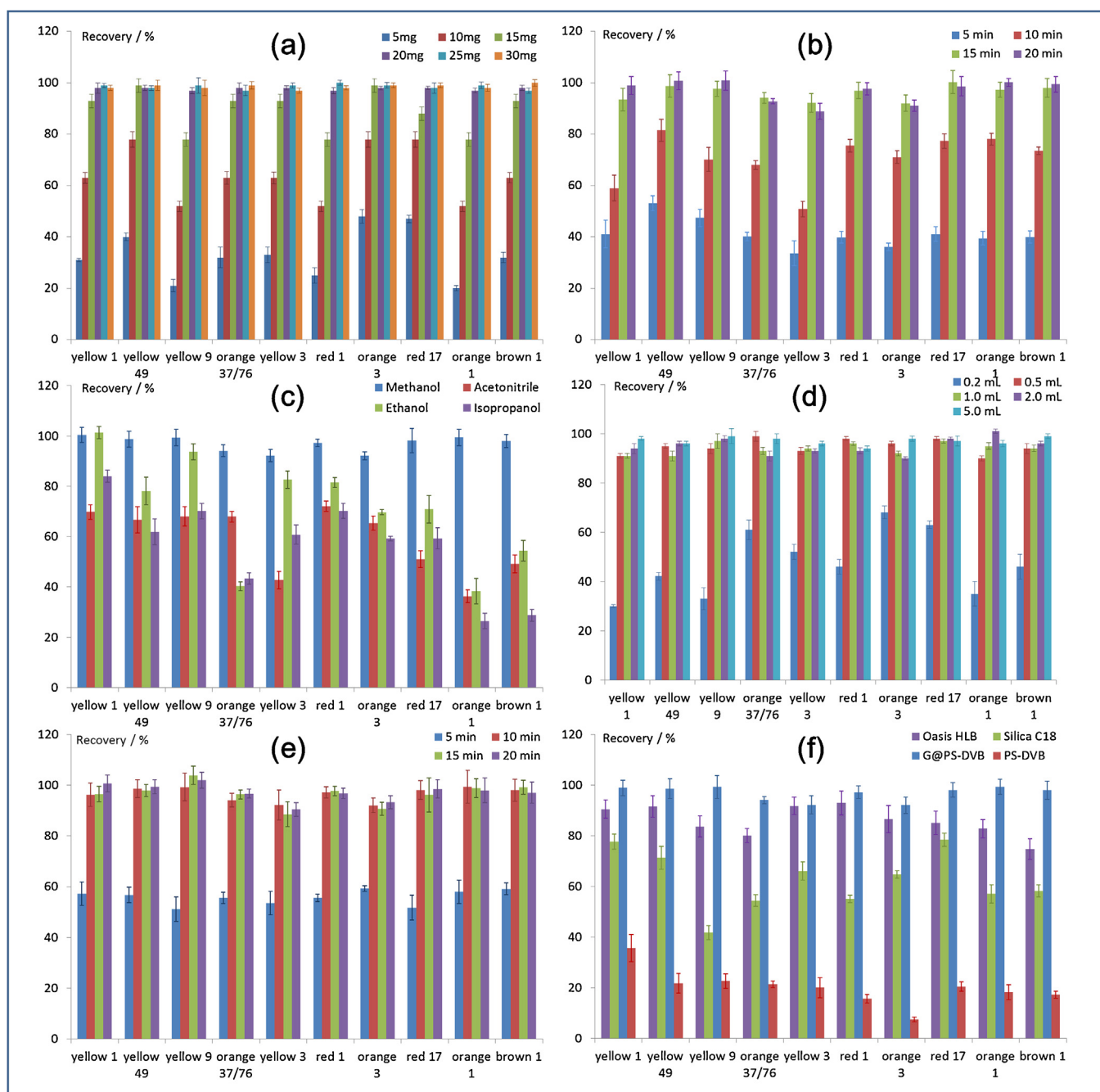


Fig. 2. Optimization of d-SPE conditions. (a) The amount of G@PS-DVB sorbent (5–30 mg); (b) The effect of extraction time (5–20 min); (c) The selection of desorption solvent (methanol, acetonitrile, ethanol and isopropanol); (d) The selection of desorption volume (0.2–5.0 mL); (e) The effect of desorption time (5–20 min); (f) The comparison of G@PS-DVB with PS-DVB, Silica C18 and Oasis HLB sorbents. Error bars represent the standard deviations obtained from three independent experiments. The experiments were conducted by using 10 mL real samples spiked with 0.5 $\mu\text{g/mL}$ allergenic disperse dyes standards.

volume, the effect of methanol volume on recovery was studied. The results in Fig. 2-d indicate that acceptable recoveries of all dyes are obtained when the volume of methanol is equal or higher than 0.5 mL. A smaller desorption volume can yield a more concentrated sample solution. Therefore, a minimal volume of 0.5 mL was selected to guarantee the complete desorption of all dyes and the enrichment factor was calculated to be 20.

3.2.4. Optimization of desorption time

The effect of desorption time was examined in the range of 5–20 min. Fig. 2-e demonstrates that the desorption efficiency increases rapidly within 10 min. Then it keeps steady with the des-

orption time further increasing from 10 to 20 min. Thus, 10 min was selected as the optimum desorption time in this work.

3.2.5. Comparison of G@PS-DVB with other sorbents

In order to evaluate the performance of the synthesized G@PS-DVB sorbent toward the allergenic disperse dyes, it was compared with unmodified PS-DVB and two commonly commercial sorbents called Silica C18 and Oasis HLB. The detailed optimum operating conditions for different sorbents were complemented in Table S3, respectively. Generally, two factors were taken into account to reflect the effectiveness of the sorbents: (1) extraction efficiency, which was evaluated by the recoveries of the spiked samples; (2)

matrix effect, which was reflected by interference peaks (signal-to-noise ratio) in the chromatogram. The extraction efficiency of these sorbents in d-SPE process was evaluated by determining the recoveries of samples spiked with 0.5 $\mu\text{g/mL}$ each of allergenic disperse dyes. As can be seen in Fig. 2-f, G@PS-DVB sorbent exhibits the best extraction efficiency among the four sorbents. The large delocalized π -electron system on the surface of G@PS-DVB has a strong affinity for the target dyes by π -stacking interaction with the benzene rings. The responses of the analytes using G@PS-DVB sorbent are approximately 1.2–2.4 times as high as those using Silica C18 sorbent. This can be explained by the fact that the specific surface area of Silica C18 is much smaller than that of G@PS-DVB. The performance of PS-DVB sorbent is even poorer than that of Silica C18, which is probably due to its strong hydrophobicity. As a hydrophobic polymer, PS-DVB hardly disperses in aqueous solutions so that the factual contact area is decreased significantly. As an efficient commercial sorbent, the behavior of Oasis HLB is comparable with that of G@PS-DVB. The matrix effect of different sorbents in d-SPE process was evaluated from the chromatograms of blank wastewater sample. As depicted in Fig. S6, G@PS-DVB as well as Oasis HLB provide a good sample cleanup as the signal-to-noise ratio is quite low and no peak is obtained at the retention times of the ten disperse dyes. The results verify the elimination of false-positive signals caused by the sample matrix. However, peaks of matrix substances are noticed using Silica C18 sorbent or PS-DVB sorbent, which demonstrates that the extraction selectivity of Silica C18 and P-DVB is worse than G@PS-DVB. Based on these comparisons with other available sorbents, G@PS-DVB microspheres are confirmed to be an effective sorbent for the target compounds under the optimized experimental conditions.

The excellent performance of G@PS-DVB for extracting the ten allergenic disperse dyes has several possible explanations. Obviously, the extraction capacity is mainly attributed to the large delocalized conjugated π -electron system of graphene, which results in π - π stacking interaction with conjugated π bonds of the benzene ring in dyes molecules. Moreover, the sufficient surface area of G@PS-DVB offers abundant binding sites to interact with the polar dyes via non-covalent forces, such as Van der Waals Force and electrostatic interactions. π - π stacking is a kind of non-covalent bond, so when methanol eluted, the bonding force was weakened or broken. As a result, the analytes were desorbed from the G@PS-DVB sorbents.

3.2.6. Regeneration and reproducibility of G@PS-DVB

The regeneration of the G@PS-DVB microspheres was examined. The reusability test was evaluated by performing 20 consecutive extractions on the same G@PS-DVB sorbent. After each run of d-SPE process, the G@PS-DVB microspheres were sequentially regenerated by ultrasonic in methanol in order to get rid of any possible cross-contamination. The effectiveness of regenerated G@PS-DVB was studied with real samples spiked with allergenic disperse dyes at a concentration level of 1.0 $\mu\text{g/mL}$. Fig. S7 presents the chromatograms of the extracted allergenic disperse dyes by using 20 batches of the same G@PS-DVB sorbent. As shown in Fig. S7, no observable carry-over is detected and the performance of the sorbents shows no significant difference within 20 times of extractions. Larger recyclable times have not been explored since the lifespan to a great extent depends on the complexity of the real samples. According to the experimental results, the G@PS-DVB sorbents can be reused for about 20 times in the d-SPE procedure of allergenic disperse dyes in water samples without sacrifice of the extraction capability, illustrating that the G@PS-DVB sorbents has good repeatability and reproducibility in d-SPE preparation procedure.

3.3. Optimization of SFC conditions

In order to well separate the 10 disperse dyes, SFC conditions were optimized. Firstly, a column screening experiment was carried out with four stationary phases. Then the effects of modifier, flow rate, column temperature and backpressure on the separation efficiency were investigated, respectively. The wavelength of the UV detector was maintained at 440 nm.

3.3.1. Column screening

In SFC, a proper chromatographic column is crucial for acceptable separation of the target analytes. Column screening has a predominant influence on the peak shape, separation efficiency and resolution. In this study, four columns: (1) Ultimate XB-C18 (5 μm , 4.6 mm $\times$ 250 mm), (2) WondaCract ODS-2 (5 μm , 4.6 mm $\times$ 250 mm), (3) Zorbax RX-C8 (5 μm , 4.6 mm $\times$ 250 mm) and (4) Ultimate Cellu-D (5 μm , 4.6 mm $\times$ 250 mm) were tested. Column screening of the four stationary phases was conducted under the beneficial chromatographic conditions as described in Fig. 3. As depicted in Fig. 3, the WondaCract ODS-2 column gives the best result where the compounds are successfully separated in 11 min though peaks labeled 6/7 are not fully resolved ($R_s = 1.366$, see Table S4). Ultimate XB-C18 fails to well separate the dyes although the retention times of the compounds are dramatically lessened. Among the three reversed-phase columns, Zorbax RX-C8 behaves worst as the targets can't be separated. Worse still, peak broadening with poor peak symmetry is noticeable when the experiment is carried out on RX-C8. As for the normal-phase column Ultimate Cellu-D, the ten dyes can't be completely separated and the separation time is much longer, which is not suitable for the analysis of dyes. In summary, the ODS-2 column is considered as the stationary phase for the analysis of the dyes in SFC.

3.3.2. Effects of modifiers

Neat supercritical CO_2 is a weak elution solvent with low polarity, thus polar modifier needs to be added in order to tune the eluent strength as well as enhance the solubility of disperse dyes in the mobile phase. Here, several organic modifiers including methanol, acetonitrile, ethanol and isopropanol were used to optimize the separation of the target dyes on ODS-2 column. Peak assignments with four modifiers are depicted in Fig. 4-a while the influence of different modifiers on the resolution is presented in Table S5. As shown in Fig. 4-a, satisfactory separation with good peak shape and rapid analysis is achieved in the case of methanol. When ethanol or isopropanol were used as modifiers, the elution order of the 10 dyes was quite similar, however, the retention times of these compounds were significantly prolonged and the 10 dyes failed to separate completely. This was probably because modifiers with hydrogen bond donor character (methanol, ethanol and isopropanol) could compete with the dyes to interact with the functional sites on ODS-2 column so that bonding force between the stationary phase and the dyes were weakened. Considering the capabilities of hydrogen bond donor, methanol was much stronger than ethanol or isopropanol, that was why ethanol and isopropanol had inferior eluent strength. When acetonitrile was added into supercritical CO_2 , the target dyes couldn't be separated and peak tailing was exhibited obviously. Considering the above results, methanol was adopted as the modifier for the following investigations.

Subsequently, the proportion of methanol ranging from 6% to 12% was examined in terms of resolution, peak shape and retention time. As shown in Fig. 5, all the dyes are separated with the addition of 6% methanol. When the percentage increases to 8%, 10% or 12%, the resolution tends to deteriorate, as a result, the peaks are unable to be sufficiently resolved (2 or more compounds are overlapped). Besides, the elution order of some dyes in the chromatograms is observed to be inversed in the range of 8%–12%. The retention inver-

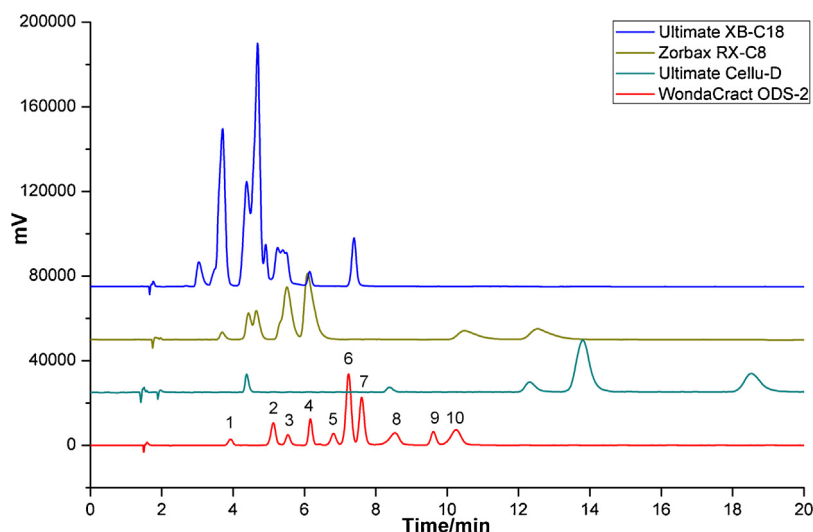


Fig. 3. Column screening among four stationary phases (Ultimate XB-C18, WondaCract ODS-2, Zorbax RX-C8 and Ultimate Cellu-D). Conditions: mobile phase, $\text{CO}_2/\text{CH}_3\text{OH}$ (93.7/6.3, v/v) for Ultimate XB-C18, WondaCract ODS-2 and Zorbax RX-C8; mobile phase, $\text{CO}_2/\text{CH}_3\text{OH}$ (80/20, v/v) for Ultimate Cellu-D; temperature, 38 °C; backpressure, 10.5 MPa; flow rate, 2.0 mL/min; UV wavelength, 440.0 nm; sample volume, 5 μL . Samples spiked with 1.0 $\mu\text{g}/\text{mL}$ of dyes standards were pretreated by d-SPE and the extracts were injected into SFC for analysis. Peaks: (1) disperse yellow 1, (2) disperse yellow 49, (3) disperse yellow 9, (4) disperse orange 37/76, (5) disperse yellow 3, (6) disperse red 1, (7) disperse orange 3, (8) disperse red 17, (9) disperse orange 1, (10) disperse brown 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

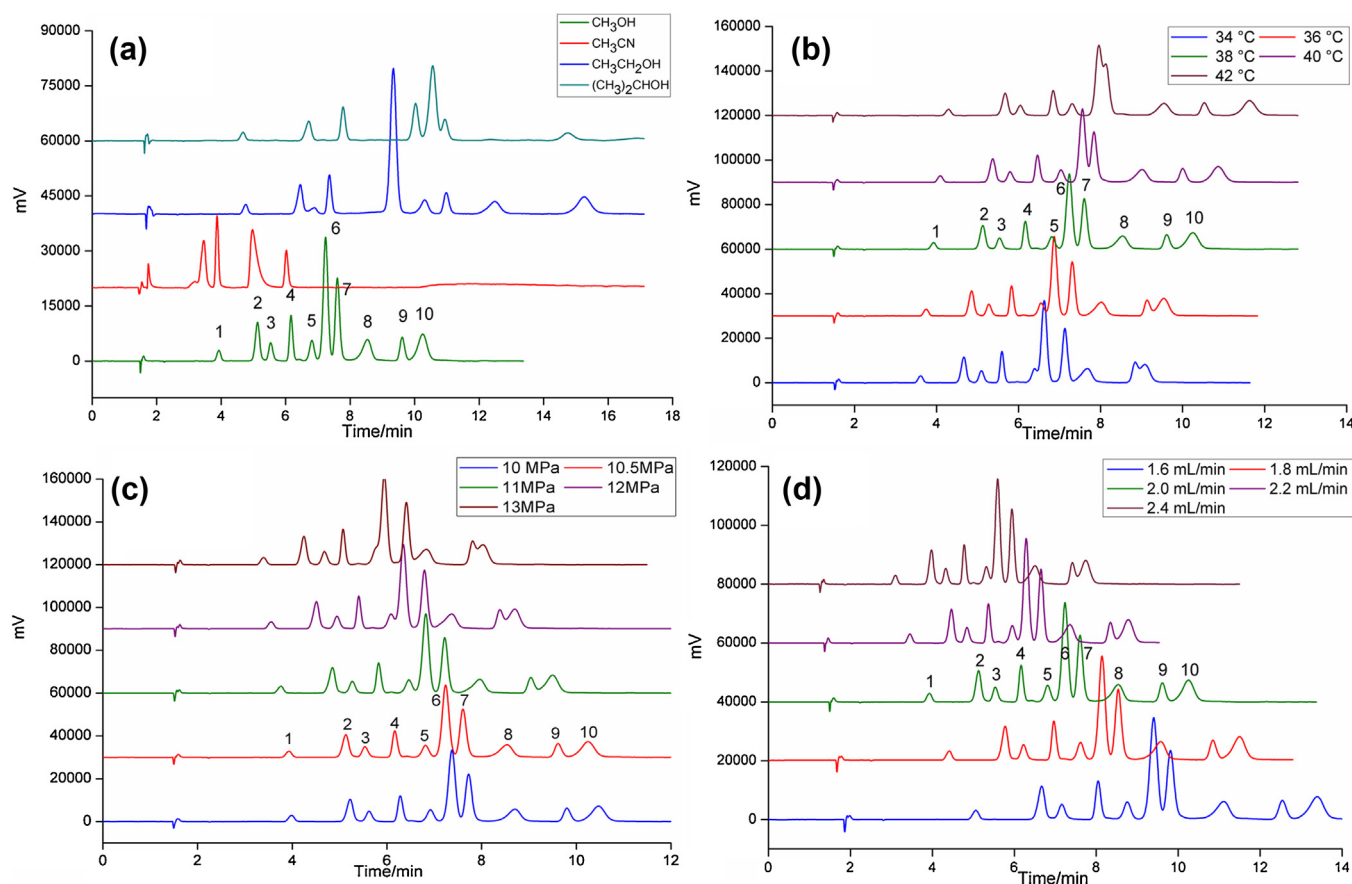


Fig. 4. (a) The effect of different modifiers on separation. (b) The effect of temperature on separation. (c) The effect of back pressure on separation. (d) The effect of flow rate on separation. Other chromatographic conditions are as described in Section 2.2. Samples spiked with 1.0 $\mu\text{g}/\text{mL}$ of dyes standards were pretreated by d-SPE and the extraction was injected into SFC for analysis. Peaks: (1) disperse yellow 1, (2) disperse yellow 49, (3) disperse yellow 9, (4) disperse orange 37/76, (5) disperse yellow 3, (6) disperse red 1, (7) disperse orange 3, (8) disperse red 17, (9) disperse orange 1, (10) disperse brown 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sions are apparent between disperse orange 37/76 (peak 4) and disperse yellow 3 (peak 5), disperse orange 3 (peak 7) and disperse

red 17 (peak 8), disperse orange 1 (peak 9) and disperse brown 1 (peak 10). In these cases, peaks 5, 8 and 10 elute early than peaks

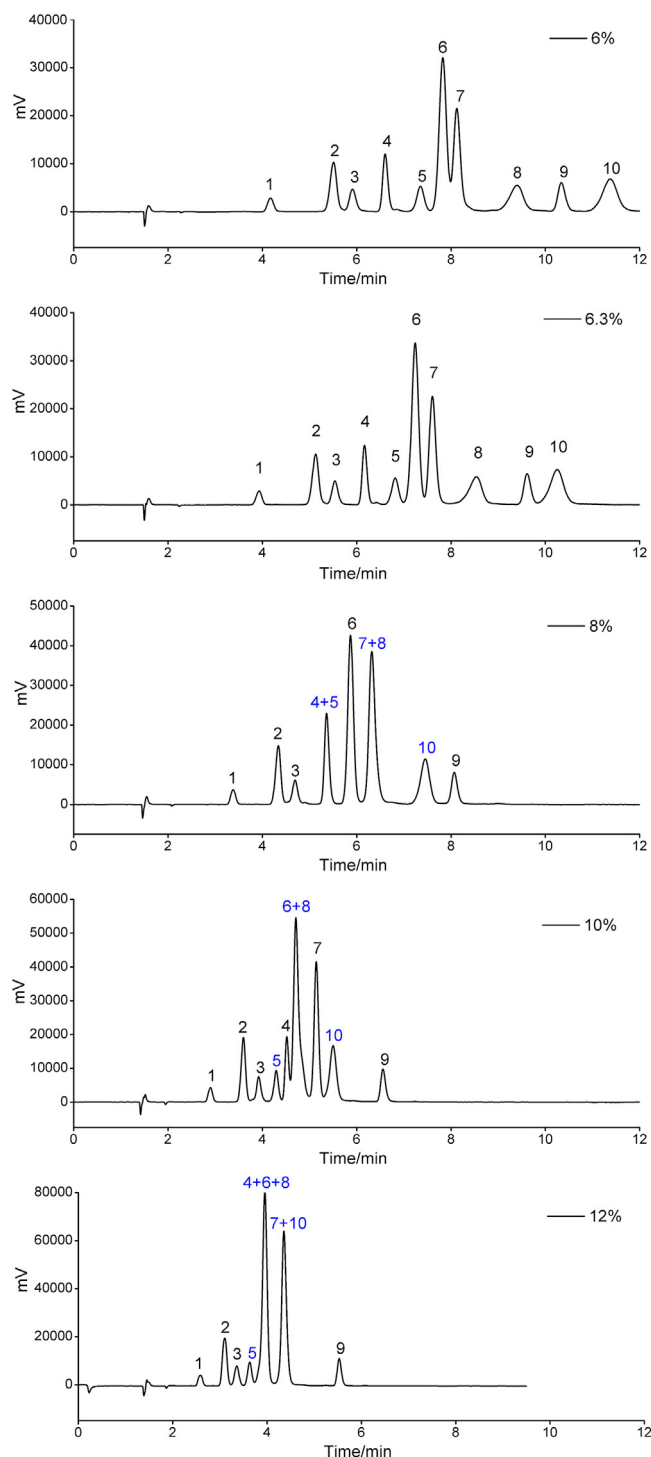


Fig. 5. Selection of the proportion of methanol in mobile phase. Other chromatographic conditions: modifier, CH₃OH; temperature, 38 °C; backpressure, 10.5 MPa; flow rate, 2.0 mL/min; UV wavelength, 440.0 nm; sample volume, 5 μ L. Samples spiked with 1.0 μ g/mL of dyes standards were pretreated by d-SPE and the extraction was injected into SFC for analysis. The labeled peaks are as follows: (1) disperse yellow 1, (2) disperse yellow 49, (3) disperse yellow 9, (4) disperse orange 37/76, (5) disperse yellow 3, (6) disperse red 1, (7) disperse orange 3, (8) disperse red 17, (9) disperse orange 1, (10) disperse brown 1.

4, 7 and 9, respectively. The variation in selectivity is probably due to the various polarities of allergenic disperse dyes and the difference is magnified at high amount of modifier in mobile phase. In order to obtain adequate separation of each compound, we further explored the resolution of the selected dyes at 6.3% percentage of

methanol. According to Table S6, under the tested conditions, the resolution between peaks 6 and 7 was improved ($R_s = 1.366$) with all the other dyes baseline separated. In conclusion, supercritical CO₂ with 6.3% methanol inside was employed as the final mobile phase for further studies.

3.3.3. Effects of temperature

In SFC, column temperature can affect the separation to a certain extent by influencing the density and viscosity of supercritical CO₂ fluid. Unlike in reversed-phase liquid chromatography, the temperature effect on separation is quite different in SFC. With the increase of column temperature, the density and viscosity of supercritical CO₂ are reduced, leading to the decrease in elution ability of the targets, resulting in greater retention. In contrast, the decrease of the column temperature increases the density and viscosity of supercritical CO₂ which would enhance elution capacity to the targets.

In this study, the column temperature was investigated at 34, 36, 38, 40 and 42 °C. As was expected, the retention times of all the dyes were prolonged when the temperature elevated. The impact of temperature on the separation of the 10 dyes is exhibited in Fig. 4-b. When the column temperature is 34 or 36 °C, peaks 5/6 and 9/10 cannot be sufficiently resolved (resolution presented in Table S7). Higher temperature (40 °C and 42 °C) improves the resolution of peaks 5/6 and 9/10 ($R_s > 1.5$), but it decreases the resolution between peaks 6 and 7. The best overall separation is obtained at 38 °C wherein all allergenic disperse dyes are well separated. Hence, considering the above-mentioned observation, a compromising temperature of 38 °C was chosen for subsequent experiments.

3.3.4. Effects of backpressure

In SFC, backpressure impacts the retention behavior by regulating the density of the mobile phase. Different backpressures ranging from 10 to 13 MPa were studied based on the separation efficiency and retention behavior of the target dyes. As shown in Fig. 4-c, when the backpressure elevated over 11 MPa, peaks 5/6 and 9/10 were not fully resolved, although the analysis time decreased. On the contrary, 10 MPa achieved acceptable separation where all the target dyes were baseline separated except peaks 6 and 7 ($R_s = 1.207$). In order to fine tune the resolution of peak 6/7, we further investigated the separation of all dyes under 10.5 MPa. According to Tables S8, 10.5 MPa improved the resolution of peaks 6/7 ($R_s = 1.366$) with all other targets exhibited baseline separation. In summary, 10.5 MPa was set as the optimal backpressure.

3.3.5. Effects of flow rate

Basically, Van Deemter equation shows the relationship between plate height and linear velocity in chromatography and is an important tool for the optimization of the flow rate. It is expressed as $H = A + B/\mu + C\mu$, where A , B , C represent eddy diffusion parameter, longitudinal diffusion coefficient and resistance to mass transfer coefficient, respectively. H is the height equivalent to a theoretical plate (HETP) and μ is the linear velocity of the mobile phase. Differentiating the Van Deemter equation with respect to velocity, we can get the first derivative of the equation " $H' = C - B/\mu^2$ ". Theoretically, when setting the resulting expression equal to zero, the HETP achieves a minimum value (H_{min}). Therefore, when $\mu = \sqrt{B/C}$, the flow velocity is theoretically calculated to be the optimum. At this flow rate, the resolving power of the column is maximized. In practice, due to the higher diffusion coefficient and lower viscosity of supercritical fluid, the C term of Van Deemter equation is much smaller in SFC than in HPLC and the linear velocity of the mobile phase reaches higher values than those encountered in HPLC. Accordingly, the flow rate of mobile phase for SFC was

Table 1Linear range, correlation coefficient, LOD and LOQ of 10 allergenic disperse dyes (seven data points, $n = 3$).

Compounds	Linear range ($\mu\text{g/mL}$)	Regression equation	Correlation coefficient (r)	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Disperse yellow 1	0.05–10.0	$Y = 8681X - 8.60$	0.9998	15.6	52.0
Disperse yellow 49	0.02–10.0	$Y = 43033X - 30.38$	0.9992	3.1	10.5
Disperse yellow 9	0.02–10.0	$Y = 15472X - 18.64$	0.9991	8.7	29.1
Disperse orange 37/76	0.02–10.0	$Y = 33370X - 22.02$	0.9992	4.0	13.5
Disperse yellow 3	0.02–10.0	$Y = 17671X - 38.59$	0.9992	7.6	25.4
Disperse red 1	0.02–10.0	$Y = 1232358X + 90.38$	0.9996	1.1	3.7
Disperse orange 3	0.02–10.0	$Y = 72874X - 30.91$	0.9992	1.9	6.2
Disperse red 17	0.02–10.0	$Y = 40764X - 18.42$	0.9989	3.3	11.0
Disperse orange 1	0.02–10.0	$Y = 23719X - 26.58$	0.9998	5.7	19.0
Disperse brown 1	0.02–10.0	$Y = 47082X + 26.84$	0.9995	2.9	9.6

evaluated in the range of 1.6–2.4 mL/min in the present study. As shown in Fig. 4–d, flow rate has a predominant impact on retention time. When the flow rate was elevated, the density of mobile phase was increased, resulting in a reduction of retention time and narrow symmetric peaks. However, as shown in Table S9, resolution of peaks 5/6 and 9/10 became less satisfying with flow rate exceeding 2 mL/min. The best overall separation occurred at 2.0 mL/min while all the dyes exhibited baseline separation except peaks 6 and 7 ($R_s = 1.366$).

3.4. Method validation

In order to validate the potential application of the proposed method for allergenic disperse dyes, the performance of the G@PS-DVB based d-SPE combined with SFC method was evaluated under the optimum conditions. In this study, external standard method was used for the determination of 10 dyes. To minimize the matrix

effects, a series of matrix matched standards solutions were prepared to establish the calibration curves. All the standard working solutions were dealt with the d-SPE process prior to SFC so that calibration errors were eliminated during quantifying the contents of dyes in complicated real samples. Favorable linearity was obtained for the target dyes over a wide concentration range of 0.02–10.0 $\mu\text{g/mL}$ with all the correlation coefficients (R) values higher than 0.9989. Spiked samples with low concentration of 10 dyes were prepared by spiking standards into blank real wastewater samples and were used to determine the limit of detection (LOD, $S/N = 3$) and limit of quantification (LOQ, $S/N = 10$) values. The LODs and LOQs values of the 10 disperse dyes were calculated to be in the range of 1.1–15.6 $\mu\text{g/L}$ and 3.7–52 $\mu\text{g/L}$, respectively. According to some reports [42–44], the investigated dyes encountered in environmental samples, e.g. waste waters, were typically at ppb to ppm levels. Hence, the sensitivity of the proposed method was adequate for the determination of disperse dyes in wastewater.

Table 2Recoveries and precision in blank wastewater samples ($n = 5$).

Compounds	Spiked level ($\mu\text{g/mL}$)	Average recovery (%)	RSD (%)	
			Intra-day	Inter-day
Disperse yellow 1	0.050	90.1	6.7	6.1
	0.100	95.8	5.9	6.7
	0.200	94.3	8.0	7.5
Disperse yellow 49	0.050	95.7	6.9	7.6
	0.100	98.6	6.4	4.1
	0.200	96.9	4.2	5.8
Disperse yellow 9	0.050	92.6	5.1	7.0
	0.100	90.8	6.4	5.2
	0.200	93.1	3.2	3.9
Disperse orange 37/76	0.050	94.3	5.2	5.4
	0.100	98.0	4.3	6.4
	0.200	97.8	5.7	4.3
Disperse yellow 3	0.050	89.1	5.1	7.2
	0.100	90.3	9.3	10.5
	0.200	93.5	7.2	6.5
Disperse red 1	0.050	96.7	4.6	5.9
	0.100	98.2	7.2	7.7
	0.200	97.8	5.3	4.5
Disperse orange 3	0.050	94.5	8.4	10.2
	0.100	96.8	7.9	7.2
	0.200	98.5	4.1	4.6
Disperse red 17	0.050	97.6	5.3	6.6
	0.100	99.7	8.2	8.6
	0.200	98.1	4.4	4.1
Disperse orange 1	0.050	95.2	5.4	6.2
	0.100	91.5	6.7	6.5
	0.200	94.6	5.0	4.3
Disperse brown 1	0.050	95.5	5.4	6.7
	0.100	98.3	5.3	6.0
	0.200	97.9	6.8	9.5

Table 3
Results of allergenic dyes in real samples by the proposed G@PS-DVB based d-SPE-SFC method (n = 3).

Samples	Allergenous disperse dyes content (µg/mL)									
	disperse yellow 1	disperse yellow 49	disperse yellow 9	disperse orange 37/76	disperse yellow 3	disperse red 1	disperse orange 3	disperse red 17	disperse orange 1	disperse brown 1
Sample 1	0.090	ND	ND	ND	ND	0.034	0.017	0.063	ND	ND
Sample 2	ND	0.023	ND	ND	ND	0.012	ND	ND	ND	ND
Sample 3	ND	0.093	ND	0.053	ND	0.026	ND	ND	ND	ND
Sample 4	0.306	0.428	ND	ND	ND	ND	ND	ND	ND	0.109
Sample 5	ND									
Sample 6	ND									
Sample 7	ND									
Sample 8	ND									

ND, not detected (<LOQ).

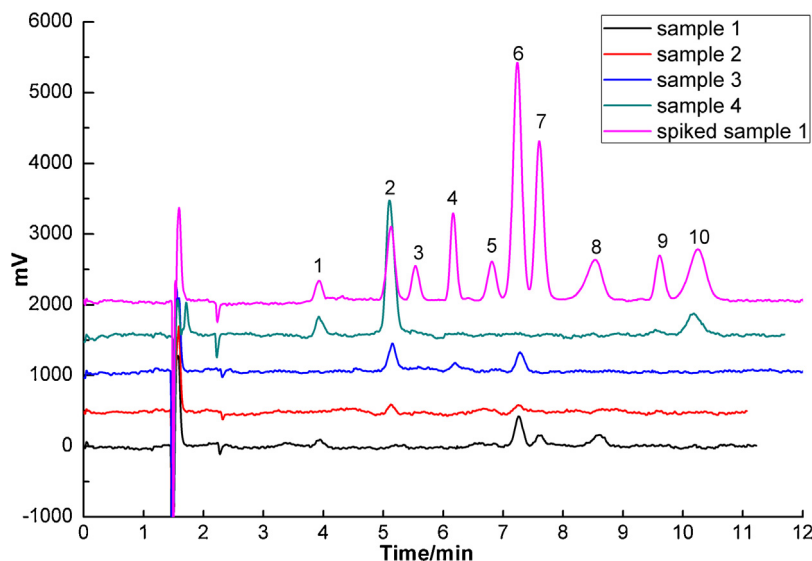


Fig. 6. Chromatograms of four real wastewater samples and spiked sample 1 (spiked with 0.2 µg/mL of each dyes) analyzed by d-SPE-SFC methodology. All the samples were pretreated with d-SPE process under optimum conditions and the chromatographic conditions were the same as those described in Section 2.2. Peaks: (1) disperse yellow 1, (2) disperse yellow 49, (3) disperse yellow 9, (4) disperse orange 37/76, (5) disperse yellow 3, (6) disperse red 1, (7) disperse orange 3, (8) disperse red 17, (9) disperse orange 1, (10) disperse brown 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ater samples. All the results including linear ranges, LODs, LOQs and calibration curves are summarized in Table 1. Subsequently, to evaluate the precision and the accuracy of the present method, the relative standard deviation (RSD) and recovery were investigated by spiking blank wastewater samples with the low (0.05 µg/mL), moderate (0.10 µg/mL), and high (0.20 µg/mL) levels of mixed dyes standards. The spiked samples were routinely pretreated by G@PS-DVB based d-SPE process and analyzed with SFC method. Since the target disperse dyes were unstable when dissolved in solutions, both intra-day and inter-day precision tests were conducted. The intra-day and the inter-day RSD of the 10 dyes were less than 6.3% and 8.7%, respectively. The mean recoveries of the disperse dyes in spiked samples varied from 89.1% to 99.7%. The intra-day and inter-day RSDs and recoveries of different spiking levels are listed in Table 2, which implies acceptable reproducibility, precision and high accuracy of this method for analyzing dyes in industrial wastewaters.

Furthermore, the performance of the proposed G@PS-DVB based d-SPE-SFC method for dyes analysis was compared with some reported works in the literature. The results in terms of LODs, recoveries and linearity are summarized in Table S10. As illustrated in Table S10, the proposed d-SPE SFC method is appropriate for the analysis of dyes in real samples. However, the values obtained in Table S10 indicate that the LOD of the present method is not comparable to some of the reported works with mass spectrometry (MS) detection. This is because the sensitivity of UV detection used in

the present study is much lower than MS detection. The sensitivity of this methodology can be further improved by coupling SFC with MS detection in our future work. Apart from the sensitivity, several advantages of the proposed method are evidenced in Table S10. Compared with reported methods, d-SPE-SFC methodology owns a significant saving of time and also provides an efficient procedure for reducing the costs and work involved in the control of allergenic dyes in real samples. Moreover, the current method is more environmentally friendly with less consumption of toxic reagents, whereas the literature methods always require lots of organic solvents. In conclusion, it is clear that the current SFC method with G@PS-DVB d-SPE preparation process is a simple, rapid, eco-benign and robust technique, which has advantages in the analysis of disperse dyes in wastewater samples.

3.5. Applications to real samples

The proposed methodology was applied to the determination of allergenic disperse dyes in industrial wastewater and environmental water samples. These samples were all collected from different textile industries where the contamination of allergenic disperse dyes might probably be found. The real samples were extracted by G@PS-DVB based d-SPE preparation prior to SFC analysis. The detailed results are summarized in Table 3. For the samples tested, the allergenic disperse dyes were presented in four of the eight samples with the contents ranging from 0.012 to 0.428 µg/mL while

other samples were found to be free of allergenic disperse dyes contamination (<LOQ). The obtained results indicated that such dyes were released into effluents in some cases. Representative chromatograms of the examined samples are given in Fig. 6.

4. Conclusions

In this study, a simple, green, rapid and robust method was developed for the separation and determination of 10 allergenic disperse dyes in wastewater samples utilizing SFC coupled with G@PS-DVB based d-SPE preparation. G@PS-DVB microspheres were successfully synthesized in laboratory and used as a novel sorbent in d-SPE procedure. G@PS-DVB possessed several merits such as high adsorption capacity, good reproducibility, less consumption of sorbent and organic solvent, simple handling as well as long lifespan (about 20 extractions), which made it a potential sorbent for the isolation and enrichment of the 10 dyes from complicated samples. Under the optimal conditions, G@PS-DVB based d-SPE procedure exhibited high extraction efficiency for the studied dyes. For the optimization of SFC conditions, variety of parameters including modifier composition, flow rate, column temperature and backpressure have been studied. Under optimal conditions (flow rate, 2.0 mL/min; temperature, 38 °C; BPR, 10.5 MPa), the target dyes were well separated by WondaCract ODS-2 column (5 µm, 4.6 mm × 250 mm) within 11 min under an isocratic elution of methanol and CO₂ (6.3/93.7, v/v). Moreover, the proposed SFC method is a much more environmentally friendly method since the consumption of organic solvent is reduced dramatically. The performance of the proposed method (linearity, LODs, recoveries and RSDs) was evaluated. The results obtained demonstrated that G@PS-DVB based d-SPE-SFC method was an efficient alternative and a complementary method for the routine analysis of disperse dyes in real samples and might have a prospective application in other areas, such as biological samples, food samples and other environmental samples.

Acknowledgments

This research was financially supported by Key Laboratory of Health Risk Appraisal for Trace Toxic Chemicals of Zhejiang Province (Nos. 2014006, 2014007), Zhejiang Provincial Natural Science Foundation of China (Nos. LZ16B050001, LY15B050001 and LY15B010005) and National Science Foundation of China (Nos. 21405141).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.chroma.2018.03.040>.

References

- [1] J. Garcia-Lavandeira, E. Blanco, C. Salgado, R. Cela, Fast throughput, highly sensitive determination of allergenic disperse dyes in textile products by use of sample composition, *Talanta* 82 (2010) 261–269.
- [2] J. Mathieu-Denoncourt, C.J. Martyniuk, S.R. de Solla, V.K. Balakrishnan, V.S. Langlois, Sediment contaminated with the azo dye disperse yellow 7 alters cellular stress- and androgen-related transcription in silurana tropicalis larvae, *Environ. Sci. Technol.* 48 (2014) 2952–2961.
- [3] J.H. Choi, A.D. Towns, Acetate dyes revisited: high fastness dyeing of cellulose diacetate and polyester-polyurethane, *Color. Technol.* 117 (2001) 127–133.
- [4] E.J. Weber, R.L. Adams, Chemical-mediated and sediment-mediated reduction of the azo-dye disperse blue 79, *Environ. Sci. Technol.* 29 (1995) 1163–1170.
- [5] D. Brown, H.R. Hitz, L. Schafer, The assessment of the possible inhibitory effect of dyestuffs on aerobic waste-water bacteria experience with a screening test, *Chemosphere* 10 (1981) 245–261.
- [6] K. Singh, S. Arora, Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies, *Crit. Rev. Environ. Sci. Technol.* 41 (2011) 807–878.
- [7] L. Malinauskienė, E. Zimerson, M. Bruze, K. Ryberg, M. Isaksson, Are allergenic disperse dyes used for dyeing textiles, *Contact Dermatitis* 67 (2012) 141–148.
- [8] G. Coman, N. Blickenstaff, A. Edwards, H. Maibach, Dermatotoxicologic clinical solutions: textile dye dermatitis patch testing, *Cutan. Ocul. Toxicol.* 34 (2015) 68–71.
- [9] C. Hansson, S. Ahlfors, O. Bergendorff, Concomitant contact dermatitis due to textile dyes and to colour film developers can be explained by the formation of the same hapten, *Contact Dermatitis* 37 (1997) 27–31.
- [10] K.L. Hatch, P.S. Magee, A discriminant model for allergic contact dermatitis in anthraquinone disperse dyes, *Quant. Struct. Act. Relat.* 17 (1998) 20–26.
- [11] K.L. Hatch, H.I. Maibach, Textile dye dermatitis, *J. Am. Acad. Dermatol.* 32 (1995) 631–639.
- [12] Y. Zhou, Z. Du, Y. Zhang, Simultaneous determination of 17 disperse dyes in textile by ultra-high performance supercritical fluid chromatography combined with tandem mass spectrometry, *Talanta* 127 (2014) 108–115.
- [13] V. Suryavathi, S. Sharma, S. Sharma, P. Saxena, P. Pandey, R. Grover, S. Kumar, K.P. Sharma, Acute toxicity of textile dye wastewaters (untreated and treated) of Sangar on male reproductive systems of albino rats and mice, *Reprod. Toxicol.* 19 (2005) 547–556.
- [14] R. Stahlmann, M. Wegner, K. Riecke, M. Kruse, T. Platzek, Sensitising potential of four textile dyes and some of their metabolites in a modified local lymph node assay, *Toxicology* 219 (2006) 113–123.
- [15] Hohenstein Institutes, Oeko-Tex Standard 100, Melliand, China, 2017, pp. 37.
- [16] DIN 54231-Textiles-Detection of Disperse Dyestuffs, Deutsches Institut Fur Normung E. V. (German National Standard), 2005 (01 November, 11 pp.).
- [17] G.A.R. Oliveira, E.R.A. Ferraz, F.M.D. Chequer, M.D. Grando, J.P.F. Angeli, M.S. Tsuboy, J.C. Marcarini, M.S. Mantovani, M.E. Osugi, T.M. Lizier, M.V.B. Zanoni, D.P. Oliveira, Chlorination treatment of aqueous samples reduces but does not eliminate, the mutagenic effect of the azo dyes Disperse Red 1, Disperse Red 13 and Disperse Orange 1, *Mutat. Res.* 703 (2010) 200–208.
- [18] D.P. Oliveira, P.A. Carneiro, M.K. Sakagami, M.V.B. Zanoni, G.A. Umbuzeiro, Chemical characterization of a dye processing plant effluent-Identification of the mutagenic components, *Mutat. Res.* 626 (2007) 135–142.
- [19] P.A. Carneiro, G.A. Umbuzeiro, D.P. Oliveira, M.V.B. Zanoni, Assessment of water contamination caused by a mutagenic textile effluent bearing disperse dyes, *J. Hazard. Mater.* 174 (2010) 694–699.
- [20] Y.G. Zhao, X.P. Li, S.S. Yao, P.P. Zhan, J.C. Liu, C.P. Xu, Y.Y. Lu, X.H. Chen, M.C. Jin, Fast throughput determination of 21 allergenic disperse dyes from river water using reusable three-dimensional interconnected magnetic chemically modified graphene oxide followed by liquid chromatography-tandem quadrupole mass spectrometry, *J. Chromatogr. A* 1431 (2016) 36–46.
- [21] L. Zhou, L. Shi, J. Liu, F. Lv, Y. Xu, Determination of nine sensitizing disperse dyes in activated sludge by ultrasound-assisted liquid-liquid extraction-ultra-performance liquid chromatography-electrospray ionization-tandem mass spectrometry, *Anal. Bioanal. Chem.* 408 (2016) 487–494.
- [22] Y. Zhang, W.E. Zhou, S.H. Li, Z.Q. Ren, W.Q. Li, Y. Zhou, X.S. Feng, W.J. Wu, F. Zhang, A simple, accurate, time-saving and green method for the determination of 15 sulfonamides and metabolites in serum samples by ultra-high performance supercritical fluid chromatography, *J. Chromatogr. A* 1432 (2016) 132–139.
- [23] L. Novakova, V. Desfontaine, F. Ponzetto, R. Nicoli, M. Saugy, J.L. Veuthey, D. Guilleme, Fast and sensitive supercritical fluid chromatography-tandem mass spectrometry multi-class screening method for the determination of doping agents in urine, *Anal. Chim. Acta* 915 (2016) 102–110.
- [24] S. Qu, Z. Du, Y. Zhang, Direct detection of free fatty acids in edible oils using supercritical fluid chromatography coupled with mass spectrometry, *Food Chem.* 170 (2015) 463–469.
- [25] F. Jumaah, S. Larsson, S. Essen, L.P. Cunico, C. Holm, C. Turner, M. Sandahl, A rapid method for the separation of vitamin D and its metabolites by ultra-high performance supercritical fluid chromatography-mass spectrometry, *J. Chromatogr. A* 1440 (2016) 191–200.
- [26] A.R. Fontana, R. Bottini, Filter-vial dispersive solid-phase extraction as a simplified clean-up for determination of ethylphenols in red wines, *Food Chem.* 230 (2017) 405–410.
- [27] S.M. Yousefi, F. Shemirani, S.A. Ghorbani, Deep eutectic solvent magnetic bucky gels in developing dispersive solid phase extraction: application for ultra trace analysis of organochlorine pesticides by GC-micro ECD using a large-volume injection technique, *Talanta* 168 (2017) 73–81.
- [28] Y. Pashaei, F. Ghorbani-Bidkorbeh, M. Shekarchi, Shekarchi, Superparamagnetic graphene oxide-based dispersive-solid phase extraction for preconcentration and determination of tamsulosin hydrochloride in human plasma by high performance liquid chromatography-ultraviolet detection, *J. Chromatogr. A* 1499 (2017) 21–29.
- [29] O. Filippou, E.A. Deliyanni, V.F. Samanidou, Fabrication and evaluation of magnetic activated carbon as adsorbent for ultrasonic assisted magnetic solid phase dispersive extraction of bisphenol A from milk prior to high performance liquid chromatographic analysis with ultraviolet detection, *J. Chromatogr. A* 1479 (2017) 20–31.
- [30] T.P. Fellingner, A. Thomas, J. Yuan, M. Antonietti, 25th Anniversary article: cooking carbon with salt: carbon materials and carbonaceous frameworks from ionic liquids and poly (ionic liquid)s, *Adv. Mater.* 25 (2013) 5838–5855.

- [31] B. Socas-Rodriguez, A.V. Herrera-Herrera, M. Asensio-Ramos, J. Hernandez-Borges, Recent applications of carbon nanotube sorbents in analytical chemistry, *J. Chromatogr. A* 1357 (2014) 110–146.
- [32] X. Liang, S. Liu, S. Wang, Y. Guo, S. Jiang, Carbon-based sorbents: carbon nanotubes, *J. Chromatogr. A* 1357 (2014) 53–67.
- [33] A.K. Geim, Graphene: status and prospects, *Science* 324 (2009) 1530–1534.
- [34] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of graphene oxide, *Chem. Soc. Rev.* 39 (2010) 228–240.
- [35] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and graphene oxide: synthesis, properties and applications, *Adv. Mater.* 22 (2010) 3906–3924.
- [36] R. Sitko, B. Zawisza, E. Malicka, Graphene as a new sorbent in analytical chemistry, *TrAC Trends Anal. Chem.* 51 (2013) 33–43.
- [37] X. Luo, F. Zhang, S. Ji, B. Yang, X. Liang, Graphene nanoplatelets as a highly efficient solid-phase extraction sorbent for determination of phthalate esters in aqueous solution, *Talanta* 120 (2014) 71–75.
- [38] Y. Zhong, W. Zhou, H. Zhu, X. Zeng, M. Ye, P. Zhang, Y. Zhu, A single pump column-switching technique coupled with polystyrene-divinylbenzene-carbon nanotubes column for the determination of trace anions in different concentrated organic matrices by ion chromatography, *Anal. Chim. Acta* 686 (2011) 1–8.
- [39] Z. Huang, Z. Zhu, Q. Subhani, W. Yan, W. Guo, Y. Zhu, Simultaneous determination of iodide and iodate in povidone iodine solution by ion chromatography with homemade and exchange capacity controllable columns and column-switching technique, *J. Chromatogr. A* 1251 (2012) 154–159.
- [40] K. Zhang, M. Cao, C. Lou, S. Wu, P. Zhang, M. Zhi, Y. Zhu, Graphene-coated polymeric anion exchangers for ion chromatography, *Anal. Chim. Acta* 970 (2017) 73–81.
- [41] D. Li, M.B. Muller, S. Gilje, R.B. Kaner, G.G. Wallace, Processable aqueous dispersions of graphene nanosheets, *Nat. Nanotechnol.* 3 (2008) 101–105.
- [42] P.P. Zhang, Y. Zhang, J.C. Liu, Y. Zhu, Y.G. Zhao, Directly-coupled-column ultra-fast liquid chromatography with diode array detection method for the rapid quantification of allergenic disperse dyes in water preconcentrated by magnetic solid-phase extraction, *J. Sep. Sci.* 40 (2017) 4294–4302.
- [43] S. Sahin, C. Demir, S. Gucer, Simultaneous UV-vis spectrophotometric determination of disperse dyes in textile wastewater by partial least squares and principal component regression, *Dyes Pigm.* 73 (2007) 368–376.
- [44] D.P. Santos, M.A.G. Trindade, R.A.G. Oliveira, M.E. Osugi, A.R. Bianchi, M.V.B. Zaroni, Electrochemical method for quantitative determination of trace amounts of disperse dye in wastewater, *Color. Technol.* 130 (2013) 43–47.