



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[☆]



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ABSTRACT

We report the template-free fabrication of three-dimensional hierarchical nanostructures, *i.e.*, three-dimensional interconnected magnetic chemically modified graphene oxide (3D-Mag-CMGO), through a simple and low-cost self-assembly process using one-pot reaction based on solvothermal method. The excellent properties of the 3D-Mag-CMGO are characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), FTIR, elementary analyzer (EA) and X-ray photoelectron spectroscopy (XPS). The easiness-to-handle of the magnetic dispersive solid phase extraction (Mag-dSPE) procedure is developed for preconcentration of 21 allergenic disperse dyes from river water. The obtained results show the higher extraction capacity of 3D-Mag-CMGO with recoveries between 80.0–112.0%. Furthermore, an ultra-fast liquid chromatography–tandem quadrupole mass spectrometry (UFLC–MS/MS) method for determination of 21 allergenic disperse dyes in river at sub-ppt levels has been developed with pretreatment of the samples by Mag-dSPE. The limits of quantification (LOQs) for the allergenic disperse dyes are between 0.57–34.05 ng/L. Validation results on linearity, specificity, trueness and precision, as well as on application to the analysis of 21 allergenic disperse dyes in fifty real samples demonstrate the applicability to environment monitoring analysis.

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1. Introduction

Disperse dyes (azo, anthraquinone) are the most commonly used type of dyes in the textile, leather, printing ink, and cosmetic industries, accounting for 60–70% of all organic dye production worldwide [1–3]. Some reports indicate that approximately 12% of the synthetic textile dyes used every year are lost to waste stream during processing and manufacturing operations, and 20%

of the losses will enter the environment through effluents from wastewater treatment plants [4]. Regrettably, according to Hatch and Maibach [5], 49 dyes have been identified as contact allergens and two thirds of these are disperse dyes. Their presence in effluent and industrial wastewater is of considerable interest because of the potential for contamination of groundwater and drinking water supplies by compounds that may produce health risks [6]. Especially, in Ningbo, the textile, leather and printing ink industry developments are booming. And the three main rivers in Ningbo, *i.e.*, Yaojiang River, Yongjiang River, and Fenghua River, are source water of drinking water supply. In order to prevent the rivers from being polluted by allergenic disperse dyes from wastewater treatment plants, a simple, rapid and efficient methods for the determination of allergenic disperse dyes residue in river samples

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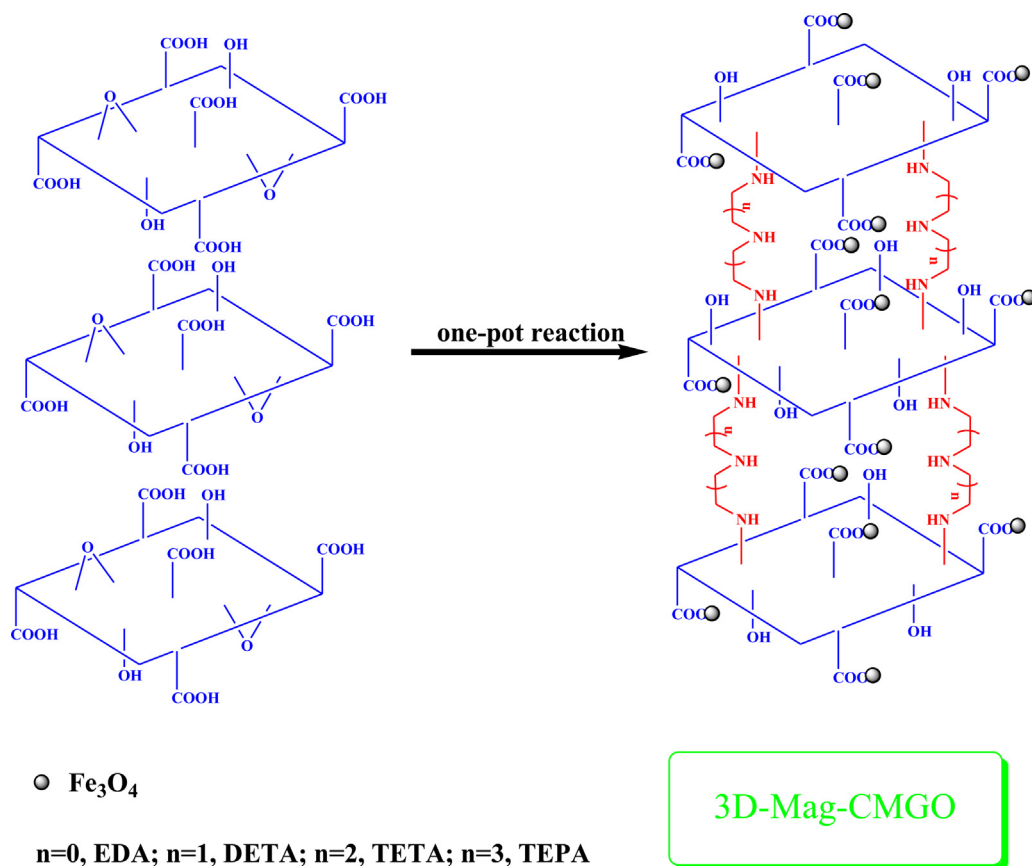


Fig. 1. Schematic procedure of 3D-Mag-CMGO.

at sub-ppt levels must be developed for environment monitoring analysis.

Complete overviews on the development of the analysis of allergenic disperse dyes in various matrices can be found in the literature. And some papers have been published about the determination of disperse dye residues in wastewaters [7,8], food and toys [9,10], and in the context of forensic studies [11]. Generally, in these methods, solid-phase extraction (SPE) or Liquid-Liquid extraction (LLE) procedure are used for sample preparation. Although SPE is more flexible and efficient than LLE in terms of simplicity, flexibility and low consumption of the organic solvents, extraction time is very long because of the limited interface between the sorbent and the aqueous sample. Thus, a clear trend in analytical chemistry is reduction of extraction time [12,13]. In order to overcome the problem, a simple, fast, and inexpensive common technique of dispersive-solid phase extraction (d-SPE) was introduced [14]. Farahani and Shemirani applied magnetic ferrofluid for extraction one cationic dye at trace levels in aqueous [14]. Although the separation of sorbent from the aqueous bulk was achieved quickly by a magnet within few seconds, low adsorption capacity limited its application for further use in multi-component analysis. Nowadays, simultaneous determination of multi-component organic pollutants is becoming main development trend to analytical chemists due to more and more organic pollutants discharged into the environment. Therefore, to explore efficient magnetic sorbent for extraction multi-allergenic disperse dyes has become a new great challenge.

Graphene is a new type of two-dimensional carbon nanostructure with excellent properties, such as extraordinary mechanical, electrical and thermal properties [15–22]. Also, its ultrahigh specific surface areas ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$) and huge aromatic domains make graphene an excellent choice for adsorbents of aromatic

organic contaminants for wastewater treatment via van der Waals, π - π stacking interaction and other noncovalent interactions [16,23–26]. Graphene and graphene oxide (GO) were reported as effective adsorbents toward cationic and anionic dyes [27]. Especially, GO is a lamellar flexible material with a large number of functional groups such as epoxy (C–O–C), hydroxyl (OH) and carboxyl (COOH) groups on both basal planes and edges [28]. Now, chemically modified GO nanocomposite have been extensively studied because of their unique structures, excellent properties, and potential applications in environmental pollutant removal and preconcentration procedure [29–34]. Sergi et al. have synthesized a graphene oxide magnetic nanocomposite (GO/ Fe_3O_4) by an inverse chemical co-precipitation method. Although the GO/ Fe_3O_4 is an effective adsorbent for the magnetic solid-phase extraction of trace quantities of malachite green from fish and water samples, the chemically modified GO nanocomposite is two-dimensional hierarchical, especially, the magnetic Fe_3O_4 installed on the surface of GO are amorphous [34]. We inspired that a novel three-dimensional interconnected magnetic chemically modified graphene oxide (3D-Mag-CMGO) nanocomposite contained magnetic component, amide and amino groups and six-membered carbon rings would be probably become a wide-spectrum sorbent to carry out magnetic dispersive solid phase extraction (Mag-dSPE) procedure for extraction allergenic disperse dyes from water samples. According to our knowledge, no published articles are reported in the literature about the 3D-Mag-CMGO for extraction 21 allergenic disperse dyes from water samples.

In this article, 3D-Mag-CMGO nanocomposite has been synthesized by a simple and environmental friendly one-pot method. The excellent 3D-Mag-CMGO nanocomposite, which is used as sorbent in Mag-dSPE procedure, has been applied for the extraction of 21 allergenic disperse dyes from environmental water. Parameters

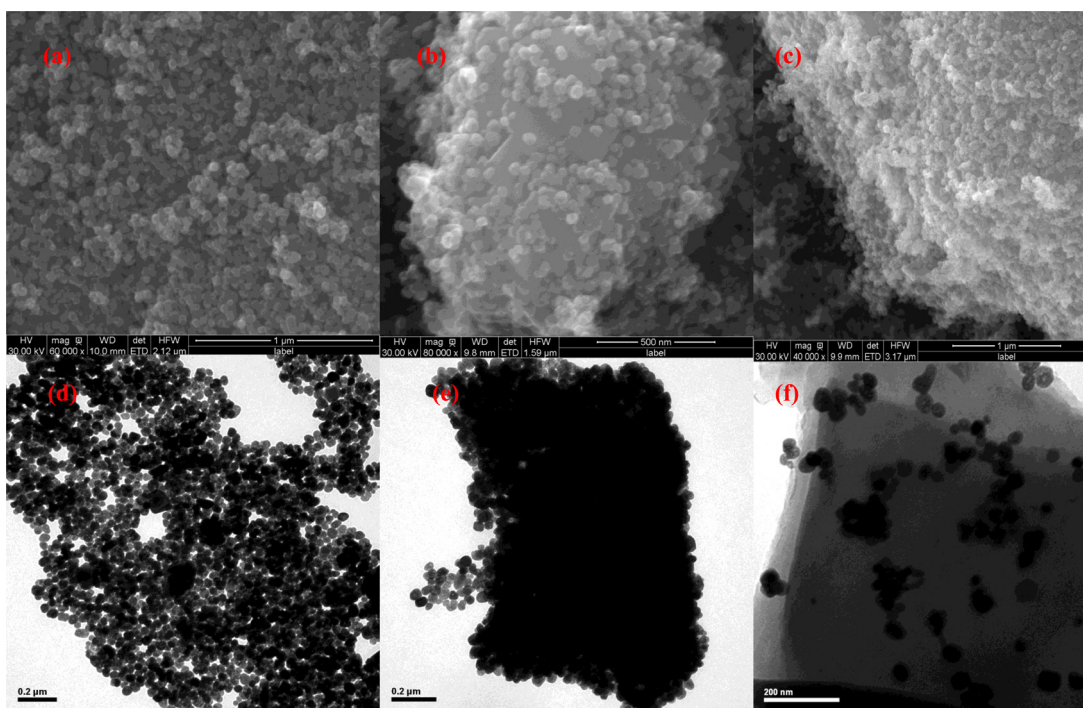


Fig. 2. SEM of EDA@Mag-Fe₃O₄ (a), whole (b) and part morphological (c) of 3D-Mag-CMGO; TEM of EDA@Mag-Fe₃O₄ (d), whole (e) and part morphological (f) of 3D-Mag-CMGO.

that can affect the adsorption and recovery efficiency of allergenic disperse dyes, such as pH value, the shaking time, the sample volume *etc.*, were assessed and optimized from laboratory batch tests. Furthermore, an ultra-fast liquid chromatography-tandem quadrupole mass spectrometry (UFLC-MS/MS) method for determination of 21 allergenic disperse dyes in environmental water at sub-ppt levels has been developed with pretreatment of the samples by Mag-dSPE.

2. Experimental

2.1. Reagents and materials

Acetonitrile, methanol and formic acid of HPLC grade were purchased from Merck (Darmstadt, German). Ammonium acetate used for mobile phase was of HPLC-grade obtained from Sigma (Steinheim, Germany). Water for all applications was obtained from an in-house Milli-Q ultra-pure water system (Millipore, Bedford, MA, USA) with resistivity equal to or higher than 18.2 MΩ × cm. The standards of disperse blue 1 (68%), disperse blue 3 (24%), disperse blue 7 (98%), basic red 9 (100%), basic violet 14 (99%), disperse blue 102 (100%), disperse blue 106 (100%), disperse blue 124 (71%), disperse yellow 1 (82%), disperse yellow 3 (30%), disperse yellow 9 (89%), disperse yellow 39 (56%), disperse yellow 49 (90%), disperse brown 1 (50%), disperse red 1 (98%), disperse red 11 (73%), disperse red 17 (83%), disperse orange 1 (80%), disperse orange 3 (85%), disperse orange 11 (92%) and disperse orange 37 (44%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Ferric chloride hexahydrate, sodium hydroxide, sodium acetate anhydrous, ethylene glycol (EG) and ethylenediamine (EDA) of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphene oxide was purchased from Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China). River water was collected from the Yaojiang River, Yongjiang River, and Fenghua River, which are three main rivers in Ningbo, China. The pH value of the water sample was adjusted to 5.0–8.0 with 0.1 mol L⁻¹ HCl

and 0.1 mol L⁻¹ NaOH, filtered through a polytetrafluoroethylene membrane (0.22 μm), and then stored in pre-cleaned polyethylene bottles prior to use.

2.2. Equipment

The magnetic and morphological characteristics of 3D-Mag-CMGO were carried out by using Lake Shore 7410 vibrating sample magnetometer (VSM) (Westerville, USA), Hitachi H-7650 transmission electron microscopy (TEM) (Hitachi, Japan) and Hitachi S-4800 Field emission scanning electron micrographs (SEM) (Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation (VG Scientific, UK). FT-IR characterization was performed with a Thermo Nicolet NEXUS-470 FTIR spectrometer (Thermo Nicolet, USA). Spectra were obtained from 4000 cm⁻¹ to 400 cm⁻¹ in transmission mode, accumulating 32 scans at a resolution of 4 cm⁻¹. The nitrogen percentages of the 3D-Mag-CMGO nanoparticles were analyzed with a ThermoFisher Flash-1112 elementary analyzer (ThermoFisher, USA). A vortex mixer Hualida WH-866 (Taicang, China) was used during extraction. LC-MS/MS analyses were performed with AB SCIEX TRIPLE QUAD 5500 mass spectrometer (Applied Biosystems, Foster City, CA, USA) and Prominence UFLC XR system equipped with a LC-30AD pump system, a CTO-20AC column oven, a DGU-20A₃ degasser and a SIL-20AC autosampler (Shimadzu Corporation, Tokyo, Japan).

2.3. Synthesis of 3D-Mag-CMGO

The 3D-Mag-CMGO was synthesized by a simple one-pot reaction based on the solvothermal method [35,36]. Briefly, FeCl₃·6H₂O, NaAc and NaOH in a weight ratio of 1.0:3.0:0.4 were dissolved in 20 mL EG at 50 °C to give a transparent solution. Then 10 mL EDA was added to the above system under ultrasonication. Finally, 50 mg of GO was added. And the mixture was stirred vigorously for 30 min at 50 °C and then transferred to a teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated to and

maintained at 200 °C for 6 h and then naturally cooled to room temperature. The brown magnetic 3D-Mag-CMGO nanoparticles were obtained and washed three times with methanol under ultrasonic conditions to remove the adsorbed solvent. The nanoparticles were dried in a vacuum oven at 60 °C and stored in a sealed bottle for further use. The schematic procedure of 3D-Mag-CMGO synthesis is shown in Fig. 1. EDA-functionalized magnetic Fe₃O₄ nanoparticles (EDA@Mag-Fe₃O₄, in the absence of GO) were also prepared and treated in an identical manner, which was used in characterization as model for comparison.

2.4. Mag-dSPE procedure

Exactly 200.0 mL of water sample (pH 5.0–8.0) was transferred to a 500 mL stopper conical flask and then 50.0 mg of 3D-Mag-CMGO was added. The mixture was immediately machine-shaken for 10.0 min and the adsorbed 3D-Mag-CMGO was isolated under magnetic field for 1 min. The adsorbed 3D-Mag-CMGO was washed sequentially with 2 mL of water and 2 mL of 10% aqueous methanol/water, and then was finally eluted by 5.0% ammonia solution/methanol (3 × 500 µL, v/v). And the elution concentrated to dryness with a nitrogen stream and was redissolved with 1.0 mL of initial mobile phase and filtered using a 0.22 µm membrane prior to its injection into the UFLC–MS/MS system.

2.5. UFLC–MS/MS analysis

The chromatographic separation was performed on a Shim-pack XR-ODS II (150 mm × 2.0 mm i.d., 2.2 µm) by using 5.0 mmol/L AmAc and 0.1% formic acid (v/v) in acetonitrile as eluent (A), and 5.0 mmol/L AmAc and 0.1% formic acid (v/v) in water as eluent (B) as the mobile phase. The linear gradient was: 0 → 1.00 min, 10.0 → 40.0% B; 1.00 → 3.00 min, 40.0 → 80.0% B; 3.00 → 8.00 min, 80.0 → 90.0% B; 8.00 → 8.01 min, 90.0 → 10.0% B; 8.10 → 10.00 min, 10% B. The column was thermostated at 40 °C to increase the retention time reproducibility. The injection volume was 10.0 µL. The separation was accomplished at a constant flow of 0.40 mL/min. Mass spectrometry analysis was performed using an electrospray ionization source in positive mode. Nitrogen was used in all cases. The operation conditions were as follows: ion spray voltage, 5500 V; curtain gas (CUR), 40 psi and interface heater was on; the turbo spray temperature, 500 °C. Applied Biosystems/MDS Sciex Analyst software (versions 1.5.1) was used for data acquisition and processing.

2.6. Method validation

2.6.1. Standard preparation

Individual stock standard solutions were prepared at 1000 mg/L level by exact weighing and dissolution in acetonitrile:water (60:40, v/v). The stock mixture standard solution (1.0 mg/L) was prepared by appropriate dilution of the stock solutions with water. “Matrix-calibration standards in blank samples with concentrations at 25.0, 50.0, 100.0, 200.0, 500.0, 1000 and 2500 ng/L were prepared for the calibration curves of disperse yellow 9, 50.0, 100.0, 200.0, 400.0, 1000, 2000 and 5000 ng/L were prepared for the calibration curve of disperse yellow 1, and 5.0, 10.0, 20.0, 40.0, 100, 200 and 500 ng/L were prepared for other 19 allergenic disperse dyes, respectively.”

2.6.2. Spiked sample

Spike recoveries were performed at concentrations of 40.0, 400.0 and 2000 ng/L for disperse yellow 9, 80.0, 800 and 4000 ng/L for disperse yellow 1, 8.0, 80.0 and 400 ng/L for other 19 allergenic disperse dyes, respectively. For each spiked sample, stock mixture

solution of the standards was added to 200.0 mL water sample, which was free from the target compounds.

2.6.3. Validation parameters

The method was evaluated by linearity, LOD, LOQ, trueness and precision. Calibration curves of peak area of quantitative ion pairs (see Table 1) against the determinant concentration were used to calibrate the UFLC–MS/MS system and spike samples in recovery experiments. The LOD and LOQ were estimated in accordance with the baseline noise method at a signal-to-noise ratio (S/N) of 3 and 10. It was experimentally determined by injecting samples with concentration at 40.0 ng/L for disperse yellow 9, 80.0 ng/L for disperse yellow 1 and 8.0 ng/L for other 19 allergenic disperse dyes, respectively. The method bias (trueness) was expressed as the recoveries, and the method precisions were expressed as the intra-day and inter-day relative standard deviations (RSDs). The inter-day RSDs were obtained by repeating the three levels of spiked samples in triplicate on 6 separate days within a 2-week period. And the intra-day RSDs were obtained by repeating the three levels of spiked samples six times within a day.

3. Results and discussion

3.1. Characterization of 3D-Mag-CMGO

Up until now, hierarchical nanostructures, i.e., self-assembly of the basic building blocks into well defined 3D nanostructures, have attracted much attention due to their unique physiochemical properties and potential applications [37]. In this work, a novel 3D nanostructures of 3D-Mag-CMGO was synthesized, and the excellent properties of the 3D-Mag-CMGO were characterized by TEM, SEM, VSM, FTIR, EA and XPS.

3.1.1. Morphological characteristics

The morphological features of EDA@Mag-Fe₃O₄ and 3D-Mag-CMGO were observed by TEM and SEM (Fig. 2). The EDA@Mag-Fe₃O₄ nanoparticles exhibited a uniform morphology with an average particle size of about 55 nm (Fig. 2(a) and (d)). The SEM image of 3D-Mag-CMGO is shown in Fig. 2(b) and (c). And it is interestingly observed that the magnetic nanoparticles own quasi-monodisperse size, and evenly installed on the surface of GO substrates because of the electrostatic interaction between negative GO and positive Fe₃O₄. On the other hand, the particles of GO look very dense with the layers stacked together to form sandwich-like 3D nanostructures as a result of the strong specific interactions between the surface epoxy groups (C–O–C) on the GO layers and amino groups (–NH₂) in EDA@Mag-Fe₃O₄ nanoparticles. Furthermore, the morphological features of the 3D-Mag-CMGO obtained by TEM were similar to those of the SEM, as shown in Fig. 2(e) and (f).

3.1.2. Magnetic property

Fig. S1 shows the magnetic hysteresis loop analysis of the nanoparticles. Similar general shapes of the two curves with symmetry about the origin may be observed, illustrating a response to an external magnetic field but without magnetization transfer. The saturation value of the EDA@Mag-Fe₃O₄ was 77.2 emu/g. The 3D-Mag-CMGO achieved a saturation magnetization value of 72.6 emu/g. This 3D-Mag-CMGO characteristic could ensure to separate more quickly and easily in two-phase (solid/liquid phase) systems due to the stronger magnetism.

3.1.3. FTIR and EA analysis

The infrared spectra of EDA@Mag-Fe₃O₄ and 3D-Mag-CMGO nanoparticles were obtained (Fig. S2). The main functional groups of the predicted structures can be observed from corresponding

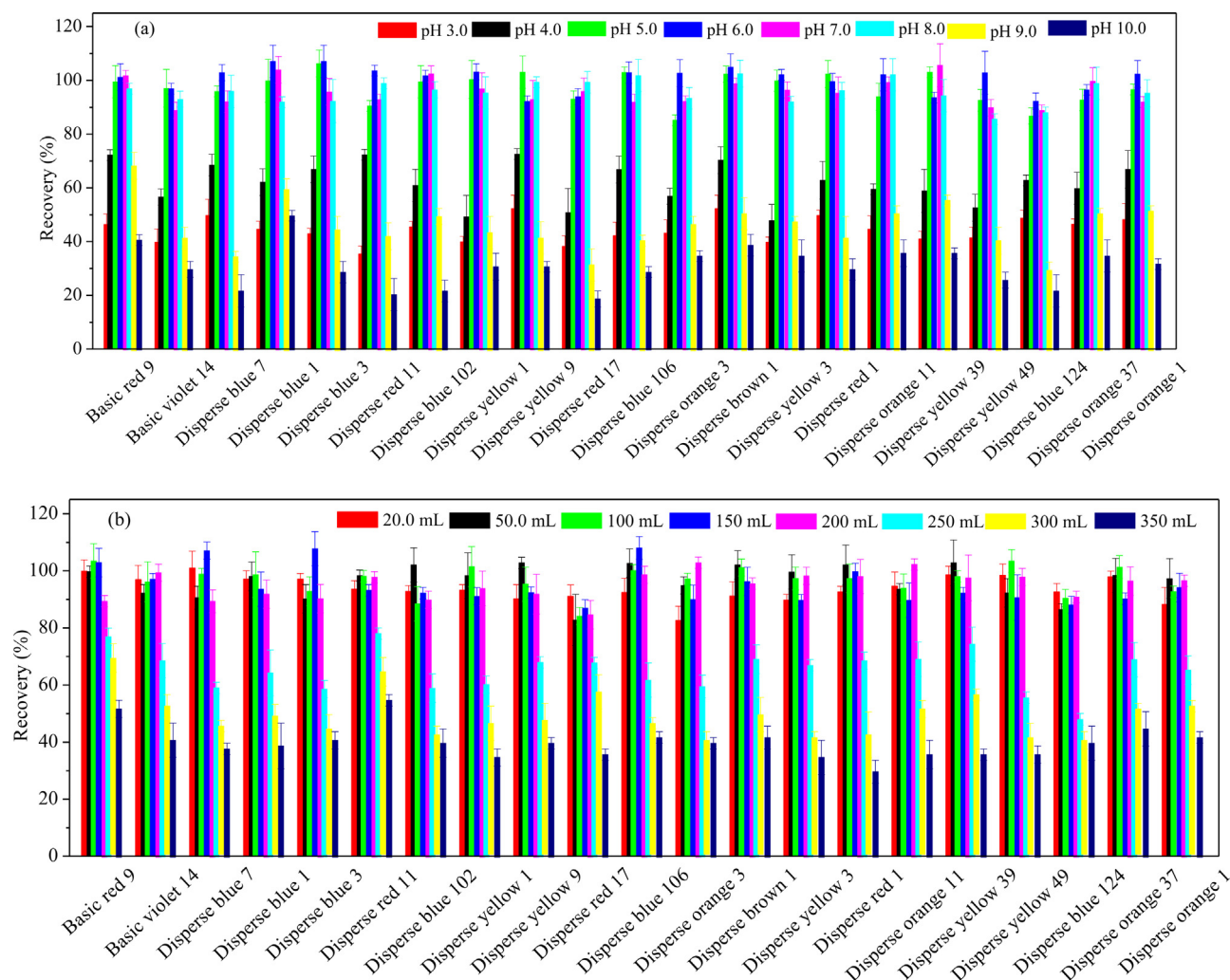


Fig. 3. Effect of pH value of water sample (a) and the volume of water sample (b) on the recoveries of 21 allergenic disperse dyes ($n = 3$), batch experiments were performed by mixing 50 mg 3D-Mag-CMGO with 200.0 mL sample spiked at low levels (40.0 ng/L for disperse yellow 9, 80.0 ng/L for disperse yellow 1, 8.0 ng/L for other 19 allergenic disperse dyes).

Table 1

Q1/Q3 ion pairs, declustering potential (DP), collision energy (CE) of MRM and retention time for 21 allergenic disperse dyes.

Allergenic disperse dyes	Precursor ion (Q1, m/z)	Fragment ion (Q3, m/z), (reference ion ratio ^a , %)	CE (eV)	DP (V)	Retention time (min)
Basic red 9	289.2	196.1 ^b , 169.1 (94.5)	42, 52	200	2.70
Basic violet 14	303.2	210.0 ^b , 196.1 (59.4)	42, 45	200	2.85
Disperse blue 7	359.2	283.1 ^b , 327.9 (46.3)	42, 29	180	3.66
Disperse blue 1	269.2	107.0 ^b , 253.0 (15.8)	45, 39	190	4.10
Disperse blue 3	297.3	252.2 ^b , 235.0 (12.6)	27, 43	180	4.12
Disperse red 11	269.1	254.1 ^b , 226.1 (98.1)	30, 40	150	4.15
Disperse blue 102	366.1	208.2 ^b , 147.2 (37.7)	26, 35	130	4.20
Disperse yellow 1	276.1	229.1 ^b , 182.9 (59.3)	32, 40	150	4.30
Disperse yellow 9	275.1	258.1 ^b , 228.0 (71.0)	20, 30	120	4.35
Disperse red 17	345.1	164.1 ^b , 177.1 (63.7)	32, 39	150	4.42
Disperse blue 106	336.1	178.1 ^b , 147.1 (13.8)	19, 40	120	4.65
Disperse orange 3	243.1	122.0 ^b , 91.9 (43.5)	25, 34	130	4.85
Disperse brown 1	433.3	356.9 ^b , 197.0 (81.4)	42, 42	150	4.85
Disperse yellow 3	270.2	107.0 ^b , 150.1 (86.7)	35, 22	150	4.95
Disperse red 1	315.1	134.1 ^b , 255.1 (68.6)	32, 40	150	5.25
Disperse orange 11	238.1	223.1 ^b , 195.0 (67.1)	23, 30	180	5.30
Disperse yellow 39	291.1	130.1 ^b , 245.1 (82.0)	36, 38	120	5.35
Disperse yellow 49	375.2	238.1 ^b , 164.1 (13.9)	21, 24	120	5.81
Disperse blue 124	378.2	220.0 ^b , 160.1 (35.0)	24, 30	120	6.09
Disperse orange 37	392.1	351.0 ^b , 218.0 (13.3)	32, 48	150	7.35
Disperse orange 1	319.1	169.1 ^b , 122.0 (58.3)	34, 25	150	8.15

^a Qualitative ion/Quantitative ion, reference ion ratios are calculated from solvent standard.

^b Quantitative ion.

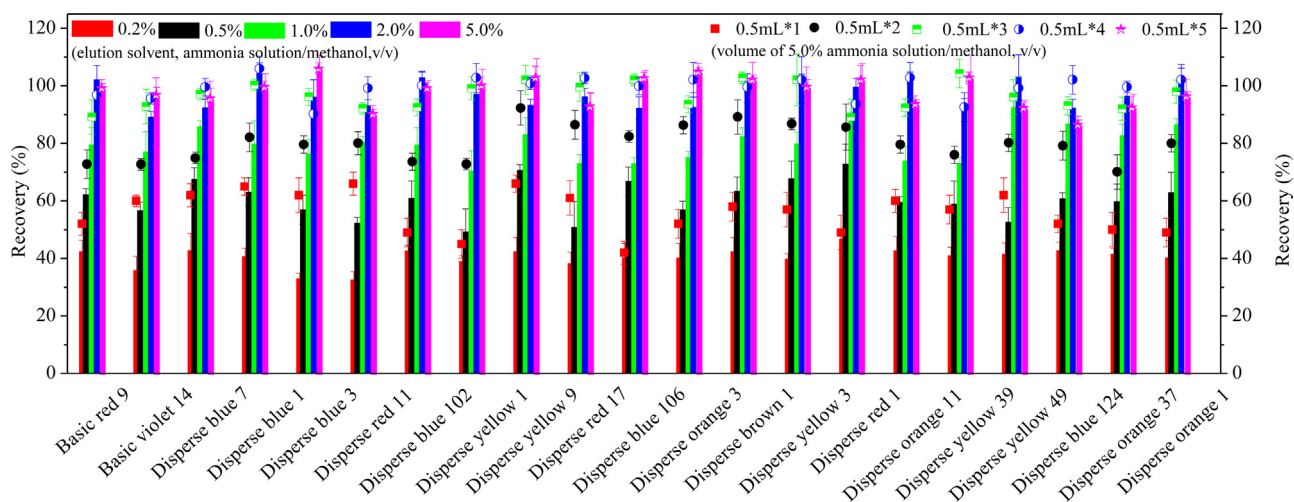


Fig. 4. Effect of the type and volume of elution solvent on the recoveries of 21 allergenic disperse dyes ($n=3$), batch experiments were performed by mixing 50 mg 3D-Mag-CMGO with 200.0 mL sample spiked at low levels (40.0 ng/L for disperse yellow 9, 80.0 ng/L for disperse yellow 1, 8.0 ng/L for other 19 allergenic disperse dyes).

infrared absorption peaks. A broad absorption band at 3438 cm^{-1} in the spectra of EDA@Mag- Fe_3O_4 and 3D-Mag-CMGO corresponded to stretching vibrations of N–H bonds in the amino groups of EDA molecules (active groups). The absorptions band at 2995 and 2920 cm^{-1} in the spectra of EDA@Mag- Fe_3O_4 and 3D-Mag-CMGO corresponded to the stretching vibrations of C–H bonds. Typical band of the 3D-Mag-CMGO was observed at 1730 cm^{-1} (C=O bonds on carbonyl groups of GO), whereas no characteristic signal for carbonyl groups (C=O) at 1730 cm^{-1} in the spectra of EDA@Mag- Fe_3O_4 was observed. Other absorption bands at 1638 and 568 cm^{-1} in the spectra of EDA@Mag- Fe_3O_4 and 3D-Mag-CMGO corresponded to the stretching vibrations of C–N bonds of EDA and Fe–O bonds of Fe_3O_4 , respectively. Furthermore, the nitrogen percentages of EDA@Mag- Fe_3O_4 and 3D-Mag-CMGO obtained from EA were 5.2% and 4.8%, respectively.

3.1.4. XPS spectra

To further identify the chemical bonding information in the composites, the 3D-Mag-CMGO was examined by XPS. As shown in Fig. S2, the C 1s high-resolution scan of 3D-Mag-CMGO could be fitted into four peaks (Fig. S3-a) with binding energies of 281.1, 282.7, 283.2, and 284.9 eV, which are attributed to aliphatic carbon (C–C/H), ether (C–O), C–N, and ester carbon (O–C=O), respectively. These results are perfectly consistent with the FT-IR and EA analysis (Fig. S2). The O 1s high-resolution scan of 3D-Mag-CMGO could be fitted into two peaks (Fig. S2-b) with binding energies of 526.3 and 527.9 eV, which are attributed to an ester oxygen (O–C=O) and ether oxygen (C–O), respectively. The N 1s high-resolution scan of 3D-Mag-CMGO could be fitted into one peak (Fig. S2-c) with binding energies of 396.0 eV, which is attributed to aliphatic nitrogen (C–N). The Fe 2p high-resolution scan of 3D-Mag-CMGO could be fitted into two peaks (Fig. S2-d) with binding energies of 707.0 and 720.5 eV, which is attributed to Fe $2p_{3/2}$ and Fe $2p_{1/2}$. And the ratio of Fe(II)/Fe(III) on the surface of the magnetic was 0.5021, which is very close to those of magnetite (Fe_3O_4) reported in literatures [38,39].

Based on the discussion above, the successful preparation of 3D-Mag-CMGO by a simple one-pot reaction based on the solvothermal method may be confirmed by the full characterization provided by the TEM, SEM, VSM, FT-IR, EA and XPS analyses. The synthesized nanoparticles were also proven to be useful for the adsorption of allergenic disperse dyes.

3.2. 3D-Mag-CMGO Mag-dSPE procedure and its optimization

In the study, the effect of pH value of water samples, the shaking time, the sample volume on the Mag-dSPE enrich properties were investigated in detail. Batch experiments were performed by mixing 50 mg 3D-Mag-CMGO with sample spiked at low levels (40.0 ng/L for disperse yellow 9, 80.0 ng/L for disperse yellow 1, 8.0 ng/L for other 19 allergenic disperse dyes) in a 500 mL stopper conical flask, and the results were shown in Fig. 3.

First, various pH values from 3.0 to 10.0 were used to optimize the Mag-dSPE procedure, and the results were shown in Fig. 3(a). It indicated that with the increasing of pH values from 3.0 to 5.0, the recoveries of allergenic disperse dyes increased significantly. With the increasing of pH values from 5.0 to 8.0, the satisfactory recoveries of the 21 allergenic disperse dyes were consistently in the range of 80.6–107%. Above pH 8.0, the recoveries of allergenic disperse dyes decreased with the increase in pH within the studied pH range. The dependence of allergenic disperse dyes adsorption on pH can be explained from the perspective of surface chemistry in aqueous phases. The primary driving force for the rebinding process, i.e., hydrogen bonding, is strongly related to the sample pH, which is suppressed in strongly acidic or basic solutions due to the ionic state of allergenic disperse dyes and amino groups in the surface of 3D-Mag-CMGO. Furthermore, π – π stacking interactions between six-membered carbon rings in GO and aromatic rings in allergenic disperse dyes is also a driving force for the dispersive dyes on adsorbents. And it could be used for explaining that the dispersive dyes was also adsorbed onto 3D-Mag-CMGO especially under strongly acidic or basic solutions. Thus, pH values ranging from 5.0 to 8.0 were selected for subsequent experiments. Ideally, river water is neutralized and this is an advantage for application of adsorbent in extraction allergenic disperse dyes from water samples.

Second, the effect of extraction time on the recovery was studied with various extraction time from 1.0 min to 120.0 min. And the results showed that with the increasing of the extraction time from 1.0 min to 120.0 min, the recoveries of 21 allergenic disperse dyes were gradually increased and reached to an equilibrium of 81.9–106% in 10.0 min. And the adsorption kinetic data obtained from batch experiments were analyzed using a pseudo-second-order rate equation, which indicates that the binding amounts of the 3D-Mag-CMGO are proportional to the number of active sites on the nanoparticle surface result in faster diffusion from the liquid into the binding sites of the 3D-Mag-CMGO and reduce the adsorption equilibrium time. Therefore, short extraction time of

Table 2
Validation parameters ($n=9$) obtained for 21 allergenic disperse dyes at three concentration levels in blank river samples.

Analytes	Linear equation	Confidence intervals (95%) ^a		Linear range (ng/L)	Average recovery ^b , % (RSD, %)			LOQ (ng/L)	LOD (ng/L)	r
		Slope	Intercept		Low level ^c	Medium level	High level			
Basic red 9	$Y = 3.56 \times 10^5 X - 7.04 \times 10^4$	$3.36 \times 10^5 - 3.76 \times 10^5$	-6.86×10^4 to -7.22×10^4	5.0–500	90.6 (3.6 ^d , 3.6 ^e)	98.0 (5.5, 6.2)	96.2 (5.0, 6.2)	2.05	0.6	0.9991
Basic violet 14	$Y = 1.88 \times 10^4 X - 5.51 \times 10^3$	$1.68 \times 10^4 - 2.08 \times 10^4$	-5.31×10^3 to -5.71×10^3	5.0–500	92.5 (2.5, 4.8)	90.2 (2.0, 5.8)	86.0 (5.1, 7.2)	4.9	1.45	0.9999
Disperse blue 7	$Y = 1.51 \times 10^5 X + 1.16 \times 10^4$	$1.36 \times 10^5 - 1.66 \times 10^5$	$1.08 \times 10^4 - 1.24 \times 10^4$	5.0–500	90.8 (5.2, 5.4)	102 (3.8, 5.0)	101 (6.4, 8.0)	0.65	0.19	0.9999
Disperse blue 1	$Y = 1.58 \times 10^4 X - 3.27 \times 10^3$	$1.42 \times 10^4 - 1.74 \times 10^4$	-3.16×10^3 to -3.38×10^3	5.0–500	80.0 (2.3, 6.6)	106 (5.0, 7.3)	92.1 (2.5, 6.3)	4.25	1.3	0.9997
Disperse blue 3	$Y = 1.87 \times 10^5 X - 1.58 \times 10^4$	$1.72 \times 10^5 - 2.02 \times 10^5$	-1.46×10^4 to -1.70×10^4	5.0–500	90.2 (3.9, 6.0)	90.9 (3.2, 5.6)	89.0 (5.7, 5.9)	2.05	0.6	0.9986
Disperse red 11	$Y = 9.89 \times 10^4 X + 1.57 \times 10^3$	$9.58 \times 10^4 - 1.02 \times 10^4$	$1.38 \times 10^3 - 1.76 \times 10^3$	5.0–500	92.0 (3.7, 6.2)	100 (5.0, 6.3)	100 (4.2, 6.6)	3.05	0.92	0.9989
Disperse blue 102	$Y = 1.40 \times 10^5 X - 3.73 \times 10^3$	$1.32 \times 10^5 - 1.48 \times 10^5$	-3.56×10^3 to -3.90×10^3	5.0–500	98.2 (3.0, 6.7)	91.2 (4.2, 5.6)	89.3 (3.2, 5.2)	2.95	0.9	0.9992
Disperse yellow 1	$Y = 3.77 \times 10^3 X + 5.68 \times 10^2$	$3.65 \times 10^3 - 3.89 \times 10^3$	$5.48 \times 10^2 - 5.88 \times 10^2$	50.0–5000	87.0 (3.1, 7.8)	98.3 (2.2, 6.2)	99.2 (4.2, 7.8)	34.05	10.2	0.9996
Disperse yellow 9	$Y = 1.36 \times 10^4 X + 5.12 \times 10^3$	$1.20 \times 10^4 - 1.52 \times 10^4$	$4.88 \times 10^3 - 5.36 \times 10^3$	25.0–2500	101 (3.4, 8.8)	99.0 (5.0, 7.8)	102 (3.6, 7.0)	13.2	3.95	0.9991
Disperse red 17	$Y = 2.53 \times 10^5 X - 8.07 \times 10^3$	$2.40 \times 10^5 - 2.66 \times 10^5$	-7.86×10^3 to -8.28×10^3	5.0–500	93.2 (3.5, 6.9)	86.8 (2.9, 5.7)	88.9 (2.9, 5.0)	1	0.3	0.9992
Disperse blue 106	$Y = 2.09 \times 10^5 X - 4.44 \times 10^4$	$1.92 \times 10^5 - 2.26 \times 10^5$	-4.26×10^4 to -4.62×10^4	5.0–500	96.0 (2.7, 4.2)	109 (5.0, 7.3)	112 (5.2, 6.6)	1	0.3	1
Disperse orange 3	$Y = 8.05 \times 10^4 X - 1.21 \times 10^3$	$7.75 \times 10^4 - 8.35 \times 10^4$	-1.06×10^3 to -1.36×10^3	5.0–500	92.2 (3.0, 7.7)	93.2 (4.2, 3.6)	97.3 (4.2, 6.2)	1.85	0.55	1
Disperse brown 1	$Y = 4.07 \times 10^4 X - 1.62 \times 10^3$	$3.87 \times 10^4 - 4.27 \times 10^4$	-1.46×10^3 to -1.78×10^3	5.0–500	88.0 (5.1, 7.8)	90.3 (2.1, 6.2)	91.2 (4.0, 7.8)	4.85	1.45	0.9993
Disperse yellow 3	$Y = 1.34 \times 10^5 X - 4.61 \times 10^4$	$1.20 \times 10^5 - 1.48 \times 10^5$	-4.46×10^4 to -4.76×10^4	5.0–500	101 (5.4, 7.1)	90.2 (6.0, 6.8)	102 (4.6, 8.0)	4.75	1.42	0.9999
Disperse red 1	$Y = 1.14 \times 10^5 X - 1.41 \times 10^4$	$1.10 \times 10^5 - 1.18 \times 10^5$	-1.26×10^4 to -1.56×10^4	5.0–500	92.1 (3.5, 6.3)	89.9 (3.7, 5.5)	100 (5.0, 5.3)	2.7	0.8	1
Disperse orange 11	$Y = 1.73 \times 10^5 X + 5.13 \times 10^4$	$1.60 \times 10^5 - 1.86 \times 10^5$	$4.88 \times 10^4 - 5.36 \times 10^4$	5.0–500	98.0 (1.7, 5.7)	90.6 (3.0, 5.6)	90.9 (4.7, 5.8)	3.34	1	0.9996
Disperse yellow 39	$Y = 3.09 \times 10^5 X + 5.7 \times 10^4$	$2.89 \times 10^5 - 3.29 \times 10^5$	$5.58 \times 10^4 - 5.82 \times 10^4$	5.0–500	94.0 (6.6, 6.7)	92.9 (6.8, 6.9)	90.3 (2.9, 6.2)	0.7	0.22	0.9997
Disperse yellow 49	$Y = 1.58 \times 10^5 X + 7.04 \times 10^4$	$1.45 \times 10^5 - 1.71 \times 10^5$	$6.78 \times 10^4 - 7.30 \times 10^4$	5.0–500	92.6 (3.8, 6.9)	90.5 (4.9, 7.8)	99.8 (6.0, 7.8)	1.8	0.55	0.9991
Disperse blue 124	$Y = 6.65 \times 10^5 X + 6.67 \times 10^4$	$6.50 \times 10^5 - 6.80 \times 10^5$	$6.48 \times 10^4 - 6.86 \times 10^4$	5.0–500	103 (6.4, 6.7)	99.2 (3.8, 6.8)	89.9 (5.2, 5.5)	0.57	0.17	0.9996
Disperse orange 37	$Y = 1.74 \times 10^5 X - 6.41 \times 10^3$	$1.60 \times 10^5 - 1.88 \times 10^5$	-6.16×10^3 to -6.66×10^3	5.0–500	90.8 (3.5, 7.6)	91.9 (4.2, 4.8)	101 (2.0, 4.8)	2.3	0.7	1
Disperse orange 1	$Y = 2.88 \times 10^5 X + 1.49 \times 10^4$	$2.78 \times 10^5 - 2.98 \times 10^5$	$1.28 \times 10^4 - 1.70 \times 10^4$	5.0–500	98.1 (2.8, 6.0)	96.6 (3.3, 5.9)	89.9 (4.2, 6.3)	1.6	0.49	0.9996

^a The linearity was monitored on 7 consecutive days.

^b The mean value was determined in one day ($n=9$ replicates).

^c Spiked level: low, medium and high level mean 40.0, 400.0 and 2000 ng/L for disperse yellow 9, 80.0, 800 and 4000 ng/L for disperse yellow 1, 8.0, 80.0 and 400 ng/L for other 19 allergenic disperse dyes, respectively.

^d Intra-day, $n=9$ replicates.

^e Inter-day, $n=3$ replicates $\times$ 9 days within a 2-week period.

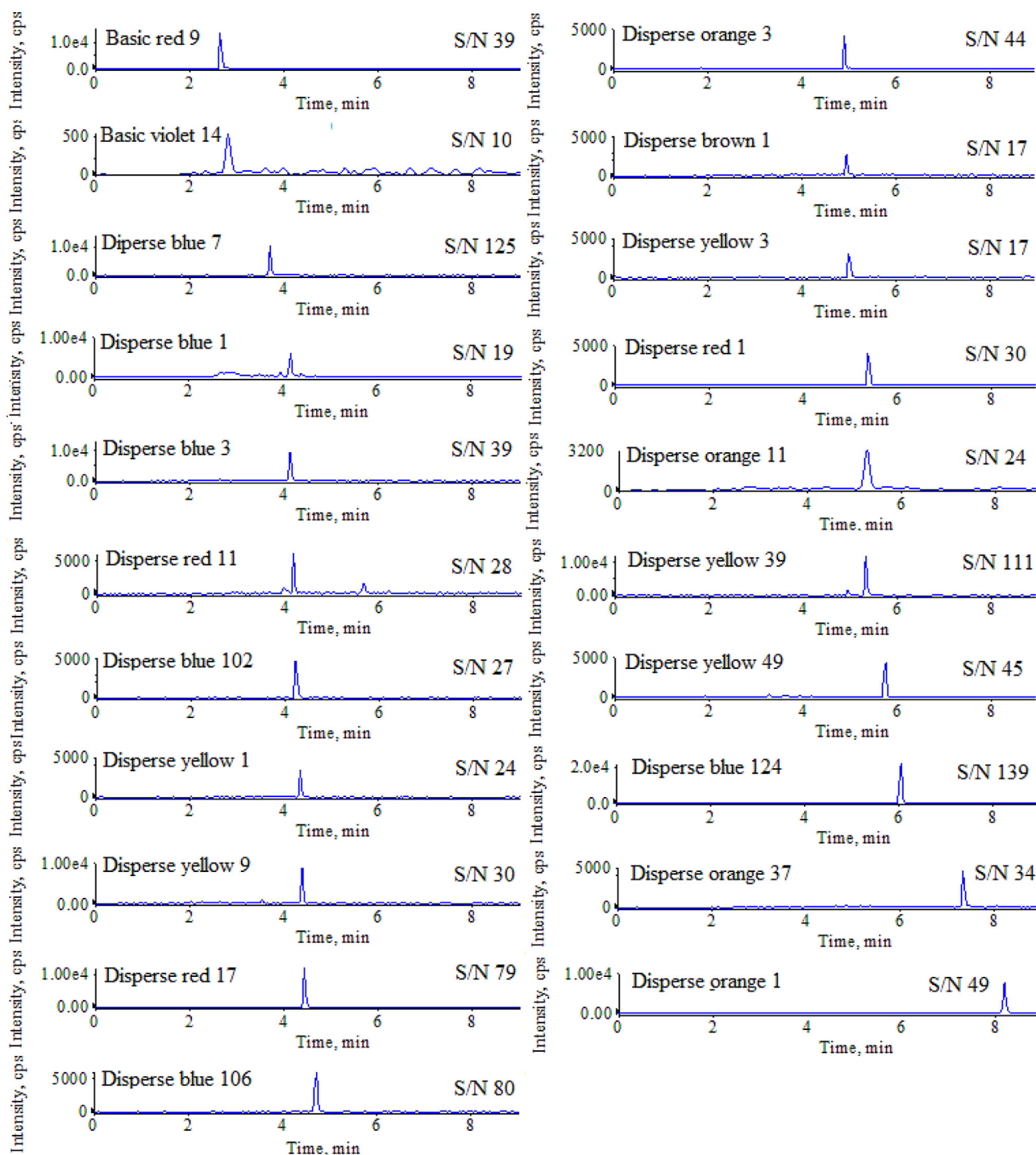


Fig. 5. MRM chromatograms for river water sample spiked with 21 allergenic disperse dyes at 40.0 ng/L for disperse yellow 9, 80.0 ng/L for disperse yellow 1 and 8.0 ng/L for other 19 allergenic disperse dyes, respectively, under Mag-dSPE extraction procedure.

10.0 min was chosen as the optimal extraction time for further studies.

Thirdly, to obtain reliable and reproducible analytical results and a high enrichment factor, obtaining satisfactory recoveries of the allergenic disperse dyes studied from a large volume of sample solutions is important. The maximum volume was studied ranging from 20 mL to 350 mL. Following the experimental procedure, the recoveries of the allergenic disperse dyes at different volumes were obtained, and the results indicate that the maximum volume was as high as 200 mL with recovery >82.9% (Fig. 3(b)). And then, the recoveries of allergenic disperse dyes gradually decreased with

the increase of sample volumes ranged from 200 mL to 350 mL. In the adsorption process, with the decreasing of the solid-to-liquid ratio from 2.5 to 0.14 (usage amount of adsorbent/the sample volume, mg/mL), the chance of the analytes adsorbed onto the adsorbent decreased resulted in low recoveries. Furthermore, the similar results were also obtained in high level (2000 ng/L for disperse yellow 9, 4000 ng/L for disperse yellow 1, 400 ng/L for other 19 allergenic disperse dyes) and medium level (400 ng/L for disperse yellow 9, 800 ng/L for disperse yellow 1, 80.0 ng/L for other 19 allergenic disperse dyes), respectively. Therefore, 200 mL of the sample solution was adopted for the preconcentration of analytes

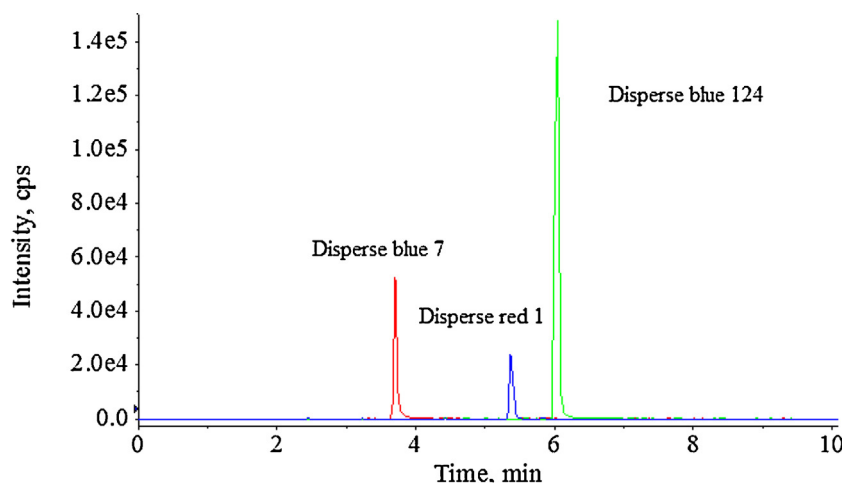


Fig. 6. MRM chromatograms for one examined samples.

from sample solutions. A high enrichment factor of 200 times was obtained because the final solution was 1.0 mL in these experiments.

Furthermore, the type of elution solvents, i.e., ammonia solution, ammonia solution/methanol, formic acid, formic acid/methanol have been investigated. And the results showed that higher recoveries could be obtained by using ammonia solution/methanol as elution solvent than others. Therefore, various concentration of elution solvent (ammonia solution/methanol), i.e., 0.2%, 0.5%, 1.0%, 2.0%, 5.0% (v/v), and the volume of elution solvent have been investigated deeply. The results were shown in Fig. 4. First, it can be seen that with the increasing of the concentration of ammonia solution/methanol from 0.2% to 2.0% (v/v), the recoveries of analytes increased significantly. With the increasing of the concentration of ammonia solution/methanol from 2.0% to 5.0% (v/v), the satisfactory recoveries of the 21 allergenic disperse dyes were consistently in the range of 90.2–106%. In this work, to obtain higher elution efficiency, 5.0% ammonia solution/methanol (v/v) has been used as elution solvent. Secondly, with the increasing of the volume of elution solvent from 0.5 mL to 2.5 mL, the recoveries of 21 allergenic disperse dyes were gradually increased and reached to an equilibrium of 86.9–108% above 1.5 mL. Finally, 5.0% ammonia solution/methanol (3×0.5 mL, v/v) has been selected for eluting the adsorbents.

3.3. Regeneration and reproducibility of 3D-Mag-CMGO

The 3D-Mag-CMGO-adsorbed could be conveniently regenerated by treating the 3D-Mag-CMGO-adsorbed sequentially with 5.0 mL 5.0% ammonia solution/methanol (v/v) and 20 mL water, allowing for them to be used repeatedly for Mag-dSPE method, extracting allergenic disperse dyes from water samples. Therefore, the effectiveness of regeneration of 3D-Mag-CMGO on recoveries of analytes were studied with the blank sample spiked with allergenic disperse dyes at low, medium and high concentration levels (40.0, 400.0 and 2000 ng/L for disperse yellow 9, 80.0, 800 and 4000 ng/L for disperse yellow 1, 8.0, 80.0 and 400 ng/L for other 19 allergenic disperse dyes, respectively). And the results showed that sorbent could be reused at least ten times in the extraction of allergenic disperse dyes from water samples without much sacrifice of the extraction efficiency.

Furthermore, the preparative reproducibility of the 3D-Mag-CMGO was evaluated. The results show that the relative deviations of the recoveries for 21 allergenic disperse dyes by using six batches of the sorbents are in the range of 4.6–8.0%. This indicates that the

preparation procedure of 3D-Mag-CMGO has good repeatability and reproducibility.

3.4. Analytical performances

The linearity of the matrix-calibration curves made by peak area of quantitative ion pairs against the determinant concentration was studied. The response function was found to be linear with a determination coefficient (r^2) higher than 0.9980 in the tested range listed in Table 2 for 21 allergenic disperse dyes. Trueness and precision were assessed based on the analysis of 21 allergenic disperse dyes spiked at low, medium, high level in blank river samples. The results are summarized in Table 2. It shows that the majority of mean recoveries are in the range of 80.0–112% at the three spiking levels with associated intra-day relative standard deviations (RSDs) ranging from 1.7–6.8% and inter-day relative standard deviations (RSDs) ranging from 3.6–8.8%.

The LODs and LOQs values for the analyzed allergenic disperse dyes are shown in Table 2. The LODs and LOQs, which were calculated on the analysis of analytes spiked at low level in blank samples that yielded a signal-to-noise (S/N) ratio of 3 and 10 were in the range of 0.17–10.20 ng/L and 0.57–34.05 ng/L, respectively. LC-MS/MS extracted ion chromatograms obtained by analysing spiked sample at low level are shown in Fig. 4. As can be seen in Fig. 5, no interference peak was observed in the LC-MS/MS extracted ion chromatograms of allergenic disperse dyes. It indicates that the proposed 3D-Mag-CMGO Mag-dSPE UFLC-MS/MS method has excellent sensitivity and selectivity.

Furthermore, a published work about LC-MS-based analysis for the determination of allergenic disperse dyes in water samples have been compared with the new developed method [40]. In the published work, Lue et al. reported a SPE LC-MS/MS method for the determination of nine allergenic disperse dyes in dyeing wastewater, and the LOQs were in the range of 0.05–2.48 $\mu\text{g/L}$. Comparing the proposed Mag-dSPE procedure with SPE procedure, the 3D-Mag-CMGO do not need to be packed into the SPE cartridge but dispersed in sample instead. Enrichment, the most time-consuming procedure in sample pretreatment, could be fulfilled fast. In a word, the proposed method gives a simpler and faster way for the extraction of allergenic disperse dyes in samples and provides relatively lower LOQs.

3.5. Verification of the proposed method

To further validate the feasibility of the proposed method, it was used for the analysis of fifty real samples. A blank sample spiked at

low level was used to control the extraction efficiency. The results showed the presence of disperse blue 7, disperse red 1 and disperse blue 124 in two out of the fifty collected samples with concentrations of 8.82 ng/L, 7.02 ng/L and 11.2 ng/L, respectively, and other allergenic disperse dyes were not detected because of lower than the LODs of the proposed method in the analyzed samples. And the MRM chromatogram for one examined samples was shown in Fig. 6. The findings indicate that illegal emit effluents may exist in some textile, leather or printing ink industries.

4. Conclusions

In summary, we have developed a simple template-free method to construct porous hierarchical nanostructures. And the Mag-dSPE extraction procedure using 3D-Mag-CMGO with rapid magnetic separation is optimized for the enrichment of 21 allergenic disperse dyes at sub-ppt levels in river waters. A high enrichment factor of 200 times is obtained under the optimal condition. Acceptable recoveries for the 21 allergenic disperse dyes are obtained in the range of 80.0–112.0%. The present work reveals that the 3D-Mag-CMGO has potential applications in the rapid effective enrichment procedure for allergenic disperse dyes at sub-ppt levels from natural water. Although the 3D-Mag-CMGO Mag-dSPE procedure is environmental friendly, less time and efficiency, and the proposed 3D-Mag-CMGO Mag-dSPE UFLC–MS/MS method has excellent sensitivity and selectivity, the main drawback is the low productivity of 3D-Mag-CMGO. Therefore, in our further study, high productivity of the adsorbent would be investigated deeply.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2015.12.089>.

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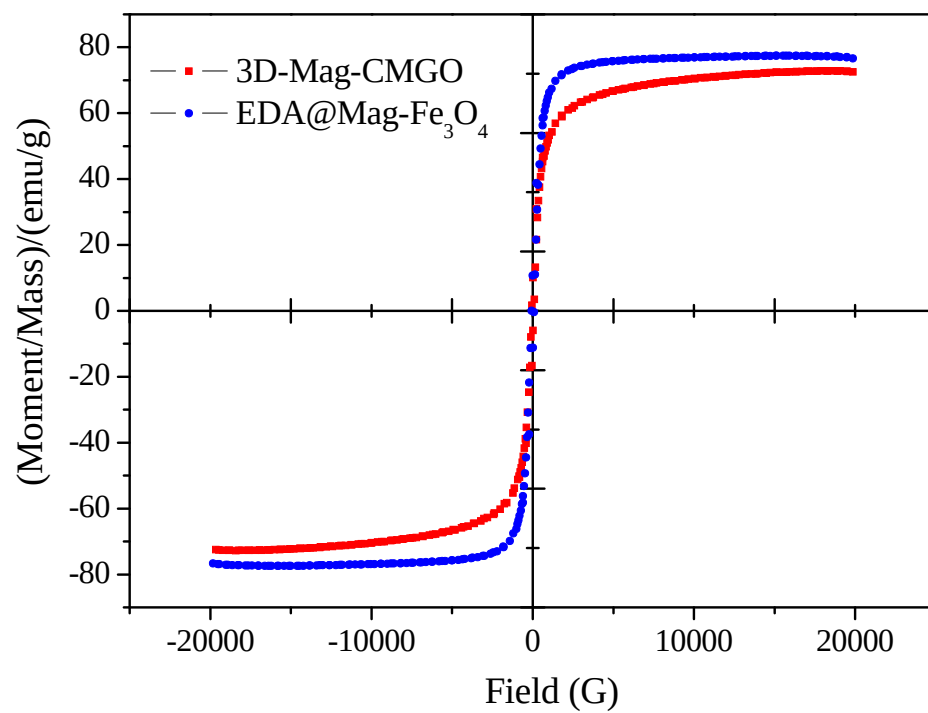


Fig. S1 VSM of EDA@Mag- Fe₃O₄ and 3D-Mag-CMGO

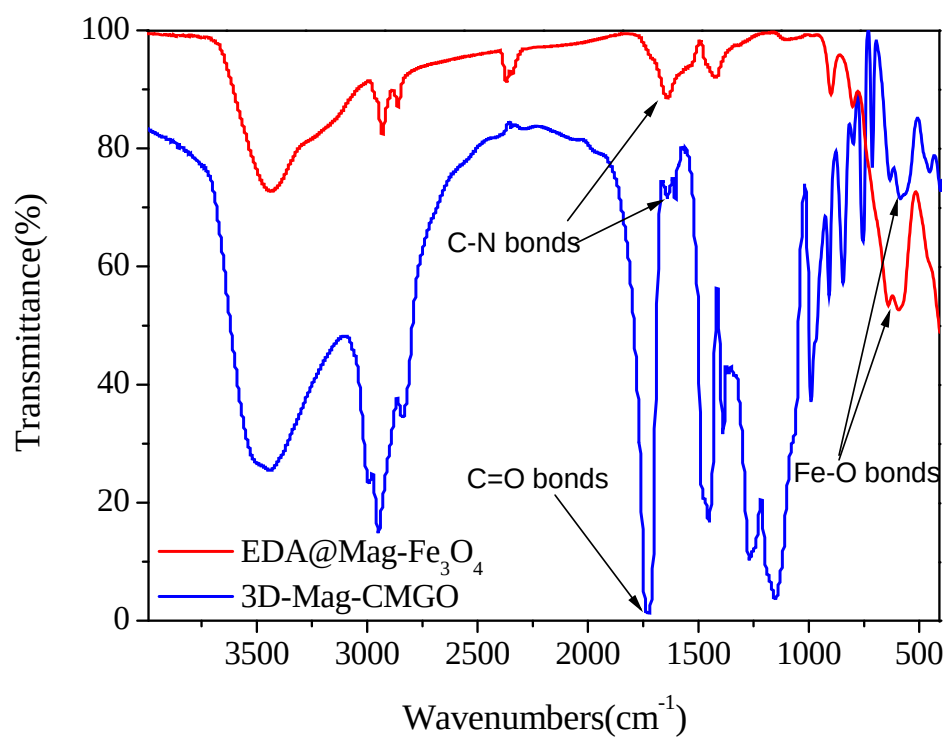
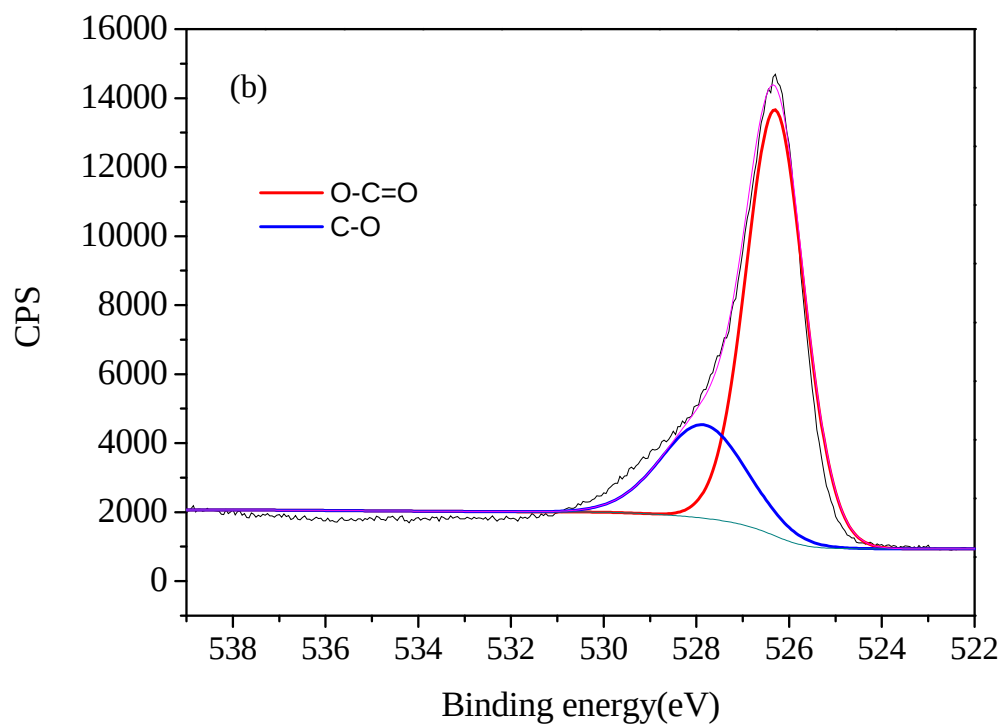
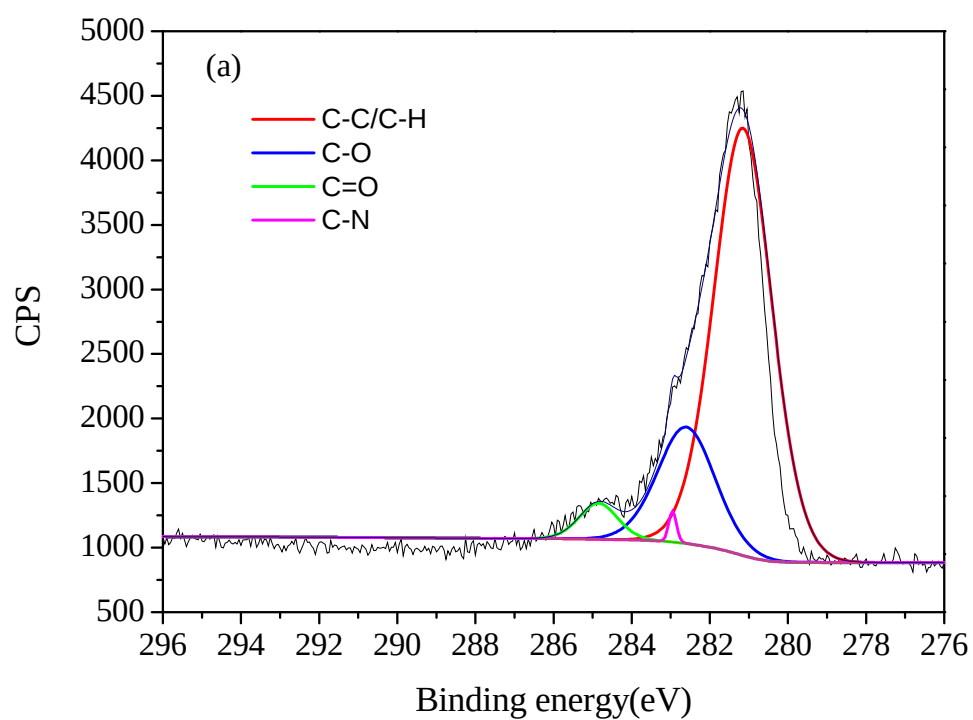


Fig. S2 FTIR spectra of EDA@Mag- Fe_3O_4 and 3D-Mag-CMGO



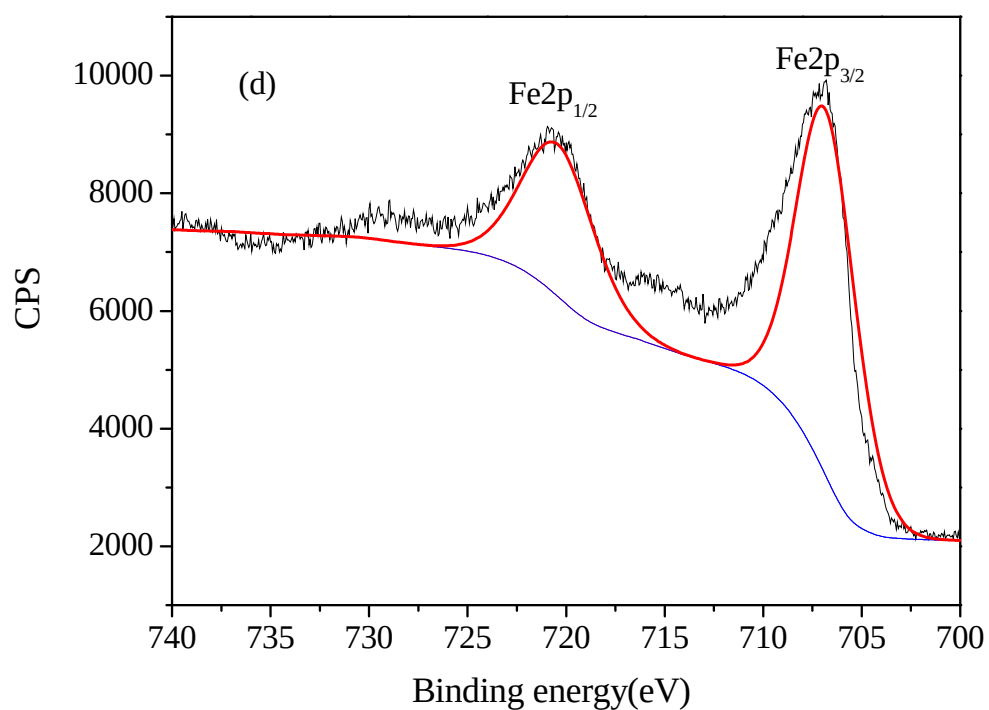
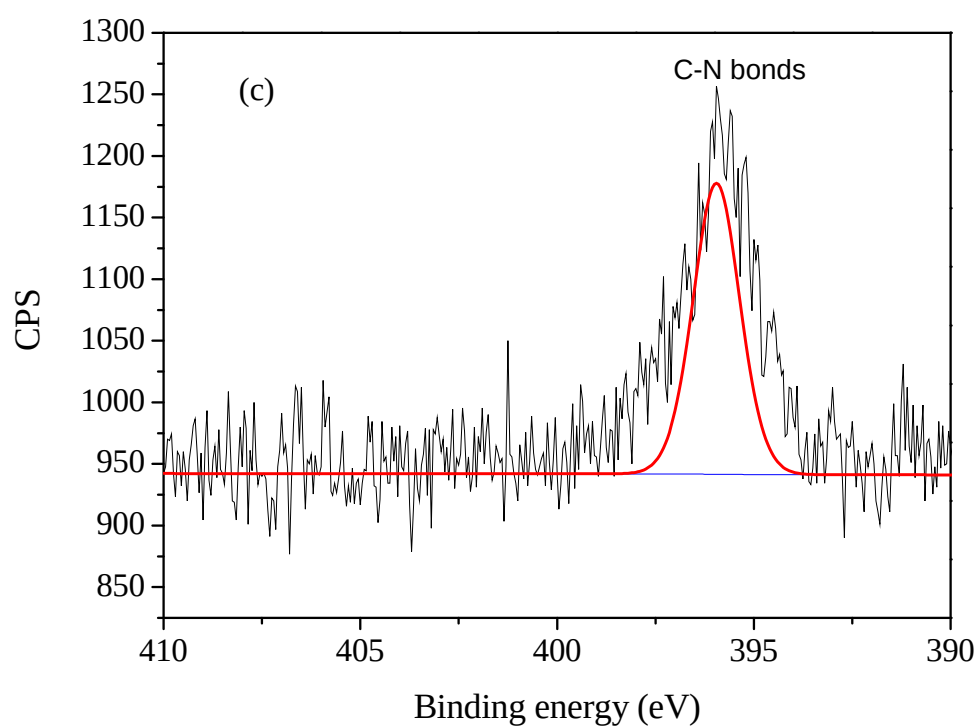


Fig. S3 The fit of the C1s XPS spectrum (a), the fit of the O1s XPS spectrum (b), the fit of the N1s XPS spectrum (c) and the fit of the Fe2p XPS spectrum (d) of 3D-Mag-CMGO