Surfactant-modified flowerlike layered double hydroxide-coated magnetic nanoparticles for preconcentration of phthalate esters from environmental water samples

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ABSTRACT

A novel type of layered, flowerlike magnetic double hydroxide (MLDH) nanoparticles modified by surfactants has been successfully synthesized and was applied as an effective sorbent for pre-concentration of several phthalate ester pollutants (PAEs) from water prior to quantification. The MLDH was obtained via a simple ultrasound-assisted method by using silica coated Fe₃O₄ as the core and anisotropic Mg–Al layered double hydroxide (Mg–Al LDH) nanocrystals as the shell to which analytes were absorbed. Orientation and dimensionality hierarchical structure as well as the large expandable interlayer free space and positive charge of the Mg–Al LDH shell make it easier to form anionic surfactant micelles on its surface via self-assembly. Due to its high adsorption area, compared with non-mesoporous nano solid-phase extraction agents, mesoporous channel shell and reduction diffusion path, MLDH exhibited high extraction efficiency of organic target residues. Under optimized conditions, with a total of 30 mg of adsorbant added to from samples containing 400 mL water from the environment recoveries of DPP, DBP, DCP and DOP were consistent with ranges of 69–101%, 79–101%, 86–102% and 63–100%, respectively. Standard deviations of recoveries ranged from 1 to 7%, respectively and the method was sensitive with limits of detection of 12.3, 18.7, 36.5 and 15.6 ng L⁻¹. To the best of our knowledge, this is the first report of use of surfactant-modified MLDH nanoparticles and its application as adsorbent to pre-concentration of PAEs from environmental water samples prior to instrumental analyses.

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1. Introduction

Recently, due to their large adsorption area and high speed of equilibrium, nanomaterials have attracted attention for preconcentration [1–3]. However, there are several limitations, such as large backpressure and long sample loading time when they are packed into cartridges. To avoid these limitations, a novel (MSPE) method that uses magnetic nanoparticles as sorbents has been developed [4–8]. Most commonly used non-porous magnetic extractants tend to aggregate and agglomerate and be contaminated in complex

matrices, which results in relatively poor adsorption capacities. Therefore, it was necessary to develop a novel MSPE agent which has a larger surface area and enrichment capability as well as better dispersity.

Layered, magnetic double hydroxide (MLDH) nanoparticles with large surface area, provide a low cost, three-dimensional structure that has demonstrated potential for use in drug delivery, catalysis, sensing, molecules and biology [9–15]. Orientation and dimensionality hierarchical structure as well as the large expandable interlayer free space make it easier to be further modified. Making MLDH magnetic facilitated an otherwise difficult solid–liquid separation, while the shell-type mesoporous structure shortens the diffusion path and increases the effective area, thus improving the adsorption capacity and extraction efficiency. Therefore, MLDH

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nanomaterials would be an idea candidate sorbents for MSPE. Fe_3O_4 -LDH has been used as a dissolvable sorbent for extraction of PPCPs and phenolic acids, respectively [16,17]. After adsorption and extraction from water, analytes were eluted from the MLDH by dissolving the double hydroxide layers containing the analytes by changing the pH of the solution. To date, however, there have been few reports on application of MLDH in MSPE by use of hemimicelles/admicelles.

There are primarily two methods for producing MLDH. One is in situ growth, in which a continuous and uniform AIOOH coating is deposited on surfaces of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microspheres by use of a layer-by-layer method of assembly, which is then reacted with a divalent nitrate to produce the magnetic $\text{M}(\text{II})\text{Al}$ -LDH ($\text{M}=\text{Ni}$, Co , Zn , Mg). Previous studies have established possible applications [18,19]. Previously flowerlike $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NiAl}$ -LDH were synthesized via in situ growth then applied for separation of a histidine (His)-tagged green fluorescent protein [18]. The other method, coprecipitation, uses synthesis of magnetic $\text{M}(\text{II})\text{Al}$ -LDH in a single step, without first forming the surface layer of AIOOH [10,12]. However, because the reaction in separate synthesis solutions for at least 10 repetitions each lasting 2 h, the in situ growth of the AIOOH layer was time consuming. In addition, the LDH nanosheet needs to be heated in an autoclave at 100°C for 48 h. The coprecipitation method also requires reaction for about 24 h under continuous heating. Therefore, it was deemed useful to develop a time-saving and simple method to obtain MLDH.

To further increase capacity for extraction and dispersity of nano-materials, their surfaces can be modified with special functional groups. Several groups, including ours, have synthesized various magnetic nanoparticles with various properties and applied them to the separation of target contaminants [3,20,21]. Among the many modified methods, one of the more mature techniques is to use a surfactant to form hemimicelles/admicelles on surfaces of magnetic nanoparticles via self-assembly behavior and then use hydrophobic interactions and electrostatic interactions between micelles and organic pollutants to achieve solid-phase extraction of the target compounds [22–26]. By combining the advantages of hemimicelles/admicelles and MLDH nanoparticles, a new hybrid type of admicelle MSPE sorbents with greater surface areas, chemical stability and good magnetic separability can be obtained.

In this study, a simple method to fabricate well dispersed flowerlike $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg-Al}$ MLDH via ultrasound assisted direct growth of MgAl -LDH nanosheets on the surface of silica spheres is presented. The new MSPE sorbent was obtained by modification of MLDH with surfactant. The outstanding features of this MSPE method are: (1) The synthetic procedure of MLDH is efficient and saves time, uses lesser amounts of reagents, and has an excellent efficiency of production of MLDH without the need to heat the solution during formation; (2) The flowerlike and mesoporous shell structure of the MLDH increases the effective area, reduces lengths of pathways of diffusion, and thus improves extraction capacity and efficiency; (3) Self-assembly of the MLDH coated with surfactant improves capacity for extraction without requiring any special conditions such as high temperature or pressure; (4) Due to the rapidity of separation of the MLDH particles from water, the entire extraction process can be completed within 15 min. To examine the feasibility of this approach, several phthalate ester pollutants (PAEs) were selected as model compounds. Coupling this novel SPE technique with high-performance liquid chromatography for separation and fluorescence for detection, a highly selective SPE HPLC with a PDA-100 ultraviolet detector analytical method was established. The reliability of this method was demonstrated by extraction and analysis of the four target compounds in environmental water samples.

2. Experimental

2.1. Materials and instrumentation

Dipropyl phthalate (DPP), dibutyl phthalate (DBP), dicyclohexyl phthalate (DCP), dioctyl-phthalate (DOP) and tetraethoxysilane (TEOS) were purchased from AccuStandard (New Haven, USA). Standard stock solutions (500 g mL^{-1}) containing these compounds were prepared in methanol and stored at 4°C . Working solutions were prepared daily by appropriate dilution of the stock solutions with water. Sodium hydroxide and hydrochloric acid were guarantee grade reagents (Beijing Chemicals Corporation, Beijing, China). HPLC-grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). Ammonium hydroxide (28%, w/w), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaCl, absolute ethyl alcohol, sodium dodecyl sulfate (SDS), sodium hydroxide, sodium bicarbonate and hydrochloric acid were purchased from Beijing Chemical Reagent Company, without further purification before use. Ultrapure water used in all of the experiments was prepared by using Milli-Q SP reagent water system (Millipore, Bedford, MA, USA).

2.2. Preparation of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg-Al}$ LDH particles

Herein, we present a simple method to fabricate well dispersed $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg-Al}$ LDH via ultrasound assisted direct growth of Mg-Al LDH nanosheets on the surface of silica spheres (Fig. 1). Uniform-sized, magnetite nanoparticles of approximately 200 nm were synthesized and used as the magnetic core that allows rapid separation by use of a magnet [27]. Briefly, 2.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1.0 g sodium citrate and 4.8 g NaAc were dissolved in 80 mL ethylene glycol. A uniform, yellow liquid formed after magnetically stirring for half an hour. The above mixed liquor was then transferred to a Teflon-lined stainless-steel autoclave and heated at 200°C for 10 h. The resultant Fe_3O_4 microspheres were collected, washed with ethanol several times, and dried at 50°C under vacuum.

In order to improve stability of the magnetic core and generate regular LDH shell, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microspheres were obtained through a versatile sol-gel method. In brief, magnetite Fe_3O_4 (0.85 g) was dispersed in a round-bottom flask charged with ethanol (200 mL), water (50 mL) and concentrated ammonia solution (3.60 mL, 28 wt.%). The suspension was ultrasonicated for 30 min (ultrasonic cleaner, KQ-500DE, 500 W, 40 kHz). Then, 2.5 mL of tetraethyl orthosilicate (TEOS) was added drop-wise followed by continuous mechanical stirring for 8 h. The resultant $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microspheres were collected from the reaction mixture under an external magnetic field, washed with ethanol several times, and dried at 50°C under vacuum.

Fig. 1. Schematic illustration of the preparation of surfactants modified $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg-Al}$ MLDH and its application for enrich analytes as SPE sorbents.

Nanoflakes of Mg–Al LDH were perpendicularly deposited onto $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microspheres by use of a sonication method to form $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg–Al LDH}$ (denoted as MLDH). Compared with other methods, the MLDH systems described here that apply ultrasound can be completed within 2 h at room temperature. Also, the procedure for making MLDH uses lesser amounts of reagents, and provided high throughput without heating. A mass of 0.1 g $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microsphere particles were dispersed in 50 mL deionized water, with the pH adjusted to 10 (the pH buffered solution for adjusting was obtained by dissolving 1.28 g Na_2CO_3 and 1.6 g NaOH in 100 mL of a 1:1 (v:v) methanol–water solution. Then 20 mL aqueous solution containing 1.44 mmol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.48 mmol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added drop-wise to the suspension of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ at a rate of 1 mL min^{-1} controlled by peristaltic pump under vigorous stirring and the solution pH maintained at pH 10. The above reaction was under ultrasonication for 1 h, and then products were collected and redispersed in 70 mL of deionized water for further ultrasound dispersion for 1 h. Particles of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg–Al LDH}$ were collected from the reaction mixture under an external magnetic field, and dried at 50°C under vacuum.

2.3. Characterization of adsorbents

Transmission electron microscopy (TEM; H-7500, Hitachi, Tokyo, Japan) was used to observe morphology and sizes of particles of various magnetic nanoparticles. Magnetic properties of materials were acquired by a vibrating sample magnetometer (VSM, LDJ9600, Troy, MI) at room temperature with the magnetic field intensity varied from +20,000 to –20,000 Oe. Fourier transform IR (FTIR) spectra of MLDH and intermediate products were measured by using a Nicolet AVATAR 360 FTIR spectrometer (IR, Nicolet Avatar 360, Waltham, MA). The phase analysis was conducted for each material by using a PANalytical X'pert Pro X-ray diffraction crystal analyzer (XRD, PANalytical, Almelo, Netherlands) with nickel-filtered $\text{CuK}\alpha$ radiation with a scan rate of $4.0^\circ \text{ min}^{-1}$ and scanning range from 10° to 80° . The nitrogen adsorption – Brunauer–Emmett–Teller (BET) adsorption method (ASAP2000V3.01A; Micromeritics, Norcross, GA) was adopted for measuring specific surface areas of materials, and the Barrett–Joyner–Halenda (BJH) method were adopted for measuring pore volume and distribution of pore size of the materials. X-ray photoelectron spectroscopy (XPS) was conducted by applying an ESCA-Lab-200i-XL spectrometer (Thermo Scientific, Waltham, MA) with monochromatic Al $\text{K}\alpha$ radiation (1486.6 eV).

2.4. Solid-phase extraction process

A magnetic field was used to separate solids from suspension during solid-phase extraction. This was similar to that of magnetic nano extracting agent that has been reported previously by our group [22,28]. In brief, 30 mg of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg–Al LDH}$ and 20 mg of SDS were added to 400 mL of phthalate esters (PAEs) water sample under ultrasonication for 30 s and pH was adjusted to 4.5 with 0.1 M NaOH or HCl. The mixture was then placed into a beaker and allowed to equilibrate for 20 min to completely trap target analytes. After reaching equilibrium, a Nd–Fe–B rectangle strong magnet ($150 \text{ mm} \times 130 \text{ mm} \times 50 \text{ mm}$) was deposited at the bottom of the beaker to isolate $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg–Al LDH}$ that adsorbed target compound from the suspension. After about 5 min, the suspension became clarified and the supernatant was decanted. Finally, pre-concentrated PAEs analytes were eluted from the MLDH sorbent with 12 mL (4 mL for each time) of acetonitrile. The eluate was concentrated to 0.5 mL with a stream of nitrogen, and 20 μL of this solution was injected into HPLC system for analysis.

2.5. Analysis of HPLC

Identification and quantification of analytes was performed by use of a liquid chromatography system (Dionex, Sunnyvale, CA USA). The HPLC equipment included a DIONEX P680 pump, a TCC-100 thermostated column compartment, an ASI-100 automatic sampler and a PDA-100 ultraviolet detector. Chromatographic separation was conducted by use of in the Diamonsil C18 column ($250 \text{ mm} \times 4.6 \text{ mm}$; particle size, $5 \mu\text{m}$) (Dikma Technologies, Beijing, China). The detector was set to a wavelength of 226 nm. Separation was achieved by use of gradient elution where 50% aqueous acetonitrile and pure acetonitrile were used respectively as mobile phase B and A, with 1 mL min^{-1} for velocity of flow. The procedures of gradient elution were as follows: Mobile phase B was remained at 40% in the first 15 min; then it increased to 100% within 10 min, and kept at that value for 10 min before the mobile phase B was returned to its initial state within 3 min.

2.6. Sample collection and quality control

Samples of surface waters were collected from different districts of Beijing, China in October 2014. River water was collected from 10 cm under the surface of the Beiyun and Juma Rivers in Beijing. Samples of tap-water were taken from laboratory of Research Center for Eco-environment Science, Chinese Academy of Science, Haidian District, Beijing. Water was filtered with $0.22 \mu\text{m}$ of nylon filter membrane and then stored in the refrigerator at 4°C . Measurements were completed within one week. In order to eliminate possible contamination of containers or equipment in the processes of sampling and conducting experiments, all containers and equipment should be rinsed with methyl alcohol for more than 3 times, and then dried at 150°C under vacuum. Blanks were performed with ultrapure water following similar procedures, and none of the target PAEs was detected in the result.

3. Results and discussion

3.1. Particle size and morphology of materials

TEM and SEM images depict the size and structure of nanoparticles. Prepared magnetic Fe_3O_4 possessed a homogeneous spherical structure with a mean diameter of 200 nm and disperse well in aqueous solution (Fig. 2A). After being coated with a smooth silica layer, typically core-shell $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microspheres with a thin silica layer of 25 nm in thickness were obtained (Fig. 2B). $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg–Al LDH}$ particles were composed of a compact core and a lower density shell (Fig. 2C). The $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg–Al LDH}$ microspheres had a uniform lamellar, flowerlike structure with numerous nanoflakes perpendicularly grafted to the surface of SiO_2 , which leaves open space among them, with a gap between nanosheets sufficient to provide positions for subsequent modifications. These are the correct conditions to allow further reactions with analytes.

3.2. Analysis of crystalline phase for materials

Crystal phases of materials were investigated by use of XRD analysis. All the curves showed that the crystalline structure of the magnetic core at different stages of formation was face-centered cubic Fe_3O_4 (JCPDS card 19-629) (Fig. 3A) [29]. After being coated by the layer of silica, the characteristic diffraction peaks of amorphous SiO_2 were increased, which indicated that the surface of Fe_3O_4 NPs had formed the dense outer layer of SiO_2 . On the curve of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mg–Al LDH}$, the greater peaks at $2\theta = 10.25^\circ$, 23.01° , 38.43° and 61.77° can be ascribed to typical and highly crystallized Mg–Al LDH shell [9].

Fig. 2. TEM and SEM images of (A) Fe_3O_4 , (B) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (C) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$.

Fig. 3. XRD spectra of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (c) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ (Diffraction Peaks: ●: Fe_3O_4 ; *: LDH; ○: Amorphous Silica) (A) and XPS curve of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ (B).

3.3. XPS spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$

Concentrations of metals on surfaces of the particles were obtained from the XPS analysis. The XPS curve for $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ had characteristic peaks of Mg1s and Al2p (Fig. 3B), which further indicated that the prepared nanomaterials had the typical core-shell structure; surface of the materials was the double metal layer structure of Mg-Al, proving the successful synthesis of magnetic Mg-Al LDH, which was consistent with the analysis of the surfaces by use of TEM, SEM, XRD and FTIR.

3.4. Infrared spectra of all the materials

Functional groups on surfaces were investigated by use of infrared spectra. In the infrared spectra of Fe_3O_4 , the absorption peak at 1400 cm^{-1} was due to COO^- which was modified on the surface of Fe_3O_4 , and the peak at 1626 cm^{-1} was due to overlapping vibrations of COO^- and O-H groups [30,31]. The peaks observed at 585 and 3434 cm^{-1} were due to stretching vibrations of Fe-O and O-H groups [32]. The peak at 585 cm^{-1} was observed for all three materials; however, the strengths became less as they were coated by layers of SiO_2 and LDH, which was mainly caused by core-shell structures of the prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$. Compared with the standard infrared spectrum of Fe_3O_4 , magnetic silica particles of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and magnetic particles with double metal hydroxides of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ synthesized during this project, had more characteristic peaks of Si-O keys at 1080 cm^{-1} , but the absorption peaks of COO^- disappeared at the same time,

which indicated that the iron core of Fe_3O_4 was completely covered [8]. With introduction of the LDH layer, strengths of peaks at 3434 and 1626 cm^{-1} increased. Simultaneously, a new absorption peak was caused by the NO_3^- group. It was also shown that $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ materials exhibited a typical Mg-Al LDH feature that was the ideal core-shell structure and surface for adsorption of organic molecules.

3.5. Magnetic properties of materials

Magnetic properties of the as-synthesized microspheres prepared for MSPE at different stages all exhibited typical superparamagnetism, and the remanence and coercive force on the magnetization curve were almost zero. With increase of non-magnetic components, saturation magnetization of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ decreased slightly compared with that of Fe_3O_4 . Maximal magnetization of prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ was 29.62 emu g^{-1} , which fully met the requirements for magnetic separation during SPE for organic molecules. Superparamagnetism of the extracting agent MLDH, which fully dispersed in the water in the absence of an external magnetic field, allowed it to be rapidly scavenged in the presence of a magnetic field.

3.6. Specific surface area and distribution of pore size of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$

The specific surface area and pore size of magnetic sorbents can affect efficiency of extraction. Curves for adsorption and desorption of N_2 by particles of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ exhibits IV-type

Fig. 4. Nitrogen adsorption curve (A) and pore size distribution curve (B) of Fe₃O₄@SiO₂@Mg-Al LDH.

with a H3-type hysteresis loops, indicating that the pore size is close to being mesoporous (Fig. 4C). The curve of pore size distribution had a sharp peak (Fig. 4B), which indicated that the pore structure of mesoporous materials was rather clear and neat, and that most sizes of mesoporous were uniform with fewer micropores. The special surface area, pore volume and pore diameter of MLDH were calculated to be 354.82 m² g⁻¹, 1.63 cm³ g⁻¹, and 2.73 nm, respectively.

3.7. Effect of pH on extraction of PAEs

Hydrogen ion activity of the solution, represented by pH, might affect the type and density of charges on the surface of nanomaterials, as well as the state of aggregation of surface active agent. Therefore, adsorption of target PAEs might have an effect on the extracting agent. Anionic, surface-active agent was absorbed onto the oxide surface through electrostatic attraction, and the charge density on the oxide surface had a significant effect on the process of self-assembly on the ionic surface-active agent. The charge density

on the oxide surface changed as a function of pH. When the pH was less than the isoelectric point of the oxide, the oxide surface carried a net positive charge; if the pH was greater than the isoelectric point, the oxide surface carried a net negative charge. The isoelectric point of Fe₃O₄@SiO₂@Mg-Al LDH was approximately 11 [33]. Thus, under neutral or acidic conditions, surfaces of the extracting agent carried a stronger positive charge, such that the hydrophilic ends with negative charge on the sodium dodecyl sulfate (SDS) of the anionic surface active agent were strongly adsorbed onto the surface of the metal oxide particles by electrostatic attraction, which could then form mixed micelles through absorption and self-assembly. When the pH was greater than 4, efficiency of extraction of PAEs was inversely proportional to pH (Fig. 5A). This was because the surface of Mg-Al LDH carried a net positive charge, and the isoelectric point was approximately 11, such that with the greater pH, it was nearer the isoelectric point, such that the density of surface charge gradually decreased [33]. Effective absorption of SDS micelles decreased, so that efficiency of extraction was reduced. When pH was 3, efficiency of extraction was reduced as well. This was because when pH was less than 4, LDH would slowly dissolve, thereby affecting the effective surface area of MLDH, which also led to lesser adsorption of surfactant micelles, as well as efficiency of extraction [34]. Thus, to offset these contradictory forces and optimize conditions for adsorption a pH of 4.5 was chosen in subsequent experiments which were designed to investigate the effects of other conditions on efficiency of extraction.

3.8. Effect of amount of MLDH on efficiency of extraction

Large specific surface area and extraction capacity were both advantages of the use of a solid-phase nanomaterial as an extraction agent. Effects of amount Fe₃O₄@SiO₂@Mg-Al LDH on efficiency of extraction was investigated by use of static equilibrium experiments similar to those described above. In this experiment, MLDH and SDS were added at a defined proportion (3:2), and then recoveries of various target chemicals were measured (Fig. 5B).

Fig. 5. Effect of pH on recovery of extraction (A); Effect of MLDH amount on efficiency of recovery of extraction (B); Effect of ionic strength on extraction (C) and Effect of humic acid on efficiency of extraction (D).

In general, efficiency of extraction was proportional to amount of MLDH used. Efficiency of extraction of PAEs gradually increased with the amount of MLDH added to a maximum at 25 mg MLDH. For this reason 25 mg of MLDH was chosen as the optimal amount for use in subsequent experiments. The optimal amounts of semi-micelle/extracting agent used as the solid phase was less than that reported by other researchers [22,23,28,35,36]. In fact, the optimal amount of extracting agent determined in this study was 1/20 of that of the amount of Al_2O_3 and SiO_2 particles modified by surfactant that was observed in previous studies [28]. Also, when the results of this study were compared with those of previous studies using nano-particles of Fe_3O_4 , the amount of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg}-\text{Al}$ LDH was only a quarter of the amount required previously, which demonstrated the greater efficiency of MLDH as the solid-phase extraction agent [23].

3.9. Effect of SDS amount on extraction recovery

Efficiency of recovery of spiked materials was initially directly proportional to the amount of surfactant, up to a maximum, thereafter the efficiency of extraction was inversely proportional to the amount of surfactant added. This was because when surfactant was not added, the efficiency of extraction PAEs by MLDH was inversely proportional to the amount of, semi-micelles, mixed-micelles and micelles formed on the surface of the MLDH. Although when an excessive amount of SDS was added, the extra SDS would be dispersed and remain in the aqueous phase, thereby creating a competitive adsorption with that of MLDH, which led to the lesser efficiency of extraction. Since the SDS is an anionic surfactant and PAEs are anionic compounds, the interaction between SDS–MLDH and PAEs was through hydrophobic groups, with few if any electrostatic interactions. Thus, in the phases of semi-micelles, mixed-micelles and micelles, they could be absorbed with target chemicals. Therefore, a larger range of concentrations of SDS was added. Greater efficiency of extraction was observed when 10–50 mg SDS/30 mg MLDH was used. Finally, 20 mg SDS/30 mg MLDH was chosen for the subsequent experiments.

3.10. Effect of adsorption equilibrium time on extraction

Shorter absorption path is another advantage of nano SPE agent, which helps equilibrium achieved quickly. This characteristic was demonstrated by results of studies with the mesoporous magnetic LDH, extraction agent. To ensure sufficient contact between MLDH, SDS, and PAEs were evenly dispersed in aqueous solutions by use of ultrasonic treatment, which formed a homogeneous, turbid liquid. The extraction agent has a strong adsorption capacity for PAEs and a short diffusion path so the absorption equilibrium will be achieved quickly. This was demonstrated by the observation that the effect of equilibrium time to the efficiency of extraction was relatively small. Efficiency of extraction was more than 90% at equilibrium, which was reached within 5 min. To insure efficient extraction with the minimum time, an optimum time for extraction of 10 min was selected for use in subsequent experiments.

3.11. Effect of resolving condition on extraction

PAEs adsorbed onto solid-phase nano extraction agent can be eluted by a small amount of organic solvent. Volumes and concentrations of acetonitrile and methanol as eluents were investigated. Acetonitrile had better elution capacity than did methanol. For instance, 12 mL of acetonitrile ($4\text{ mL} \times 3$ times) can elute analytes off MLDH. Finally, 12 mL acetonitrile ($4\text{ mL} \times 3$ times, processed with ultrasound for 10 s during the elution) was selected for elution of target analytes.

3.12. Effect of solution volume on extraction

Breakthrough volume is a major parameter in SPE and preconcentration of samples. It significantly affects preconcentration factor, reproducibility and reliability of results. Efficiency of extraction was inversely proportional to volume of eluent in the range of 100–550 mL. Extraction recovery for DBP, DCP, and DOP from water being extracted with a set mass of MLDH (30 mg), but always greater than 85%, which demonstrated that the capacity for absorbance was dynamic and the conditions selected sufficient to allow for optimal recovery of analytes. A volume of 400 mL was chosen for use in subsequent studies. Target analytes adsorbed onto SDS–MLDH were then eluted by use of acetonitrile. By concentrating the eluents (12 mL of acetonitrile solution) to 0.5 mL with nitrogen flow, a preconcentration factor of 800 was achieved.

3.13. Effect of ionic strength on extraction

Ionic strength can change the chemical activity of charged ions and molecules in solution as well as that of the adsorbent, and then effects the adsorption efficiency. To investigate the effect of ionic strength on efficiency of adsorption a range of concentrations (0.0–0.2 M) of NaCl were studied (Fig. 5C). Increasing ionic strength improved the hydrophobic effect between the SDS hydrophobic grouping on the extraction agent and PAEs, which will improve adsorbance. Maximum efficiency was observed at approximately 0.05 M, while greater ionic strength increased viscosity of the solution and slowed migration of target analytes to the solid phase, which lead to lesser efficiency of adsorption. Thus, an ionic strength of 0.05 M was selected for use in subsequently experiments.

3.14. Effect of humic acid on efficiency of extraction

Humic acids (HAs) and fulvic acids (FAs), are typical natural organic matters (NOM) that are common in environmental samples of water. Concentrations of HA/FA in environment samples are in the range $0.2\text{--}50\text{ }\mu\text{g mL}^{-1}$ [8]. FAs are generally smaller with nominal molecular mass of greater than 500 daltons while HAs are typically greater than 500 Da in molecular mass. Many organic compounds can be adsorbed onto HAs due to the fact that the quinonyl, carboxyl, and phenolic hydroxyl groups on the polyphenolic structural framework that consists of both alkyl and aromatic groups. HAs can be adsorbed onto the surface of solid-phase adsorbents of extracting organics from water. They can thus block these sites of adsorption and interfere with extraction of target analytes. Efficiency of extraction was found to be inversely proportional to the concentration of HA/FA which suggest that there is competitive adsorption between the HA/FA and target, organic analytes for sites on the MLDH sorbent (Fig. 5D). This can be explained by the fact that, under acidic conditions (pH4.5), HA/FA carry net negative charges and MLDH carries a net positive charge. Thus, HA/FA will be adsorbed by electrostatic attraction onto the extraction agent and therefore occupy potential sites of adsorption to SDS. This results in target analytes, such as PAEs to combine with free SDS in water, and results in lesser recoveries. Also, it is possible that, due to the strong adsorbent capacity of HA/FA, PAEs directly react with free HA/FA in water which results in poorer efficiencies of extraction. We expect that the extraction of PAEs onto MLDH would not be affected in water samples in which concentration of natural organic matter is less. Magnetic extraction sorbent with strong anti-interference capacity will be developed in our further study.

Table 1

PAEs detecting concentration and standard recovering concentration in several environment water samples.

Water sample	Analytes	Detected ^a (ng mL ⁻¹)			Recovery ^b (%) ± RSD	
		Blank	0.5 ng mL ⁻¹ spiked	5 ng mL ⁻¹ spiked	0.5 ng mL ⁻¹ spiked	5 ng mL ⁻¹ spiked
Tap water	DPP	ND ^c	0.466	5.01	93 ± 6	100 ± 3
	DBP	ND	0.478	4.65	96 ± 2	93 ± 4
	DCP	ND	0.512	4.73	102 ± 4	95 ± 5
	DOP	ND	0.501	3.19	100 ± 3	64 ± 6
Beiyun river	DPP	0.07	0.493	4.41	99 ± 2	88 ± 1
	DBP	<LOQ	0.490	5.08	98 ± 1	101 ± 3
	DCP	ND	0.428	5.06	86 ± 4	101 ± 2
	DOP	ND	0.504	4.11	101 ± 5	82 ± 5
Juma river	DPP	<LOQ	0.428	3.47	86 ± 6	69 ± 4
	DBP	<LOQ	0.507	3.94	101 ± 3	79 ± 5
	DCP	ND	0.461	5.09	92 ± 4	102 ± 3
	DOP	ND	0.501	3.14	100 ± 5	63 ± 6

^a Three parallel determination results.^b RSD of three determinations.^c Not detected.**Table 2**

Linearity range, calibration equations, correlation coefficient and limit of detection of the working curve.

Analytes	Linearity range (ng mL ⁻¹)	Calibration equations	Correlation coefficient (r^2)	RSD (%)	LOD (ng L ⁻¹ , S/N = 3)
DPP	0.1–10	$y = 2.01x - 0.464$	0.9897	6.867	12.3
DBP	0.1–10	$y = 1.286x - 0.3123$	0.9864	6.976	18.7
DCP	0.1–10	$y = 1.0856x - 0.2398$	0.9852	3.379	36.5
DOP	0.1–10	$y = 0.5614x + 0.0988$	0.9925	2.175	15.6

Table 3

Comparison of the present method with other sorbent-based methods for the determination of PAEs.

Method	Extraction technique ^a	Sorbent/cartridge	LOD (ng L ⁻¹)	RSD (%)	Sample volume (mL)	Sorbent amount (mg)	Extraction time (min)	Ref.
HPLC–UV	AHMSPE	Fe ₃ O ₄ /meso-SiO ₂	12–32	2.3–5.4	250	100	20	[36]
HPLC–UV	MSPE	ALG@C ₁₈ –Fe ₃ O ₄ –TN	11–36	0.3–11	500	70	50	[20]
HPLC–UV	MSPE	Fe ₃ O ₄ @C ₁₈ @Ba ²⁺ –ALG	–	1–9	500	100	35	[37]
HPLC–UV	EPS	CTAB–TN	–	0.4–7	250	100	>60	[2]
GC–MS	DI-SPME	MWCNTs–PPy	50–100	9.3–12.1	10	–	25	[38]
GC–MS	MSPE	Fe ₃ O ₄ @PPy	6–68	3.4–11.7	20	30	15	[39]
HPLC–UV	MSPE	Fe ₃ O ₄ @SiO ₂ –G	70–100	2.7–6.1	100	15	10	[6]
HPLC–UV	AHMSPE	MLDH–SDS	12–36	1–7	400	30	10	This work

^a AHMSPE, admicelles/hemimicelles magnetic solid-phase extraction; MSPE, magnetic solid-phase extraction; EPS, extraction by packed sorbent in cartridge column; DI-SPME, direct immersion solid-phase microextraction.

3.15. Relevant parameters of MSPE–HPLC analysis methods for PAEs

By using the optimized solid-phase extraction methods (Table 1), based on magnetic solid-phase extraction–chromatography, PAEs were extracted from water. The linear working range of the standard curve is 0.1–10 ng mL⁻¹, with a coefficient of determination (r^2) of >0.985. The limit of detection (LODs) for analytes, defined as 3 times of SNR (S/N = 3) for DPP, DBP, DCP, and DOP were 12.3, 18.7, 36.5, and 15.6 ng L⁻¹, respectively. The relative standard deviation (RSD) of the method was 2–7%.

3.16. Methods validation with field samples

To examine the utility of the method, concentrations of DPP, DBP, DCP, and DOP of several environment water samples were determined by use of the optimized method (Table 2). Concentrations of PAEs in the Beiyun and Juma River were low and none of the PAEs were detected in samples of Beijing tap water. The recovery

Fig. 6. MSPE–HPLC–UV chromatogram of PAEs in the Juma River water sample and its standard sample. (a) Juma River water sample; (b) add 0.50 ng mL⁻¹ of analyte in the Juma River sample; (c) add 5.0 ng mL⁻¹ of analyte in the Juma River sample and (d) blank sample. 1, DPP; 2, DBP; 3, DCP; 4, DOP.

of DPP, DBP, DCP, and DOP from three water samples are 69–101%, 79–101%, 86–102%, and 63–100%, respectively, with RSD of 1–6% (Fig. 6).

To compare the present method with other sorbent-based extraction techniques used for the determination of PAEs, analytical performance data of the methods have been summarized in Table 3. The LOD of the proposed method was lower than most of those obtained by other HPLC-based techniques. Compared to cartridge, the procedure for preconcentration was simplified and time to complete the extraction was lesser. To pretreat 400 mL of water samples, by use of MLDH adsorbents required only 10 min. The enrichment factor has up to 800 with 30 mg of MLDH.

4. Conclusion

The method combines the advantages of nanometer/mesoporous materials, self-assembly modification, and magnetic separation technology. Compared with solid-phase extraction that is based on modification of surface active agents, the advantages of this method are: (i) Rapid synthesis of MLDH and milder conditions for formation, high throughput, low cost; (ii) The mesoporous materials have a large specific surface area and adsorption capacity is high; the amount of extraction agent required is small (need only 30 mg MLDH and 20 mg SDS); (iii) Magnetic separation can be achieved in a short time; and the speed with which large volumes of water from the environment is greatly improved. The analytical method developed based on these adsorbents is stable, reproducible, and can be used to simultaneously process multiple samples. The mesoporous diameter can be controlled by methods used in its preparation to give the material some size exclusion which allows the micromolecule pollutant to enter and keeps the macromolecule such as protein, nucleic acid, and HA out. For complex samples of water from the environment, the method can be adapted for use with a range of organic pollutants.

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