Magnetic polyamidoamine dendrimers for magnetic separation and sensitive determination of organochlorine pesticides from water samples by high-performance liquid chromatography

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ABSTRACT

Organochlorine pesticides (OCPs) have received much attention due to their toxicity. Reliable methods to monitor their residues in the environment are needed. Here, magnetic polyamidoamine dendrimers were prepared by co-precipitation, Michael addition, and amidation. The magnetic polyamidoamine dendrimers demonstrated good adsorption ability for OCPs—this feature was utilized to construct a sensitive tool for monitoring OCPs in water samples. The proposed method provided remarkable linearity from 0.1 to 500 μg/L and satisfactory limits of detection from 0.012 to 0.029 μg/L. The spiked recoveries of the four target analytes were 91.8%–103.5% with relative standard deviations less than 4.5%. The magnetic materials had good reusability. The results indicated that the resulting method was an efficient, easy, rapid, economical, and eco-friendly tool for monitoring OCPs in aqueous samples.

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Introduction

Pesticides are extensively used in modern agriculture to increase crop protection and yields. However, their impact is sub-par once they enter soil and water (Rejczak and Tuzimski, 2017). Insecticides and herbicides are especially important because of their effects on pests (Rani et al., 2017).

Organochlorine pesticides (OCPs) are used broadly, and dichlorodiphenyltrichloroethane (DDT) is a typical member of this class. DDT is a persistent organic pollutant and endocrine-disrupting substance. DDT and its isomers dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) are stable and liposoluble endocrine disrupter chemicals (EDCs) with neurotoxicity, genotoxicity, and carcinogenicity. This results in human health effects due to bioaccumulation and biomagnification with even worse ecological effects (Kim et al., 2017; Stehle et al., 2018). For example, DDT can remain in the body for 50 years and lead to serious diseases and even death (Akhil and Sujatha, 2012). Thus, it has been either restricted or banned in many western countries since 1972 (Yadav et al., 2015). The Ministry of Environmental Protection

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of China has also forbidden the production and usage of DDT since 2009. However, the large consumption of DDT in the past implies that its residuals still exist in the environment. Hence, effective and accurate technologies for measuring OCPs are urgently needed.

Many analytical methods have been established for analysis of OCPs based on different principles including gas chromatography-mass spectrometry (GC-MS). GC-MS is a favorite analytical method for OCPs due to its simplicity, rapidness, high sensitivity, and selectivity (Durak et al, 2020). However, its running cost is very expensive. Liquid phase chromatography (HPLC) is a common and important alternative because of its rapidness, effectiveness, sensitivity, and low cost (Farooqi et al., 2015).

Environmental samples have complicated matrices and the analytes are present at low concentrations (Liu et al., 2016). Hence, sample pretreatment is crucial to achieve effective separation and enrichment. Many methods have been successfully developed for the pretreatment of OCPs—two representative methods are solid phase extraction (SPE) (Marsin et al., 2020) and liquid phase extraction (LLE) (Mondal et al., 2018). However, they suffer from the consumption of toxic organic solvents and more time. Recently, some new miniaturization micro-extraction technologies, including dispersive liquid-phase microextraction (DLPME), microwave-assisted extraction combined with solid phase extraction (MAE/SPE), and dSPE, have been introduced for effective enrichment of pollutants (Fang et al., 2012; Deme et al., 2014; Nadaf et al., 2016).

Magnetic solid-phase extraction (MSPE) is an important branch of dSPE which has achieved extensive applications in environmental applications and other fields, since it was introduced by Šafařňková and Šafařňk (1999). Here, the magnetic adsorbents are fully dispersed in the sample solution increasing the contract area between the adsorbents and targets. Adsorbents can then be rapidly isolated using an external magnetic field. They can be reused after elution, and this approach is affordable, fast, easy, and efficient (Hubetska et al., 2018).

Magnetic or magnetically modified materials play a key role in MSPE. Magnetite nanoparticles (MNPs) are usually used as the core materials. To increase the enrichment factor, MNPs often must be modified or functionalized with various materials, such as metal−organic frameworks (MOFs), carbon nanotubes, graphene, and polymer materials (Zhou et al., 2016; He et al., 2019).

Polyamidoamine (PAMAM) dendrimers have received wide interest in the past few decades due to its special structure and properties. PAMAM dendrimers earn three-dimensional (3D), monodispersed, highly branched, and symmetrical structures. Thus, they have been employed in many fields, such as gene diagnosis, drug delivery, and ultrasensitive sensors (Li et al., 2018a; 2018b; Zhang et al., 2018). Furthermore, high-density functional groups facilitate heavy metal ion complexation (Hayati et al., 2018). PAMAM dendrimers and its decorated materials have been used to adsorb Cu^{2+}, Pb^{2+}, Cr^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} (Sohail et al., 2020; Yuan et al., 2020). In addition, PAMAM dendrimers with huge hydrophobic cavities or modified functional groups may adsorb organic pollutants by hydrophobic interaction, hydrogen bonds, and intermolecular forces (Sajid et al., 2018). Therefore, this is an excellent attempt to combine the merits of PAMAM dendrimers and MNPs.

Here, MSPE coupled with HPLC-UV based on magnetic PAMAM dendrimers was developed for the detection of four ultra-trace OCPs. The parameters, such as generation of dendrimers, adsorbent amount, sample pH, adsorption time, ionic strength, type and volume of eluent, and sample volume, were investigated.

1.   Experimental

1.1.   Reagents and instruments

The stock standard solutions of OCPs at 1000 μg/mL in acetone including p,p'-DDT, o,p'-DDT, p,p'-DDE and p,p'-DDD were supplied from Beijing Putian Genesis Biotechnology Co., Ltd. (Beijing, China), which were stored at 4 °C in darkness. The mixed stock standard solution was prepared in methanol and further diluted as working solution. The other reagents and main instruments for characterization and analysis are as the same as that reported (Wu et al., 2019). A Shimadzu LC-20 system with an Eclipse XDB-C18 column (150 × 4.6 mm, 5 μm) was used for the separation and analysis. The mixture of methanol and water (88:12, V/V) was used as the mobile phase and the flow rate was kept at 1.0 mL/min. The column temperature was set at 30 °C and the detection wavelength was set at 238 nm. Additionally, the injection volume was set at 50 μL.

MNPs-G0 was prepared by the same procedure by Wu et al. (2019). MNPs-Gn was prepared by a divergent method with iterative sequence co-precipitation, Michael addition and amidation reactions with MNPs-G0 as the primary core. Moreover, all synthetic procedures were carried out under nitrogen protection and in dark conditions. The information of synthesis of the MNPs in detail is provided in supplementary materials. The synthetic procedure of MNPs-Gn is demonstrated in Fig. 1.

1.2.   MSPE procedure

Initially, 80 mg of magnetic PAMAM dendrimers was mixed with 60 mL aqueous sample with OCPs spiked at 20 μg/L. The solution pH was adjusted to pH 7, and the ionic strength was adjusted with NaCl to 25% (W/V). The mixture was then oscillated for 40 min at 200 r/min and 25 °C. The supernatant was removed after separation using a strong external magnet. The target analytes were desorbed from the adsorbent with 4.5 mL ethanol for 6 min. The eluent was blown to near dryness with a mild nitrogen stream at 40 °C, and the residue was diluted to 500 μL using methanol; then, 50 μL was taken for HPLC analysis.

2.   Results and discussion

2.1.   Material characterization

The fabricated magnetic PAMAM dendrimers were characterized by TEM, EDS, XRD, FTIR, and EA (the MNPs-Gn mentioned here was synthesized by route 1). Fig. 2A−D displays TEM images of MNP-G0 and MNPs-G2.0. Fig. 2A and B shows the images of MNPs-G0 at different magnifications, while Fig. 2C and
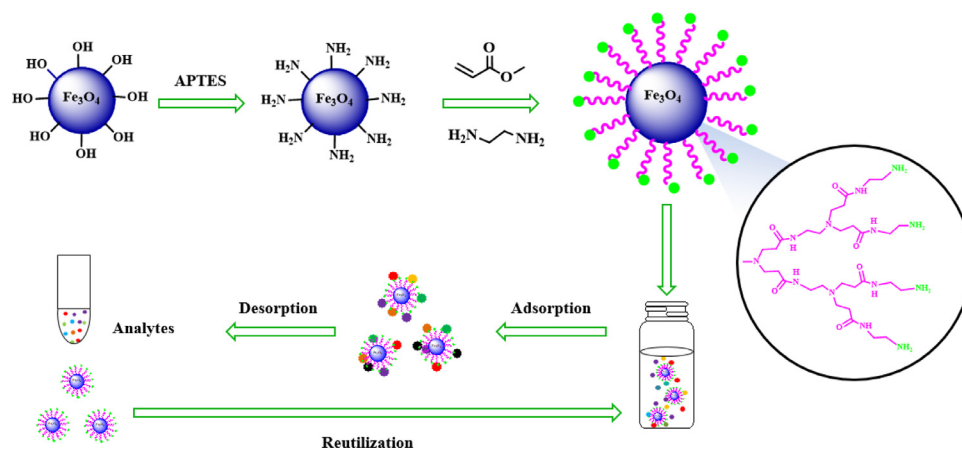
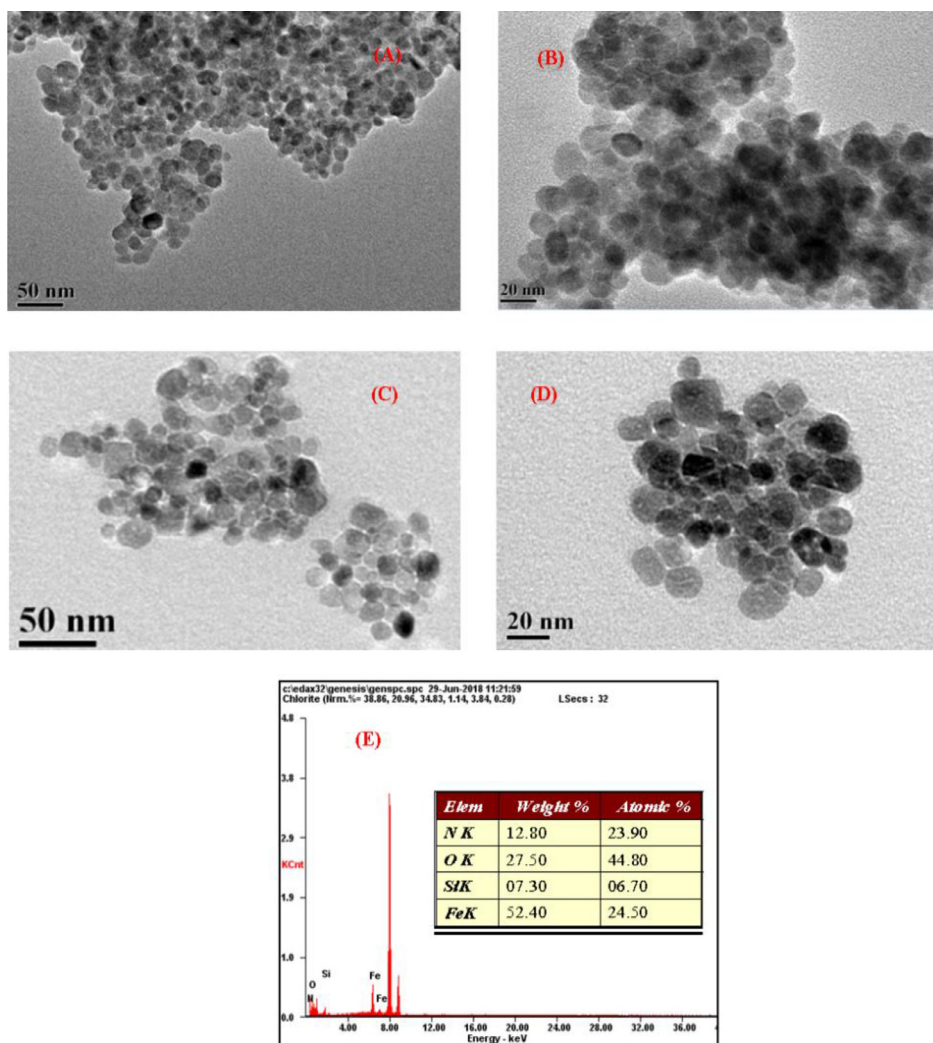Fig. 1 – Synthetic procedure of MNPs-Gn and representative MSPE procedure.

Fig. 2 – (A) and (B) TEM images of MNPs-G0 under different magnifications; (C) and (D) TEM images of MNPs-G2.0 under different magnifications; and (E) EDS image of MNPs-G2.0.
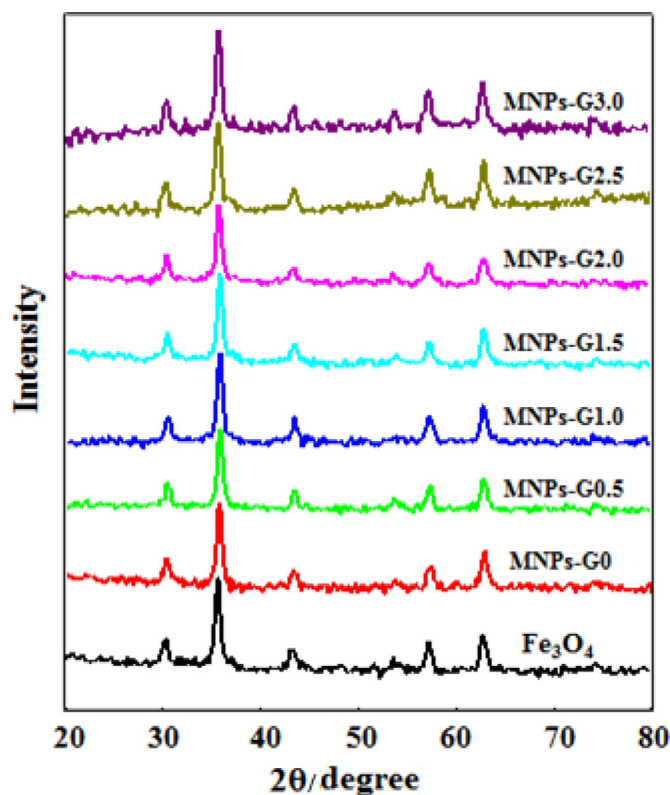
Fig. 3 – XRD patterns of MNPs and MNPs-Gn.

D describes the images of MNPs-G2.0. Compared with MNPs-G0, MNPs-G2.0 with a spherical shape were better dispersed due to the steric-hindrance effects and electrostatic repulsive interactions after the PAMAM coating (Wang et al., 2016). The mean diameter of MNPs-G0 was statistically determined to be ca. 10.8 nm, while MNPs-G2.0 was ca. 13 nm. The EDS spectrum in Fig. 2E suggests that MNPs-G2.0 contained Fe, Si, N, and O elements; this offers further evidence for successful grafting of PAMAM onto the surface of the magnetic materials.

The crystal structure of bare MNPs and MNPs-Gn was characterized by XRD, and Fig. 3 shows XRD patterns. The six strong special diffraction peaks at $2\theta = 30.3°, 35.3°, 43.0°, 53.6°, 57.2°$, and $62.8°$ were due to crystal indexes of (220), (311), (400), (422), (511), and (440) of Fe_3O_4, which affirmed the cubic spinel phase of naked MNPs (Fig. 3) (Murugan and Jebaran-jitham, 2015). Moreover, there was no significant change in the XRD peak characteristics of MNPs in the MNPs-Gn after decoration of PAMAM dendrimers, indicating that the crystal structure was not changed during this processes.

Fig. 4 shows the FT-IR spectra of the materials. The typical absorption peaks at 571 cm^{-1} and 988 cm^{-1} represent Fe−O and Si−O bonds, respectively. The characteristic peak at 3430 cm^{-1} suggested the stretching vibration of the N-H group. Moreover, the absorption peak at 1630 cm^{-1} was related to bending vibration of the N-H group and stretching vibration of the CO-NH group. These peaks confirmed the primary amine and amide bond. In addition, two characteristic bonds at 2927 cm^{-1} and 2847 cm^{-1} agreed with the symmetric and asymmetrical stretching vibration of C-H, confirming that alkyl groups were observed. Notably, the peak
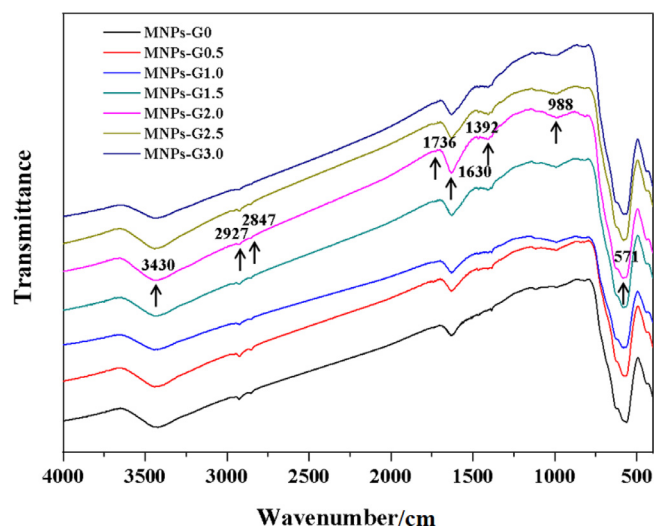

Fig. 4 – FT-IR spectra of MNPs-Gn.

at 1392 cm^{-1} described the deformation vibration of the C-H group that became much stronger along with an increase in PAMAM dendrimer generation. Another interesting finding was that the adsorption peak at 1736 cm^{-1} —which describes the stretching vibration of C=O in the ester groups—existed in the spectra of MNPs-Gn with a half-generation PAMAM dendrimers. This characteristic bond disappeared or weakened in the spectra of MNPs-Gn with full-generation PAMAM den-

drimers (Yu et al., 2018). These observations confirmed that MNPs were successfully modified with PAMAM dendrimers.

Elemental analysis of MNPs-G0 and MNPs-G2.0 were performed, and the results showed that the contents of carbon (C), hydrogen (H), and nitrogen (N) of MNPs-G0 and MNPs-G2.0 were 0.88%, 0.58%, 0.22%, and 1.4%, 0.72%, and 0.27%, respectively. In contrast to MNPs-G0, the content of the three elements in MNPs-G2.0 increased, which confirmed the successful introduction of PAMAM on MNPs-G0.

2.2.　*Optimization of MSPE parameters*

Four synthetic routes were designed to screen materials with good enrichment efficiencies. All of the materials offered higher extraction efficiencies, except those from route #4 (Fig. 5A). This might be due to more side effects including intramolecular cyclization, incomplete Michael addition, and retro-Michael reactions occurring at 50 °C in the procedure of PAMAM grafting. Besides, the synthesis of materials by route #1 was simple and fast. Thus, route #1 was used as the synthetic scheme of the subsequent experimental materials.

The impact of PAMAM generation on enrichment was studied next. The results are shown in Fig. 5B and suggests that the recoveries of OCPs increased with increasing PAMAM generations to MNPs-G2.0. The recoveries of p,p'-DDT and p,p'-DDD slightly increased, and the recoveries of the other two OCPs slowly decreased. Based on all parameters, the best extraction performance was obtained with MNPs-G2.0. It is quite probable that the number of special functional groups and inner cavities increased with PAMAM generation. Thus, the adsorption capacity increases. In contrast, the steric-hindrance effect and intra-molecular crosslinking generated in higher-generation PAMAM dendrimers decrease the recoveries. Song and Zhu reported similar results in the adsorption of heavy metal ions (Song et al., 2017; Zhu et al., 2018). Based on these results, MNPs-G2.0 was used for subsequent experiments.

There is no doubt that eluent was crucial in the desorption process. Herein, five appropriate solvents, including methanol, ethanol, acetonitrile, acetone, and dichloromethane, were evaluated to obtain satisfactory recoveries. Fig. 5C shows good eluting performance with ethanol and acetonitrile as the eluting solvent; the eluting performance of methanol, acetone, and dichloromethane was very poor. The eluting performance of ethanol for all of the four OCPs was a little better than that with acetonitrile. Therefore, ethanol was used as the final desorption solvent.

Both the amount of adsorbent and adsorption time are essential in a MSPE process. In this experiment, they were optimized in the range of 20−120 mg and 10−50 min, respectively. Fig. 5D shows the results from different amounts of adsorbent. The enrichment efficiencies of the OCPs quickly increased along with increased adsorbent dose because more adsorbents were used and more active sites and functional groups were available for adsorption. When the amount of adsorbent was more than 80 mg, the expected higher recoveries were not observed because the adsorption rate of the OCPs was similar to the desorption rate of OCPs from the adsorbent. The effect of adsorption time is shown in Fig. 5E, which indicated that the recoveries of OCPs increased quickly in the first 20 min and then slightly up to 40 min. Further increases in

time decrease the recoveries of p,p'-DDD with no change for the other three OCPs. Thus, 80 mg adsorbent and 40 min were used for subsequent experiments.

The elution volume was a crucial parameter and was examined from 1.5 mL to 9.0 mL. Fig. 5F shows the results from different volumes. The elution performance of the targets increased as the volume increased up to 4.5 mL. The elution volume continued to increase until there was no obvious change in recoveries, indicating that 4.5 mL eluting solvent was adequate for desorption of the targets.

Elution time is another important factor for achieving completely or almost eluting performance. There is low elution efficiency with short times due to incomplete elution; longer times can be wasteful. We empirically optimized the elution time from 3 to 9 min (Fig. 5G). It was obvious that the enrichment efficiencies of OCPs sharply rose by increasing the elution time from 3 min to 4.5 min and then slightly increased up to 6 min. The recoveries remained almost unchanged up to 9 min. Thus, 6 min was used as the elution time.

The pH is a vital parameter in MSPE because the pH can influence the stability of analytes as well as the charge and density of the characteristic groups on the adsorbent. The pH was studied from pH 5 to pH 9. Fig. 5H indicates that the highest recoveries of OCPs were at pH 7. The adsorbent earned more terminal amino groups which were easily protonated under acidic conditions decreasing the enrichment efficiencies resulting from electrostatic repulsion. The analytes tend to hydrolyze in alkaline media and meanwhile the adsorbents would be degraded, which would resulted the lower recoveries of analytes (Sun et al., 2016). So at pH, the adsorbents would be not protonated and have higher hydrophobicity, and the DDTs are stable and more hydrophobic, which will enhance the higher recoveries due to higher hydrophobic interactions and Van der waals forces between adsorbents and analytes. Therefore, the sample pH was adjusted to pH 7.

Usually, the increase in ionic strength is an effective way to improve the enrichment efficiencies by decreasing the solubility of targets in aqueous solution according to destroying the formation of hydration spheres around analytes (salting-out effect). For higher enrichment efficiency, the effect of ionic strength was investigated in the NaCl concentration range of 5–30% (W/V). Fig. 5I indicates that the recoveries of four OCPs decreased as the ionic strength increased to 5%. This was due to the salting-in effect, while the extraction efficiencies slowly increased by increasing ionic strength from 5% to 25% due to salting-out. The recoveries had no further change as the ionic strength further increased up to 30%. The highest recoveries were at ionic strength of 25%. With the increase of ionic strength, he solubility of the analytes decreased and the viscosity of the solution increased which would inhibit the diffuse rate of the analytes indicating that the analytes would be easily adsorbed on to the adsorbents due to hydrophobic interactions.

To investigate the sample penetration volume, different sample volumes from 20 mL to 100 mL were evaluated. Fig. 5J displays the effect of sample volume, and the results show no remarkable change in the extraction recoveries of OCPs when the sample volume changed from 20 to 60 mL. The recoveries slightly decreased when the sample volume was over 60 mL. This might be because a fixed amount of adsorbent cannot ad-
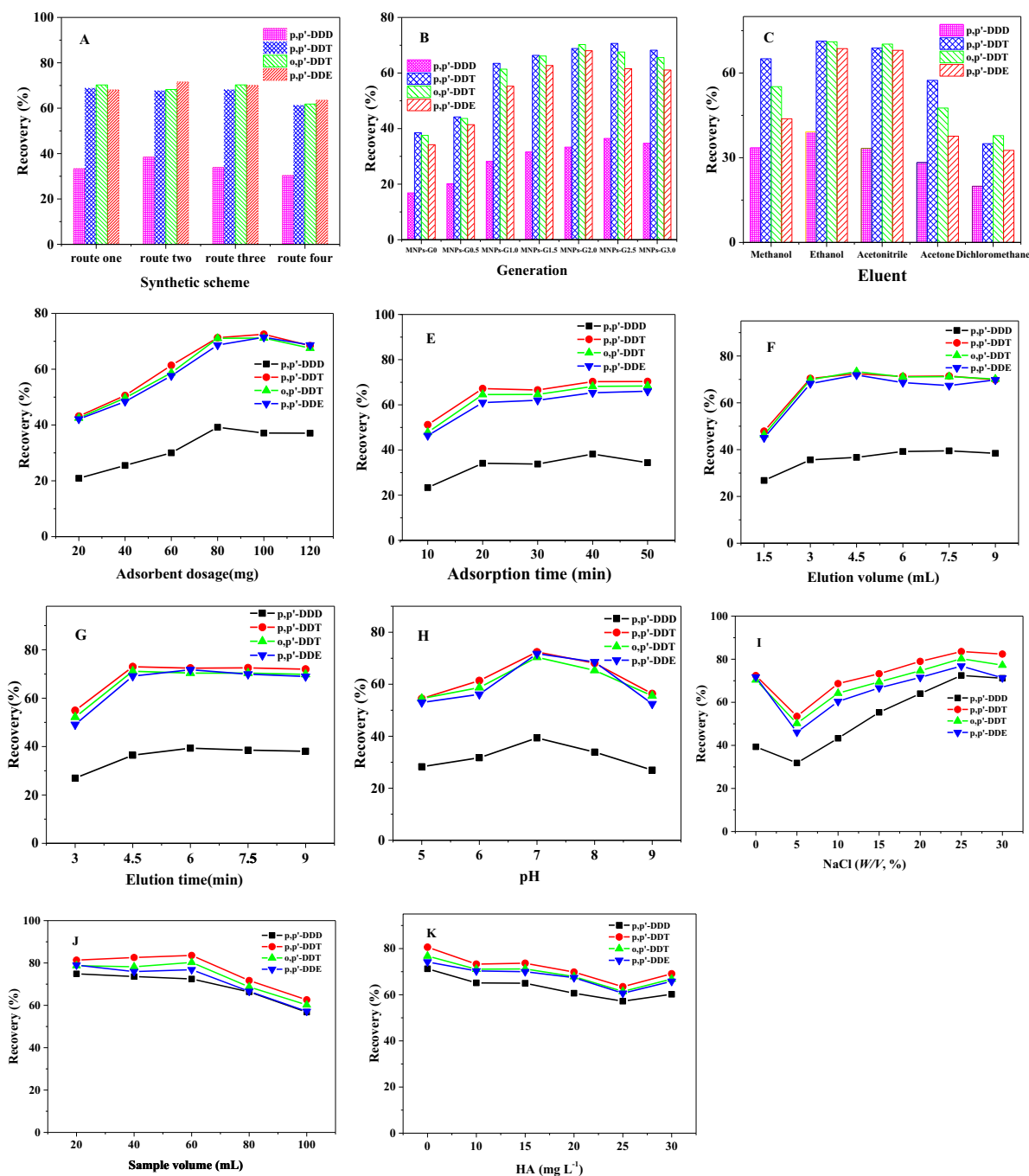
Fig. 5 – Optimization of MSPE parameters. (A) Selection of synthetic scheme; (B) selection of PAMAM generation; (C) effect of eluent; (D) effect of adsorbent dosage; (E) effect of adsorption time; (F) effect of elution volume; (G) effect of elution time; (H) effect of pH; (I) effect of ionic strength; (J) selection of sample volume; and (K) effect of humic acid. Experimental conditions: spiked concentration of analytes, 20 μg/L; PAMAM generation, MNPs-G2.0; eluent, acetonitrile; adsorbent amount, 80 mg; adsorption time, 40 min; elution volume, 6 mL; elution time, 6 min; pH, 7; ionic strength, 0% (W/V); sample volume, 60 mL; concentration of humic acid, 0 mg/L. Each parameter was optimized while holding the other parameters constant. The optimal value was used in the subsequent optimization process.

sorb much more OCPs. On the other hand, a specific volume of eluent and elution time cannot elute much more OCPs.

Humic acid is widely found in real water samples. This is disfavors extraction due to its competitive adsorption. To investigate the influence of humic acid, different concentrations

of humic acid (10–30 μg/mL) were tested (Fig. 5K). The enrichment efficiencies of OCPs slightly decreased along with the increase of humic acid concentration up to 25 μg/mL as a result of competitive adsorption. Moreover, a slight increase was observed with continuous increase in the humic acid concen-

Table 1 – Analytical performance of the proposed method.						
Compound	Linearity (μg/L)	R	Precision (%)		LOD (μg/L)	LQD (μg/L)
			Intra-day (n=6)	Inter-day (n=3)		
p,p'-DDT	0.1-500	0.999	4.1	4.5	0.012	0.04
o,p'-DDT	0.1-500	0.999	4.4	4.0	0.029	0.097
p,p'-DDE	0.1-500	0.998	4.4	2.7	0.012	0.04
p,p'-DDD	0.1-500	0.999	2.9	2.9	0.016	0.053

Table 2 – Comparison of different methods for the analysis of OCPs.								
Analytical Method	Matrix	Linearity (μg/L, ng/g)				LOD (μg/L)	Intra-day RSD (%)	Ref.
		p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-DDD			
MSPE-HPLC-UV	Water	0.1–500	0.1–500	0.1–500	0.1–500	0.012–0.029	2.9–4.4	Present work
MAHSCTLPME[a]-GC-ECD[b]	Water	0.15–3.0	0.1–2.0	0.05–1.0	0.15–3.0	0.02–0.03	3.2–11.3	Kumar and Jen, 2011
HS-LPME-HPLC	Water	0.3–30	0.3–30	0.2–30	0.3–30	0.05–0.08	6.8–8	Ye et al., 2006
MSPE-GC-MS	Water	0.002–0.5	0.002–0.5	0.002–0.5	0.002–0.5	0.00039–0.00060	5.5–7.6	Liu et al., 2017
HFSPME[c]-UHPLC[d]	Water		0.5–50	0.5–50	0.5–50	0.33–0.38	4–6	Pang et al., 2017
DLLME-HPLC-UV	Water	1–50	1–50	1–50	1–50	0.32–0.51	2.8–7.5	Zhou et al., 2009

[a] Microwave-assisted headspace controlled-temperature liquid-phase micro-extraction.
[b] ECD: Electron-capture detector.
[c] Hollow-fiber solid-phase microextraction.
[d] Ultra high performance liquid chromatography.

tration to 30 μg/mL. The humic acid might adsorb the OCPs onto the surface of the magnetic adsorbents. Thus, no humic acid was added in the following experiments.

2.3. Feature parameters of the proposed method

To assess the performances of the proposed method, important parameters, such as linear range, LOD, and precision, were examined under optimal conditions (Table 1). Excellent linearity was seen between the peak areas and the concentration of OCPs (0.1–500 μg/L). Correlation coefficients (R) were seen from 0.998 to 0.999. The LOQs (S/N = 10) and LODs (S/N = 3) were very low over the range of 0.04–0.097 μg/L and 0.012−0.029 μg/L, respectively. The intra-day (n = 6) and inter-day (n = 3) precisions were all lower than 4.5%. Moreover, the analytical merits of this method were compared with the existed methods (Table 2). This proposed method has a wider linearity, higher sensitivity, and better repeatability. Thus, this method has good application prospects and is a good alternative to routine methods for the determination of DDTs and related metabolites.

2.4. Reusability of the adsorbent

In order to evaluate the stability of magnetic adsorbent, the used materials were washed with ethanol and water for several times to keep adsorbent clean for reuse investigation under the optimal conditions and the results were shown in Fig. 6. It was obvious that the adsorbent can be used at least eight times without significant loss of the extraction recoveries of targets, which demonstrated the magnetic material earned good reusability.
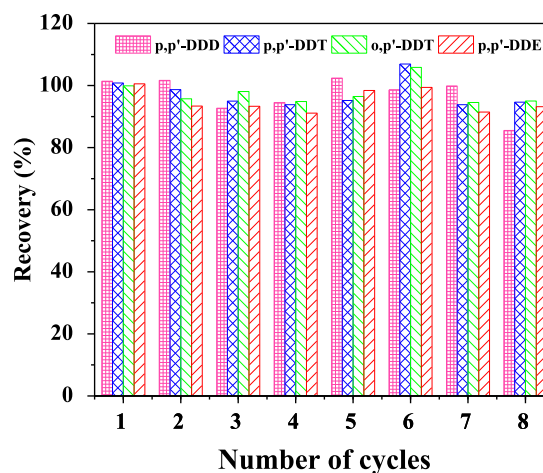

Fig. 6 – Reusability test of MNPs-G2.0 under the optimal conditions.

2.5. Analysis of real environmental water samples

Four water samples, such as West Sea, Olympic Park, Taoranting Park, and Yuyuantan Park, were taken to evaluate the practicability of this proposed approach. The analytical results are shown in Table 3. No OCP residue was found. The spiked recoveries at two levels were also obtained. The obtained spiked recoveries were satisfied from 90.6% to 103.5%, which demonstrated that the present method has good enrichment efficiency and precision, and matched the requirements for de-

Table 3 – Analytical results for the determination of OCPs in real water samples.

Water sample	Spiked level (μg/L)	Recovery (%)			
		p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-DDD
West Sea Water	0	nd[a]	nd	nd	nd
	10	96.2[b] ± 0.9[c]	99.3 ± 1.0	97.5 ± 3.1	97.5 ± 3.5
	20	96.6 ± 4.6	96.0 ± 2.3	91.8 ± 0.7	93.4 ± 3.6
Olympic Park Water	0	nd	nd	nd	nd
	10	99.9 ± 2.1	99.2 ± 2.1	98.5 ± 3.6	99.6 ± 2.2
	20	98.3 ± 0.5	95.4 ± 0.6	92.8 ± 1.9	102.7 ± 1.1
Taoranting Park Water	0	nd	nd	nd	nd
	10	96.3 ± 1.7	94.6 ± 1.6	92.8 ± 4.3	102.8 ± 1.4
	20	103.3 ± 3.4	103.5 ± 2.4	98.4 ± 0.9	95.8 ± 2.8
Yuyuantan Park Water	0	nd	nd	nd	nd
	10	96.6 ± 2.1	97.3 ± 2.0	97.0 ± 4.1	103.5 ± 2.5
	20	98.1 ± 3.4	98.9 ± 3.3	95.3 ± 1.8	90.6 ± 4.6

[a] Not detected.
[b] Mean value of three determinations.
[c] Relative standard deviation for three determinations.
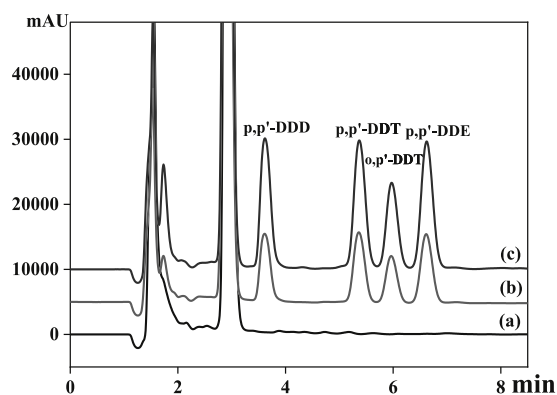
Fig. 7 – Typical chromatograms of Olympic Park water sample. (a) blank; (b) spiked at 10 μg/L; (c) spiked at 20 μg/L.

tecting four OCPs in natural water samples. Fig. 7 displays the typical chromatograms of Olympic Park water.

3. Conclusions

Here, PAMAM dendrimer-modified MNPs were successfully synthesized and investigated to develop an effective magnetic solid phase extraction coupled with HPLC-UV for measuring DDTs and their metabolites from real environmental water samples. This study integrated the excellent adsorption property of PAMAM dendrimers attributed to their multifunctional groups and the strong magnetism of MNPs. The expected excellent enrichment ability of ultra-trace OCPs in water samples was achieved. This method was fast, easy, and sensitive with high enrichment efficiency. It could measure four OCPs in real samples. These results confirmed that this new material was a promising adsorbent for the extraction of OCPs and is a good alterative adsorbent for other organic pollutants in different samples. The developed magnetic solid phase ex-

traction method reduced the consumption of organic solvents compared with conventional liquid-liquid extraction, and decreased the analytical time due to the rapid separation using a magnet. Meanwhile, this method is an excellent analytical and monitoring tool for OCPs in environmental and food samples.

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.09.005.

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