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Ultrasonic assisted extraction combined with titanium-plate based solid phase extraction for the analysis of PAHs in soil samples by HPLC-FLD

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ABSTRACT

In this work, ultrasonic assisted extraction combined with solid phase extraction (SPE) was applied in the analysis of polycyclic aromatic hydrocarbons (PAHs) in environment samples. A titania nanotubes/titanium plate was modified with n-octadecanethiol monolayer-protected Ag nanoparticles, and developed as the adsorbent in SPE of PAHs. Six different PAHs in soil samples were analyzed with high performance liquid chromatography-fluorescence detection. The experiment conditions including the deposition time of Ag nanoparticles, extraction solvent properties, the amount of extraction solvent, the amount of organic modifier, extraction time, and desorption solvent properties were optimized. Under the optimized conditions, good linearity and low limits of detection of 0.0015–0.4 ng g^{-1} were obtained. The analysis of PAHs in real soil samples gave satisfactory recoveries ranging from 70.32% to 115.51% with 3.14%–13.56% intra-day relative standard deviations (RSD) and 4.92%–14.87% inter-day RSD.

1. Introduction

PAHs are a group of more than 100 chemically different organic substances that are generally formed by two or more benzene rings [1]. For this reason, these compounds are classified as hydrophobic organic compounds. PAHs are formed during the incomplete combustion of coal, oil, diesel or gasoline, and other organic substances at high temperature (500–800 °C) or subjection of organic material at low temperature (100–300 °C) for long periods [2]. PAHs exhibit recalcitrant and strong mutagenic/carcinogenic properties for the living beings [3]. Soil is the major terrestrial environmental reservoir and one of the major sinks for persistent organic pollutants (POPs) and the occurrence of PAHs in soils and other environmental media has received much attention since these chemicals were first found by Blumer in 1961 [4]. PAHs are very persistent in soils due to the properties such as low volatility, low water solubility and low biodegradability [5]. These characteristics make it very difficult to remove them from soils.

The analysis of PAHs can be carried out by a number of analytical techniques, for instance, gas chromatography (GC) with flame ionization (FID) or mass spectrometry (MS) detector and reverse-phase high performance liquid chromatography (RP-HPLC) with photometric (UV) or fluorescence detector (FLD) [6]. Among them, FLD has been found to be very suitable for the quantification of PAHs in a variety of environmental samples because of the high fluorescence quantum yields of PAHs. FLD has sensitivity of about 20–320 times higher than UV detection, and 0.8–50 times higher than MS [7]. What is more, the HPLC-FLD method which requires no carrier gas allows the determination of non-volatile, thermally labile molecules without derivatization [8]. Due to all the advantages mentioned above, HPLC-FLD is a preferable method for PAHs' analysis.

Due to the complexity of soil samples and the low content of PAHs in them, the sample preparation step which need good clean-up and concentration is very important in order to enhance the sensitivity and selectivity before detection. Many extraction techniques have been exploited, such as soxhlet extraction [9], pressurized liquid extraction (PLE) [10], accelerated solvent extraction (ASE) [11], microwave-assisted extraction (MAE) [12] and so on. Ultrasonic assisted extraction (UAE) is a common method for the extraction of organic compounds from complex

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Abbreviations: Ant, anthracene; ASE, accelerated solvent extraction; BaA, benzo[a]anthracene; BbF, benzo[b]fluoranthene; BkF, benzo(k)fluoranthene; C18-Ag NPs, n-octadecanethiol monolayer-protected Ag nanoparticles; EDX, energy dispersive X-ray; FlA, fluoranthene; GC–MS, gas chromatography with mass spectrometry; HPLC-FLD, high performance liquid chromatography with fluorescence detector; MAE, microwave-assisted extraction; MSPD, matrix solid-phase dispersion; LLE, liquid–liquid extraction; PAH, polycyclic aromatic hydrocarbons; PLE, pressurized liquid extraction; POPs, persistent organic pollutants; Pyr, pyrene; R^2, correlation coefficient; SPE, solid phase extraction; SPME, solid phase microextraction; TiO_2 NTs/Ti, titania nanotubes/titanium plate; UAE, ultrasonic assisted extraction

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samples due to its advantages of less time-consuming and easy operation. After the extraction of analytes from soil samples, a further clean-up step which is usually performed by SPE is necessary due to the interferences co-extracted along with the target compounds [13]. Co-extractives having similar fluorescence properties sometimes cannot be removed and negatively affect the precision and accuracy of PAHs analysis by HPLC-FLD [7]. SPE is established on liquid–liquid extraction (LLE) but has the advantages of high recovery, high pre-concentration factor, low consumption of organic solvent, simplicity, easy automation and operation and so on over LLE [14]. It has been used extensively for the analysis of PAHs in environment samples. Various kinds of adsorbents have been applied in SPE, such as ionic liquid [15], molecular imprinted polymer [16], carbon nanotubes [17] and so on. C18 is one of the mostly used adsorbents due to its hydrophobic nature.

Titanium is a newly developed material in sample preparation step. Several works have reported the use of titanium wire in solid phase microextraction (SPME) as the substrate instead of silica fiber due to its high strength [18–20]. Titanium can be easily oxidized to form high-ordered titania nanotubes (TiO_2 NTs) on the titanium surface. The TiO_2 NTs is with large surface area, which benefits the further modification and the consequent extraction [21–24].

In this work, UAE and SPE were used in sequence for the extraction of PAHs in soil samples to achieve extraction, clean-up and concentration. A titania nanotubes/titanium plate (TiO_2 NTs/Ti) modified with n-octadecanethiol monolayer-protected Ag nanoparticles (C18-Ag NPs) was developed as the adsorbent in SPE of PAHs. Six different PAHs in soil samples were analyzed with HPLC-FLD.

2. Materials and methods

2.1. Reagents and materials

Titanium plates (99.8% pure, 0.127 mm thick) were purchased from Aldrich (Milwaukee, WI). n-Hexane, acetone, ethanol, cyclohexane, hydrofluoric acid and methylene dichloride of analytical reagent grade were purchased from Sinopharm Chemical Reagent (Shanghai, China), while methanol and acetonitrile of chromatographically reagent grade were purchased from Sigma-Aldrich (Madrid, Spain). n-Octadecanethiol (97% in purity) was obtained from Aladdin Chemistry and silver nitrate was purchased from Sigma-Aldrich (Madrid, Spain). Ultrapure water was prepared using a Milli-Q system (Bedford, USA) and used throughout the experiment. The PAHs including anthracene (Ant) , fluoranthene (FlA), pyrene (Pyr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF) and benzo(k)fluoranthene (BkF) were purchased from Acros Organics (NJ, USA). Stock solutions of PAHs were prepared by dissolving each compound in methanol at concentrations of 0.1 mg mL^{-1} (Ant, Pyr), 1 mg mL^{-1} (FlA, BaA), and 0.05 mg mL^{-1} (BbF, BkF), respectively. A standard mixture of PAHs composed of Ant (4 μg L^{-1}), FlA (2 μg L^{-1}), Pyr (1 μg L^{-1}), BaA(1 μg L^{-1}), BbF (0.75 μg L^{-1}), and BkF (0.1 μg L^{-1}) was prepared by diluting the stock solutions with methanol and used as working solution. Using different concentrations of each PAH in the mixture is because of their different sensitivities to FLD and different concentration levels in environmental samples. n-Octadecanethiol was dissolved in ethanol at a concentration of 200 mM. All standard and working solutions were stored at 4 °C. Soil samples A and B collected from Yuelu Mountain and Xiangjiang River (Changsha, China), respectively, were dried carefully, sieved to less than 2 mm after collection, and stored at room temperature.

2.2. Apparatus

The liquid chromatographic system (Shimadzu, Kyoto, Japan) used in this work was consisted of two LC-20AT pumps, a CTO-10AS VP column oven and an RF-10A XL FLD system. They were connected via a communication bus module (Model CBM-20A), and controlled by a Shimadzu LC Solution workstation. A Shimadzu Shimpack vp-ODS column (250 mm × 4.6 mm, 5 mm) was employed for the separation. The mobile phase was consisted of 25% water (solvent A) and 75% acetonitrile (solvent B) at a flow rate of 1 mL min^{-1}. The injection volume was 20 μL.

The morphology of the surface of the titanium plate was characterized by a field-emission scanning electron microscope operating at 10 kV (S4800; Hitachi, Japan). Fourier transform infrared (FT-IR) spectra were recorded on a WQF-410 instrument (Braic Crop, China). Energy Dispersive X-Ray (EDX) spectrum was recorded by EMAX instrument (Horiba, Japan).

2.3. Preparation of the adsorbent

Titanium plates were cut into pieces of 3.5 cm × 1 cm. Another 12 cm long titanium wire (Φ0.28 mm) was tied to the top of the plate to facilitate the operation in the SPE procedures. Prior to anodization the titanium plate was ultrasonically cleaned in HF solution (< 1%) for 2–3 min to remove the surface impurities. The cleaned titanium plate was anodized at 15 V in an electrolyte containing HF solution (0.5%) at room temperature for 20 min in a conventional two-electrode system with a graphite slice counter electrode. Electroplating Ag NPs on the TiO_2 NTs substrate was performed by employing the multi-potential step mode of an electrochemical workstation (Chenhua, Shanghai) with a platinum sheet as the counter electrode. The electroplating conditions were as follows: electrolyte, 5 mM $AgNO_3$ solution; running voltage, −1 V; disconnecting voltage, 0 V; open/close ratio: 0.2/1 s; efficient depositing time: 500 sequences. After electro-deposition, the Ag NPs-modified titanium plate was washed by ultrapure water, and then put into a 100 mM n-octadecanethiol solution for about 40 h to form a self assembled monolayer (SAM). The excess n-octadecanethiol was washed with ethanol. After drying in air, the plate was stored at room temperature.

2.4. UAE and SPE procedure

The analysis of blank soil samples (collected from Yuelu Mountain in Changsha, Hunan Province, China) gave values below the limits of detection (LODs) of the method for all the studied PAHs. These soil samples were used in the optimization and validation experiments.

In all experiments, 1 g soil samples were spiked with certain amount of stock solution in a 50 mL centrifugal tube. The mixture was mixed together by a mechanical shaker for about 1 min, and then kept in dark atmosphere overnight. Afterwards 30 mL dichloromethane was added into 1.0 g spiked soil sample. The mixtures were then placed in ultrasonic bath for 30 min at room temperature and centrifuged at 10,000 rpm for 10 min in sequence. The supernate was collected into a vacant 50 mL centrifugal tube, dried under a stream of nitrogen at 30 °C, and dissolved in 20 mL deionized water in which 400 μL methanol was added as the organic modifier under ultrasonic bath for 5 min. SPE was carried out at room temperature for 90 min under stirring using the prepared C18-Ag NPs/TiO2/Ti. After extraction, the plate was soaked immediately in 3.5 mL acetonitrile for 20 min to achieve desorption in a static desorption mode. The acetonitrile solution was collected and dried under a stream of nitrogen at 30 °C. The analytes were re-dissolved by 500 μL methanol, and 20 μL of this solution was injected directly into the HPLC-FLD system for analysis.

3. Results and discussions

3.1. Characterization

The characterizations of the adsorbent were carried out by FE-SEM and FT-IR. Fig. 1 is the FE-SEM images which show the surface morphology of the TiO_2 NT-modified, Ag NPs/TiO_2 NT-modified and C18-Ag NPs/TiO_2 NT-modified titanium plate. Fig. 1a shows the cross-sectional view of the anodized titanium plate, a layer of TiO_2 NTs are formed on the plate with a pore size of about 80 nm. Fig. 1b shows that the AgNPs at a size of 50 nm are evenly distributed on the surface of TiO_2 NTs. There is no difference between Fig. 1c and b because n-Octadecanethiol could not be observed by FE-SEM.

n-Octadecanethiol was self-assembled on the surface of Ag NPs via Ag-thiol bonding so that long carbon-chains were introduced. Fig. 2a shows the FT-IR spectra of the Ag NPs/TiO_2 NT/Ti, C_{18}-Ag NPs/TiO_2 NT/Ti and C_{18}-SH. The absorptions at 2918, 2849, 1462 and 1472 cm^{-1} are attributed to the stretching and bending of C–H bonds , the peaks appeared at 719 and 730 cm^{-1} correspond to the stretching of C–S bonds of n-octadecanethiol. The FT-IR spectra confirms the successful assembling of n-octadecanethiol on the Ag NPs. The EDX analysis of the C18-Ag NPs/TiO2 NT-modified titanium plate surfaces is shown in Fig. 2b. The presence of peaks at 3 keV corresponds to Ag, confirming that Ag NPs has been deposited on the plate. The peaks of 0.28 keV, 0.38 keV and 0.52 keV correspond to the atoms of carbon, oxygen and sulfur, respectively, which indicate that n-octadecanethiol has been modified to titanium plate.

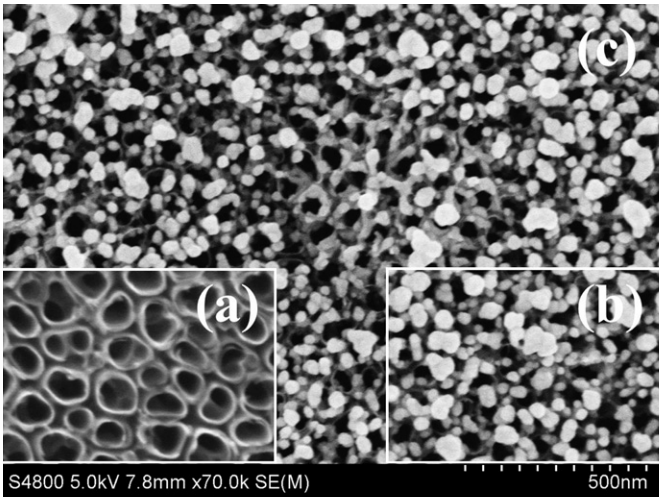

Fig. 1. The FE-TEM images of the titanium-plate surface at a magnification of 50,000 after the modifications of (a) TiO_2 NTs; (b) Ag NPs/TiO_2 NTs; (c) C_{18}-Ag NPs/TiO_2 NTs.

3.2. Optimization of the adsorbent

The extraction efficiency would be highly related to the loading amount of n-octadecanethiol which was dependent on the Ag NPs loading. The effect of electro-deposition time on the extraction efficiency was therefore investigated. As the results shown in Fig. 3a, the peak areas of all the analytes follow an increase tendency with increasing the deposition sequences. Further increasing the deposition time would result in blocking of the TiO_2 NT entry, deposition of 500 sequences was therefore applied in this work with a view to both extraction efficiency and saving time.

3.3. Optimization of UAE

Both the extraction solvent and the volume of the extraction solvent were optimized for UAE. Acetone, methylene dichloride, methanol, acetonitrile, ethanol and cyclohexane were tested as the extraction solvents for the extraction of six PAHs from soil samples. As shown in Fig. 3b, methylene dichloride performs the best for all the analytes, and is consequently chosen as the extraction solvent.

In order to determine the optimum volume of the extraction solvent, 1 g of spiked soil was sonicated for 30 min with different volume of methylene dichloride. The results are shown in Fig. 4a. For all the analytes, the peak areas follow an increasing tendency with increasing the volume from 10 to 30 mL. For Pyr, BaA, BkF, and BbF, increasing the volume from 25 to 30 mL results in no further increase in the peak areas. Taking into consideration of environmental protection, 30 mL methylene dichloride was used in UAE.

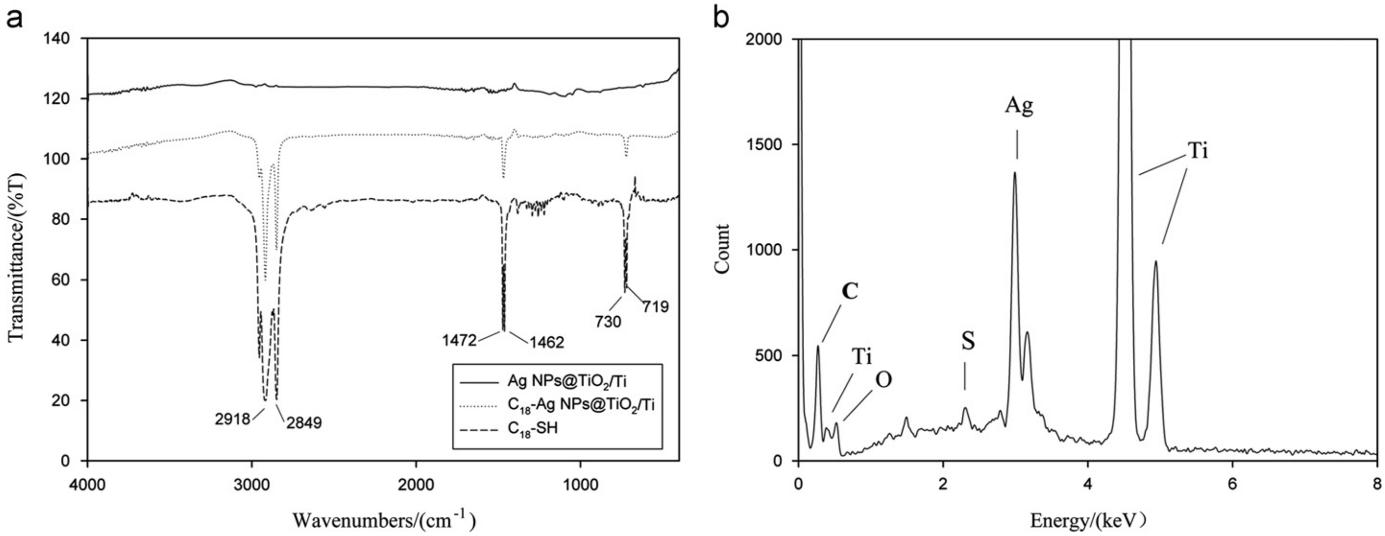

Fig. 2. (a) The FT-IR spectra of the Ti-plate after the modifications of Ag NPs TiO_2 NTs,C_{18}-Ag NPs/TiO_2 NTs and n-octadecanethiol; (b) EDX spectrum of the C_{18}-Ag NPs/TiO_2 NT-modified titanium plate.

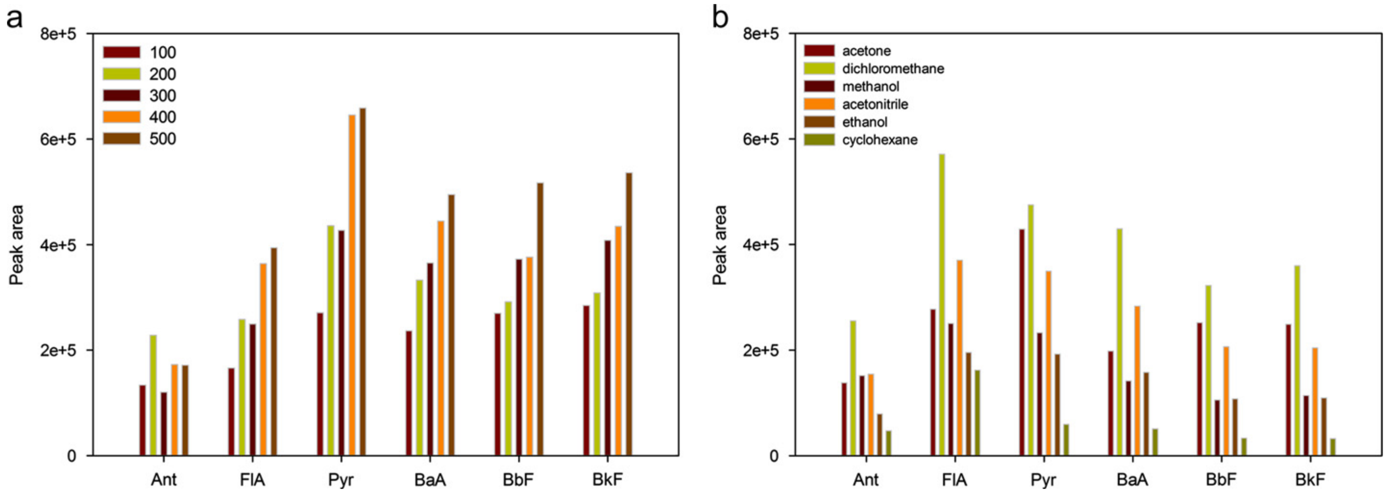

Fig. 3. (a) Effect of electro-deposition time on peak areas of the analytes. Extraction solvent: methylene dichloride; volume of extraction solvent: 30 mL; extraction time: 60 min; desorption solvent: acetonitrile. (b) Effect of extraction solvent on peak areas of the analytes. Electro-deposition time: 500 sequences; volume of extraction solvent: 30 mL; extraction time: 60 min; desorption solvent: acetonitrile.

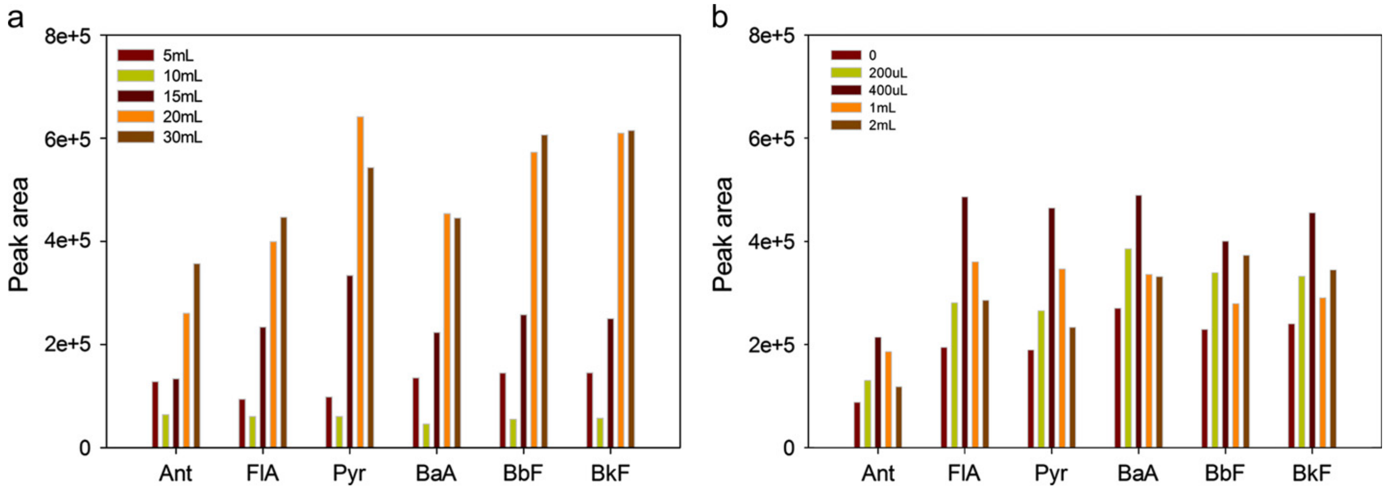

Fig. 4. (a) Effect of volume of the extraction solvent on peak areas of the analytes. Deposition time: 500 sequences; extraction solvent: methylene dichloride; extraction time: 60 min; desorption solvent: acetonitrile. (b) Effect of volume of organic modifier on peak areas of the analytes Electro-deposition time: 500 sequences; extraction solvent: methylene dichloride; volume of extraction solvent: 30 mL; extraction time: 60 min; desorption solvent: acetonitrile.

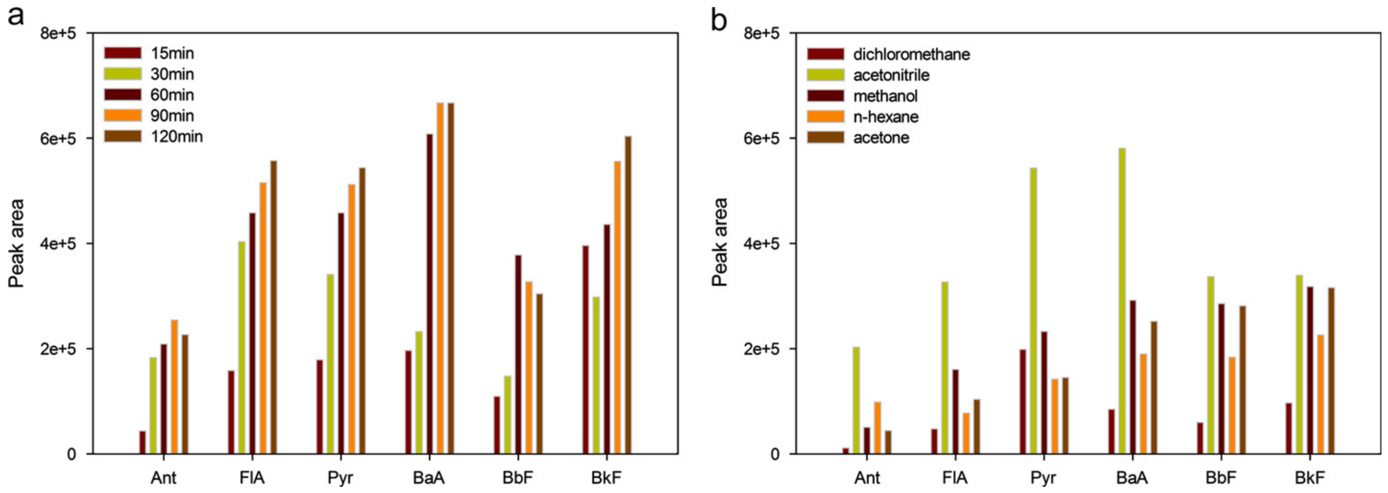

Fig. 5. (a) Effect of extraction time on peak areas of the analytes. Electro-deposition time: 500 sequences; extraction solvent: methylene dichloride; volume of extraction solvent: 30 mL; volume of organic modifier: 400 μL; desorption solvent: acetonitrile. (b) Effect of desorption solvent on peak areas of the analytes. Electro-deposition time: 500 sequences; extraction solvent: methylene dichloride; volume of extraction solvent: 30 mL; volume of organic modifier: 400 μL; extraction time: 90 min.

3.4. Optimization of SPE

The optimization of SPE includes the optimizations of the amount of organic modifier, the extraction time and desorption solvent.

After UAE, the target compounds collected in a 50 mL centrifugal tube were dissolved in 20 mL deionized water. According to the preliminary experiments, the target compounds were easily adsorbed on the container wall due to their high hydrophobicity, resulting in a decrease in the recovery rate. Organic modifier was therefore added to improve the extraction efficiency of SPE. Excessive organic modifier, however, would result in an increase in the solubility of analytes, decreasing the extraction efficiency. The amount of the organic modifier was therefore needed to be optimized. Methanol was selected as the organic modifier according to our previous studies [24]. Fig. 4b displays that 400 μL methanol performs the best for all the analytes, 400 μL methanol was therefore applied as the organic modifier.

Table 1
The linearity ranges, linearity curves, correlation coefficients and LODs of the proposed method under optimization conditions.

Compounds	Linearity range/ng g^{-1}	Linearity curve	Correlation coefficient (R^2)	LOD/ ng g^{-1}
Ant	4–600	$y=580x+34{,}356$	0.9933	0.4
FlA	2–400	$y=1503x+146{,}528$	0.9964	0.01
Pyr	1–200	$y=3036x+388{,}980$	0.9969	0.02
BaA	1–200	$y=7870x+104{,}743$	0.9977	0.2
BbF	0.75–150	$y=6212x+47{,}496$	0.9962	0.0015
BkF	0.1–20	$y=40518x+106{,}119$	0.9940	0.002

Table 2
The comparison of the proposed method to reported literatures.

Compound	Method			
	LOD(ng g^{-1})			
	Proposed method	MAE(HPLC-FLD) [25]	PLE(GC-MS) [26]	MSPD(HPLC-FLD) [27]
Ant	0.04	2	4	0.02
FlA	0.01	1	8	0.1
Pyr	0.02	2	9	0.04
BaA	0.2	0.5	4	0.007
BbF	0.0015	1	2	0.02
BkF	0.002	0.3	2	0.004

Extraction time is a key factor influencing the extraction efficiency. As shown in Fig. 5a, the peak areas of most analytes increase with increasing time from 15 min to 120 min. However, 90 min extraction time performs about the same with 120 min extraction time for most of the analytes. Taking both the saving-time and good extraction efficiency into consideration, 90 min was used as the extraction time.

In order to get higher sensitivity of the proposed method, complete desorption of analytes from the adsorbent is very important. Different desorption solvent including methylene dichloride, acetonitrile, methanol, n-hexane, and acetone were investigated as the desorption solvents. As is shown in Fig. 5b, acetonitrile performed the best for all the analytes and was chosen to enhance the sensitivity.

3.5. Method validation

Under the conditions optimized above, the analytical performance of the proposed method was assessed with spiked soil samples. The results including linearity, correlation coefficients (R^2) and LODs are given in Table 1. All the PAHs showed good linearities over a wide concentration range with correlation coefficients (R^2) ranging from 0.9933–0.9977. The LODs calculated as three times the signal to noise ratio (S/N) were ranged from 0.0015 to 0.4 ng g^{-1}. Table 2 shows the comparison of the present method with published ones. The merits of the present

Table 3
Analytical results for the determination of PAHs in real soil samples.

Compound	Spiked (ng/L)	Sample A						Sample B					
		Detected (ng/L)		Recoveries (%)		RSD (%)		Detected (ng/L)		Recoveries (%)		RSD (%)	
		Intra-day	Inter-day	Intra-day	Inter-day	Intra-day	Inter-day	Intra-day	Inter-day	Intra-day	Inter-day	Intra-day	Inter-day
Ant	0	–	–	–	–	–	–	63.94	64.31	–	–	10.12	11.13
	10	10.81	10.98	108.10	109.83	12.43	13.80	73.92	74.10	99.76	101.58	12.32	14.87
	50	55.08	54.75	110.16	109.51	6.80	6.14	118.62	118.94	109.36	109.99	10.40	11.06
	200	231.03	231.081	115.51	115.91	7.68	10.16	276.62	274.34	106.34	105.20	11.26	12.31
FlA	0	–	–	–	–	–	–	41.19	41.66	–	–	8.49	10.52
	10	10.93	11.26	109.26	112.56	13.56	11.62	49.06	49.09	78.69	79.02	9.94	11.80
	50	53.58	53.03	107.16	106.07	9.10	11.38	84.59	82.79	85.80	83.20	8.78	10.43
	200	220.11	222.59	110.05	111.29	8.18	8.25	218.87	219.71	88.84	89.26	4.05	5.16
Pyr	0	–	–	–	–	–	–	67.84	66.26	–	–	7.97	11.94
	10	7.99	8.09	79.89	80.89	8.37	10.67	78.00	77.86	101.63	100.22	7.93	9.93
	50	36.48	35.63	72.97	71.25	8.56	14.86	118.29	119.45	100.90	103.23	8.73	5.76
	100	77.46	78.92	77.46	78.92	6.92	9.78	170.29	168.07	102.45	100.23	6.82	7.22
BaA	0	4.48	4.29	–	–	7.13	11.33	42.21	42.49	–	–	6.58	4.58
	10	13.72	13.24	92.42	87.65	4.57	10.49	51.22	51.17	90.11	89.55	11.90	14.06
	50	50.95	50.98	92.94	93.03	5.91	7.00	91.65	92.81	98.87	101.20	3.97	6.27
	100	100.16	98.84	95.68	94.36	3.80	5.65	139.48	141.10	97.27	98.89	3.14	5.37
BbF	0	0.80	0.75	–	–	11.01	14.55	45.11	45.03	–	–	4.52	7.66
	5	5.41	5.24	92.23	88.81	7.71	8.23	50.33	50.51	104.49	108.00	11.31	13.15
	37.5	35.54	36.16	92.64	94.69	7.38	10.38	83.69	83.40	102.90	103.16	5.21	9.33
	75	71.82	72.27	94.69	95.29	6.85	5.61	123.91	123.49	105.08	104.51	4.30	5.74
BkF	0	1.48	1.44	–	–	10.53	13.17	17.32	17.21	–	–	4.87	7.80
	1	2.18	2.21	70.32	73.61	10.12	8.36	18.28	18.25	96.11	92.61	13.10	14.49
	5	5.27	5.32	75.71	76.74	5.71	8.30	22.41	22.66	101.85	106.79	7.78	9.47
	10	9.56	9.67	80.83	81.92	6.10	4.92	27.23	27.51	99.10	101.92	6.78	7.06

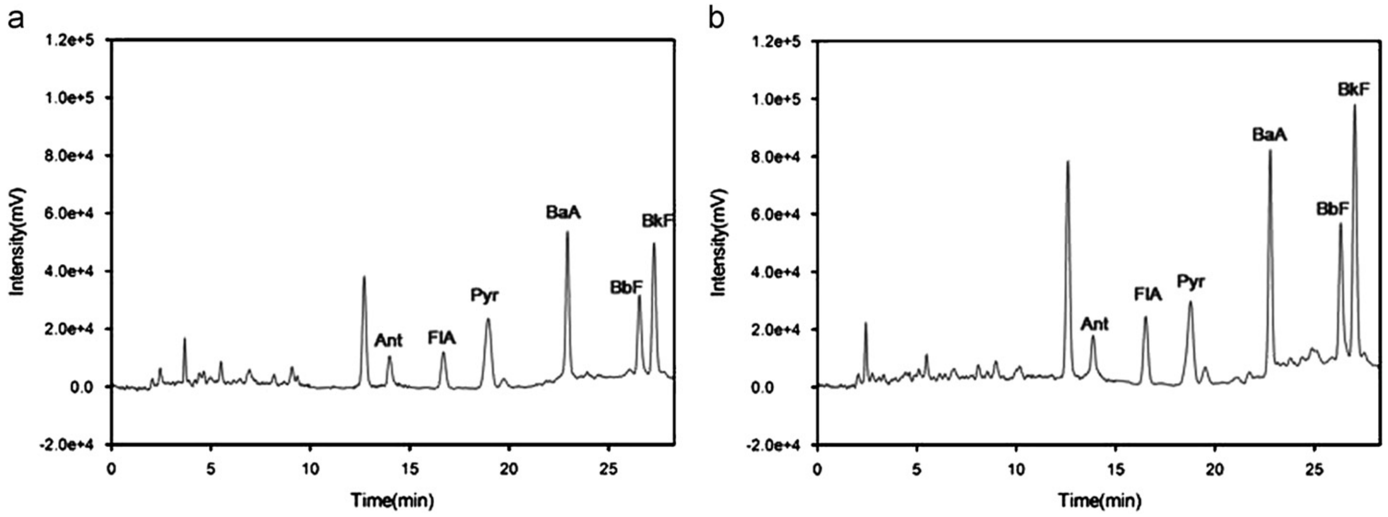

Fig. 6. The chromatograms of the analysis of spiked real soil samples by the proposed method (a) sample A (b) sample B.

method are obvious over the references presented in Table 2 including low LODs, as well as fast and simple analytical procedure [25–27].

The proposed method was applied to the analysis of real soil samples. Quintuplicate analysis were performed. As is shown in Table 3, BaA, BbF and BkF were detected in sample A which was collected from Yuelu Mountain. For sample B which was collected from Xiangjiang River, the concentrations of PAHs were much higher than those detected in Sample A because of the higher pollution that might be caused by heavy traffic and industrial pollution. Then both real soil samples were spiked with PAHs at concentrations within the linearity ranges. The concentrations of each PAH in the spiked samples were listed in Table 3. The spiked samples were handled in intra- and interday to test the precision and accuracy. Recoveries ranging from 70.32% to 115.51% were achieved for both samples. The RSDs for the analysis of real soil samples are also summarized in this table which gives results of 3.14%-13.56% for intraday tests and 4.92%–14.87% for interday tests. There is no significant difference between the intra-and interday RSDs. The chromatograms revealed the analysis of spiked real soil samples were shown in Fig. 6. According to the results obtained above, the proposed method is a promising mean for the analysis of PAHs in soil samples.

4. Conclusion

In this work, a novel adsorbent was developed based on TiO_2 NTs/Ti which was modified by C18-Ag NPs for SPE of PAHs. As the adsorbent possesses both large surface area and hydrophobic nature, it shows high extraction efficiency in the SPE of PAHs in soil samples with combining with UAE. Real soil samples were analyzed with using HPLC-FLD. The procedure shows good selectivity, low LODs, wide linear ranges for PAHs, as well as cost-effectiveness and easy-operating. It can be applied in the analysis of PAHs in complex environmental samples.

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