TiO$_2$ nanotubes as solid-phase extraction adsorbent for the determination of polycyclic aromatic hydrocarbons in environmental water samples

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Abstract

An analytical method based on TiO$_2$ nanotubes solid-phase extraction (SPE) combined with gas chromatography (GC) was established for the analysis of seven polycyclic aromatic hydrocarbons (PAHs): acenaphtylene, acenaphthene, anthracene, fluorene, phenanthrene, fluoranthene and pyrene. Factors affecting the extraction efficiency including the eluent type and its volume, adsorbent amount, sample volume, sample pH and sample flow rate were optimized. The characteristic data of analytical performance were determined to investigate the sensitivity and precision of the method. Under the optimized extraction conditions, the method showed good linearity in the range of 0.01–0.8 μg/mL, repeatability of the extraction (RSD were between 6.7% and 13.5%, $n = 5$) and satisfactory detection limits (0.017–0.059 ng/mL). The developed method was successfully applied to the analysis of surface water (tap, river and dam) samples. The recoveries of PAHs spiked in environmental water samples ranged from 90% to 100%. All the results indicated the potential application of titanate nanotubes as solid-phase extraction adsorbents to pre-treat water samples.

Key words: TiO$_2$ nanotubes; hydrothermal treatment; solid phase extraction; gas chromatography; polycyclic aromatic hydrocarbons

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants throughout the environment and originate mainly from anthropogenic sources such as the combustion of fossil fuels and the direct release of oil products (Poster et al., 2006). They present an important class of organic contaminants, and many of them with four or more rings are carcinogenic and mutagenic because of their metabolic transformation capacities (Li et al., 2001; ATSDR, 1995). Due to the extensive amount of data suggesting the hazards of these compounds, the European Water Framework Directive (WFD) establishing a list of six PAHs priority substances (anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, ideno[1,2,3-cd]pyrene) are classified as priority hazardous substances, and naphthalene, as well as fluoranthene as priority substances (Directive 2000/60/EC; Decision No 2455/2001/EC).

International standardised methods for analysing PAHs in surface waters are available, including ISO 17993 method based on high-performance liquid chromatography (HPLC) with fluorescence detection after liquid-liquid extraction, and ISO/CD 28540 method based on gas chromatography–mass spectrometry after either liquid-liquid or solid phase extractions. EPA method 525.1 using C18 silica adsorbent for PAH extraction, is also widely used.

Solid phase extraction (SPE) is a well-established technique for the extraction of various pollutant species at low concentration level. This technique is extinguished from the liquid-liquid extraction because of its advantages of high recovery, high enrichment factor, short extraction time, and low consumption of organic solvents. Recently, carbon nanotubes divided into single-walled carbon nanotubes and multi-walled carbon nanotubes (MWCNT) (Cai et al., 2003a, 2003b, 2005; Yang and Xing, 2006; Yang et al., 2006a, 2006b) have attracted more attention as SPE adsorbent. Wang et al. (2007) used MWCNT as adsorbent for solid-phase extraction of PAHs in environmental waters. Moreover, many nanotubes materials have been synthesised such as: titanium dioxide (TiO$_2$),

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zirconium dioxide, silica, V_2O_5, MoO_3 (Liu et al., 2007; Mor et al., 2006; Jung et al., 2002). It is reported that TiO_2 nanotubes have larger surface area than the starting titanium, and contain more ion-exchangeable OH groups in the interlayer and surface (Kasuga, 2006; Liu et al., 2005). TiO_2 nanotubes has also gained great interests in analytical chemistry because of its high chemical stability, durability, corrosion resistance, non toxicity and cost effectiveness. Micro-scaled TiO_2 has been used as stationary phase in HPLC applications (Nawrocki et al., 2004) as well as a solid phase extraction adsorbent for the enrichment of metal ions (Vassileva et al., 1996; Camel, 2003; Zhang et al., 2005) and selective extraction of phosphates (Kawahara et al., 1989; Matsuda et al., 1991; Ikeguchi and Nakamura, 1998), phospholipids (Ikeguchi and Nakamura, 1999, 2000) and phosphopeptides (Sano and Nakamura, 2004a, 2004b; Pinkse et al., 2004). TiO_2 nanotubes were demonstrated to be excellent adsorbents of inorganic cations and anions as well as organic compound (Diebold 2004; Liang et al., 2001; Li et al., 2004; Li and Deng, 2002; Chen and Chen, 2005). Zhou et al. (2007) investigated the feasibility of TiO_2 nanotubes as SPE adsorbent for the extraction of dichlorophenyltrichloroethane (DDT) and their metabolites in environmental water samples.

However, there was no literature about application of TiO_2 nanotubes to the enrichment of PAHs from environmental water samples. In the present work, we demonstrated for the first time the applicability of TiO_2 nanotubes as SPE adsorbent. We investigated the selective separation of acenaphthene, acenaphthylene, anthracene, fluorene, phenanthrene, fluoranthene and pyrene (cited among the 16 PAHs considered as priority by the EPA) as PAHs model compounds. Factors that may influence the enrichment efficiencies of the target PAHs (kind and volume of eluent, sample flow rate, sample pH, sample volume and adsorbent amount) were optimised. Furthermore, efficiency of the TiO_2 nanotubes as adsorbent for the enrichment of selected PAHs at trace levels in tap and surface waters was investigated.

1 Experimental

1.1 Reagents

Organic solvents, acetonitrile (ACN), methanol, dichloromethane (DCM) and hexane were of the HPLC grade. Ultra pure water was prepared in the laboratory using a Milli-Q system (Millipore, Elix, France). Certified PAHs reference standards acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), fluorene (Flo), phenanthrene (Phn), fluoranthene (Flr) and pyrene (Pyr) were purchased from Sigma-Aldrich (USA). These standards were dissolved in DCM at 0.1 μg/mL. Stock solutions were protected from light and stored at 4°C. Working solutions were prepared daily by an appropriate dilution of the stock solutions with methanol.

Titanium dioxide (68% anatase and 32% rutile, P25, Degussa-Hüls AG); sodium, hydroxide (Fisher Chemicals, UK), and hydrochloric acid (Panreac Quimica SA, Spain)

were used without further purification.

Acetate buffer solution (CH_3COO^-/CH_3COOH) was prepared by mixing appropriate volumes of 0.1 mol/L acetic acid and 0.1 mol/L sodium acetate solutions at pH 4. Ammonium buffer solution was prepared by mixing appropriate amounts of 0.1 mol/L ammonia and 0.1 mol/L ammonium chloride solutions at pH 9.

1.2 Materials characterization

The N_2 adsorption-desorption isotherms at 77 K were performed using a Micromeritics ASAP 2000 analyzer (USA). The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area (S_{BET}). Mean pore diameter (d_p) was obtained using the Barrett-Joyner-Halenda (BJH) model in the range of mesopores. X-ray diffraction (XRD) patterns were obtained by a PANalytical X'Pert Pro (the Netherlands) apparatus using Cu$K\alpha$ radiation (λ = 1.542 Å) for investigating the crystallization behaviour. Low magnification TEM images were taken at an accelerating voltage of 200 kV on a JEOL-2010 (Japan) instrument. HRTEM images were taken at an accelerating voltage of 400 kV. Specimens for the TEM studies were prepared by depositing a drop of aqueous suspension of the samples onto 300 mesh Cu grid, coated with a lacey carbon film.

PAHs were analyzed using an Agilent 689ON Network GC System (USA) with flame ionization detector (FID). An HP-5MS column coated with 5% phenyl methylsiloxane (30 m × 0.25 mm, with 0.25 μm film thickness) was used for separation of studied compounds. Helium (1 mL/min) was used as carrier gas. The GC oven temperature was kept at 50°C for 2 min and programmed to 250°C at a rate of 8°C/min. The split ratio was adjusted at 1:10 and the injector temperature was maintained at 250°C. The FID detector temperature was kept at 300°C.

1.3 Preparation of titanate nanotubes

The alkaline hydrothermal method, as described by Kochkar et al. (2009) was used to prepare the titanate nanotubes. Specifically, a commercial TiO_2 (0.50 g) was dispersed in a 15 mL aqueous solution of 11.25 mol/L NaOH and placed into a teflon-lined autoclave with an 80% filling factor. The autoclave was then heated at 403 K for 20 hr to prepare the hydrogenotitanate nanotubes (HNTs) samples. A white precipitate was isolated upon filtration and washed repeatedly with 1000 mL of hot ultra pure water until the supernatant pH value attained 9. In a second step, an aqueous solution containing the precipitate was neutralized using a 0.1 mol/L HCl solution until a pH value of 7 was reached. The precipitate was then subsequently washed with 500 mL ultra pure water to remove NaCl formed in excess. The obtained wet solids were dried in an oven at 353 K for 24 hr. Finally, HNTs nanotubes were calcined at 773 K under air for 2 hr.

1.4 SPE procedure

TiO_2 nanotubes packed cartridges were prepared by modifying an Agilent ZORBAX SPE C18 cartridge (0.2 g, 3 mL, polypropylene). The C18 packing was evacuated,

and 0.1 g TiO$_2$ nanotubes were packed in the cartridge. The polypropylene upper and lower frits remained at each end of the cartridge to hold their packing TiO$_2$ nanotubes in place. The packed cartridge was placed in a vacuum elution apparatus. This solid phase was first conditioned with 10 mL of methanol and 10 mL of deionised water. Then a known volume of ultra pure water or sample water spiked with the seven target analytes was applied to the column. After that, the retained PAHs were eluted with an optimum volume of DCM and finally the extract was dried to 1 mL with nitrogen gas in water bath at 35°C.

1.5 Water samples

Tap water and surface water samples were selected for validating the proposed method. Tap water sample was collected from our own laboratory after it was flowing for 10 min at very large rate. However, dam water samples were obtained from Sidi Salem and Sejnene reservoirs. All the collected water samples were filtered through a Millipore membrane with pore size 0.45 μm immediately after sampling and were maintained in amber glass bottles at 4°C. To avoid PAHs adsorption in the glass of bottles, samples were rapidly extracted.

2 Results and discussion

2.1 TiO$_2$ nanotubes characterization

The change in the crystal structure from the starting P25 powder to one dimensional titanate structures was studied by XRD. All peaks in the XRD patterns (Fig. 1) were assigned to the H$_2$Ti$_2$O$_5$·H$_2$O, which showed an orthorhombic system with the lattice constants a_0 = 1.926 nm, b_0 = 0.378 nm and c_0 = 0.300 nm (Yang et al., 2003). Up-on calcination of TiO$_2$ nanotubes at 773 K, it can be seen from Fig. 1, that the intensity of the diffraction peak (110) near $2\theta \approx 30°$ was decreased and shifted towards a higher angle value, indicating a decrease in the interlayer distance in this plane. This contraction of layers may be due to the release of water molecules adsorbed and presented in the spacing. New peaks appeared showing the transformation of the initial HNT sample to anatase phase.

The effect of calcination temperature on the pore size distribution, mesoporous volume and surface area has been investigated and the results are illustrated in Table 1. For temperature > 403 K, the surface area was found to be strongly influenced by the calcination temperatures; it decreases to 99 m^2/g at 773 K, indicating sintering of the nanotubes. However, the pore distribution increases due to the aggregation of formed nanoparticles. The drop in surface area and mesoporous volume is in accordance with previous observations by Edisson et al. (2006) for Na$_x$H$_{2-x}$Ti$_3$O$_7$.

Changes in the morphology of the nanotubes occurring with respect to temperature were followed using TEM analysis. Figure 2 shows transmission electron micrographs of the starting material as well as after calcination at 773 K for 2 hr. It can be seen from fig. 2a that the initial material is quite homogeneous with a large number
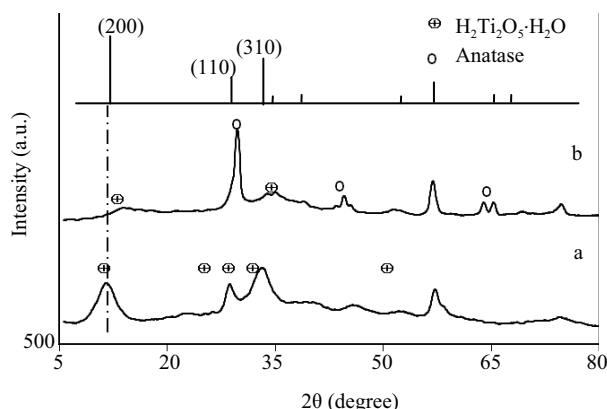
Fig. 1 XRD patterns of titanate nanotubes support (line a) and comparison with the expected XRD peak intensities of the H$_2$Ti$_2$O$_5$ phase (line b) after calcination at 773 K.

Table 1 Textural properties of TiO$_2$ nanotubes

Temperature (K)	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)
403	269	0.67	9
773	99	0.63	23

S_{BET}: BET surface area; V_p: porous volume; d_p: mean pore diameter.

of nanotubes. The outer diameters of tubes were 6–8 nm and inner diameters were 4–6 nm, and the lengths were measured to be several hundreds of nanometres. All the tubes were open at both ends. The HRTEM analysis shows that the walls of the nanotubes were amorphous (Fig. 2b). The morphology of the nanotubes remained hardly affected up to 773 K even the outer and inner diameters decrease to 7–5 nm (Fig. 2c). However, HRTEM analysis showed that the initially amorphous nanotubes walls were transformed into crystalline anatase (Fig. 2d). This was also consistent with the XRD results showing that the patterns drastically changed after calcination at 773°C.

Nanotubes were successfully obtained directly from TiO$_2$ (P25) following a hydrothermal process in the presence of sodium hydroxide. The nanotubes retained their morphology up to 773 K. Only a change in the structure related to the transformation of orthorhombic HNTs into anatase TiO$_2$ was observed.

The anatase TiO$_2$ nanotubes were used as adsorbent for the SPE of PAHs at trace levels in water samples. There are many factors that may influence the enrichment efficiencies of the PAHs compounds such as the kind of elution solvent and its volume, the sample volume, the sample pH, the sample flow rate and the mass of adsorbent. To determine optimum factors that ensure the entire recovery of all the analytes adsorbed, Milli-Q water was spiked with the seven PAHs compounds at 0.1 μg/mL concentration level.

2.2 Effect of elution solvent

To ensure the completely elution of the target PAHs from the cartridge, an optimum solvent polarity should be chosen. For this purpose, four solvents with different polarities were tested: hexane < DCM < acetonitrile < methanol. Elution of PAHs from cartridge was performed
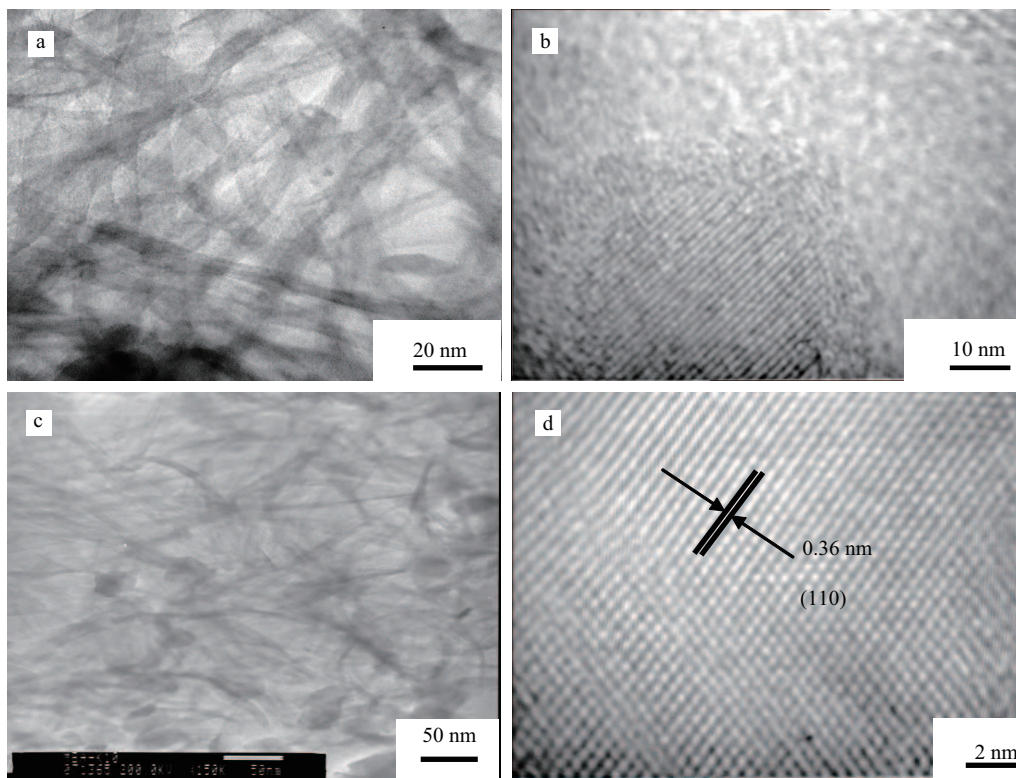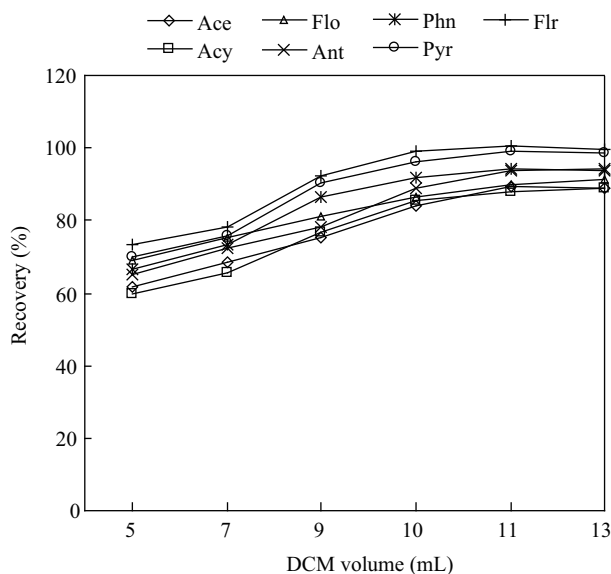
Fig. 2　TEM (a) and HRTEM (b) images of H$_2$Ti$_2$O$_5$·H$_2$O; TEM (c) and HRTEM (d) images after calcination at 773 K.
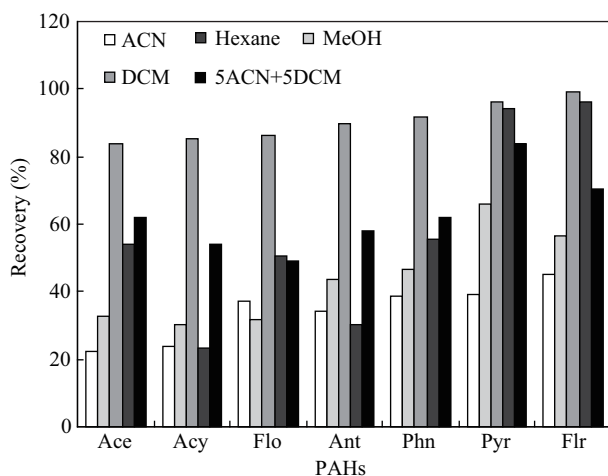
Fig. 3　Influence of elution solvent on analytes recovery. Spiked sample concentration: 0.1 μg/mL for each compound; eluent volume: 10 mL; sample flow rate: 3 mL/min; sample pH: 6 and sample volume: 100 mL. ACN: acetonitrile; MeOH: methanol; DCM: dichloromethane.

Fig. 4　Effect of eluent volume on analyte recoveries. Other conditions are the same as in Fig. 3.

with 10 mL of the selected organic solvent. An intermediate solvent polarity was obtained by mixing acetonitrile and DCM (5:5, *V/V*). It seems clear that the recovery of PAHs compounds is related to the solvent polarity (Fig. 3). This is due to different partition constants of PAHs between TiO$_2$ nanotubes (solid phase) and solvent (liquid phase). The experimental results demonstrated that DCM, with a medium polarity, gave the much high elution efficiency than other organic solvents for all of the target analytes, therefore it was selected as the elution solvent for the next optimisation steps.

The volume of the eluent has an great effect on the elution performance and efficiency. To find out the required DCM volume to recover all the analytes from TiO$_2$

nanotubes packed cartridge, eluent volumes in the range of 5–13 mL were tested. From Fig. 4, it suggested that PAHs compounds needed a volume of eluent more than 11 mL to get the best recoveries. Thus, to achieve complete elution of the seven analytes, 12 mL DCM was utilized in following experiments.

2.3 Effect of sample flow rate

The influence of sample flow rate was investigated over the range of 1–8 mL/min with the other conditions kept constant. The experimental results shown in Fig. 5 indicated that 3 mL/min was optimal flow rate which was
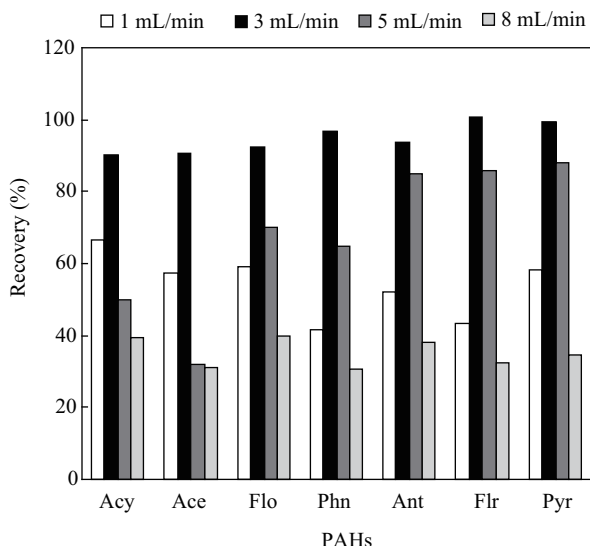
Fig. 5 Effect of the sample flow rates on PAHs recoveries. Eluent: 12 mL DCM; other conditions were same as in Fig. 3.
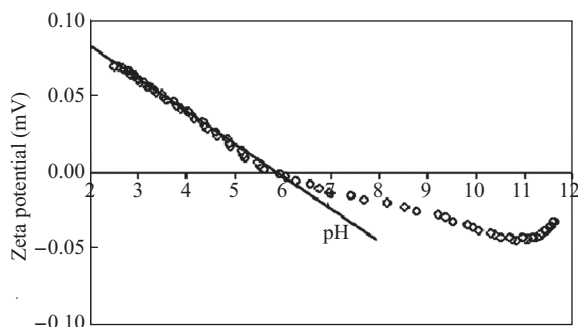
Fig. 6 Zeta potential values of TiO$_2$ nanotubes as a function of solution pH.

selected for further use in the following experiment.

2.4 Effect of sample pH

Sample pH plays an important role in the SPE procedure and affects the extraction efficiency. pH factor determine the surface charge of the TiO$_2$ nanotubes. The OH group can be protonated in acidic solution then TiO$_2$ nanotubes have positive surface charge. However, in alkaline media the OH group can be deprotonated and they have negative surface charge. The effect of sample pH on the recoveries of selected PAHs was examined in a range of 4–9. For most of objectives satisfactory recoveries were obtained at pH 6 (Fig. 6). This result is in agreement with that of Zhou et al. (2007) who studied the feasibility of TiO$_2$ nanotubes for the enrichment of the DDT and its metabolites in environmental water samples. Zeta potential (ZP) of titanium nanotubes as function of solution pH was determined (with zetasizer 2000 apparatus). Figure 6 shows the ZP-pH curve of the TiO$_2$ in aqueous media (1 g/L). Three different surface charges (positive, zero, and negative) were detected, depending on the solution pH. The zero zeta potential (pH between 5.5 and 6) coincides with the sample pH allowing maximum extraction recoveries.

2.5 Effect of sample volume

In order to obtain reliable and reproducible analytical results and satisfactory recoveries for all the studied compounds, the breakthrough volume in the solid phase extraction was investigated. Different volumes (100–500 mL) of ultra pure water spiked with 0.1 μg/mL of each PAH analytes were preconcentrated by TiO$_2$ nanotubes packed cartridges. As described in Fig. 7, recovery levels obtained for studied PAHs decrease when the treated water volume increases from 100 to 400 mL. Based on these results, the sample volume of 100 mL was selected in the subsequent analysis.

2.6 Effect of amount of cartridge packing

The efficiency of the TiO$_2$ nanotubes amount on the recovery of analytes was studied. Three solid phase amounts were tested (100, 200 and 300 mg) for the preconcentration of PAH compounds in spiked Milli-Q water. Obtained results (Fig. 8) showed insignificant differences in recoveries among the different amounts of cartridge packing. Therefore, the TiO$_2$ nanotubes amount of 100 mg was recommended for the extraction of PAHs compounds.

## 2.7 Characteristics of the method

For the precision of this method, five replicate samples spiked at 0.1 μg/mL were carried out using the optimum conditions described above. The recoveries of Acy, Ace, Flo, Ant, Phn, Pyr and Flr were 90.2%, 90.8%, 92.2%, 93.9%, 97.0%, 99.5% and 100.9% respectively. The relative standard deviations (RSD) were 7.3% for Acy, 12.4 for Ace, 6.7 for Flo, 6.8 for Phn, 11.2 for Ant, 13.0 for Flr and 13.4 for Pyr. As a new adsorbent for SPE, TiO$_2$ nanotubes present some limitation in terms of stability and repeatability (RSD > 5%), this can be improved by enlarging the surface area and controlling the pore size.

Under the conditions selected above, calibration graphs were linear in the range of 0.01–0.80 μg/mL for each PAH compounds. Calibration equations, correlation coefficient as well as the detection limit ($S/N = 3$) of each analyte are illustrated in Table 2. TiO$_2$ nanotubes, as SPE adsorbent,
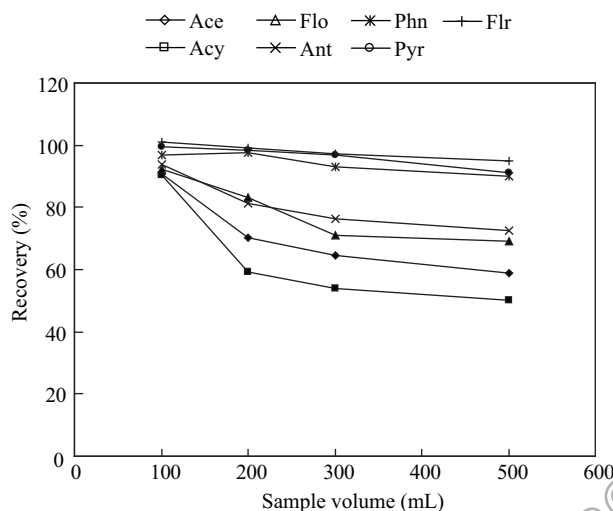
Fig. 7 Effect of sample volume on PAHs recoveries. Conditions are the same as in Fig. 5.
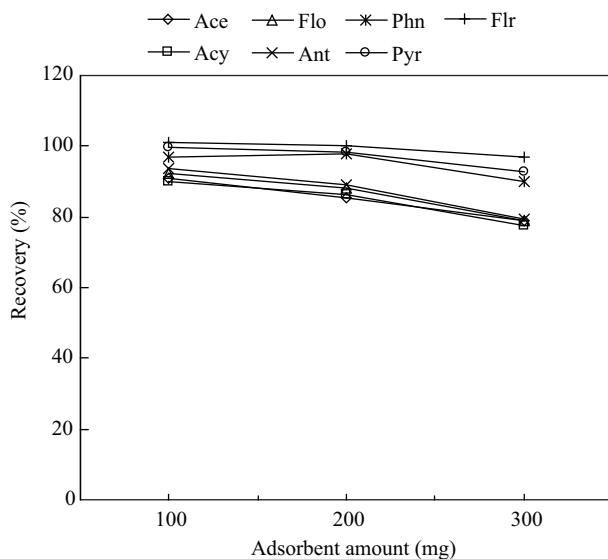
Fig. 8   Effect of TiO$_2$ nanotubes amount on the PAHs recoveries. Conditions are the same as in Fig. 7.

provided reproducible and reliable analytical results and showed good linear correlation $R^2 \geqslant 0.994$.

2.8 Comparison study

The present results with TiO$_2$ nanotubes, as new sorbent for the SPE, were compared to traditional method using C18 silica sorbent. PAHs were extracted from water samples by C18 procedure as described by Oleszczuk and Stanisław (2004). Results were also compared to that presented by Wang et al. (2007) using MWCNTs sorbent. Figure 9 shows that TiO$_2$ nanotubes presented its comparable adsorbent properties to MWCNTs but superior to C18. The three SPE procedures applied to PAHs presented competitive results. But sometimes it is necessary to take into account the cost of adsorbent in addition to its analytical performance. However, MWCNTs and C18
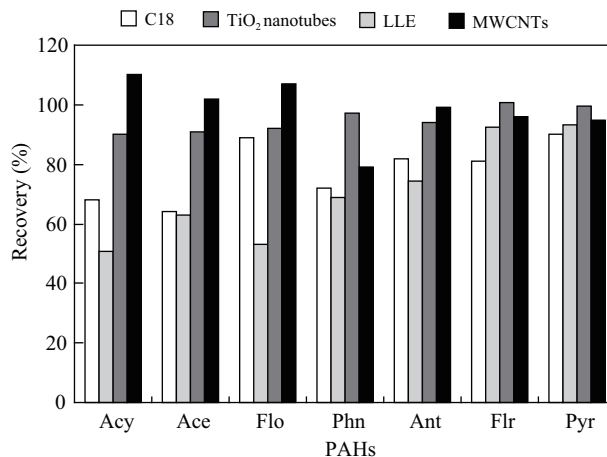
Fig. 9   Extraction recoveries obtained with C18, MWCNTs and TiO$_2$ nanotubes sorbents and with liquid-liquid extraction.

silica sorbents are more expensive than the TiO$_2$ nanotubes elaborated with the simple hydrothermally method.

Liquid-liquid extraction (LLE) of PAHs from water samples was done as described by Brum et al. (2008) and experimental results were compared to that obtained with TiO$_2$ nanotubes sorbent. According to the results shown in Fig. 9, the difference of recoveries between the two extraction procedures was important with the exception of Flr and Pyr cases. SPE method presents more advantages than LLE especially when using nanoscaled materials as sorbents. Indeed, their strong adsorption affinity to a wide variety of organic compounds, together with their large adsorption surface make them excellent material for SPE.

2.9 Application to environmental water samples

In order to investigate the feasibility of TiO$_2$ nanotubes in the application of environmental sample analysis, all retained SPE conditions were assessed on real spiked water samples (tap, river and dam waters). Firstly, blanks of

Table 2   Calibration equation, correlation coefficient and the detection limit of each PAH analyte

Compound	Linear range (μg/mL)	Calibration equation	R^2	Detection limit* (ng/mL)
Acy	0.01–0.50	$y = 1.6690x - 10^{-4}$	0.9999	0.031
Ace	0.05–0.40	$y = 1.8504x - 10^{-4}$	0.9998	0.017
Flo	0.05–0.40	$y = 1.2195x - 10^{-4}$	0.9971	0.026
Phn	0.05–0.80	$y = 2.2420x + 3 \times 10^{-4}$	0.9997	0.053
Ant	0.05–0.80	$y = 1.3812x - 2 \times 10^{-4}$	0.9982	0.015
Flr	0.05–0.40	$y = 2.5889x - 3 \times 10^{-5}$	0.9944	0.017
Pyr	0.01–0.80	$y = 1.8366x - 8 \times 10^{-5}$	0.9959	0.059

* Detection limits were calculated using $S/N = 3$.

Table 3   Recovery percentages of tap and surface water samples spiked at two concentrations levels

Compound	Recovery of tap water (%)		Recovery of surface water (%)			
			Sidi Salem		Sejnane	
	0.05 μg/mL	0.1 μg/mL	0.05 μg/mL	0.1 μg/mL	0.05 μg/mL	0.1 μg/mL
Acy	85.4	93.3	82.4	84.3	85.0	88.4
Ace	83.4	94.1	87.5	90.3	81.7	88.5
Flo	86.2	94.9	89.2	91.1	87.3	90.3
Phn	88.9	97.2	88.8	94.5	91.0	93.8
Ant	85.5	93.0	88.1	90.7	89.3	89.5
Flr	94.3	99.5	93.5	97.6	90.5	96.2
Pyr	92.6	98.4	90.5	96.7	89.7	94.9
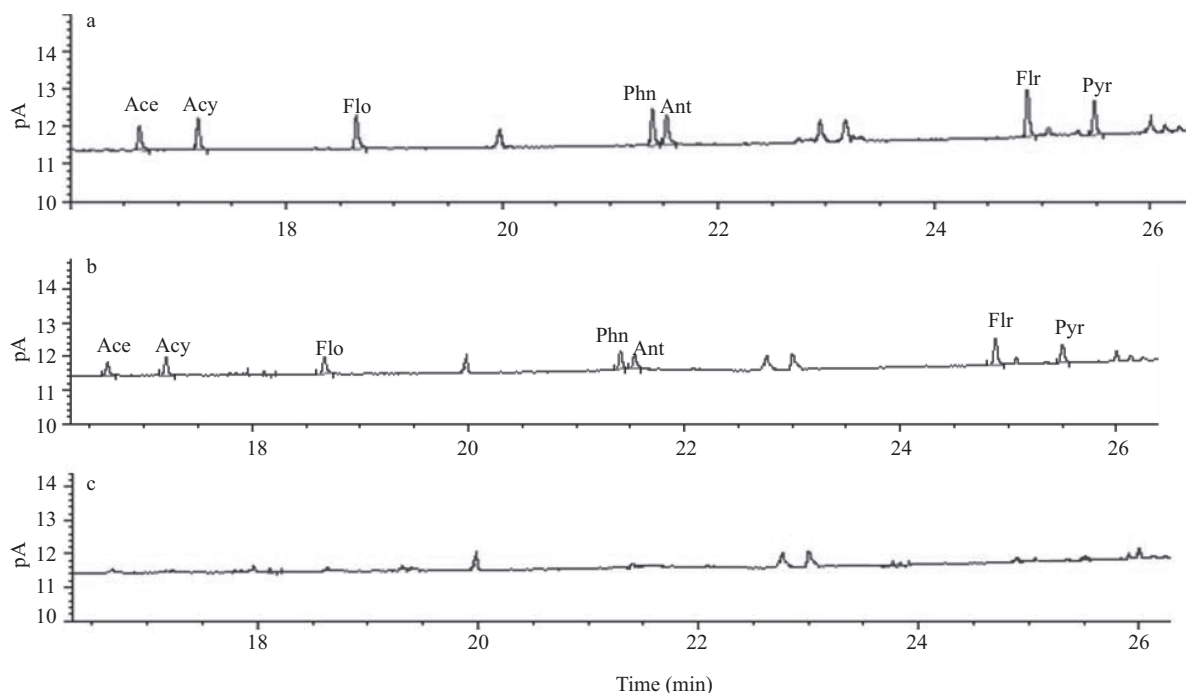
Fig. 10 Chromatograms of surface water samples. (a) blank of tap water, (b) tap water sample spiked with 0.05 μg/mL of each compound, and (c) tap water sample spiked with 0.1 μg/mL of each compound. Eluent: DCM; 12 mL; sample flow rate: 3 mL/min; sample pH: 6; sample volume: 100 mL and TiO$_2$ nanotubes amount: 100 mg.

all samples were run then 100 mL waters spiked at 0.05 and 0.1 μg/mL were passed through the SPE cartridge. The analytical results of the proposed method are given in Table 3 and the chromatograms of the blank and spiked tap waters are exhibited in Fig. 10. Using this method, little matrix effect was found for the SPE of PAHs. The recoveries obtained were between 81.7% and 99.5%.

3 Conclusions

In this study, a simple, efficient and reliable method was set up to determine PAHs in the aqueous solution using titanate nanotubes as SPE sorbent coupled with GC. According to our experimental results, titanate nanotubes packed cartridge has good analytical potential for the extraction of some PAHs compounds such as acenaphthene, acenaphthylene, anthracene, fluorene, phenanthrene, fluoranthene and pyrene from real environmental water samples. Taking into account the simplicity and low cost of TiO$_2$ nanotubes elaboration, as well as the good extraction efficiencies, this nanostructured titania has great potential of becoming a cost effective and useful extraction tool in analytical methods.

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