



# Investigation of the applicability of highly ordered TiO<sub>2</sub> nanotube array for enrichment and determination of polychlorinated biphenyls at trace level in environmental water samples

Qingxiang Zhou<sup>a,b,\*</sup>, Yunrui Huang<sup>b,d</sup>, Guohong Xie<sup>c</sup>

<sup>a</sup> College of Geosciences, China University of Petroleum Beijing, Beijing 102249, China

<sup>b</sup> School of Chemistry and Environmental Sciences, Henan Normal University, Key Laboratory for Yellow River and Huaihe River Water Environment and Pollution Control, Ministry of Education, Xinxiang 453007, China

<sup>c</sup> College of Resources and Environment, Henan Institute of Science and Technology, Xinxiang 453003, China

<sup>d</sup> College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, China

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## ABSTRACT

Present study investigated the applicability of ordered TiO<sub>2</sub> nanotube arrays for the enrichment and determination of polychlorinated biphenyls (PCBs) in water samples. A new and reliable method was developed for the preconcentration and determination of PCBs by micro-solid phase equilibrium extraction in combination with gas chromatography and electron capture detection (GC-ECD), which exploited the special physical and chemical properties of ordered TiO<sub>2</sub> nanotube arrays. The experimental results indicated that low LODs were easily achieved in the range of 0.02–0.10 μg L<sup>-1</sup> for PCB-28, PCB-52, PCB-101, PCB-153, PCB-138, and PCB-180. The proposed method was validated with several real water samples, and good spiked recoveries have been obtained in the range of 95.8–110.5%. The experimental results demonstrated that TiO<sub>2</sub> nanotube arrays could be reused for over 200 times without the loss of the extraction efficiency. All these showed that TiO<sub>2</sub> nanotube arrays would be very useful in the enrichment and determination of trace pollutants.

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## 1. Introduction

Recently, TiO<sub>2</sub> nanotubes have received considerable attention because of its higher surface area, better adsorption ability and higher photocatalytic activity in comparison with TiO<sub>2</sub> powders [1–4]. However, it was difficult to separate and reuse the TiO<sub>2</sub> nanotubes from the solution. It would be helpful to solve this question if the TiO<sub>2</sub> nanotubes were aligned on a substrate or a template. Zwilling et al. firstly reported that the ordered TiO<sub>2</sub> nanotubes arrays could be obtained through a simple anodization process [5], and Mor et al. successfully prepared highly ordered TiO<sub>2</sub> nanotube array film for fabricating the solar cell [6]. Ordered TiO<sub>2</sub> nanotube array has been an attractive approach for many important engineering applications. These potential applications include photoelectrochemical hydrogen generation [7–11], solar cells [12–14], hydrogen storage [15], gas sensing [16–18], catalyst supports [19] and photoelectrocatalytic activity electrode for organic contaminant degradation [20–24]. However, to the best of our knowledge, there has very few reports using TiO<sub>2</sub>

nanotube array on the enrichment and measurement of environmental contaminants.

Polychlorinated biphenyls (PCBs), up to 209 individual chlorinated compounds, have been used widely in heat exchangers and dielectric fluids as stabilizers in paints, polymers, and adhesives, and lubricants in various industrial processes. They are hazardous substances due to their hydrophobic character and toxic potential and resist to degradation and have high bioaccumulation potential [25]. Therefore, the occurrence of PCBs in natural environment has become a major problem in the world.

Determination of PCBs at trace level is usually performed by gas chromatography (GC) combined with a preconcentration step including traditional liquid–liquid extraction (LLE) [26], solid phase extraction (SPE) [27,28], solid phase microextraction (SPME) [29–31], dispersive liquid–liquid microextraction (DLLME) [32], ultrasound-assisted emulsification–microextraction (USAEME) [33], pressurized liquid extraction (PLE) [34,35], supercritical fluid extraction (SFE) [36,37], bead injection (BI) in the miniaturized lab-on-valve (LOV) [38], stir bar sorptive extraction (SBSE) [39], dynamic hollow fiber liquid–phase microextraction (dynamic HF-LPME) [40], and ultrasound-assisted pressurized solvent extraction (PSE) [41], etc. These pretreatment methods have been applied to the enrichment and determination of PCBs. SPE has been the popular one because the procedure is very easy and the

\* Corresponding author at: College of Geosciences, China University of Petroleum Beijing, Beijing 102249, China. Tel.: +86 10 89732300; fax: +86 10 89732300.

E-mail addresses: [zhouqx@cup.edu.cn](mailto:zhouqx@cup.edu.cn), [zhouqx@henannu.edu.cn](mailto:zhouqx@henannu.edu.cn) (Q. Zhou).

operation is very simple. However the enrichment performance is determined by the characteristics and the physical and chemical properties of the used adsorbents. As we know, even if the same material is used, the different structure may also result in different enrichment performance. Highly ordered  $\text{TiO}_2$  nanotube array is a new kind nanomaterial of  $\text{TiO}_2$  materials, and has been widely used as mentioned above. However, there are few applications of highly ordered  $\text{TiO}_2$  nanotube array in the analysis of pollutants [42,43]. The goal of present study is to investigate the enrichment ability and applicability of  $\text{TiO}_2$  nanotube arrays for the monitoring of PCBs. A convenient micro-solid phase equilibrium extraction ( $\mu\text{SPEE}$ ) for the extraction of PCBs was developed with  $\text{TiO}_2$  nanotube arrays as the adsorbents and this process would avoid the low flow rate of the conventional solid phase extraction with  $\text{TiO}_2$  nanotubes cartridge and the difficulty in separation from dispersion in solution, which would broaden the application field of  $\text{TiO}_2$  nanotube arrays.

## 2. Experimental

### 2.1. Reagents and materials

A mixed standard solution with each concentration of  $10.00 \text{ mg L}^{-1}$  for 2,4,4'-trichlorobiphenyl (PCB-28), 2,2',5,5'-tetrachlorobiphenyl (PCB-52), 2,2',4,5,5'-pentachlorobiphenyl (PCB-101), 2,2',3,4,4',5'-hexachlorobiphenyl (PCB-138), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153), and 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB-180) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). The working stock solution with a concentration of  $1.00 \text{ mg L}^{-1}$  of PCBs was prepared in HPLC grade methanol with the mixed standard solution. All the standard solutions were stored at  $4^\circ\text{C}$  in the refrigerator. The aqueous solutions were prepared daily by diluting the standard mixture with ultrapure water. HPLC grade methanol and acetonitrile were obtained from Jiangsu Guoda Chemical Reagent Co., Ltd. (Huaian, China). Ultrapure water was prepared in the laboratory using a Millipore (Billerica, MA, USA) water generator system and all the other solvents were analytical reagent grade unless stated. One percent (w/v) sodium hydroxide and  $1 \text{ mol L}^{-1}$  hydrochloric acid were used for adjusting the pH value of the water samples.

Titanium sheets (99.6% purity) from Beijing Hengli Taiye Co., Ltd. (Beijing, China), Pt electrode was obtained from Shanghai Dian-guang Device Factory. 30V potentiostat was obtained from The Fourth Wearless Factory of Shijiazhuang (JWY-30G, Shijiazhuang, China).

### 2.2. Preparation of $\text{TiO}_2$ nanotube array

Titanium sheets (0.2 mm thick,  $10 \text{ mm} \times 20 \text{ mm}$  size) with 99.6% purity (Beijing, China) were polished with metallographic abrasive paper, and then were degreased by sonicating in acetone, methanol and ultrapure water, and then the sheets were air-dried. The anodic oxidation was accomplished by using titanium sheet as anode and platinum as cathode. The distance between two electrodes was 3 cm in all experiments. The electrolyte was composed of  $0.14 \text{ mol L}^{-1}$  sodium fluoride and  $0.5 \text{ mol L}^{-1}$  phosphoric acid [44]. The anodic oxidation was carried out at 20V for 1 h. After electrolysis, titanium sheet was rinsed with ultrapure water and then air-dried.

### 2.3. Scan electron microscopy (SEM)

SEM images of  $\text{TiO}_2$  nanotube arrays prepared were obtained with a field emission scanning electron microscope (S-4800 FESEM, Hitachi, Japan) (Fig. 1).

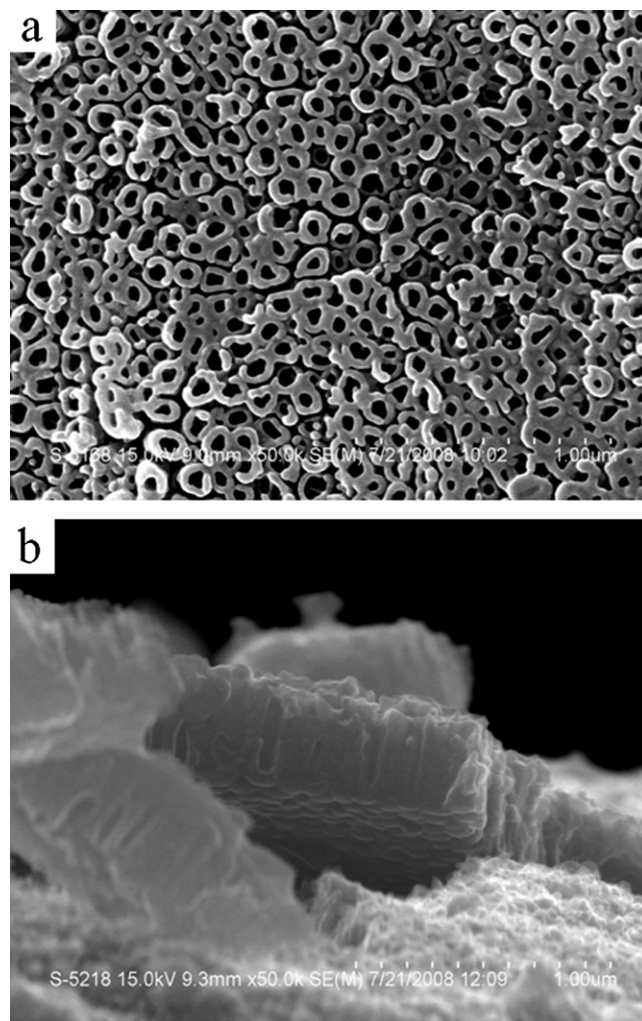


Fig. 1. FESEM images of  $\text{TiO}_2$  nanotube arrays: (a) top-view; (b) cross-view.

### 2.4. $\mu\text{SPEE}$ procedure

The  $\text{TiO}_2$  nanotube array sheet was directly immersed in 10 mL solution with a constant depth and then sealed the sample vial. The extraction conditions were as the same of the optimized conditions. A magnetic stirrer was used at 500 rpm. After the equilibrium between adsorption and desorption basically reached, the  $\text{TiO}_2$  nanotube array sheet was removed, rinsed with ultrapure water in order to remove co-adsorbed matrix materials and then air-dried, and eluted for desorption of analytes.  $\text{TiO}_2$  nanotube array sheet was directly immersed in a small amount of n-hexane in order to make the target analytes desorbed completely. After 10 min, the  $\text{TiO}_2$  nanotube array sheet was removed, and n-hexane was removed with a mild stream of nitrogen gas. Then the residues were dissolved in  $100 \mu\text{L}$  methanol. Finally,  $1 \mu\text{L}$  of the solution was injected for GC analysis.

### 2.5. GC analysis

GC analyses were performed on an Agilent 7890A gas-chromatographic system, equipped with an ECD. Separations were carried out on a HP-5 film column ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$ ). Nitrogen (99.999%) was employed as the carrier gas ( $1.0 \text{ mL min}^{-1}$ ).  $1.0 \mu\text{L}$  of a standard solution or sample solution were injected with splitless mode at  $300^\circ\text{C}$  using the following program:  $100^\circ\text{C}$  (held 1 min), then  $25^\circ\text{C min}^{-1}$  ramp to  $150^\circ\text{C}$  held for 1 min, then

8 °C min<sup>-1</sup> ramp to 280 °C held for 1 min, then 20 °C min<sup>-1</sup> ramp to 320 °C held for 1 min. Total run time was 24.2 min. The ECD was maintained at 320 °C.

## 2.6. Water samples

In this work, four water samples such as melted snow water, lake water and wastewater from a factory in Xinxiang City were selected for validating the proposed method. Snow sample was collected from Henan Normal University in Xinxiang City, Henan Province, China. Lake water samples were collected from Donghu Lake in Xinxiang City, Henan province, China and Shouxihu Lake in Yangzhou City, Jiangsu Province, China. Wastewater sample was taken from a wastewater treatment factory in Xinxiang City, Henan province, China. All the collected water samples were filtered through 0.45 μm micropore membranes after sampling and were stored in glass containers at 4 °C.

## 3. Results and discussion

### 3.1. Optimization of μSPEE procedure

In this μSPEE procedure, the extraction is affected by several factors. There are three processes in the whole process. First, the analytes would migrate between gas and liquid phases due to the vapor pressure for the volatile or half volatile compounds. This process will reach equilibrium. This equilibrium obeys Henry's law:

$$p_B = k_H x_B \quad (1)$$

where  $p_B$  is the partial pressure of the analytes in the gas above the solution,  $x_B$  is the concentration of the analytes and  $k_H$  is known as the Henry's law constant, which depends on the solute (analytes), the solvent and temperature.

The second process is the dissociation of the analytes which also occurred in the liquid phase due to the sample pH. Due to the fact that PCBs are difficult to be dissociated usually, the second process would be ignored. The final one is the adsorption of analytes onto the adsorbents and it is also a reversible process. Some of the PCBs may adsorb on the surface of the adsorbents and some of them will be desorbed at the same time. Finally, they will reach equilibrium. This equilibrium obeys Freundlich adsorption isotherm equation:

$$\lg Q = \lg K_F + \left(\frac{1}{n}\right) \lg x_B \quad (2)$$

where  $Q$  is the weight adsorbed per unit area of TiO<sub>2</sub> nanotubes array sheet,  $K_F$  and  $(1/n)$  are constants for a given adsorbate and adsorbent at a particular temperature,  $x_B$  is the concentration of the analyte. We substituted Eq. (1) into Eq. (2):

$$\lg Q = \lg K_F - \left(\frac{1}{n}\right) \lg k_H + \left(\frac{1}{n}\right) \lg p_B \quad (3)$$

In general, these three processes reach the equilibrium and the best enrichment will be achieved. If the concentrations of analytes are larger, maybe they do not obey the Henry's law. Suppose the amount of volatile part of the analytes is transferred to concentration form as  $C_v$ , and the concentration of analytes in solution will be  $C_0 - C_v$ , so,

$$\lg Q = \lg K_F + \left(\frac{1}{n}\right) \lg (C_0 - C_v) \quad (4)$$

Because the volatility of PCBs is very small, they will obey Eq. (2). The primary experiments have indicated that it was true.

In order to obtain appropriate extraction efficiency, the parameters including the kind of organic solvents, sample pH, extraction time, desorption time and the salting-out effect were investigated to obtain optimal enrichment conditions.

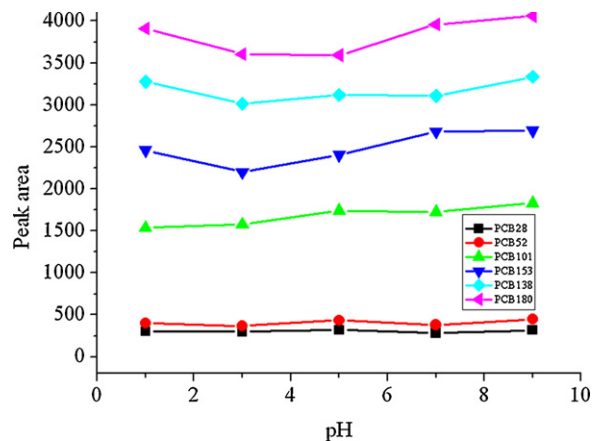


Fig. 2. Effect of sample pH. Equilibrium time: 40 min; NaCl: 0%; desorption time: 5 min; spiked sample concentration: 1 μg L<sup>-1</sup> for each compound.

#### 3.1.1. Effect of the kind of organic solvents

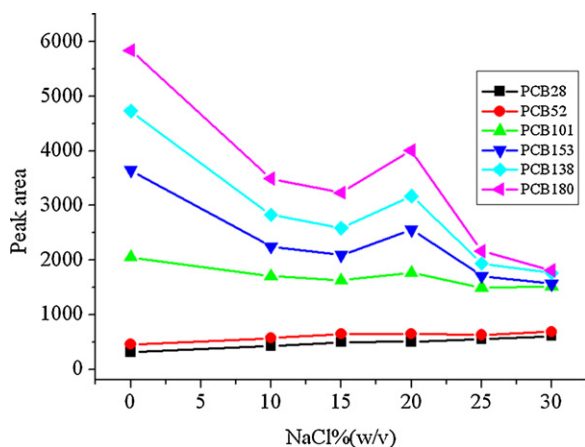
As this μSPEE procedure is concerned, different desorption efficiency would be obtained when different solvents are used because of the physical and chemical properties of the organic solvents and the characteristics of the target analytes. In this experiment, methanol, acetonitrile, acetone, n-hexane and dichloromethane were tested for desorption of PCBs. It was found that hexane was the most effective solvent for the six analytes. So it was used as the solvent for desorption.

#### 3.1.2. Effect of sample pH

Sample pH plays an important role in the μSPEE procedure because pH value determines the existing form of the analytes, and then the pH of the sample solution affects the extraction efficiency. In this experiment, the effect of sample pH on the enrichment of PCBs was evaluated in a range of pH 1.0–9.0 (see Fig. 2), the peak area of PCBs remained basically constant. The reason is that these compounds are stable compounds and will not dissociate under the common conditions. Hence, it need not adjust the pH value of the water samples in the following experiments.

#### 3.1.3. Salting-out effect

Salting-out effect is often an important factor in the extraction process. Addition of salt would enhance the enrichment performance in most cases, and also decrease the enrichment performance in some cases. The main reason is related to the physical and chemical properties of the analytes. Some studies showed the enhancement of extraction efficiency with the addition of ionic salts [45,46], while the others showed negative [47] or no direct correlations [48,49] between extraction efficiency and salt addition, and this result has also been seen by other authors [50,51]. In these experiments, it was investigated in the range of 0–30% (w/v). It can be seen from Fig. 3. The results showed that the results with no NaCl were much better than that with addition of NaCl. When the concentration of NaCl is in the range of 0–15%, the peak area decreases with the increase of salt concentration. When the concentration of NaCl is in the range of 15–20%, the peak area increases with the increase of salt concentration. When the concentration of NaCl is in the range of 20–30%, the peak area decreases with the increase of salt concentration. The reason is that salting-out effect is present in two aspects, one is enhancing dissolving, and the other is salting out. Fig. 3 has demonstrated the phenomena very well. When the salt concentration is very small, it makes more PCBs dissolved in the solution, which is the function of enhancing dissolving. The concentration of NaCl changed in the range of 15–20%, the peak area increased, which is the function of salting out. However, the



**Fig. 3.** Effect of ionic strength. Extraction time: 40 min; pH: 7; desorption time: 5 min; spiked sample concentration:  $1 \mu\text{g L}^{-1}$  for each compound.

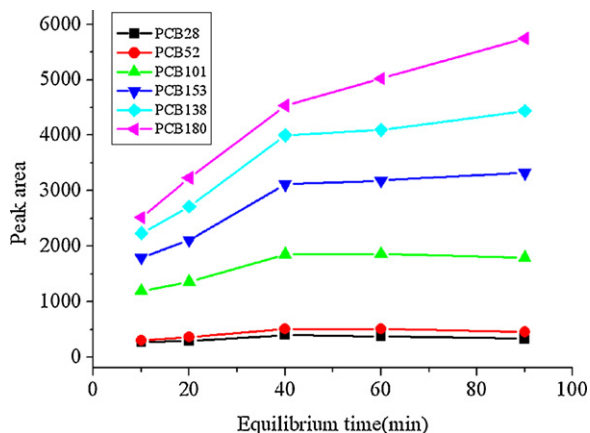
peak areas of PCBs decreased which was due to the fact that more NaCl would adsorb some of PCBs and this part of PCBs would not adsorb on the surface of the adsorbents. Hence, no NaCl was added in the further experiments.

### 3.1.4. Effect of extraction time

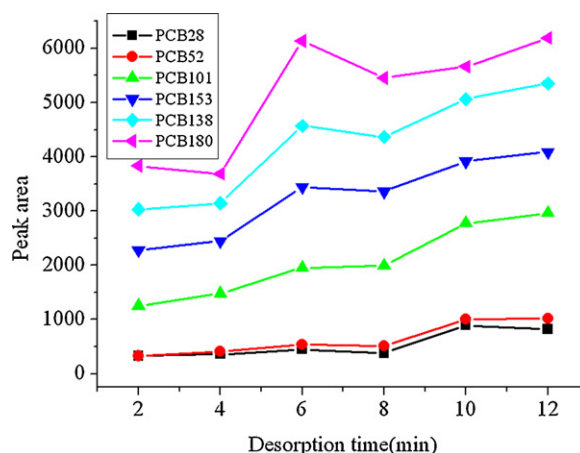
Extraction time is an important parameter in the  $\mu\text{SPEE}$  procedure. In order to achieve a reasonable extraction time, the effects of extraction time were studied over the time range of 10–90 min. The results were shown in Fig. 4. It was obviously that the extraction efficiency increased significantly when the extraction time increased up to 40 min after 40 min, the extraction efficiencies of PCBs increased very few except for PCB-180, whose extraction efficiency still increase slightly. So, 40 min was utilized as the final extraction time for time saving.

### 3.1.5. Effect of desorption time

In the  $\mu\text{SPEE}$  procedure, two steps are very important, one is the adsorption of analytes on the surface of adsorbents and the other is desorption of analytes from the adsorbents. Ideally these two procedures are very rapid. In fact, the procedure may be various due to different conditions. Desorption of PCBs from the  $\text{TiO}_2$  nanotube array sheet in *n*-hexane is influenced by time. In order to desorb PCBs completely, the desorption time was investigated in the range of 2–12 min and the results were exhibited in Fig. 5. It was found that the desorption was completed for all the test analytes in 10 min.



**Fig. 4.** Effect of equilibrium time. NaCl: 0%; pH: 7; desorption time: 5 min; spiked sample concentration:  $1 \mu\text{g L}^{-1}$  for each compound.



**Fig. 5.** Effect of desorption time. NaCl: 0%; pH: 7; extraction time: 40 min; spiked sample concentration:  $1 \mu\text{g L}^{-1}$  for each compound.

## 3.2. Analytical performance

To develop a new method, parameters such as linear range, correlation coefficients, limits of detection (LODs) and relative standard deviation (RSD) were important and they were evaluated (see Table 1). Calibration curves were performed using 10 mL ultrapure water spiked with  $0.1\text{--}50 \mu\text{g L}^{-1}$  for each PCB. Each PCB exhibited good linearity with correlation coefficient ( $R^2$ ) > 0.99 in the studied range. The limits of detection, calculated on the basis of signal to noise ratio of 3 ( $S/N=3$ ), were in the range of  $0.02\text{--}0.10 \mu\text{g L}^{-1}$ . The LODs of PCB-28, PCB-52 and PCB-101 were obviously higher than the other three PCBs. That is to say that the sensitivities of PCB-28, PCB-52 and PCB-101 were lower than the other three PCBs. The reason may be that the volatilities of PCB-28, PCB-52 and PCB-101 were higher than the other three PCBs, which could be found from Figs. 2–4, the peak areas of them were significantly lower than that of the others. The precision of proposed method was investigated using six replicate experiments with each PCB at a spiked concentration of  $1.0 \mu\text{g L}^{-1}$ , and precisions for intra day and inter day (RSDs) were all lower than 10.0%. Enrichment factor is an important parameter when a preconcentration method is developed. Generally, the enrichment factors are simply calculated by the ratio of the initial sample volume to the final volume enriched the target analytes, which is often right with the supposition that the analytes have the same enrichment or adsorption performance. However, different analytes will have different volatility and adsorption properties, and the enrichment behavior will be different. The often used volume ratios will not exhibit the real enrichment factor. In general, the calibration curve will not be through the origin of coordinates due to the reality that the analytes are not enriched at all, and the slope of the calibration curve would demonstrate the enrichment ability. So it is a very good way to use the ratio of the slope of the calibration curves with and without extraction as the enrichment factors. The enrichment factors, defined as the ratio of the slope of the calibration curves with and without extraction, were calculated and listed in Table 1. Moreover, in our experiments, it was found that one piece of Ti sheet with  $\text{TiO}_2$  nanotube array could be reused more than 200 times without the decrease of the enrichment performance, which made it competitive to be an alternative as an routine enrichment method for analytes.

## 3.3. Analysis of real water samples

To demonstrate the applicability of the  $\text{TiO}_2$  nanotube array sheet as  $\mu\text{SPEE}$  adsorbents, the proposed procedure has been applied to four real environmental water samples, and the results

**Table 1**  
Linear range, correlation coefficient, precision and detection limits (S/N=3).

Compound	Linear range ( $\mu\text{g L}^{-1}$ )	$R^2$	RSD% ( $n=6$ )		LOD ( $\mu\text{g L}^{-1}$ )	Enrichment factor
			Intra day	Inter day		
PCB-28	0.4–50	0.9907	5.53	7.22	0.100	41.2
PCB-52	0.3–50	0.9925	3.26	9.67	0.092	41.5
PCB-101	0.2–50	0.9903	2.42	8.92	0.042	75.8
PCB-153	0.1–50	0.9900	3.72	9.87	0.029	76.1
PCB-138	0.1–50	0.9901	3.70	4.25	0.025	72.8
PCB-180	0.1–50	0.9937	4.54	7.14	0.020	75.8

**Table 2**  
Recoveries of real water samples spiked at three concentration levels.

Water samples	Blank	Added ( $\mu\text{g L}^{-1}$ )	PCB-28	PCB-52	PCB-101	PCB-153	PCB-138	PCB-180
Donghu Lake water	N.D.	0.4	105.2 $\pm$ 3.8	106.2 $\pm$ 4.2	108.5 $\pm$ 4.3	101.2 $\pm$ 2.8	102.3 $\pm$ 3.1	102.7 $\pm$ 2.5
	N.D.	1.0	98.6 $\pm$ 1.0	101.3 $\pm$ 1.9	102.3 $\pm$ 1.0	105.3 $\pm$ 1.9	98.8 $\pm$ 1.1	99.5 $\pm$ 1.8
	N.D.	5.0	99.2 $\pm$ 2.2	99.8 $\pm$ 2.2	95.8 $\pm$ 2.5	99.8 $\pm$ 3.8	99.6 $\pm$ 3.1	100.2 $\pm$ 2.8
Snow water	N.D.	0.4	103.3 $\pm$ 7.8	101.3 $\pm$ 6.5	99.8 $\pm$ 8.8	102.3 $\pm$ 2.5	103.5 $\pm$ 3.8	106.2 $\pm$ 1.8
	N.D.	1.0	99.8 $\pm$ 2.5	105.6 $\pm$ 3.5	102.3 $\pm$ 4.1	99.5 $\pm$ 4.2	98.7 $\pm$ 3.8	95.8 $\pm$ 1.8
	N.D.	5.0	101.3 $\pm$ 1.1	100.4 $\pm$ 2.3	97.8 $\pm$ 0.8	100.1 $\pm$ 2.1	99.1 $\pm$ 2.4	99.6 $\pm$ 1.8
Shouxihu Lake water	N.D.	0.4	95.6 $\pm$ 2.3	99.6 $\pm$ 2.7	101.5 $\pm$ 4.2	102.3 $\pm$ 5.1	100.2 $\pm$ 5.8	101.2 $\pm$ 4.6
	N.D.	1.0	98.9 $\pm$ 3.8	98.4 $\pm$ 3.2	99.3 $\pm$ 3.1	95.6 $\pm$ 4.5	101.5 $\pm$ 1.6	98.4 $\pm$ 7.8
	N.D.	5.0	102.3 $\pm$ 0.5	108.9 $\pm$ 3.5	95.8 $\pm$ 2.4	98.7 $\pm$ 3.3	99.6 $\pm$ 0.6	99.2 $\pm$ 2.6
Wastewater	N.D.	0.4	110.5 $\pm$ 6.2	105.6 $\pm$ 5.8	105.2 $\pm$ 6.1	101.2 $\pm$ 4.5	101.8 $\pm$ 1.0	104.3 $\pm$ 6.7
	N.D.	1.0	101.5 $\pm$ 6.6	102.8 $\pm$ 6.1	99.1 $\pm$ 4.5	108.6 $\pm$ 1.0	101.9 $\pm$ 0.7	102.2 $\pm$ 1.9
	N.D.	5.0	105.3 $\pm$ 6.1	98.7 $\pm$ 3.8	98.2 $\pm$ 2.1	99.8 $\pm$ 0.4	100.2 $\pm$ 1.2	96.8 $\pm$ 1.5

were shown in Table 2. The results indicated that no PCBs were found in water samples. These samples were then spiked with PCBs at three different concentrations to investigate the effect of sample matrices. The spiked recoveries were satisfied in the range of 95.8–110.5%. A comparison between present method and conventional C18 SPE method was carried out. 0.2 g C18 was used for SPE, and the conditions were as described in Ref. [52]. The results were listed in Table 3. The results showed that the spiked recoveries at lower levels were good for these two adsorbents, however the spiked recoveries at higher level (for example, 5  $\mu\text{g L}^{-1}$ ) decreased markedly and was about 50% as C18 was used for enrichment, and these results were similar with that in reference [52]. Thome et al. had found that at low PCB concentrations ranging from 0.01 to 1 ppb, high and reproducible recovery percentages supported the idea that the adsorption of PCB onto microcartridges was efficient enough to retain a significant amount of the PCB present in analyzed water. Conversely, at higher PCB concentrations ranging from 2 to 10 ppb, the extraction efficiency dropped down to 50% [52]. As  $\text{TiO}_2$  nanotube array was used as the adsorbents, all the spiked recoveries were higher than 95.5%, and no marked drop was found in the concerned ranges. As the LODs were concerned, we also investigated the LODs of the method with 0.2 g

C18 as the adsorbent for SPE, the LODs were 0.047, 0.03, 0.023, 0.018, 0.014, and 0.02  $\mu\text{g L}^{-1}$  for PCB-28, PCB-52, PCB-101, PCB-153, PCB-138 and PCB-180, respectively. From Table 1, LODs of present study was in the range of 0.02–0.1 ppb, there has very small difference between them. The  $\text{TiO}_2$  nanotube arrays on the titanium sheet were two much thin layers, and the effective amount of  $\text{TiO}_2$  nanotubes were very small. Because the total mass of the sheet including  $\text{TiO}_2$  nanotube arrays is 400 mg, if the length of  $\text{TiO}_2$  nanotube arrays is 500 nm, the two layers of  $\text{TiO}_2$  nanotube arrays is about 1  $\mu\text{m}$ , and the thickness of the sheet is 0.2 mm. So the mass of  $\text{TiO}_2$  nanotube arrays used for enrichment is lower than 2 mg. That is to say, the amount of C18 used for enrichment is 100 times larger than that of  $\text{TiO}_2$  nanotube arrays. As mentioned above, the effective amount of C18 was much higher than that of  $\text{TiO}_2$  nanotube array. If this factor was taken into consideration, the present method should give better results. Dai et al. [53] reported a dispersive liquid–liquid microextraction (DLLME) and gas chromatography–electron capture detection (GC–ECD) for the extraction and determination of five polychlorinated biphenyls (PCBs), in which the analytes included PCB-28, PCB-101, PCB-138, PCB-153 and PCB-180. The LODs reported was in the range of 0.2–0.5 ppb, and it was obvious that there were a great difference

**Table 3**  
Recoveries of real water samples spiked at three concentration levels by C18 SPE method.

Water samples	Blank	Added ( $\mu\text{g L}^{-1}$ )	PCB-28	PCB-52	PCB-101	PCB-153	PCB-138	PCB-180
Donghu water	N.D.	0.4	98.6 $\pm$ 2.1	101.8 $\pm$ 3.1	110.5 $\pm$ 1.7	99.8 $\pm$ 4.2	98.5 $\pm$ 2.3	100.2 $\pm$ 2.6
	N.D.	1.0	103.6 $\pm$ 3.5	106.1 $\pm$ 4.3	99.8 $\pm$ 2.1	93.5 $\pm$ 1.8	98.7 $\pm$ 1.6	102.1 $\pm$ 1.7
	N.D.	5.0	56.8 $\pm$ 2.6	49.9 $\pm$ 2.6	52.6 $\pm$ 1.7	51.8 $\pm$ 4.2	50.2 $\pm$ 4.3	51.1 $\pm$ 2.5
Snow water	N.D.	0.4	102.3 $\pm$ 2.3	98.6 $\pm$ 2.7	104.1 $\pm$ 3.4	99.6 $\pm$ 2.1	104.5 $\pm$ 3.4	110.2 $\pm$ 1.9
	N.D.	1.0	99.8 $\pm$ 1.8	97.6 $\pm$ 4.1	102.3 $\pm$ 4.1	110.2 $\pm$ 4.3	106.8 $\pm$ 4.5	99.2 $\pm$ 2.3
	N.D.	5.0	72.0 $\pm$ 0.7	62.3 $\pm$ 2.6	58.3 $\pm$ 3.5	58.3 $\pm$ 7.9	59.6 $\pm$ 7.0	54.8 $\pm$ 5.1
Shouxihu Lakewater	N.D.	0.4	102.3 $\pm$ 1.8	99.4 $\pm$ 5.1	110.3 $\pm$ 6.4	98.5 $\pm$ 1.4	97.8 $\pm$ 2.3	105.1 $\pm$ 4.6
	N.D.	1.0	95.6 $\pm$ 3.5	112.0 $\pm$ 7.8	100.1 $\pm$ 5.8	95.0 $\pm$ 7.1	100.2 $\pm$ 5.9	101.0 $\pm$ 6.7
	N.D.	5.0	59.1 $\pm$ 3.3	51.2 $\pm$ 4.5	50.6 $\pm$ 2.5	51.6 $\pm$ 4.2	54.2 $\pm$ 6.2	51.8 $\pm$ 2.3
Wastewater	N.D.	0.4	100.2 $\pm$ 5.7	110.2 $\pm$ 3.8	99.6 $\pm$ 2.8	102.8 $\pm$ 4.6	105.3 $\pm$ 5.1	99.8 $\pm$ 1.8
	N.D.	1.0	102.3 $\pm$ 4.6	106.8 $\pm$ 4.2	106.5 $\pm$ 6.3	99.0 $\pm$ 6.7	106.4 $\pm$ 7.9	103.3 $\pm$ 7.0
	N.D.	5.0	58.6 $\pm$ 5.7	51.2 $\pm$ 6.8	51.6 $\pm$ 5.7	50.4 $\pm$ 5.1	55.7 $\pm$ 6.2	50.7 $\pm$ 5.6

between the reported value and present study, and present study provided much better results. Ćonka et al. [54] utilized an off-line SPE method in combination with GC–ECD for the determination of PCBs containing the six PCBs mentioned in this study and selected organochlorine pesticides (OCPs) from human serum, the results showed that the LODs of PCB-28, PCB-52, PCB-101, PCB-153, PCB-138 and PCB-180 were 0.0026, 0.0051, 0.0026, 0.0037, 0.0019b, and 0.0013ppb. López et al. [55] reported a headspace solid phase microextraction method prior to GC–ECD for the enrichment and analysis of PCBs and OCPs in human serum samples, the LODs of the selected six PCBs were in the range of 0.0039–0.031 ppb. These results were better than present study. However, the final solution in SPE was not completely injected for analysis, and also this study provided a new enrichment procedure with good enrichment performance, meanwhile, it provided an alternative selection for the analysis of PCBs.

#### 4. Conclusions

This work has demonstrated for the first time that TiO<sub>2</sub> nanotube array could be used as effective micro-solid phase equilibrium extraction ( $\mu$ SPEE) materials for the extraction of six PCBs in four environmental water samples. The proposed method earned good linear range, reproducibility and detection limit, and it could be reused for over 200 times without loss of the recovery efficiency. Meanwhile, the developed extraction method was very easily to operate and the array was also easily to be prepared. Based on the experimental results, a simple and reliable method was developed for the micro-solid phase equilibrium extraction and GC determination of six analytes in environmental water samples. As a promising adsorbent, TiO<sub>2</sub> nanotube array has great potential for  $\mu$ SPEE of some pollutants. It is expected that TiO<sub>2</sub> nanotube array can be potentially applied to the enrichment and determination of many other pollutants.

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