



Original Article

In-situ sampling of nitrophenols in industrial wastewaters using diffusive gradients in thin films based on lignocellulose-derived activated carbons



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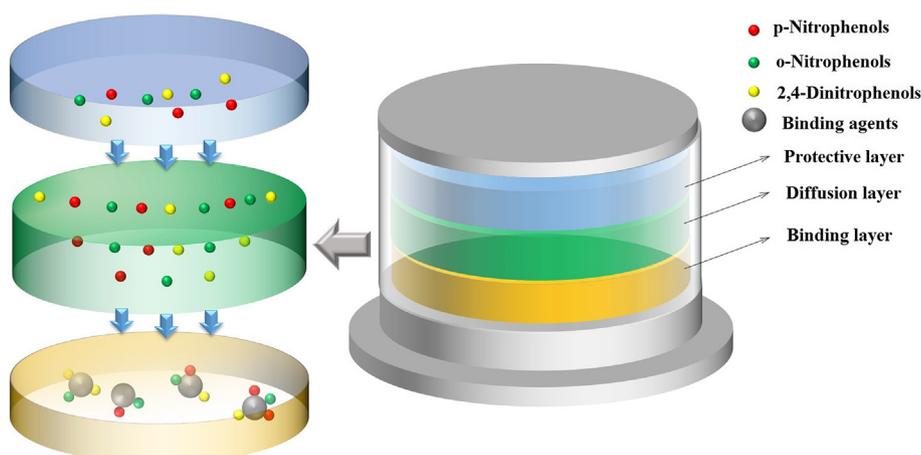
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HIGHLIGHTS

- A specific DGT sampler for measurement of nitrophenols in acidic aqueous solutions.
- Hazelnut shell-derived activated carbons as DGT binding agents.
- No interference of water matrices on the measurement of nitrophenols by DGT sampler.
- Reliable results of field deployments in acidic wastewater with relative good precision.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrophenols (such as o-nitrophenol (ONP), p-nitrophenol (PNP), and 2,4-dinitrophenol (DNP)) are priority environmental pollutants. Their toxicity is pH dependent, and these molecular species of nitrophenols exhibit higher toxicity than their anionic counterparts. Herein, for the first time, a method for the in situ measurement of nitrophenols in acidic industrial wastewater was developed using diffusive gradients in thin films (DGT) with lignocellulose hazelnut shell-derived activated carbons (HSACs) as the binding agents. Nylon membranes (0.1 μm rated) with diffusion coefficients of $(2.02 \pm 0.13) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for ONP, $(1.39 \pm 0.09) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for PNP and $(1.20 \pm 0.08) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for DNP at 25 °C were used as the DGT diffusion layers. The accumulation of ONP, PNP, and DNP in DGT samplers based on the HSAC and nylon membranes (HSAC-DGT) agreed well with the theoretical curves predicted by the DGT equation in synthetic solutions with 200 $\mu\text{g L}^{-1}$ nitrophenol. The uptake of the HSAC-DGT samplers for ONP, PNP, and DNP was found to be independent of the ionic strength of pNaNO_3 ($-\log [\text{NaNO}_3]$ (mol L^{-1})) in the range of 0.7–3 and the pH range of 3–7 for ONP and PNP and 3–6 for DNP, which is beneficial for their accumulation. The matrices of the tested water samples exhibited no notable interference during nitrophenol analysis by the HSAC-DGT samplers. The results of field deployments in acidic industrial wastewater containing $268.3 \pm 79.2 \mu\text{g L}^{-1}$ DNP were satisfactorily accurate, thus demonstrating

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that the HSAC-DGT samplers are good candidates for use in the in situ measurement of nitrophenols in acidic aqueous solutions.

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Introduction

Nitrophenols (such as o-nitrophenol (ONP), p-nitrophenol (PNP), and 2,4-dinitrophenol (DNP)) are among the most important environmental contaminants in aquatic environments, according to the priority pollutants lists of the United States of America and the European Union [1,2]. Due to their diverse application, these compounds are discharged freely into the natural aquatic environment through industrial wastewaters [3]. Therefore, monitoring them has become an important part of environmental analysis. Usually, grab samples, a traditional sampling method that can provide information on the instantaneous dissolved concentration of a target without pre-concentration and in situ information, are used to sample nitrophenols from the water environment [4]. Subsequently, the concentrations of these nitrophenols are determined by different methods (such as liquid–liquid extraction or liquid–solid extraction combined with gas or liquid chromatography) [5]. However, few methods are focused on in situ sampling and measurement of nitrophenols in natural aquatic environments. Therefore, it is desirable to develop efficient analytical methods for monitoring the concentrations of nitrophenols in water systems.

The diffusive gradients in thin films (DGT) method, based on Fick's first law, passively collects target analytes and has shown promise for the in situ long-term assessment of analytes in the ambient environment [6]. The DGT device typically consists of a binding layer containing binding agents with a high affinity for the analytes of interest and a diffusion layer, which can effectively control the diffusion of analytes [7]. To monitor different types of analytes or various speciation, it is necessary to develop binding agents with a specific binding performance. Numerous functional materials have been used as binding agents of the DGT method to analyse inorganic analytes; for example, Chelex100 was used for the quantitative determination of 24 cationic metals [8], zirconium oxide was used for the simultaneous measurements of 8 oxyanionic metalloids and metal species [9,10], zeolites were used for ammonium in water samples [11], Purolite A520E anion-exchange resins were used to measure nitrate levels in freshwaters [12], Amberlite IRA-400 anion-exchange resins were used to assess sulfate levels in soils [13], Fe-Al-Ce tri-metal oxides were used for the measurement of fluoride in waters and sediments [14], copper ferrocyanide-immobilized Chelex-100 resin gels and poly(acrylic acid) gels were used to measure stable ^{133}Cs and radioactive ^{137}Cs , respectively, in waters [15], and 3-mercaptopropyl-functionalized silica [16] and baker's yeast (*Saccharomyces cerevisiae*) [17] were used to determine MeHg. Recently, the DGT technique was used to measure organics in the ambient environment. A novel DGT sampler with an XAD18 resin as the binding agent was successfully developed for the measurement of antibiotics and polar organic contaminants [18–22]. Zheng et al. developed a new activated charcoal-based DGT device for measuring three types of bisphenols in water [23]. Dong et al. showed that conventional DGT devices equipped with a molecularly imprinted polymer as the binding agent are able to selectively measure the concentrations of 4-chlorophenol in water samples. Currently, no single device allows the measurement of nitrophenolic compounds [24]. Therefore, it is necessary to develop a new type of binding agent for the in situ sampling and measurement of nitrophenols in water.

Low-cost adsorbents, especially low-cost activated carbon, which is produced from biomass precursors such as agricultural

residues, exhibit excellent performance for the adsorption and removal of nitrophenols due to their high surface area, rich porous structure, and suitable chemical characteristics of the catalyst surface [25–28]. In this study, low-cost lignocellulose hazelnut shell-derived activated carbons (HSACs) were prepared and characterized. The performance of DGT samplers based on nylon membranes as the diffusion layer and HSAC as the binding agent (HSAC-DGT) for in situ sampling and measurement of nitrophenols in industrial wastewater was examined. The influence of pH and ionic strength on the uptake of nitrophenols by the HSAC-DGT samplers was assessed. The HSAC-DGT samplers were also validated for extended deployment in spiked water samples and in field conditions.

Experimental

General procedures

All the reagents used were of analytical grade. All solutions were prepared in deionized water. Acrylamide, N,N'-methylenebisacrylamide, ammonium persulfate, and N,N,N',N'-tetramethylethylenediamine were purchased from Sigma Aldrich (USA). Nylon membranes (0.1 μm pore size, (160 ± 8) μm thickness, 25 mm diameter) and nitrocellulose filter membranes as the protective layer (0.45 μm pore size, 120 μm thickness, 25 mm diameter) were purchased from Sartorius (Germany). Stock solutions (1000.0 mg L^{-1}) of ONP, PNP, and DNP (Sinopharm Chemical Reagent Co., Shanghai, China) were prepared individually using deionized water. All other reagents used were obtained from Shanghai Aladdin Biochemical Polytron Technologies Inc. (Shanghai, China). Prior to use, all the samplers and glassware were immersed in a 10% (v/v) HNO_3 solution for 24 h and rinsed with deionized water to eliminate any HNO_3 residue. The concentrations of the three nitrophenols from the sample extracts were measured by high-performance liquid chromatography (HPLC) with a UV detector at 280 nm, as described previously [29]. The concentrations of PNP, ONP, and DNP were analysed by injecting 10 μL of the filtered liquid samples into an HPLC (Shimadzu, LC-6A, Japan) equipped with a UV-VIS detector (SPD-6AV) and a C_{18} reverse-phase column (250 mm, 4.6 mm, 5 μm ODS, Dikma, USA). To adjust the peak symmetry, slight changes were made in the proportion and pH of the mobile phase, as described in other studies [29]. The mobile phase consisted of a 1:1 phosphoric acid solution of pH 2.4 and HPLC-grade methanol, and the flow rate was set at 1 mL min^{-1} . Prior to use, the mobile phase was filtered through a 0.45- μm filter and immediately degassed in an ultrasonic water bath. The retention times of ONP, DNP, and PNP were 4.5, 5.7, and 7.1 min, respectively. The linear ranges of ONP, DNP, and PNP were 100.0–2000.0, 75.0–2000.0, and 100.0–2000.0 $\mu\text{g L}^{-1}$, respectively, with relative standard deviations (RSD) below 5% ($n = 5$). The detection limits of ONP, DNP, and PNP were 9.7, 4.7, and 5.4 $\mu\text{g L}^{-1}$ ($n = 20$), respectively, and the corresponding quantification limits were 32.1, 15.6, and 17.9 $\mu\text{g L}^{-1}$ ($n = 20$). The recovery ranges of ONP, DNP, and PNP at concentrations of 200, 800, and 1600 $\mu\text{g L}^{-1}$ were found to be almost 95.2–104.9% ($n = 5$). Errors are represented by the standard deviations (SD) of the mean. The obtained results are expressed as the mean \pm SD. Statistical analysis was performed using the *t*-test; significant differences are defined as $p < 0.05$.

Preparation and characterization of HSAC

HSAC was prepared using phosphoric acid (H_3PO_4) as the activation agent, as described previously [30,31]. Hazelnut shells were obtained from a hazelnut processing factory near the Liaoning University of Petroleum & Chemical Technology (41°85' N, 123°80' E). Dust particles adhered on the hazelnut shells were removed using deionized water. Later, the shells were dried, ground, and screened to particles with diameters in the range of 150–200 μm . The dried shells were impregnated with phosphoric acid to achieve a phosphoric acid/precursor weight ratio of 0.9 by agitating for 2 h. After drying at 110 °C, the mixtures were carbonized at 800 °C at a heating rate of 10 °C min^{-1} for 60 min in an argon environment. After cooling, the resultant samples were cleaned with deionized water to remove excess phosphoric acid (removal was considered complete when the pH was almost neutral (pH \sim 7)). The obtained samples were dried at 110 °C overnight. HSAC particles were later characterized by scanning electron microscopy (SEM, Shimadzu SS 550) and Fourier transform infrared spectroscopy (FT-IR, 5700 Nicolet, USA) using the KBr plate method with a resolution of 1 cm^{-1} in the wavenumber range of 4000–400 cm^{-1} . Point-of-zero charge (pH_{PZC}) measurements were conducted according to the batch equilibrium method described by Babić et al. [32]. Samples of HSAC (0.2 g) were added to 40 mL of 0.01 mol L^{-1} KNO_3 and stirred for 24 h at different pH levels. The initial pH values were determined by adding a predetermined amount of KOH or HNO_3 (0.1 mol L^{-1}) to keep the ionic strength constant. The amount of H^+ or OH^- ions adsorbed by HSAC was calculated from the difference between the initial and final concentrations of H^+ or OH^- ions.

Preparation of binding gels

The binding gels were prepared following a published procedure described by Zhang and Davison [7]. The gel solution was composed of 15% acrylamide and 0.3% N,N'-methylene bisacrylamide as the cross-linker. Then, 100 mg of the HSAC was added to 10 mL of the gel solution at a dosage of 10 g L^{-1} . Subsequently, 70 μL of 10% ammonium persulfate and 25 μL of N,N,N',N'-tetra methylethylenediamine were added to 10 mL of the mixed solution mentioned above. The HSAC settled on the side of the binding gel, and then the loaded HSAC binding gels were cast at 40 °C for 1 h. Binding gel discs with a diameter of 20 mm and a thickness of 2 mm were cut and stored in 0.01 mol L^{-1} sodium nitrate (NaNO_3) solution at 4 °C prior to use. The capacity of the HSAC binding gel disc was examined by adding the disc into 25.0 mL of nitrophenol solution (individually) of varying concentrations (100–600 mg L^{-1}) at 25 °C and pH 5 for 24 h with stirring. The solutions were filtered, and the filtrates were subjected to analysis.

Possible accumulation of nitrophenols in nylon membranes

Nylon membranes were decontaminated with methanol and 1 mol L^{-1} nitric acid (HNO_3), washed with deionized water until a neutral pH was achieved, and then stored in deionized water until further use. The interaction between nylon membranes and nitrophenols was assessed by soaking the treated membranes in 10 mL of nitrophenol solutions (200, 500, 2000, and 5000 $\mu\text{g L}^{-1}$) at pH 5 for 24 h. After achieving equilibrium, the concentration of residual nitrophenols in the bulk solutions was determined by HPLC. The surface morphologies of the nylon membranes before and after soaking were analysed by SEM. The accumulation factor (AF%) was calculated as follows [7]

$$\text{AF}(\%) = 100 \times (C_i - C_f)/C_i \quad (1)$$

where C_i and C_f are the initial and final concentrations of nitrophenol in the feed solution, respectively.

Elution of nitrophenols from HSAC-based binding gel discs

To investigate the elution factor, binding gel discs were placed in 25.0 mL of 10 mg L^{-1} nitrophenol solutions and allowed to equilibrate at pH 5 for 24 h at 25 °C; later, the loaded binding gel discs were retrieved and eluted with 1 mol L^{-1} NaOH at 25 °C. Ultrasound power was used for desorption instead of stirring [33]. Sonication was performed using an ultrasonic cleaning instrument (100 W, 20 kHz, Kunshan Shumei Instrument Co., China) at a frequency of 20 kHz and power of 50 W for 2 h. The elution rate can be calculated using the amount of nitrophenols eluted from the loaded binding gel disc divided by the amount adsorbed by the binding gel obtained from the change in the nitrophenol concentration in the feed solution. Elution was performed in all subsequent trials. Unloaded binding gel discs were also treated according to this procedure, and the blank elution solutions were analysed. The results indicated that the background of the binding gel disc did not influence the accuracy of nitrophenol measurement.

HSAC-DGT samplers assembly

The binding gel disc was placed on the bottom, with the HSAC side facing up, and a nylon membrane was overlaid on it; later, a 0.45 μm -thick nitrocellulose filter membrane was placed on top of the nylon membrane. Finally, the three discs were held together with a 3.14 cm^2 effective exposure area. The mounted HSAC-DGT samplers were stored in 0.01 mol L^{-1} NaNO_3 solution at 4 °C.

Measurement of the diffusion coefficient

A two-compartment diffusion cell (source cell and receiving cell) equipped with twin stirrers, as described previously [34], was used to evaluate the diffusion coefficients of each of the tested nitrophenols through the nylon membrane at (25 \pm 0.5) °C. NaNO_3 solution (0.01 mol L^{-1}) was used as the matrix solution at pH 5. The source cell was spiked with 500 mg L^{-1} of each of the nitrophenols of interest. One millilitre of the solution from the receiving cell was used to determine the concentration of each of the nitrophenols over a period of 3 h at 30-min intervals. The diffusion coefficients (D) were calibrated by testing the relationship between the mass of each of the nitrophenols in the receiving cell (M_D) and the deployment time (t_D) using the following equation [7]

$$D = M_D \cdot \Delta g / A \cdot C \cdot t_D \quad (2)$$

where C (mg L^{-1}) is the concentration of each nitrophenol in the source cell, A (cm^2) is the effective exposure area of the nylon membrane, and Δg (cm) is the thickness of the nylon membrane. The values of C , A , and Δg are known. The value of D for each type of nitrophenol passing through the nylon membrane was obtained from the slope of Eq. (2).

Calibration experiments

Thirty litres of well-stirred bulk solutions (0.01 mol L^{-1} NaNO_3 matrix), at pH 5 and containing 200 $\mu\text{g L}^{-1}$ of nitrophenols (similar to the levels present in industrial wastewater [35]), were used to calibrate the HSAC-DGT samplers. Three HSAC-DGT samplers were retrieved after 24, 48, 72, 96, and 120 h. Pre-experiments were carried out and indicated no obvious loss of nitrophenols for 7 days under the same conditions. Grab samples (10 mL) were also collected from the bulk solutions during the deployment period. The HSAC-DGT samplers were calibrated by evaluating the relationship

between the mass of each nitrophenol in the sampler (M) and the deployment time (t) using the DGT equation shown below [7].

$$M = DAC_{DGT}/\Delta g \quad (3)$$

where C_{DGT} is the concentration of each nitrophenol as measured by the DGT method and A and Δg are the effective exposure area and thickness of the nylon membrane, respectively. The solution was stirred by an aquarium pump with a current velocity of 100 cm s^{-1} for all subsequent trials.

Effects of pH and ionic strength on the uptake of HSAC-DGT samplers

To investigate the effect of pH and ionic strength, fifteen HSAC-DGT samplers were immersed in 30 L of well-stirred 0.01 mol L^{-1} NaNO_3 solutions containing $200 \mu\text{g L}^{-1}$ of the nitrophenols of interest for 120 h; the bulk solutions differed in pH and ionic strength. The pH values of the solutions were adjusted between 3 and 8 using 0.1 mol L^{-1} HCl and NaOH. The ionic strengths of the solutions were adjusted between 0.155 and 3 at pH 5 by varying the concentration of NaNO_3 . Three HSAC-DGT samplers were retrieved every 24 h over a test period of 120 h, and the binding gels were eluted by the procedures described earlier.

Validation of the HSAC-DGT samplers in spiked water samples

The HSAC-DGT samplers were deployed in 30 L of tap water and two filtered natural freshwaters, i.e., Hun River in Shenyang section and a small eutrophic pond near the campus of Shenyang University of Chemical Technology. As shown in Table 1, none of the three nitrophenols were found by HPLC in the three water samples. Therefore, the HSAC-DGT samplers were validated by standard addition, in triplicate, to the three water samples spiked with $200 \mu\text{g L}^{-1}$ nitrophenols for 120 h. The pH values of the three water samples were adjusted to 5 using a 0.1 mol L^{-1} HCl solution. The concentrations of the nitrophenols in three spiked water samples were measured by the HSAC-DGT samplers. The physicochemical parameters and collection location of water samples are available in Table 1.

In situ deployment of HSAC-DGT samplers

The HSAC-DGT samplers were deployed 50 cm beneath the surface of industrial wastewater contaminated with nitrophenolic

compounds. The HSAC-DGT samplers were deployed for 24 h to 120 h and retrieved every 24 h for testing. The grab samples were sourced simultaneously at each time interval to determine the concentrations of the nitrophenolic compounds. The physicochemical parameters and collection locations of the wastewater samples are included in Table 1.

Results and discussion

Characterization

SEM analysis was carried out to observe the surface morphology of the prepared HSAC. Fig. 1a shows that honeycomb cavities are clearly formed on the surface of the HSAC, indicating that adsorbates can be bound quickly owing to the presence of macropores on the HSAC surface. FT-IR spectra provide valuable information on the chemical groups present on the surfaces of materials. The FT-IR spectrum of HSAC is depicted in Fig. 1b. The broad bands located at approximately 3433 and 1630 cm^{-1} are attributed to O–H stretching and O–H bending vibrations of the hydroxyl groups, respectively. The bands at 2942 , 1384 , and 777 cm^{-1} are due to C–H stretching, C–H bending, and C–H out-of-plane deformation vibrations, respectively, of methyl and methylene groups. The band at 1324 cm^{-1} is related to C–O stretching vibrations in alcohol and/or ether groups [36]. The peak at 1132 cm^{-1} is assigned to P=O stretching vibrations in phosphate-carbon ester complexes [37]. The shoulder peak at 1012 cm^{-1} may represent vibrations in the P–O–P chain [38]. Some weak bands in the range of 600 – 650 cm^{-1} are associated with C–O–H twisting vibrations [39]. These results indicate that phosphoric acid chemically activated the carbonaceous materials. Fig. 1c shows the thermogravimetric (TG) curve of HSAC in a nitrogen atmosphere. Three weight loss steps can be distinguished. The first mass loss (approximately 10%) is observed at temperatures $< 200 \text{ }^\circ\text{C}$ and mainly represents moisture loss and loss of small adsorbed molecules. The second step ($\sim 35\%$ loss) in the TG curve of HSAC between 600 and $1000 \text{ }^\circ\text{C}$ is attributed to the thermal degradation of lignocelluloses. Finally, a low mass loss of approximately 3% occurs in the range of 1000 – $1200 \text{ }^\circ\text{C}$, probably due to the volatilization of different P compounds [40]. The pH_{PZC} value of HSAC was determined to be 7.3 ± 0.4 . The HSAC surface exhibited a negative charge when the solution pH was higher than pH_{PZC} and a positive charge when the solution pH was lower than pH_{PZC} .

Table 1
Characteristics of water samples.

Measured parameters	Water samples			
	Tap water	Hun river	Xi lake	Wastewater
Location	–	41°41' N, 123°13' E	41°44' N, 123°14' E	41°73' N, 123°24' E
Conductivity ($\mu\text{s cm}^{-1}$) ^a	704	1792	1568	3233
Salinity (ppt) ^a	0.0	0.58	0.88	1.2
ORP (mV) ^a	132	187	172	448
TDS (mg L^{-1}) ^a	144	706	699	1048
DOC (mg C L^{-1}) ^b	N.D. ^c	8.8 ± 1.2	13.1 ± 2.3	88.8 ± 7.8
COD (mg L^{-1}) ^d	N.D.	64.8 ± 10.8	81.7 ± 11.2	712.8 ± 92.9
pH	6.8 ± 0.2	7.6 ± 0.2	7.4 ± 0.2	5.1 ± 0.4
PNP ^e / $\mu\text{g L}^{-1}$	N.D.	N.D.	N.D.	N.D.
ONP ^e / $\mu\text{g L}^{-1}$	N.D.	N.D.	N.D.	N.D.
DNP ^e / $\mu\text{g L}^{-1}$	N.D.	N.D.	N.D.	268.3 ± 79.2

^a Conductivity, salinity, oxidation–reduction potential and total dissolved solids were measured by pen conductivity meter (ST10C-B), pen salinity meter (ST20S), pen ORP meter (ST10R) and pen TDS meter (ST10T-B), respectively (Ohaus, Canada).

^b Dissolved organic carbon was measured using a TOC analyzer (Dohrmann DC-190, GE, USA).

^c N.D. means not detected.

^d Chemical oxygen demand was measured by potassium dichromate method.

^e The concentrations of PNP, ONP and DNP were measured by HPLC.

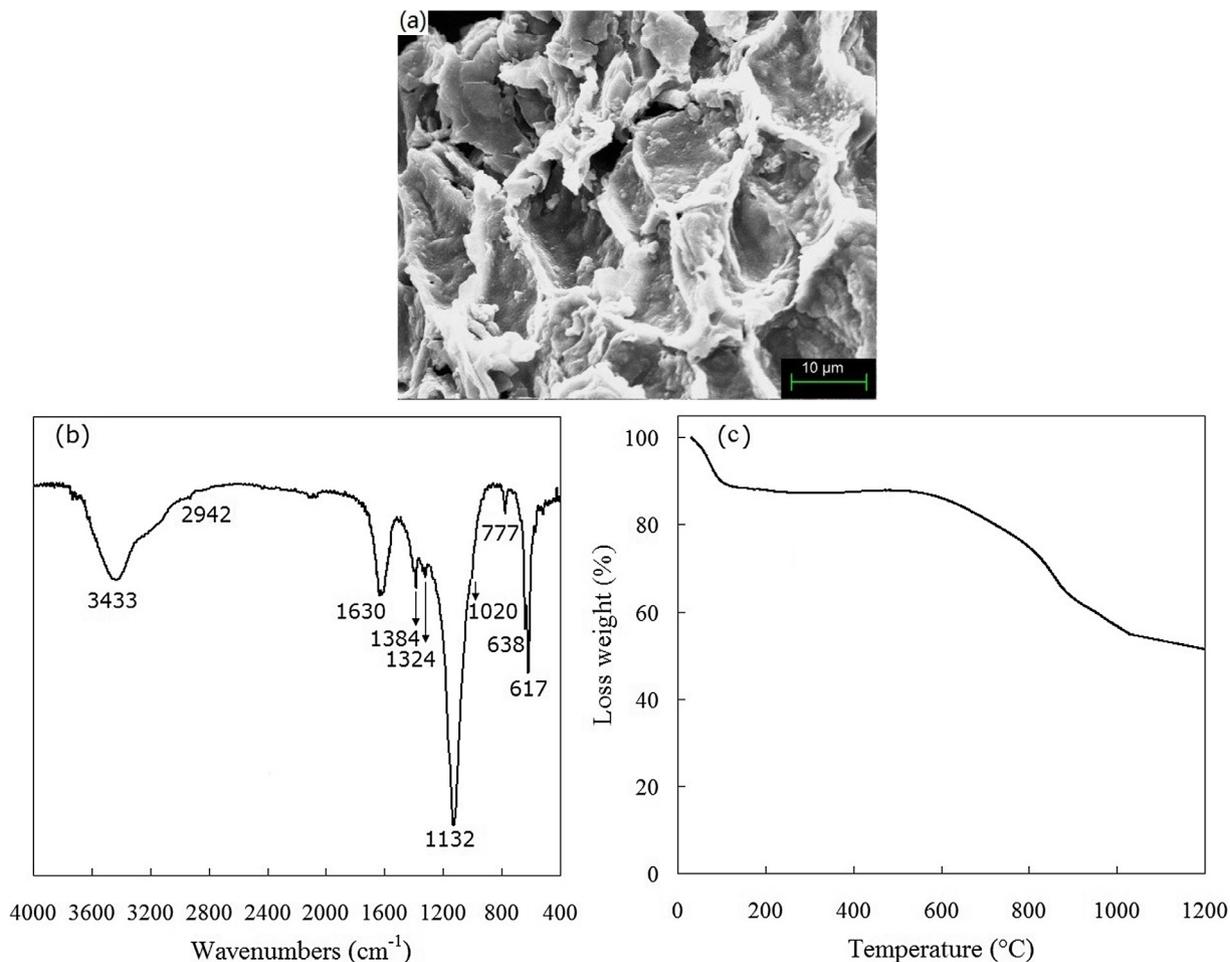


Fig. 1. (a) SEM image (a magnification of 1000×), (b) FT-IR spectrum and (c) thermogravimetric curve of the HSAC.

Accumulation of nitrophenols in the nylon membrane

The surface morphological features of nylon membranes before and after soaking in nitrophenol solutions were studied using SEM, as shown in Fig. 2a and b. The surface texture of nylon membranes

before and after soaking is macroscopically uniform with no visible cracks and is porous in nature. The pore structures and homogeneity of the nylon membranes before and after soaking exhibited no significant differences. The AF% of the nylon membranes (n = 6) for the three nitrophenols studied decreased slightly with an increase

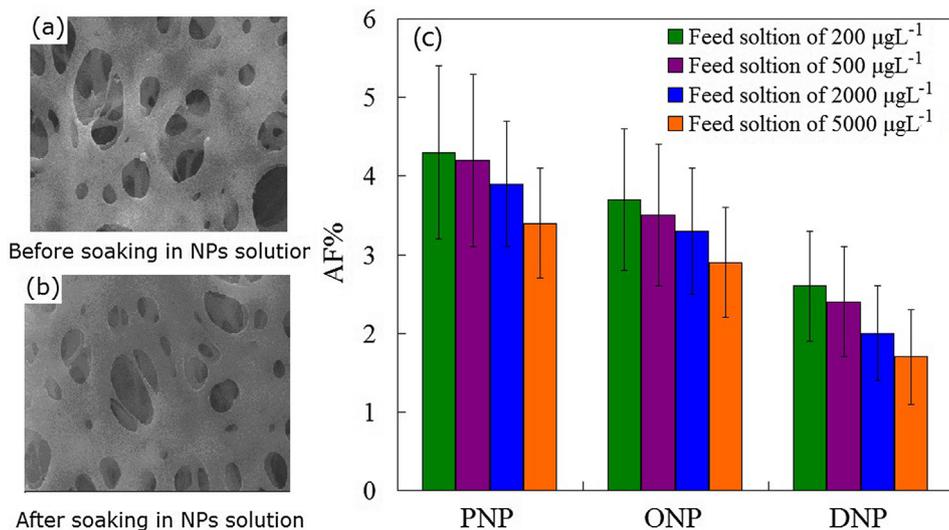


Fig. 2. SEM images (a magnification of 1000×) of the nylon membrane before (a) and after (b) soaking in the nitrophenol solution. (c) The accumulation efficiencies of PNP, ONP and DNP on the nylon membrane.

in their concentration in the feed solution (Fig. 2c), while there was no significant difference in the AF% values. The AF% values were found to be quite stable and low (<4.3%) in the tested conditions. There was no strong accumulation of nitrophenols on the nylon membranes, which may account for this result. Dong et al. also concluded that nylon membranes, such as the DGT diffusion layer, did not significantly affect the accuracy of 4-chlorophenol sampling in water [24]. These results indicate that nylon membranes are suitable as DGT diffusion layers for the measurement of nitrophenols.

Capacity of the HSAC-based binding gel

The capacity of HSAC binding gels with respect to the three nitrophenols of interest, an important parameter, can indicate if the long-term and/or high-concentration deployment of DGT samplers is viable or not. The saturation capacities of the HSAC binding gels with respect to the three tested nitrophenols can be calculated by plotting the nitrophenol mass accumulated against the initial nitrophenol concentration in bulk solutions (Fig. 3). The mass accumulated increased with an increase in the initial concentration within the range of 100–400 mg L⁻¹. The mass accumulated by the HSAC binding gels was not significantly different when the ini-

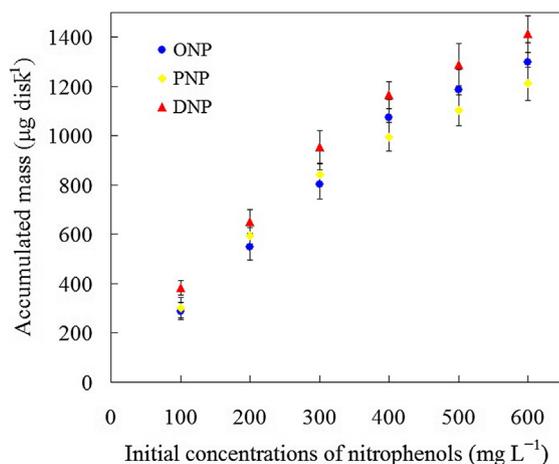


Fig. 3. The capacities of the HSAC binding gel disc for PNP, ONP and DNP.

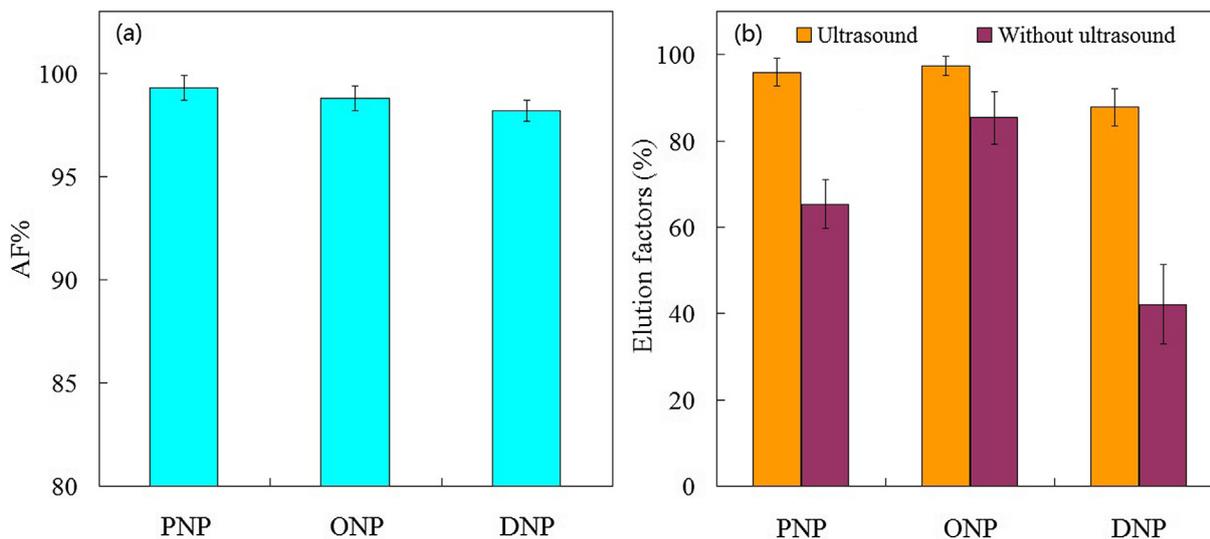


Fig. 4. (a) The accumulation efficiencies of PNP, ONP and DNP on the HSAC binding gel disc. (b) The elution efficiencies of PNP, ONP and DNP from the loaded binding gel disc.

tial concentrations were above 400 mg L⁻¹. The saturation capacities of the HSAC binding gels for ONP, PNP, and DNP were found to be (1185 ± 112), (1104 ± 108), and (1289 ± 124) µg disc⁻¹, respectively. Assuming that the HSAC-DGT samplers were deployed in contaminated water containing 1000 µg L⁻¹ nitrophenols, these capacities are sufficient to allow their deployment for over 30 days according to Eq. (3), which indicates that the HSAC-DGT samplers can be used for long-term or high-concentration analysis.

Uptake and elution factor of HSAC binding gels

The AF% values of the HSAC binding gels in 10 mg L⁻¹ nitrophenol solutions (individually) for all analytes were > 98% (n = 6) (Fig. 4a), demonstrating that the HSAC binding gels can efficiently accumulate the three nitrophenols of interest. Guilane and Hamdaoui showed in previous studies that NaOH can effectively elute nitrophenols from carbonaceous materials [41]. In this study, HSAC binding gels were eluted with 10 mL of 1 mol L⁻¹ NaOH by ultrasound-assisted extraction. The obtained elution factors for ONP, PNP, and DNP were 95.9% ± 3.2%, 97.4% ± 2.3%, and 87.8% ± 4.3%, respectively (Fig. 4b). The elution factors of ONP, PNP, and DNP from loaded HSAC binding gels not subjected to ultrasound extraction were 65.4% ± 5.7%, 85.4% ± 6.1%, and 42.1% ± 9.2%, respectively (Fig. 4b). The results indicate that ultrasound-assisted extraction can greatly improve the elution factor due to an increase in the mass transfer rate [41]. Ultrasound-assisted extraction with 1 mol L⁻¹ NaOH was conducted to elute nitrophenols in further studies.

Diffusion coefficients

The diffusion coefficients of nitrophenols passing through the nylon membrane were obtained by fitting the linear regression lines of the amounts diffused vs. time. The correlation coefficients (r²) of the linear regression lines were greater than 0.99, indicating that the diffusion of nitrophenols obeyed Fick's first law. The diffusion coefficients of ONP, PNP, and DNP in the nylon membranes were (2.02 ± 0.13) × 10⁻⁶ cm² s⁻¹, (1.39 ± 0.09) × 10⁻⁶ cm² s⁻¹, and (1.20 ± 0.08) × 10⁻⁶ cm² s⁻¹, respectively. The RSD of the *D* values corresponding to PNP, ONP, and DNP were estimated to be ± 6.4%, ± 6.5%, and ± 6.7%, respectively; these values include contributions from the uncertainties in the nylon membrane thickness (± 7.1%) and the RSD values of the measured concentrations of the

three nitrophenols in the source cell ($\pm 5.3\%$ for PNP, $\pm 4.7\%$ for ONP, and $\pm 4.8\%$ for DNP). The diffusion coefficients of PNP, ONP, and DNP in the nylon membrane are one order of magnitude smaller than the diffusion coefficients of the same analytes in aqueous solutions ($1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for PNP and $0.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for ONP) [42] due to pore confinement for the diffusion of nitrophenols through the nylon membrane [43]. The results indicate that the diffusion of nitrophenols through nylon membranes includes a control step of mass transport from the bulk solution into the DGT device.

DGT performance

The diffusive boundary layer (DBL) has a significant effect on the DGT sampler at slow current velocities ($\sim 2 \text{ cm s}^{-1}$) and static conditions. However, the issue of DBL interference is still under debate. Zhang and her team believe that the DBL needs to be cor-

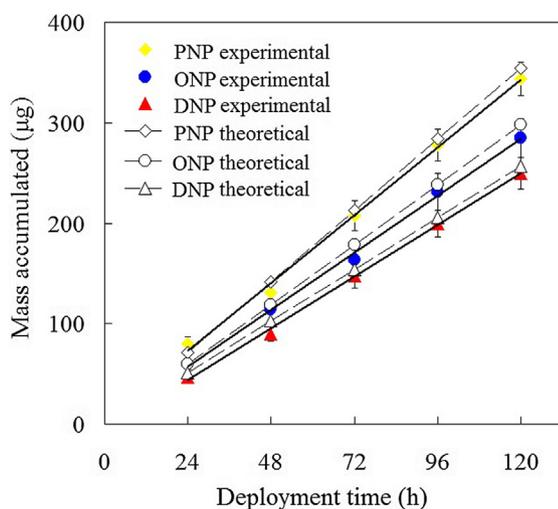


Fig. 5. (a) Uptakes of PNP (◆), ONP (●) and DNP (▲) by the HSAC-DGT samplers vs. deployment time in the tested solution with known concentrations for different time periods. The dashed lines are the theoretical slopes calculated from the known concentrations of nitrophenols in the tested solutions.

rected at slow current velocities [44,45]. However, Uher et al. [46] found that the error obtained by neglecting the DBL was lower than the average RSD of the analyte concentration and that the simplest DGT equation (as shown in Eq. (3)) is sufficient to estimate the concentration of the analytes even at a slow current velocity. The thickness of the DBL is inversely proportional to the current velocity, as described previously [47]. To validate the HSAC-DGT samplers based on the most common and simplest DGT equation, a high current velocity ($\sim 100 \text{ cm s}^{-1}$) was applied in this study to neglect the interference of the DBL.

The HSAC-DGT samplers were calibrated by testing the relationship between the mass of each nitrophenol in the samplers (M) and the deployment time (t) using Eq. (3). The performance of HSAC as the DGT binding agent was investigated by time-series deployment. The concentrations of nitrophenols measured by the DGT method (C_{DGT}) were compared to their concentrations measured from grab samples of the deployment solution (C_{SOLN}). A good linearity was observed between the mass of nitrophenols accumulated by the HSAC-DGT sampler and time ($r^2 > 0.99$), as shown in Fig. 5. The solid lines indicate the results obtained with the HSAC-DGT samplers. The dotted lines were calculated using Eq. (3). There was no significant difference between the mass of nitrophenols accumulated by the HSAC-DGT sampler and the theoretical mass calculated using the DGT equation from the solution concentrations, indicating that the uptake behaviour of HSAC-DGT samplers for nitrophenols is consistent with the theoretical DGT technique. The values of $C_{\text{DGT}}/C_{\text{SOLN}}$ for ONP, PNP, and DNP were 0.962 ± 0.046 , 0.944 ± 0.051 , and 0.970 ± 0.031 , respectively (the typical range is 0.9–1.1) [48,49]. These results demonstrate that neglecting the DBL in the DGT equation does not introduce a notable error between the theoretical and experimental curves; further, HSAC is deemed suitable as a DGT binding agent for the measurement of nitrophenols in synthetic solutions.

Effects of pH and ionic strength

The pH of the solution strongly affects the uptake of the HSAC-DGT sampler and the speciation of nitrophenols. The effect of pH on the DGT performance is shown in Fig. 6a. Nitrophenols are weakly acidic compounds ($\text{p}K_{\text{a}} = 7.02$ for PNP, $\text{p}K_{\text{a}} = 7.15$ for ONP, and $\text{p}K_{\text{a}} = 4.14$ for DNP) and exist as anionic species at $\text{pH} > \text{p}K_{\text{a}}$

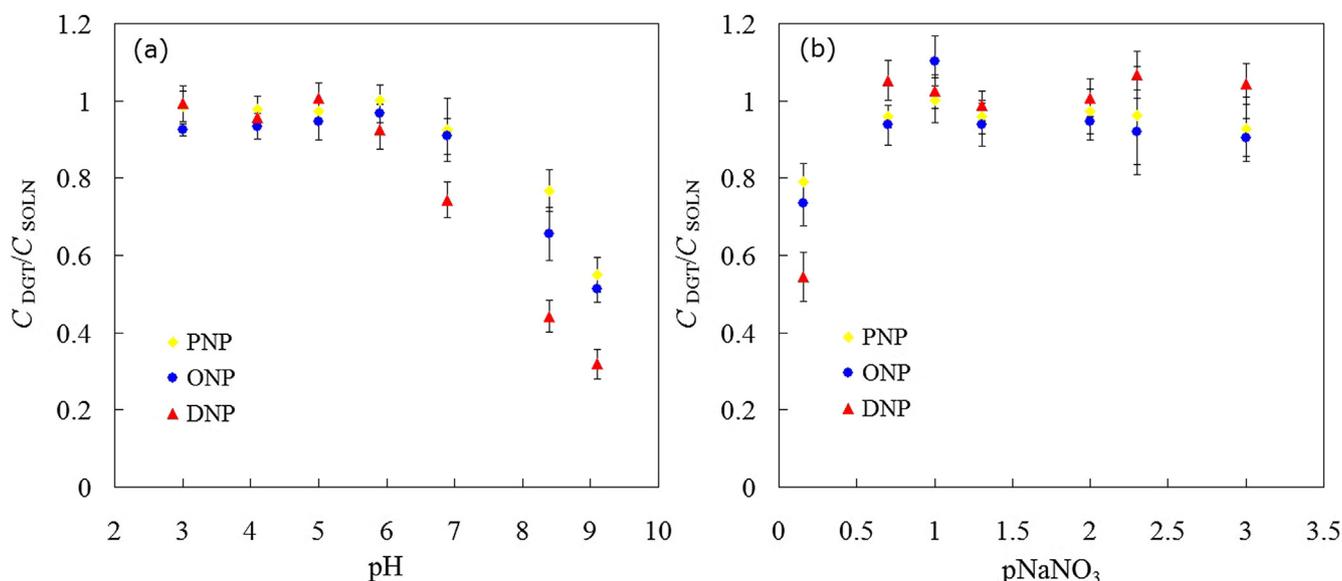


Fig. 6. Effects of pH and ionic strength (as pNaNO_3) on the performance of the HSAC-DGT samplers for PNP (◆), ONP (●) and DNP (▲) in the tested solution. The solid lines represent the accepted limits (error bars are the standard error).

and as molecular species at $\text{pH} < \text{pK}_a$ [50]. Fig. 6a shows that there is no change in the values of $C_{\text{DGT}}/C_{\text{SOLN}}$ (between 0.9 and 1.1) for all the nitrophenols within the pH range of 3–7 for PNP and ONP and 3–6 for DNP; beyond these pH values, there was a sharp decline in the $C_{\text{DGT}}/C_{\text{SOLN}}$ value, indicating that the HSAC-DGT samplers can be applied in acidic aqueous solutions. The pH_{PZC} value of HSAC was 7.3 ± 0.4 . When solution $\text{pH} < \text{pH}_{\text{PZC}}$, the HSAC surface has a net positive charge and a net negative charge at $\text{pH} > \text{pH}_{\text{PZC}}$. At $\text{pH} < 7.3$, these results were attributed to the electrostatic attraction between the positively charged HSAC surface and anion and/or the nitrophenol molecular species [51]. At $\text{pH} > 7.3$, the HSAC surface was negatively charged, and a portion of the nitrophenol molecules became anionic, resulting in a sharp reduction in the $C_{\text{DGT}}/C_{\text{SOLN}}$ values due to electrostatic repulsion [51]. The solution pH exerts a strong adverse effect on the adsorption of HSAC with respect to the anionic species of the three nitrophenols at $\text{pH} > \text{pH}_{\text{PZC}}$. These results demonstrate that HSAC is suitable as a DGT binding agent for no distinct dependence of the accumulation of PNP and ONP in the pH range of 3–7 and DNP in the pH range of 3–6. In addition, the toxicity of nitrophenols depends greatly on the ambient pH; it decreases with an increase in the pH of the medium [52]. Nałecz-Jawecki and Sawicki reported that no notable reduction could be observed in the toxicity of nitrophenols in the pH range of 6–7, but a large reduction was observed (to less than one-twentieth of the original value) at $\text{pH} > 7$ [53]. These results would be lucky to stumble across a good method for the sampling of the highly toxic molecular species of the three nitrophenols.

It is necessary to assess $C_{\text{DGT}}/C_{\text{SOLN}}$ as a function of the ionic strength of pNaNO_3 in the range of 0.155–3 to analyse the effect of ionic strength on the HSAC-DGT performance (Fig. 6b). There was hardly any variation in the $C_{\text{DGT}}/C_{\text{SOLN}}$ values in the ionic strength range of 0.7–3, suggesting that the HSAC-DGT performance for the measurement of nitrophenols is independent of the solution ionic strength in this range. At a pNaNO_3 of 0.155, slightly lower values of $C_{\text{DGT}}/C_{\text{SOLN}}$ were obtained for the three nitrophenols due to the competitive effect at high ionic strength [54]. The working ionic strength for the accurate measurement of ONP, PNP, and DNP using the HSAC-DGT samplers is in the range of 0.7–3, which covers the ionic strength range of most natural freshwaters and industrial wastewaters.

Validation

The performance of the proposed DGT samplers was assessed to determine nitrophenol concentrations in tap water and two natural freshwater samples. The matrix effect of the water samples on the HSAC-DGT performance was investigated. The C_{SOLN} values of nitrophenols in the spiked water samples and the mass of nitrophenols accumulated in the binding gel discs of the HSAC-DGT samplers during the elution procedure were also measured by HPLC. The repeatability and $C_{\text{DGT}}/C_{\text{SOLN}}$ values of the HSAC-DGT samplers are presented in Table 2. The data show that there was no significant difference between the values of C_{DGT} when compared to the values of C_{SOLN} in the $C_{\text{DGT}}/C_{\text{SOLN}}$ range of 0.9–1.1. In addition, the accuracy is fairly good for ONP, PNP, and DNP with

an RSD of $< 2.6\%$, indicating the low dispersion of data. The matrices of the tested water samples did not interfere to a significant extent in the determination of the three nitrophenols. These positive results indicate that nitrophenol measurement by the HSAC-DGT samplers is accurate and reliable, without interference from common matrices in weakly acidic conditions.

In situ field deployment

The HSAC-DGT samplers were evaluated in field deployment conditions, and the results obtained are compared with those from classical grab sampling. Protocols for the grab sampling of nitrophenols in water were obtained using the procedure described by Carlson et al. [55]. Three sets of grab samples (50 mL) were taken from industrial wastewater samples at the same deployment time intervals for comparison with the HSAC-DGT samplers. The concentration of nitrophenols in the filtered grab samples was analysed directly by HPLC; only DNP could be detected in industrial wastewater. A linear relationship was observed in the regression curves plotted between the uptake of DNP by the proposed HSAC-DGT samplers and deployment time ($r^2 > 0.949$) (Fig. 7); the concentration of DNP was calculated from the slope of Eq. (3). The concentration of DNP calculated using the HSAC-DGT samplers was $(321.3 \pm 44.4) \mu\text{g L}^{-1}$ with an RSD of 5.6%, which agrees with the value obtained by the grab sampling method ($(268.3 \pm 79.2) \mu\text{g L}^{-1}$, RSD of 11.9%). Statistical comparison of the results obtained by the DGT and grab sampling methods demonstrated no significant difference, suggesting that the proposed HSAC-DGT samplers yield accurate results for DNP measurement in industrial wastewater. The advantage of the proposed HSAC-DGT samplers over the grab sampling method lies in their good precision and supply of in situ information on DNP. The improvement in precision is mainly attributed to the enrichment

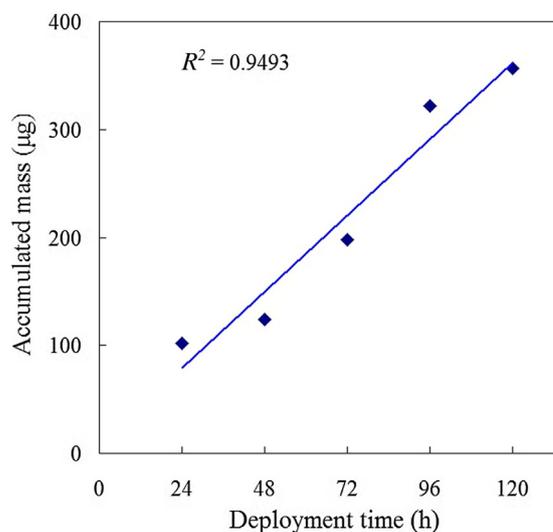


Fig. 7. The linear curve between the accumulated mass of DNP by the HSAC-DGT samplers and deployment time.

Table 2

The concentrations of PNP, ONP and DNP by HSAC-DGT in spiked waters.

Water samples	$C_{\text{DGT}}/C_{\text{SOLN}}$			RSD%		
	PNP	ONP	DNP	PNP	ONP	DNP
Spiked tap water	1.021 ± 0.053	0.991 ± 0.048	1.031 ± 0.035	2.1	1.9	1.4
Spiked lake water	0.987 ± 0.045	1.008 ± 0.032	0.948 ± 0.061	1.9	1.3	2.6
Spiked river water	0.957 ± 0.059	0.963 ± 0.044	0.953 ± 0.049	2.5	1.9	2.1

of DNP and reduction in matrix interference by HSAC [56]. Therefore, we conclude that HSAC-DGT samplers may be a practical alternative for the in situ sampling and measurement of molecular species of nitrophenols in acidic aqueous solutions.

Conclusions

HSAC with a high surface area and well-developed pores was prepared successfully from hazelnut shell precursors by H_3PO_4 activation; HSAC was successfully used as a binding agent in the DGT technique for the in situ measurement of ONP, PNP, and DNP in industrial wastewater. Relatively high elution efficiencies of ONP, PNP, and DNP from the binding gel were obtained using 1 mol L^{-1} NaOH as the elution agent. The uptake of ONP, PNP, and DNP by the HSAC-DGT samplers was independent of the solution pH (3–6 for DNP and 3–7 for PNP and ONP) and ionic strength (pNaNO_3 in the range of 0.7–3). In alkaline solutions, the poor uptake of ONP, PNP, and DNP by the HSAC-DGT samplers can be attributed to electrostatic repulsion between the anionic species of the three nitrophenols and the negatively charged surface of HSAC, indicating that the HSAC-DGT samplers can be used to measure the molecular species of the three nitrophenols. The good values of $C_{\text{DGT}}/C_{\text{SOLN}}$ (0.9–1.1) for the three nitrophenols in the three tested spiked water samples indicate the excellent accuracy of the HSAC-DGT method in determining the nitrophenol concentration in water; using this method, the matrix interference effect can be eliminated. The simplicity of the HSAC-DGT samplers, along with their high accuracy, suggests that they can be used as an alternative tool for in situ sampling and measurement of nitrophenols in acidic industrial wastewaters. Studies on the application of HSAC-DGT samplers and the DBL effect at slow current velocities are currently ongoing in our lab.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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