Application of Nylon6/Polypyrrole core–shell nanofibres mat as solid-phase extraction adsorbent for the determination of atrazine in environmental water samples

Bi-Yi Yang\textsuperscript{a}, Fei-Fei Qi\textsuperscript{a}, Xiao-Qing Li\textsuperscript{a}, Jing-Jing Liu\textsuperscript{a}, Fei Rong\textsuperscript{b} and Qian Xu\textsuperscript{a,b}\textsuperscript{*}

\textsuperscript{a}Key Laboratory of Environmental Medicine Engineering, Ministry of Education, School of Public Health, Southeast University, Nanjing 210009, China; \textsuperscript{b}Suzhou Key Laboratory of Environment and Biosafety, School of Public Health, Southeast University, Suzhou 215123, China

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A novel solid-phase extraction (SPE) system, based on a new sorbent of Nylon6/Polypyrrole (PA6/PPy) core–shell nanofibres mat and a new packing format of SPE disks, is presented in this paper. A series of related parameters that may affect the efficiency, such as the kind of eluent and its volume, the amount of nanofibres mat, ionic strength, pH of the sample, flow rate of the sample and volume of the sample, have been investigated systematically. Under the optimised conditions, the target analyte in 10 mL water samples can be completely extracted by a 3.0 mg PA6/PPy nanofibres mat and easily eluted by 400 µL acetonitrile. Around 20 µL elution was injected directly to HPLC-UV for determination, without further concentration. Besides, the nanofibres mat could be repeatedly used up to six cycles. Satisfactory linearity was achieved in the range of 0.1–40.0 ng/mL with a correlation coefficient of 0.9999. The limit of detection (LOD) (3 S/N) was 0.03 ng/mL, which could meet the determination requirements of atrazine as per the European Union legislation, US. Safe Drinking Water Act and the State Environmental Protection Administration of China. The simple, effective and economic method was proposed for the determination of atrazine in environmental water at trace level. The recoveries ranged from 94.73 to 114.92%, with relative standard deviations (RSDs) of 2.5–4.2%, and were obtained from tap water and lake water samples with atrazine at 2.0 ng/mL, suggesting the actual feasibility of the proposed method in environmental water samples.

Keywords: Nylon6/Polypyrrole core–shell nanofibres mat; disks SPE; atrazine; water samples

1. Introduction

As the most time-consuming and error-prone step, sample preparation greatly influences the final success of the whole analytical procedure, especially for trace analysis. It is because of the paramount importance of sample preparation that numerous methods have been devised for the extraction procedure since the last century [1]. Among the common extraction techniques for trace analysis, solid-phase extraction (SPE) is outstanding for it can accommodate the needs of high enrichment efficiency, low costs and green chemistry [2]. Therefore, selecting an optimal adsorbent is the key factor for the later assayed steps of SPE.

Nowadays, electrospinning (e-spinning) process has aroused great interest as a simple and convenient technique for the fabrication of polymer fibres with fine diameter sizes, from micron to nanometre scales [3]. The main benefit of these nanometre-sized materials is their large

*Corresponding author. Email: q_xu68@163.com

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specific surface area, which can provide much more analyte-interaction sites than traditional SPE adsorbents (e.g. adsorptive inorganic oxides and porous polymers) at the same amount \[4,5\]. Most of the reports have examined the perfect extracting efficiency of electrospun nanofibres when applying to different chemical species from water samples, such as pesticide and phthalate \[6–8\]. Remarkable performance could be reached with a few milligrammes (mg) of adsorbent and hundreds of microlitres (µL) of organic solvents. The advent of electrospun nanofibres is a major leap forward in the research area of SPE techniques. It opens up the possible optimal adsorbent of a new class of materials.

Polypyrrole (PPy), as one of the conducting polymers, was used to be applied in various fields such as electromechanical devices \[9\], sensors \[10\] and batteries \[11\] owing to its high conductivity, electrochemical reversibility and easy preparation. In the current decades, PPy is supposed to be an effective material to extract the contaminants from water through its multiple types of interactions such as the π–π interactions, hydrogen bonding, acid-base property, ion-exchange properties and electrostatic attractions \[12,13\]. Hence, a new potential effective adsorbent can be obtained theoretically when combining the advantages of electrospun nanofibres and PPy. Based on this reasonable assumption, a novel material of Nylon6/Polypyrrole (PA6/PPy) core–shell nanofibres mat was developed to be packed as the adsorbent of SPE.

Atrazine was chosen as the target to examine the new SPE adsorbent. Atrazine, a typical kind of triazine herbicide with high power, was popularly employed to control weeds over the past few years. The residue of atrazine in soil can be easily leached into rivers, lakes and reservoirs, thereby affecting raining and irrigation due to its high water solubility. More than that, atrazine has been confirmed to be an endocrine-disrupting chemical by recent studies \[14,15\]. Thus there is an urgent demand to develop a simple and effective method to monitor the concentration of atrazine in water environment. In this study, a novel SPE system, based on a new sorbent of PA6/PPy core–shell nanofibres mat and a new packing format of SPE disks, is applied to extract atrazine in environmental water samples. In addition, the parameters for the optimisation of SPE were investigated. Quantitative analysis of atrazine in environment water sample was conducted using high-performance liquid chromatography – ultraviolet detection (HPLC-UV).

2. Experimental

2.1. Reagents and materials

Pyrrrole monomer was purchased from Aladdin Inc, USA (purity 99.5%). Nylon6 was purchased from DeBioChem, Nanjing, China. High-purity (98.5%) atrazine standard was obtained from Shanghai Pesticide Research Institute. Standard stock solution of atrazine was prepared by dissolving appropriate amount into methanol stored at –4°C in the dark. HPLC-grade methanol, acetonitrile and acetone used in analysis were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Analytical reagent-grade anhydrous ethanol, m-cresol, formic acid, hydrochloric acid, sodium hydroxide and ferric chloride were purchased from Chemical Reagent Factory, Shanghai, China.

2.2. Apparatus and instrumentation

Quantitative analysis of atrazine was performed by high-performance liquid chromatography (HPLC, Shimadzu, Japan) including an LC-20A HPLC pump. A personal computer equipped with a Shimadzu Chromatography Workstation for HPLC was used to analyse chromatographic data. The Diamonsil C18 reverse-phase column (5 µm, 250 × 4.6 mm) was used for analysis of
atrazine at 30°C. The mobile phase consisted of acetonitrile and water (70:30, v:v). The flow rate and detection wavelength were set at 1.0 mL/min and 220 nm, respectively.

The morphological images of the PA6 nanofibres and PA6/PPy nanofibres were obtained with a scanning electron microscope (SEM, Hitachi S-3000 N, Japan), at an acceleration voltage of 5 kV. A transmission electron microscopy (TEM, JEOL2100, Japan) system was employed to examine the core–shell structure of the PA6/PPy nanofibres. Fourier transform infrared (FTIR) spectra were carried out on an FTIR Spectrophotometer (NEXUS 870, Nicolet, USA).

2.3. The preparation of PA6/PPy nanofibres mat

PA6 nanofibres mat was employed as a template by e-spinning according to our previous description [8,16,17]. Then PPy was coated on PA6 nanofibres mat by in situ polymerisation with FeCl₃ as an oxidant and Cl⁻ as a dopant. The procedure can be briefly described as follows.

The PA6 nanofibres mat was first cut into pieces of 10 cm × 10 cm size and then immersed in 50 mL anhydrous ethanol solution spiked with pyrrole monomer at 0.1 mol/L for 1 h. The polymerisation of pyrrole monomer was formed by the addition of another 50 mL of anhydrous ethanol solution of FeCl₃ (0.23 mol/L). The polymerisation lasted for 24 h at room temperature. The synthesised PA6/PPy nanofibres mat was washed with anhydrous ethanol followed by water for several times until the solution turned colourless, and then air-dried.

2.4. SPE

Benefitted from the relatively high mechanical strength of the PA6/PPy nanofibres, it was cut out to circular portions (diameter of 2.0 cm approximately), and then packed tightly in Swinnex filter (Mollipore, No. SX0001300) as nanofibres mat sorbent beds. Both ends of the filter were screwed down and connected with an SPE device (Supelco, No.57044). All collecting tubes were connected together with a vacuum pump.

The nanofibres mat was pretreated with 200 µL of methanol and 200 µL of distilled water prior to each SPE procedure. Then 10 mL water sample was passed through the filter at the optimum flow rate. The target analytes retained on the mat were eluted with an optimal volume of eluent and analysed by HPLC-DAD directly with an injection of 20 µL, without any further concentration.

2.5. Water samples preparation

The tap water sample was collected from our laboratory without further pretreatment. The three environmental water samples (100 mL, pH = 7) were collected from Xuanwu Lake, Nanjing, China. The collected water samples were stored at 4°C for further analyses. These real water samples were filtered through a 0.45 µm nylon membrane prior to analysis.

3. Results and discussion

3.1. Characterisation of the PA6/PPy nanofibres mat

3.1.1. Morphology of the PA6/PPy nanofibres

The morphology of PA6 and PA6/PPy nanofibres was studied under SEM and TEM (Figure 1). Figure 1A and B shows the SEM images of PA6 nanofibres and PA6/PPy nanofibres, respectively. The average diameter of PA6/PPy nanofibres was increased from 200 nm to 220 nm when compared with PA6 nanofibres. Besides, the smooth surface of PA6 nanofibres also
became coarse after pyrrole polymerisation. To further study the structure, the PA6/PPy nanofibres were immersed in formic acid solution for 12 h to dissolve the PA6 nanofibres template. From the TEM image of PPy hollow fibres (Figure 1C), the core–shell structure can be clearly confirmed. It demonstrates that the functionalised nanofibres can be formed by employing PA6 as core and PPy as shell.

3.1.2. Attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR) characteristic of the PA6/PPy nanofibres

The ATR-FTIR results are presented in Figure 2. The characteristic vibrational bands of PPy are observed to grow after polymerisation. The main characteristic peaks comprise pyrrole ring stretching at 1547 cm$^{-1}$, conjugated C-N stretching at 1176 cm$^{-1}$, C-H stretching vibration at 963 cm$^{-1}$ and C-H deformation at 904 cm$^{-1}$. The positions of these peaks are in agreement with the peaks reported for PPy [18]. However, compared with PA6 nanofibres, the characteristic IR peaks of PA6 disappeared in the FTIR spectrum, such as the N-H and C-H stretching vibrations at 2800–3300 cm$^{-1}$ and the coupled motions of C = O stretching and N-H in-plane bending at 1500–1700 cm$^{-1}$ [19]. In addition, the peaks at 1299 cm$^{-1}$ and 1040 cm$^{-1}$ were assigned to the in-plane vibrations of C-H and in-plane bending mode. The spectrum of PA6/PPy nanofibres clearly exhibits characteristic peaks with respect to PPy, which indicates the formation of PPy in nanofibres.
3.2. Optimisation of SPE devices

3.2.1. Evaluation of nanofibres mat as SPE sorbent

To evaluate the adsorption efficiency of the new material, functioned (PA6/PPy nanofibres mat) and non-functioned (PA6 nanofibres mat) mats were compared to extract atrazine under the same condition. The two nanofibres mats, cut out to circular portions with the same weight of 3.0 mg, were used to extract 10 mL water sample spiked with atrazine at 5.0 ng/mL ($n = 3$). The recovery of PA6 nanofibres mat (41.87% ± 7.4%) was extremely lower than PA6/PPy nanofibres mat (101.24% ± 6.2%).

The molecular structure in Figure 3 illustrates that the pyrrole ring of PPy enabled π–π interaction with the triazine ring of atrazine. However, for PA6, without unsaturated bonds in its

![Figure 2. ATR-FTIR spectra of PA6 nanofibres (A) and PA6/PPy nanofibres (B).](image)

![Figure 3. The molecular structure of atrazine, PPy and PA6.](image)
molecular skeleton, it could not adsorb atrazine through $\pi-\pi$ interactions, which resulted in distinctively lower recovery rates of atrazine adsorbed onto PA6 nanofibres mat. Moreover, usually hydrogen bonding exists in the compounds containing atoms with a lone pair of electrons, such as $\text{H}_2\text{O}$, PPy, PEI and polyaniline. The cooperative interactions can increase apparently when involving more molecules [20]. Therefore, hydrogen-bonding interaction between PPy chain and the nitrogen atom of atrazine can also be assumed as a possible mechanism. In addition, as the SEM images in Figure 1 of the two nanofibres show, the rougher surface of the PA6/PPy nanofibres mat could supply more adsorption sites due to its higher specific surface area, leading to the higher recovery. Thus, the new material, PA6/PPy nanofibres mat, can be applied as a perfect SPE adsorbent for atrazine.

3.2.2. Packing format selection

Regarding increasing the efficiency of SPE, researchers usually focused on the study of the adsorbent itself, and seldom took the packing format of SPE into consideration. Actually, an unexpected result could be obtained when choosing a fine packing format fitting the certain adsorbent. As shown in these literature [21,22], with the same adsorbent but different packing format of SPE cartridge and SPE disk, there was less demand of adsorbent and organic solvent for the SPE disk. We have even tried the packing format of SPE cartridge. The PA6/PPy nanofibres mat of 3.0 mg was cut into pieces and ground to powder. Then it was packed tightly into the cartridge (diameter 0.6 cm, height 5.5 cm), with two gaskets compressed at both ends. The height of the sorbent bed was about 0.8 cm. However, we found that the back-pressure during the SPE process was so great that it could not afford the fast analysis requirement of a large volume of water sample. Furthermore, more elution of organic solvent was needed for the SPE cartridge, thereby running in the opposite direction of green chemistry. Thus, the packing format of the SPE disk was finally chosen in this study. The PA6/PPy nanofibres mat was cut out to circular portions, and then packed as SPE disk fully utilising the mechanical strength of the nanofibres. Based on it, a novel, simple and fast method was developed for the determination of atrazine at trace level in water.

3.3. Optimisation of SPE conditions

In order to exert the maximum enrichment potential of PA6/PPy nanofibres mat as the SPE adsorbent, other related factors influencing the extraction efficiency were optimised and investigated in detail, including the kind of eluent and its volume, the amount of nanofibres mat, ionic strength, pH of the sample, flow rate of the sample and volume of the sample (see supplemental material).

Retrieval of analytes retained on the nanofibres mat into solution is necessary for subsequent quantitative analysis. The eluting capabilities of methanol, acetonitrile and acetone were inspected, respectively (10 mL of 5.0 ng/mL atrazine solution). The recovery results indicated that acetonitrile showed the best performance among the three organic solvents. Therefore, acetonitrile was selected as the eluent in the subsequent experiments. Moreover, the volume of the eluent is another factor that should be considered. In order to obtain a satisfactory recovery simultaneously without overuse of organic solvent, the volume of acetonitrile was studied by changing from 100 to 500 µL (10 mL of 5.0 ng/mL atrazine solution). It was found that the recovery increased from to 61.74% ± 4.3% to 103.36% ± 3.7% ($n = 3$) with the increase in the volumes of acetonitrile between 100 and 400 µL. However, when the volume was higher than 400 µL, the recovery remained constant. Eventually, 400 µL acetonitrile was used as elution.

To ensure the target analytes are adsorbed completely, a proper amount of nanofibres mat should be selected. The investigation was optimised in the range of 1.0–5.0 mg (10 mL of
5.0 ng/mL atrazine solution). However, the nanofibres mat below 2.0 mg was too brittle to afford the flow of the sample. According to the results of recoveries for different amounts of adsorbents, the recoveries increased from to 74.93% ± 2.8% to 103.61% ± 3.1% (n = 3) when the amount of nanofibres mat increased up to 3.0 mg. The increased amount of nanofibres mat could supply more available sites on the sorbent. But when the amount of sorbent was more than 3.0 mg, the recovery tended to reach a plateau value. As a result, 3.0 mg of PA6/PPy nanofibres mat was finally used to achieve the acceptable extraction efficiency.

Solutions containing different amounts of NaCl in the range of 0–10.0% (W/V) were prepared to accomplish this study (10 mL of 5.0 ng/mL atrazine solution). We found that the presence of salt caused an outstanding increase of recovery for atrazine. The recovery increased by 35% with a 10% increase of NaCl concentration. The addition of salt usually decreases the solubility of organic compounds in water, resulting in the improvement of extraction recovery [12]. On the other hand, electrical double layers can form near the PPy nanofibres mat surface with the mat contacting the solution. With the increase in ionic strength in the solutions, the electrolyte (e.g. NaCl) can compress the electrical double layers and then weaken the electrostatic repulsion between the adsorbates and adsorbents [23]. Accordingly, the extraction efficiency exhibited an extraordinary increase due to the addition of NaCl. Therefore, all further extractions were conducted with 10% (W/V) NaCl added.

The pH value of the solution can determine both the present state of analytes and the charge of PPy skeleton, and thus influence the extraction efficiency of atrazine. Effect of sample pH was studied in the range 3–11 (10 mL of 5.0 ng/mL atrazine solution). The recovery increased from 43.21% ± 2.4% to 101.31% ± 3.9% (n = 3) when the pH increased from 3 to 7. After that, the recovery retained no obvious changes in the alkaline condition. A possible reason for this result was that atrazine was positively charged because of protonation under acid condition (pKa = 1.65) [21]. PPy can be positively charged with a solution pH lower than 10 [24]. Then stronger electrostatic repulsive interactions formed between positively charged PPy and atrazine, leading to a lower recovery. Based on the characteristics of atrazine and PPy, a neutral or alkaline condition was distinctly helpful for a good extraction. Considering that most original water samples’ pH were at about 6–7 and the extraction efficiency was acceptable in neutral condition, the sample solution was free from the pH adjustment, leading to a more simplified sample preparation.

In general, the flow rate of the sample has a significant impact on the analysis result and the time of the procedure. Hence, it is also one of the important parameters that should be considered in the optimisation of SPE conditions. In this experiment, the flow rate was investigated in the range of 0.5–2.5 mL/min (10 mL of 5.0 ng/mL atrazine solution). The results showed that the recoveries of atrazine were constant at 101.27% ± 4.6% (n = 3) despite the flow rate of 2.5 mL/min. To satisfy the requirement of fast analysis, the flow rate of 2.5 mL/min was used finally.

To obtain the reliability of analytical results and the high enrichment factor, the maximal sample loading volume of the disk-based SPE cartridge should be inspected so as to ensure the breakthrough volume. The experiment was performed by investigating the recoveries of atrazine when loading different volumes of sample solution (10–100 mL). Volumes of 10, 50, 60, 80 and 100 mL of sample solutions with 1.0 ng/mL atrazine were passed through the PA6/PPy nanofibres mat, with the recoveries of 106.57% ± 4.7%, 95.96% ± 6.9%, 90.17% ± 5.1%, 85.36% ± 8.1% and 82.03% ± 6.3% (n = 3), respectively. When the sample volume was more than 100 mL, the recovery sharply decreased to 62.71% ± 7.4% (n = 3). In order to save the most of analysis time, 10 mL was chosen as the last loading volume.
3.4. Analytical performance

Based on the above-mentioned optimum conditions, high efficient enrichment has been achieved for the quantitative analysis of atrazine. Relevant performance of the proposed method, such as linear range, LOD, limit of quantity (LOQ) and precision, was validated with a series of designed experiments with spiked water solutions.

The linearity was studied using tap water spiked with the target analyte at five concentration levels (0.1, 0.5, 5.0, 10.0 and 40.0 ng/mL), with an excellent correlation coefficient ($R^2$) of 0.9999. The LOD and LOQ of the HPLC method, calculated at the concentrations with the signal-to-noise ratios (S/Ns) of 3 and 10, were 0.5 and 2.0 ng/mL, respectively. However, the LOD and LOQ for the SPE method were 0.03 and 0.1 ng/mL, respectively. The accuracy was studied using 10 mL samples spiked with target analyte at 2.0 ng/mL. The spiked samples were mixed in an ultrasonic bath for 10 min to ensure efficient distribution and then standing for 5 min prior to extraction. The intra-day recovery ($n = 3$) was for 107.31%, with the relative standard deviations (RSD) of 2.2%, whereas the inter-day recovery among three working days was 108.02%, with an RSD of 6.9%.

Traditional liquid–liquid extraction is employed as the sample preparation method for the National Standard Method of China (HJ587-2010, Water quality-Determination of Atrazine-High performance liquid chromatography). The proposed method in this work was compared with the national standard method, in terms of organic solvent, sample volume, linear range, LOD, LOQ, accuracy and recovery. The results were obtained and are presented in Table 1. Based on the similar recovery, the LOD and LOQ of disks’ SPE were both lower than the national standard method. For this work, the volume of the organic solvent was only 0.8 mL, which was 20 times smaller than the consumption of the national standard method. At the same time, less sample preparation time was needed for the 10 mL sample volume when compared with the national standard method of 100 mL.

Except for these advantages, the life of the nanofibres mat was investigated in this work. The PA6/PPy nanofibres mat was washed with 500 µL acetonitrile and 500 µL distilled water prior to each SPE procedure. Then 10 mL spiked sample (2.0 ng/mL) was passed through the nanofibres mat. It can be found that the recoveries for six cycles almost remained unchanged (mean recovery of 97.59% ± 8.1%), with no significant statistical differences ($P > 0.05$). The excellent performance of reusability for the nanofibres mat proved that the proposed method can be seen as an efficient and economical way to determine the concentration of atrazine in the water sample.

| Sample preparation method          | Organic solvent (mL) | Sample volume (mL) | Linear range (ng/mL) | LOD (ng/mL) | LOQ (ng/mL) | Recovery (%)$^a$ | Method                      |
|-----------------------------------|----------------------|--------------------|----------------------|-------------|-------------|------------------|-----------------------------|
| Liquid–liquid extraction          | 21                   | 100                | 0.3–10.0             | 0.08        | 0.32        | 94.60 ± 18$^b$   | This work                   |
| Disks solid-phase extraction      | 0.8                  | 10                 | 0.1–40.0             | 0.03        | 0.10        | 107.31 ± 2.2$^c$ | National Standard Method    |

Notes: $^a$±RSD.
$^b$The RSD was obtained from data of three laboratories.
$^c$The RSD was inter-day precision.
Atrazine is commonly analysed by chromatographic techniques (gas chromatography (GC) [25–28] and HPLC [29–32]). In the studies employing HPLC for the determination of atrazine, the widely used detectors comprise diode array detection (DAD) [32–35], ultraviolet detection (UV) [36–39] or mass spectrometry (MS) detection [30,40–42]. However, it is obvious that detections of DAD and UV are more familiar when compared with the MS technique because of the low cost. Meanwhile, the detection method employed in this study is HPLC-DAD. Therefore, the detection methods of the references selected for the comparison are all HPLC-DAD [43–45].

The results of SPE based on other sorbents were also selected as references for comparative studies, and the comparative information is shown in Table 2. The results proved that the proposed method based on PA6/PPy nanofibres mat required a lower consumption of sorbent amount and organic solvent than the methods in the literature. Although the LOD of this work is slightly higher than that of HLB cartridges, only 10 mL of sample volume is still quite superior for the proposed method. Besides, using just 400 µL elution can also be free of dryness by nitrogen for further concentration, greatly reducing the analysis time. Moreover, the LOD and LOQ of 10 mL loading volume have already satisfied the demand of water-quality monitoring levels required by European Union legislation (0.1 µg/L) [44], US Safe Drinking Water Act (3.0 µg/L) [46] and the State Environmental Protection Administration of China (3.0 µg/L) [46].

### Table 2. Comparison of other SPE sorbents in the literature.

| SPE sorbent                  | Amount (mg) | Organic solvent (mL) | Sample volume (mL) | LOD (ng/mL) | Spiked level (ng/mL) | Recovery (%) | Ref.   |
|-----------------------------|-------------|----------------------|--------------------|-------------|----------------------|--------------|--------|
| PA6/PPy Nanofibres mat      | 3           | 1                    | 10                 | 0.03        | 2.0                  | 107.31 ± 2.2 | This work |
| C18 cartridges              | 500         | 31                   | 50                 | 50          | 100.0                | 97 ± 3.5    | 43     |
| HLB cartridges              | 200         | 14                   | 500                | 0.011       | 2.0                  | 98 ± 6      | 44     |
| Molecularly imprinted polymer | 150        | 15                   | 500                | 0.08        | 8.0                  | 99 ± 1      | 45     |

Note: *±RSD.*

#### 3.5. Comparison between PA6/PPy nanofibres mat and other SPE sorbents in the literature

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#### 3.6. Real environmental water samples analysis

To evaluate the proposed method, two environmental water samples including tap water and lake water were collected and analysed. Around 10 mL water sample was simply filtered prior to the SPE procedure. The results indicated that the content of atrazine in these samples was below the detection limit. To prove the accuracy of the proposed method in practical applications, environmental water samples with atrazine at 2.0 ng/mL spiked level were determined. The recoveries were in the range of 94.73–114.92%, with an RSD of 2.5–4.2%. The results are presented in Table 3. Figure 4 shows the typical chromatogram of a blank lake water sample and a lake water sample spiked with 2.0 ng/mL atrazine after enrichment.

#### 4. Conclusion

PA6/PPy nanofibres mat, a novel SPE sorbent material with high extraction efficiency, was prepared and applied in the detection of trace levels of atrazine in environmental water. Compared with the national standard method and other SPE sorbents in the literature, the
The proposed method was confirmed to be a simple, rapid, sensitive and eco-friendly procedure with a lower consumption of sorbent amount, organic solvent and sample volume. It provided a low detection limit, good recovery and precision. The disks’ solid-phase extraction based on PA6/PPy nanofibres mat could be a great potential method for atrazine in real water samples.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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### Table 3. Determination and recoveries of atrazine spiked in tap water and Xuanwu Lake water sample.

| Sample           | Added (ng/mL) | Found (ng/mL) | Recovery(%)<sup>a</sup> |
|------------------|---------------|---------------|--------------------------|
| Tap water        | 0.0           | n.d.          | –                        |
|                  | 2.0           | 1.89          | 94.73 ± 4.1              |
| Lake water       | 0.0           | n.d.          | –                        |
| (sample 1)       | 2.0           | 2.30          | 114.92 ± 2.5             |
| Lake water       | 0.0           | n.d.          | –                        |
| (sample 2)       | 2.0           | 1.99          | 99.59 ± 4.2              |
| Lake water       | 0.0           | n.d.          | –                        |
| (sample 3)       | 2.0           | 2.22          | 111.10 ± 3.2             |

Notes: n.d.: not detected.
<sup>a</sup>±RSD.

Figure 4. Typical chromatogram of lake water sample spiked with 2.0 ng/mL atrazine after enrichment (A) and blank lake water sample (B).
Supplemental data

Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/03067319.2015.1085524.

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