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Determination of atrazine and simazine in environmental water samples using multiwalled carbon nanotubes as the adsorbents for preconcentration prior to high performance liquid chromatography with diode array detector

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Abstract

Multiwalled carbon nanotubes, a new nanoscale material, has been gained many interests for use in various fields, and has exhibited exceptional merit as SPE absorbents for enrichment of environmental pollutants. This paper focused on the enriching power of atrazine and simazine, two important widely used triazine herbicides and described a novel and sensitive method for determination of these two herbicides based on SPE using multiwalled carbon nanotubes as solid phase absorbents followed by high performance liquid chromatography with diode array detector. Factors that maybe affect the enrichment efficiency of multiwalled carbon nanotubes such as the volume of eluent, sample flow rate, sample pH, and volume of the water samples were optimized. Under the optimal procedures, multiwalled carbon nanotubes as the absorbents have obtained excellent enrichment efficiency for atrazine and simazine. The detection limits of the atrazine and simazine were 33 and 9 ng l^{-1}, respectively. The spiked recoveries of the two analytes were over the range of 82.6–103.7% in most cases. Good analytical performance was achieved from real-world water samples such as river water, reservoir water, tap water and wastewater after primary pretreatment with proposed method. All these experimental results indicated that the developed method could be used as an alternative for the routine analysis of atrazine and simazine in many real water samples.

Keywords: Multiwalled carbon nanotubes; Solid-phase extraction; High-performance liquid chromatography; Atrazine; Simazine

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1. Introduction

Triazines, one kind of herbicides with high power for weed control, have been often used as the selected herbicides for crop protection in agricultural domain over past years. However, they are also in the list of chemical pollutants that need to be more heavily monitored due to their toxicity, persistence and cumulation in environment and their effects on the environment and human health [1]. Atrazine and simazine are typical candidates of great importance in this family of herbicides with better efficiency for control of weed and have been applied in a large scale with a great deal of consumption. Yet atrazine is suspected as one of the endocrine disrupters in recent reports, and meanwhile it can cause multiplicate types of cancers, and it was considered to have the abilities such as interrupting regular hormone function, causing birth defects, reproductive tumors, and weight loss in mother and embryos [2,3]. In spite of application dose at the very low level, it exactly existed in the environment owing to the chemical

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and physical properties of it persistence and solubility. Thus, atrazine and simazine and their metabolites would end up in natural waters, which have to be considered as a serious problem for environmental safety and human health.

In order to protect water systems, U.S., European Unions and many other countries have established according legislations to control residual level at maximum amount for these two herbicides. European Union has set a standard that the residues of triazine herbicides are limited to $0.1\,\mu\mathrm{g\,l}^{-1}$ for single herbicides and $0.5\,\mu\mathrm{g\,l}^{-1}$ for the sum of the herbicides in drinking water [4]. With the progress of science and technique, the allowed level of herbicides in various waters will be much lower than that of current level. Therefore, it is of essential importance to set up robust and efficient methods to determine the residues of triazine herbicides in different waters at trace levels. Nowadays, many methods based on different principles have been developed and applied to analysis of atrazine and simazine, and among of them chromatographic techniques account for the most usage for quantitative detection. In general, gas chromatography (GC) with flame thermionic detection (FTD), electron capture detection (ECD), nitrogen phosphorus detection (NPD) or mass spectrometric detection (MSD) [5,6] and liquid chromatography (LC) with diode array detection (DAD), fluorescence detection or mass spectrometric detection [7–9] were employed for the determination of these triazine herbicides in most cases. Capillary electrophoresis has also been found in research reports due to its less consumption, high separation efficiency and simplicity [10], etc. Beside these analytical technologies, methods based on biological or electrochemical principles were utilized in a certain extent for sample analysis of these pollutants, e.g., biosensor [11–12], immunochemical methods [13–14], square wave voltammetry with the hanging mercury drop electrode (HMDE) [15], etc.

High-performance liquid chromatography in combination with diode array detector (HPLC-DAD) has been broadly used in determination of organic pollutants due to its ability of analyzing both polar and nonpolar themodegradable compounds. With respect to atrazine and simazine they have strong ultraviolet absorbance at 223 nm and can be easily separated on C18 chromatographic analysis column, hence HPLC-DAD was preferred as a routine detection method for trace-level determination of atrazine and simazine in water samples [16–18]. Unfortunately, the sample matrices are very complex in general and the concentrations of target analytes in real water samples are very low at trace level in most cases, so prior to quantitative analysis and high efficient separation, a reasonable sample pretreatment procedure would be required because it can reduce the interference of sample matrix and an enhanced sensitivity can be achieved at the same time. On this aspect, pretreatment is an important step in the process of successful analysis at low concentration, especially for determination at ultra-trace residual level. At present, a variety of sample pretreatment techniques were developed for further use, including solid-phase extraction (SPE) [19], solid-phase microextraction (SPME) [20], supported liquid membrane extraction (SLM) [10], microwave-assisted extraction (MAE) [21] and so on. SPE has been proved to be an effective sample handling method with advantages of higher enrichment efficiency and lower cost of organic solvents than the traditional method of liquid–liquid extraction. In addition, SPE has another merit as simplicity and easily to be automated and operated. In the procedure of SPE, the adsorbents for SPE play a more important role in obtaining higher enrichment efficiency of analytes. Until now, several kinds of materials such as C18, styrenedivinylbenzene (SDB), molecularly imprinted polymers (MIPs) as well as Oasis HLB were introduced as the adsorbents for SPE cartridge [8,19,22]. In recent years, a novel carbonaceous material, multiwalled carbon nanotubes, was successfully observed and absorbed more and more attentions due to its advantages that can be used for many different goals in terms of its special chemical and physical properties as well as the unique tubular structures of nanometer diameter and large length/diameter ratio. CNTs are to be considered as a sheet of graphite that is rolled into a tube and be classified as single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) on the principle of carbon atom layers in the wall of nanotubes. On the basis of their peculiar electronic, metallic and structural characteristics [23], they have been exploited in analytical and other fields such as biosensor [24], modified electrode [25–27], field-effect transistors [28] and so on. Because CNTs have a large specific surface area, they should possess excellent adsorption ability in theory. The results of primary study demonstrated that CNTs had high enrichment efficiency on adsorption of dioxins [29]. Cai et al. used MWCNTs as adsorbents for preconcentration of phthalate esters, bisphenol A, 4-*n*-nonylphenol and 4-*tert*-octylphenol in environmental water samples before chromatographic analysis, and favorable achievements were obtained [30,31]. Liang et al. applied MWCNTs packed cartridge which were pretreated with nitric acid beforehand to concentrate heavy metal ions of Cd, Mn and Ni, and the offered recoveries were over the reasonable range of 96–104% [32]. Because these facts the related research on the applications of CNTs in analytical field as potential SPE absorbents is still very few, and there has not been found such reports for atrazine and simazine, it will be of great value to investigate the adsorption characteristics of MWCNTs and develop a novel determination method for these compounds on the basis of the experimental results.

In presented work, the extraction performance of MWCNTs for atrazine and simazine were investigated. SPE cartridge packed with multiwalled carbon nanotubes were self-made in our lab and the two analytes in water samples were extracted, further final elutes were analyzed by high performance liquid chromatography with diode array detector throughout the experiments. The factors that maybe influence the preconcentration such as elute solvent volume, flow rate of sample, sample volume and so on also were optimized. The method based on the optimal conditions was well developed and applied to determination of real water samples.

2. Experimental

2.1. Chemicals

Simazine and atrazine standard at the concentration of 100 μg ml^{-1} were purchased from Institute of Environmental protection and monitoring, Department of Agriculture (Beijing, China). Working solutions were prepared daily by appropriate dilution of the stock solutions with water. LC-grade acetonitrile and methanol were obtained from Scharlau Chemie SA (Barcelona, Spain). Ultrapure water was prepared in the lab using a water treatment device "Ultra-Clear" (SG Wasseraufbereitungsanlagen, Barsbüttel, Germany). All other solvents and reagents used were of analytical regent grade unless stated.

Multiwalled carbon nanotubes with an average external diameter of 30–60 nm were kindly provided by Tsing-Nafine Nano-Powder Commercializition Engineering Center, Chemical Engineering Department of Tsinghua University (Beijing, China). Before use, MWCNTs were dried at 80 °C for 2 h. All the glassware used in experiments were cleaned with pure water, then soaked in 6 mol l^{-1} nitric acid for 24 h and then washed with purified water.

2.2. Apparatus

MWCNTs packed cartridge was prepared by modifying an Agilent ZORBAX SPE C18 cartridge (0.2 g, 3 ml, polypropylene), which was purchased from Agilent Cooperation, USA. The C18 packing was evacuated, and 0.1 g multiwalled carbon nanotubes were packed in the cartridge. The polypropylene upper frit and lower frit were remained at each end of the cartridge to hold the carbon nanotubes packing in place. Then the outlet tip of the cartridge was connected to a model SHZ-3 (III) vacuum pump (Yuhua Instrument Co., Ltd., Zhengzhou, Henan), and the inlet end of the cartridge was connected to a PTFE suction tube whose other end was inserted into sample solution. In order to reduce the interferences of organic and inorganic contaminants, the entire SPE assembly needed to be washed with sufficient acetonitrile and water.

HPLC analysis was performed by using an Agilent 1100 HPLC system including an autosampler, a thermostatic cartridge, a vacuum degasser, a quaternary pump and a diode array detector. The separations were performed on an Agilent Zorbax Extend C18 cartridge (250 mm × 4.6 mm, 5 μm). The mobile phase insisted of acetonitrile and water (70/30, v/v), and the flow rate of the mobile phase was set at 0.5 ml min^{-1}. Chromatographic data were acquired at the wavelength of 223 nm. Agilent LC-3D ChemStation for LC systems was used to control the chromatographic units, acquire and process chromatographic data.

2.3. SPE procedure

The MWCNTs packed cartridge was preconditioned by washing it with 5 ml acetonitrile and 5 ml ultrapure water ahead of the pretreatement procedure. Then an appropriate volume of sample solutions spiked with atrazine and simazine was passed through the cartridge at the maximum flow rate by a vacuum pump. Then the cartridge was washed with 10 ml 5% acetonitrile solution to remove the co-absorbed matrix materials from the cartridge. Subsequently, atrazine and simazine retained on the cartridge were eluted with an optimal volume of acetonitrile. At last, 50 μl of the eluent was injected into HPLC-DAD system for determination.

2.4. Water samples

In this work, four environmental water samples were used for evaluation including river water, tap water, reservoir water and wastewater from the primary treatment. River water sample was gathered from the Qingtian River in the region of Jiaozuo, Henan Province. Reservoir water sample was collected from Xiaolangdi Multipurpose Dam over the Yellow River in the region of Jiyuan, Henan Province. Tap water sample was taken from a water tap after flowing for 10 min in our laboratory. The treated sewage water sample was obtained from a wastewater treatment plant in Xinxiang city. Before use, all the environmental water samples were filtered through 0.45 μm micropore membranes and stored in brown glass bottoms, respectively.

3. Results and discussion

3.1. Optimization of enrichment procedure

To obtain appropriate extraction performance with multiwalled carbon nanotubes as SPE absorbent for concentrating atrazine and simazine, several parameters that would give rise to impact on the trapping were investigated including pH of sample, flow rate of sample, eluent and sample volume.

As atrazine and simazine absorbed on the SPE cartridge were concerned, different performance would be achieved due to the different elution power of the various solvents. Herein four organic solvents such as acetonitrile, methanol, ethanol and acetone were compared for the optimal selection. In the experiment, LC-grade acetonitrile and methanol was utilized directly as obtained, and the analytical-grade ethanol and acetone were used after being redistilled to remove the impurity before experiment. Of the solvents, it was found that acetonitrile produced the best elution performance for atrazine and simazine, which led to better separation, excellent symmetrical peak shape, yet the other solvents resulted in less perfect separation or symmetry of the chromatographic peaks. As a result, acetonitrile was optioned as the eluent in the following experiments. The amount of the acetonitrile also affected the extraction efficiency, and a series of experiments was designed to get the proper volume without lost of extraction efficiency. When the experiment was operated, another 5 ml of acetonitrile was employed passing through the MWCNTs packed cartridge before next procedure in order

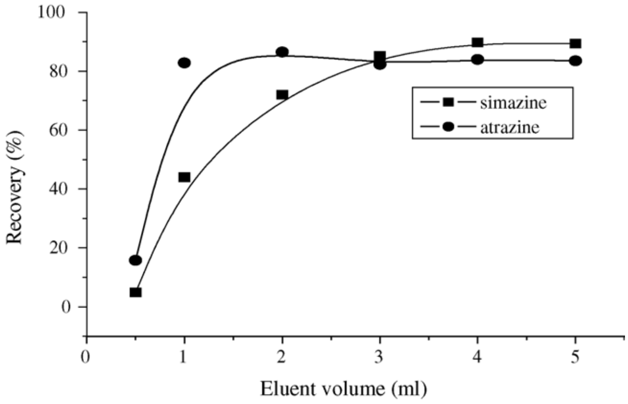

Fig. 1. Effect of eluent volume on recoveries of atrazine and simazine using MWCNTs for SPE. Concentration of sample solution: 2 ng ml^{-1} atrazine and simazine; volume of sample solution: 200 ml; flow rate of sample solution: 7 ml min^{-1}; pH of sample solution: 6–7.

to get rid of the residues, which maybe adsorbed on the cartridge. From the results exhibited in Fig. 1, it was discovered that the amounts of eluent for atrazine and simazine were different to reach higher stable extraction efficiency. The elution of atrazine was very fast and required only 1 ml acetonitrile to gain a good extraction recovery over 80%; however, simazine need more acetonitrile in the range from 4–5 ml for almost complete elution acetonitrile. In order to reduce residual on the SPE column of analytes and avoid its influence on the next run as well as the concentration factor, 4 ml acetonitrile was adopted for further use.

In the SPE procedure, analytes are absorbed onto the solid phase packing in the molecular form and eluted from the absorbed materials with a small volume of selected organic solvents to give a high concentration factor expected initially on the basis of the difference of the distribution coefficients between the solid phase and the organic phase. Without doubt the value of pH sample solution, which determined the present state of analytes in solution as ionic or molecular form, would be another crucial influence factor with respect to the adsorption of the atrazine and simazine on MWCNTs. In this way, we studied the influence of pH on the recoveries by regulating the pH value of sample solutions from 3 to 11. According to the results of experiments shown in Fig. 2, it was indicated that the recoveries at $\text{pH} < 5$ or $\text{pH} > 9$ were lower than that at the pH range of 5–9 for atrazine and simazine respectively. Possible reason for this is that atrazine and simazine may hydrolyze in strong acidic and basic aqueous environments or ionised [33]. Therefore, the pH of sample solutions was adjusted to 6–7 for well extraction based on the characteristics of the two analytes that atrazine and simazine were stable in the neutral, weak acidic or alkalescent media while they were unstable in strong acidic or alkalescent media.

Generally the flow rate of water sample solution always contributes a significant impact to the analysis time in the procedure, and is one of the important parameters considered in the process of most method development. In this experiment, it was investigated by changing the flow rate from 2 to 7 ml min^{-1}(maximum flow rate). It was found that the recoveries of atrazine and simazine were constantly even though the flow rate arrived at 7 ml min^{-1}. It illuminated that the flow rate had almost no effect on the recoveries of the atrazine and simazine. For shortening the experimental time, the maximum flow rate was employed finally.

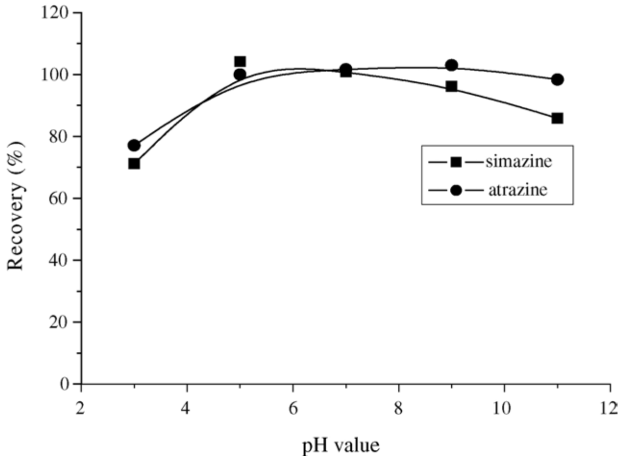

Fig. 2. Effect of pH of water sample on recoveries of atrazine and simazine using MWCNTs for SPE. Concentration of sample solution: 2 ng ml^{-1} atrazine and simazine; volume of eluent: 4 ml; flow rate of sample solution: 7 ml min^{-1}; volume of sample solution: 200 ml.

Besides of the selectivity, a higher preconcentration factor is expected in the trace level sample analysis. Before a method is well developed, the various approaches that can increase the preconcentration factor are all in the view. Generally, two main ways are utilized and the better then is optioned, one is the absorption ability of materials to the analytes which is the intrinsic nature that can be exploited for better extraction of the analytes, the other is change the volume of sample solution to reach the analytical goal. In order to obtain a satisfactory results sample volume employed for use is large as possible in the experiment. As is known to us all, the sample volume cannot be limitless to a valuable method and too large volume of sample will not lead to the maximum extraction factor because of fixed amount of solid absorbent. For the purpose of achieving a preconcentration factor as high as possible, we investigated the effect of sample volume on adsorption of atrazine and simazine. In the experiment, we made the sample solutions up to 1000 ml at a same concentration of 2 ng ml^{-1} pass the MWCNTs packed cartridge, respectively, with a flow rate of 7 ml min^{-1}. We can draw a conclusion from the experimental results that no remarkable differences were found among the enrichment efficiencies of atrazine and simazine over the range of sample volume investigated. The effect of sample volume on the preconcentration performance was very small when the solution volume was lower than 1000 ml. Comprehensive consideration of enhancing the enrichment factor and saving experimental time and

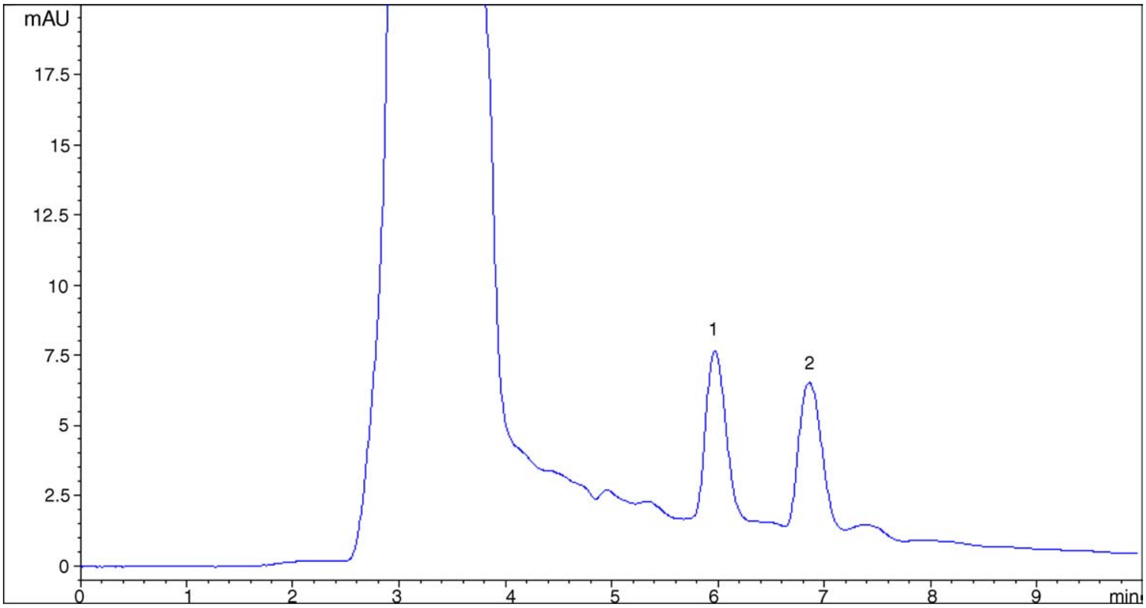

Fig. 3. Standard chromatograms from the SPE using MWCNTs as packing materials with spiked purified water. Spiked concentration, 0.8 ng ml^{-1}; volume of eluent: 4 ml; flow rate of sample solution: 7 ml min^{-1}; pH of sample solution: 6–7. (1) Simazine and (2) atrazine.

applicability for routine analysis, 500 ml was adopted as the sample volume for extraction.

3.2. Analytical performance and application to real water samples

Under the optimal conditions mentioned above, high efficient separation and enrichment has been achieved for the quantitative analysis of atrazine and simazine. The standard chromatogram of atrazine and simazine enriched with MWCNTs SPE demonstrated in Fig. 3. Based on above selected parameters a novel alternative method for determination of these two herbicides at trace level was developed. Relevant performance of the proposed method was validated with a series of designed experiments with spiked water solutions, and the results were exhibited in Table 1. It was found that there was an excellent linear correlation between the peak area and concentration from 0.2 to 100 and 0.02 to 100 ng ml^{-1} for atrazine and simazine, respectively. The detection limits of these two analytes were obtained based on the signal as three-fold the baseline noise (S/N = 3) for an extraction of 500 ml water sample, and the favorable detection limits of atrazine and simazine were 33 and 9 ng l^{-1}, respectively. Compared with the results reported by Koeber et al. with multidimensional solid phase extraction and high throughout LC–MS analysis, the detection limit of atrazine was very near (30 ng l^{-1} reported), yet the detection limit of simazine was remarkably better than that reported (50 ng l^{-1}) [35]. As an important parameter of robust method, reproducibility was also investigated by fortifying the atrazine and simazine into the 500 ml water solution with a concentration of 0.8 ng ml^{-1}, and the results indicated that precision was satisfactory at a very low level and relative standard deviations (R.S.D.) were equivalent to 0.6 and 2.1% ($n = 6$) for atrazine and simazine, respectively.

Four environmental water samples, tap water, river water, reservoir water and wastewater from the primary treatment were collected used to validate the applibility of developed method. The extraction steps were as described above and the eluent was analyzed by a HPLC-DAD system. The recoveries of atrazine and simazine in spiked water samples at a concentration of 0.8 ng ml^{-1} with standard solution for each

Table 1
Recoveries of atrazine and simazine in fortified environmental waters

Sample	Atrazine			Simazine		
	Added (ng ml^{-1})	Detected (ng ml^{-1})	Recovery (%)	Added (ng ml^{-1})	Detected (ng ml^{-1})	Recovery (%)
River water	0.8[a]	0.69[b]	86.7 ± 0.9[c]	0.8	0.83	103.7 ± 1.0
Reservoir water	0.8	0.66	82.6 ± 5.6	0.8	0.79	98.4 ± 4.9
Tap water	0.8	0.78	96.9 ± 1.2	0.8	0.82	102.8 ± 2.6
Wastewater	0.8	0.46	58.0 ± 2.8	0.8	0.58	72.0 ± 3.6

[a] The spiked concentration of 500 ml water sample.
[b] The achieved results and transferred to the concentration 500 ml water sample.
[c] The spiked recovery.

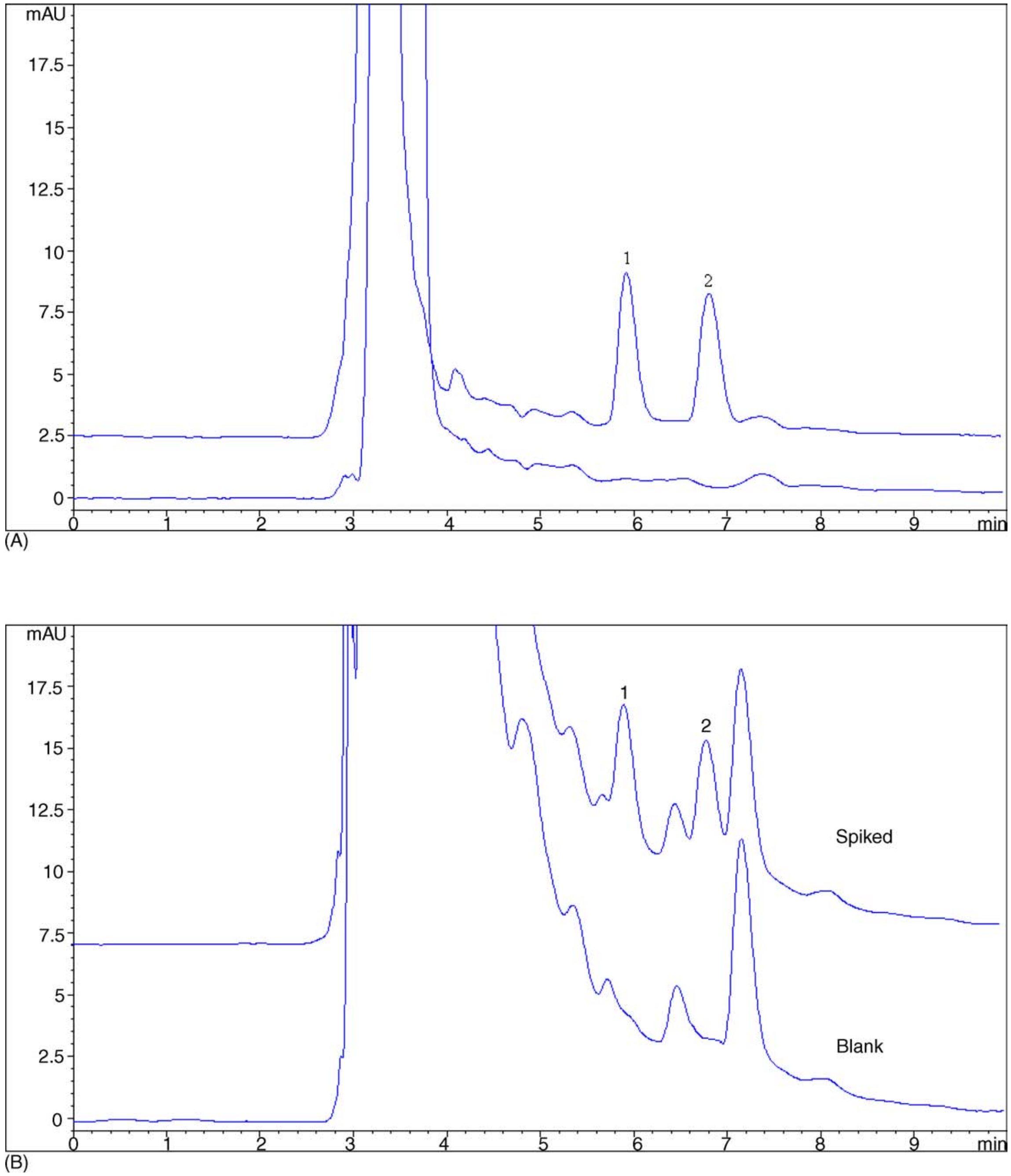

Fig. 4. HPLC-DAD chromatograms from tap water (A) sample and wastewater sample (B). Spiked concentration: 0.8 ng ml^{-1}; volume of eluent: 4 ml; flow rate of sample solution: 7 ml min^{-1}; pH of sample solution: 6–7. (1) Simazine and (2) atrazine.

compound were investigated, and the equivalent results were also listed in Table 1. No atrazine and simazine was found in the tested water samples. The chromatograms from blank and spiked tap water and wastewater samples were exhibited in Fig. 4. The recoveries of atrazine and simazine obtained from tap water, river water and reservoir water samples were excellent; however, the recoveries for them were much lower from the primarily treated wastewater. The possible reason was that the matrix of the wastewater was very complex and organic matters in them would promote the degradation of atrazine and simazine and also adsorb some of them [34], and all these facts leaded to observed results.

4. Conclusions

This paper described a sensitive, simple and reliable method for simultaneous determination of atrazine and simazine in water samples using CNTs packed cartridge for SPE extraction prior to HPLC analysis. The proposed method could provide better recoveries, wide linear range and low detection limits for atrazine and simazine, respectively. The results demonstrated multiwalled carbon nanotubes has exhibited notable merits for trapping triazine herbicides like atrazine and simazine, and described method would be much more competitive for the trace analysis of these herbicides in water samples. These results and previous reports gave rise to a conclusion that multiwalled carbon nanotubes as a tremendously potential absorbents could be used to concentrate many other environmental pollutants in water samples and have an appalling perspective for ultra-trace level analysis.

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