Electrospun polymer nanofibres as solid-phase extraction sorbents for extraction and quantification of microcystins

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Electrospun polymer nanofibres were used as novel solid-phase extraction (SPE) sorbents to extract and quantify the microcystins (MCs) including microcystin-RR (MC-RR) and microcystin-LR (MC-LR) from in-suit water samples. The parameters that influenced the extraction efficiency were studied, including the amount of nanofibre, eluted solvent, eluted volume, pH, and the water sample volume. Under optimized conditions, a linear response for MC-RR and MC-LR over the range of 0.25–4 μg/L was achieved with $r^2$ values of 0.998 and 0.997, respectively. The extraction recovery of MC-RR and MC-LR was 97–102% and 98–100%, respectively, when the MC concentration was 0.25–4 μg/L. When their concentrations ranged from 0.05 to 0.25 μg/L, the MCs could be detected with high accuracy by the nanofibre SPE sorbent combined with nitrogen gas. Due to its simplicity, environment-friendliness, high efficiency, reusability, and sensitivity, the electrospun polymer nanofibre can be applied as a novel SPE sorbent to extract and detect the MCs from in-suit water samples.

Keywords: microcystins; nanofibre; solid-phase extraction; detection; in-suit water samples

1. Introduction
Cyanobacterial blooms can cause significant damage, such as aquatic environment pollution and production of various algal toxins. Microcystins (MCs) are most commonly reported as harmful secondary metabolites of toxic cyanobacteria. The MCs can accumulate in the food chain and are toxic to human beings and animals.[1–3] Consequently, MCs have potent hepatotoxicity and carcinogenic activity in humans and animals. Approximately, 90 MC analogs have been identified, which have chemical structures that contain a cyclic heptapeptide of five amino acids; this structure is common to all MCs as well as two variable L-amino acids.[4,5] Among these analogs, microcystin-LR (MC-LR) has leucin (L) and arginine (R) residues, whereas microcystin-RR (MC-RR) has two R residues. Both analogs have received most attention because of their hepatotoxicity and neurotoxicity, as well as their frequent occurrence in water blooms.[6] The World Health Organization recommends that the MC-LR concentration in drinking water should not exceed 1 μg/L. Therefore, the concentrations of MCs should be detected to avoid using water polluted by cyanobacterial blooms.

Various analytical techniques have been developed for detection. These techniques include the mouse bioassay,[7] protein phosphatase inhibition assay,[8] liquid chromatography/mass spectrometry,[9,10] high-performance liquid chromatography (HPLC), [11] thin-layer chromatography, [12] enzyme-linked immunosorption assay,[13] tandem mass spectrometry,[14] and time-of-flight mass spectrometry.[15]

All of these MC analytical methods mainly rely on HPLC, which allows for the highly selective identification and sensitive quantification of various MCs present in a sample. However, their detection limit is relatively high, especially for the trace analysis of MCs in in-suit water environments. Therefore, the pre-concentration is often required before HPLC analysis. Several pre-concentration methods, including liquid–liquid extraction, solid-phase microextraction, freeze drying,[16] and solid-phase extraction (SPE), are commonly employed to concentrate MCs from water samples.[17] However, these pre-concentration methods are typically labour intensive and time consuming. Consequently, novel methods for the pre-concentration of MCs are still anticipated.

Electrospun nanofibres have been widely used in various fields for their remarkable properties, such as small diameter, high aspect ratio, large specific surface area, high sorption capacity, high porosity, and high stability.

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in liquid media.[18–20] The electrospun polystyrene (PS) nanofibres have been optimized in previous studies.[21] In addition, these nanofibres have been successfully applied in packed-fibre SPE to determine target compounds even in biological fluids [21–23] because of low consumption of organic solvents, simplicity, high recovery, and ease of operation.[23,24] Meanwhile, the use of electrospun nanofibres as an active system to remove environmental pollutants, including MC-LR, has been reported elsewhere.[25–28] However, the use of electrospun nanofibres as an efficient sorbent in SPE systems to extract and quantify MCs has not been reported. Therefore, a novel extraction method with electrospun polymer nanofibres as SPE sorbents was developed to extract and quantify MCs in this study. The potential use of PS nanofibres as adsorbents for SPE to extract and quantify MC-LR and MC-RR simultaneously in water samples was examined. The factors for better quality control during the extraction process were optimized, and the absolute recovery and repeatability were investigated. This method was further applied to extract and quantify MCs in in-suit water samples.

2. Materials and methods

2.1. Reagents and materials

All reagents were of analytical grade, and double-distilled water was used throughout the experiments. Standard MC-LR and MC-RR (≥ 95% purity from HPLC) were purchased from Enzo Life Sciences Inc. (USA). PS (Mw = 185,000), dimethylformamide (DMF), and tetrahydrofuran (THF) were obtained from Shanghai Chemical Agents Institute (Shanghai, China). The HPLC-grade methanol, acetonitrile, and trifluoroacetic acid were purchased from Dikma Technologies Inc. (Beijing, China).

2.2. Standards and calibration curves

The stock solutions (100 μg/mL) of MC-LR and MC-RR were prepared by dissolving a suitable amount of the compounds in methanol. The method of preparing calibration solutions was stepwise dilution. The calibration standard solutions were prepared by diluting the stock standard solutions with double-distilled water step by step to make the concentrations of interest. The model solutions at the concentration levels of interest were prepared daily from the calibration standard solutions by spiking and mixing them with double-distilled water just before experiments. In all cases, the methanol concentration in the solution before SPE was restricted to 1% (v/v). All solutions were stored at −20°C to reduce loss by evaporation.

2.3. Preparation of nanofibres

The nanofibres were synthesized as reported previously. [21,23] A 10% (w/v) PS solution was prepared by dissolving an appropriate amount of PS in a mixture of DMF and THF (4:6, v/v). This solution was loaded into a glass syringe (5 mL volume). The glass syringe was fitted to a steel needle with a tip diameter of 0.5 mm, the tip of which was filed flat. A high-voltage generator was linked with the needle through a copper pin. A grounded iron drum mantled with a copper grid was used as a collection screen. The distance between the needle tip and the collector was 12 cm. A voltage of 16 kV was supplied by a Dongwen high-voltage generator (DW-P403-1AC, Tianjin, China). The flow rate of the syringe was controlled with a syringe pump (TCI-I, Beijing Slog Medical Technology Co., Ltd, China). The feed rate of the precursor solution was fixed at 1.0 mL/h. A dense web of the nanofibres was collected on the copper grid. The morphology image of the PS nanofibres was obtained by using a scanning electron microscope (SEM, Hitachi S-3000N) with an acceleration voltage of 10 kV. The system for electrospinning [21] and the surface-to-volume ratio of PS fibres [23] were similar to those previously described for photocatalytic nanofibres as studied by Bedford et al.[28]

2.4. Instrumental analysis

MCs were analysed by Agilent 1100 liquid chromatograph (Agilent Technologies, USA) with a photo diode array detector. The column used was Extend-C18 (Agilent, 5 μm, 4.6 mm × 150 mm). The column temperature was 40°C. The mobile phase of methanol and water (0.05% trifluoroacetic acid; 52:48, v/v) was used at a flow rate of 1 mL/min. The injection volume was 20 μL. The retention times and peak areas of MCs at 238 nm were determined and compared with those of standard MCs.

2.5. SPE procedure

The SPE columns were manually prepared by packing the appropriate amount of PS fibres into a novel packed-nanofibre SPE column as described in previous experiments.[24] An SPE device purchased from Suzhou Dongqi Biological Technology Co. Ltd was used to enrich the target compounds via the SPE method (Figure S1). Prior to a pre-concentration step, the activation of the nanofibres is vital to achieve high extraction efficiency. Consequently, the nanofibres were preconditioned with 100 μL of methanol and then 100 μL of water.[21–23] With the flow rate carefully controlled in a slow drop-wise manner, the water sample was pushed through the column consisting of nanofibres by the pressure of air forced by a gastight plastic syringe. After the total mixture had been eluted through the nanofibres, the sorbed MCs were desorbed by the appropriate amount of reagents. Finally, 20 μL of the extract was injected into the HPLC system.
2.6. Optimization of extraction conditions

The performance of the extraction method is potentially affected by a large number of factors. Therefore, different amounts of nanofibres (5, 6, 7, 8, or 9 mg), eluent solutions (methanol, water, or acetonitrile), elution volumes (50, 100, or 150 μL), volumes of the water sample (10, 20, or 30 mL), and medium pH (3, 5, 7, 9, or 11) were examined to obtain the optimum conditions. The effects of different factors on the extraction efficiency were investigated using spiked water samples.

2.7. Method validation

The repeatability and linearity were investigated under optimized conditions. The internal calibration curve of MC-RR and MC-LR with different concentrations (0.25, 0.5, 1, 2, or 4 μg/L) was measured by mixing them in spiked water standards. The repeatability of the analytical procedure was assessed by determining the inter-day relative standard deviations of MC-RR and MC-LR at three different concentrations (0.25, 1, or 4 μg/L) over three consecutive days. Extraction recovery (absolute recovery) was calculated at the three aforementioned concentrations in spiked water samples by comparing the peak areas of MC-RR and MC-LR from the extracted samples with those obtained from a direct injection of the corresponding standards dissolved in methanol. The detection limits were calculated at a signal-to-noise ratio of 3 for MC-RR and MC-LR.

2.8. In-suit water samples

Three in-suit water samples were collected in April 2012. Tap water was taken from our laboratory; the other two environmental water samples were taken from Xuanwu Lake (Nanjing, China) and Taihu Lake (Wuxi, China), respectively. These samples were stored in pre-cleaned glass bottles. Extracellular MC concentrations are often extremely low in open water [29]; thus, the total MC (intracellular and extracellular) was also measured. Before the analysis of extracellular MC, the samples were filtered through 0.45-μm membrane filters. To obtain the intracellular MCs from cyanobacterial cells, the water samples were added with 5% (v/v) acetic acid overnight, followed by filtration through 0.45 μm membrane filters. Thereafter, the water samples were immediately analysed after the sampling procedures to ensure the efficient SPE of the analytes.

2.9. Data analysis

Extraction recovery was calculated as the ratio of peak areas from extracted samples over those obtained from the direct injection of the corresponding unextracted standards dissolved in methanol. Peak areas were plotted as a function of the known amounts of analytes, and the results were analysed by least-squares linear regression.

Analysing quality control samples at three different concentrations (0.25, 1, and 4 μg/L) assessed inter-assay imprecision. Each of the three quality control samples was analysed once a day on different days (n = 3). Imprecision is given as the relative standard deviation of the concentrations calculated. The extraction recovery of MC-LR and MC-RR was determined for quality control samples at three concentrations (0.25, 1, and 4 μg/L).

3. Results and discussion

3.1. Characterization of PS nanofibres

The SEM image of PS electrospun nanofibres is shown in Figure 1. The average diameter of the nanofibres was 450 nm. The 10% PS solution could continuously produce high-quality nanofibres.

3.2. Optimization of extraction conditions

3.2.1. Effect of the amount of PS nanofibres on SPE

A spiked water solution mixed with MC-LR and MC-RR (1 μg/mL, 100 μL) was the model sample. The extraction recovery was improved with the increasing nanofibre mass.
Figure 2. Effect of the amount of PS nanofibres on the recoveries of MC-RR and MC-LR. Extraction conditions were as follows: a spiked water solution (1 μg/mL, 100 μL); pH 7; eluting solvent, 100 μL methanol (n = 3).

Table 1. Effect of different eluent solutions and elution volume on the recoveries.

| Eluent solution | Volume of elution solution (μL) | Recovery of MC-RR (%) | Recovery of MC-LR (%) |
|-----------------|---------------------------------|-----------------------|-----------------------|
| Acetonitrile    | 100                             | 66.1                  | 60.1                  |
| Water           | 100                             | 57.9                  | 63.9                  |
| Methanol        | 100                             | 101.1                 | 99.6                  |
| Methanol        | 50                              | 75.8                  | 75.9                  |
| Methanol        | 150                             | 101.3                 | 97.5                  |

until the packing amount of 8 mg was reached (Figure 2). Therefore, the packing amount of 8 mg was sufficient to extract sub-microgram levels of MC-LR and MC-RR in the water sample. Higher amounts of nanofibres may lead to increasing column pressure and a large amount of solvent for elution.

3.2.2. Choice of eluting solvents

Different solutions such as methanol, water, and acetonitrile were tested to elute MCs and ensure the effective desorption of MC-LR and MC-RR from the SPE column. As shown in Table 1, the extraction recovery of MC-RR and MC-LR with 100 μL acetonitrile or 100 μL water was less than 70%. However, the extraction recovery of MC-RR and MC-LR with 100 μL methanol was 101.1% and 99.6%, respectively. Therefore, compared with the other solvents, methanol had the highest efficiency as the eluting solvent for both MC-LR and MC-RR. This difference can be explained by the fact that MC-LR and MC-RR dissolved best in methanol among the three solvents. Subsequently, the appropriate volume of methanol (50, 100, and 150 μL) was tested, and the results are shown in Table 1. For 1 μg/mL of MC-LR and MC-RR in water, the extraction recovery of MC-RR and MC-LR with 50 μL methanol was approximately 75%, whereas those with 100 and 150 μL of methanol were almost 100%. Therefore, 100 μL of methanol was obviously the appropriate solution to elute both MC-LR and MC-RR.

Figure 3. Effect of the sample volume on the recoveries of MC-RR and MC-LR. Extraction conditions were as follows: a spiked water solution (1 μg/L); PS nanofibres, 8 mg; pH 7; eluting solvent, 100 μL methanol (n = 3).

Figure 4. Effect of pH on the recoveries of SPE based on PS nanofibres. Extraction conditions were as follows: a spiked water solution (1 μg/L, 20 mL); PS nanofibres, 8 mg; eluting solvent, 100 μL methanol (n = 3).

3.2.3. Effects of water volume

The water volume may influence the recovery of MC-RR and MC-LR; thus, the experiments were performed in different volumes of the same spiked water standards (1 μg/L). The effect of water volume on recoveries was investigated (Figure 3). The recovery of MC-RR and MC-LR decreased as the water volume increased. Meanwhile, the required time for the pre-concentration process increased as the water volume increased. Therefore, 20 mL was selected as the optimum water volume.

3.2.4. Effects of pH

The effect of pH on the extraction of MC-RR and MC-LR was examined in 20 mL spiked water standards (1 μg/L) within the range of 3–11 (Figure 4). The optimal extraction pH was determined to be 5, which was appropriate to ensure the extraction of both MC-RR and MC-LR. The adsorption behaviour of MC-LR in our study was similar to that observed in other nanoparticles. The maximum adsorption of MC-LR was observed at low pH.[30]

3.3. Method validation

According to the results in Table 2, good linearity of response of both MC-RR and MC-LR was observed in the
Table 2. Linearity, repeatability, and absolute recovery of the method (n = 3).

| Analytes | Linear range (μg/L) | Linearity $r^2$ | Repeatability (RSD%) | Recovery (%) |
|----------|---------------------|----------------|----------------------|-------------|
|          |                     |                | 0.25 μg/L | 1 μg/L | 4 μg/L | 0.25 μg/L | 1 μg/L | 4 μg/L |
| MC-RR    | 0.25–4              | 0.998          |           | 3.28   | 1.02   | 5.28     | 99.64   | 97.45   | 102.01 |
| MC-LR    | 0.25–4              | 0.997          |           | 1.10   | 0.34   | 2.63     | 99.36   | 98.61   | 100.96 |

range of 0.25–4 μg/L with $r^2$ values of 0.998 and 0.997, respectively. The repeatability of the analytical procedure was assessed at three different concentrations (0.25, 1, and 4 μg/L) over three consecutive days, and the results were found to be less than 6% for both MC-RR and MC-LR. The extraction recovery (absolute recovery) was calculated at the three aforementioned concentrations. The analytical results were within acceptable limits, as summarized in Table 2. The detection limit was 0.1 μg/L for MC-RR and MC-LR. Previous ultrafiltration experiments have demonstrated that hydrophobic membranes are more efficient for the extraction of MCs [31]; thus, a hydrophobic material should be designed to improve fibre adsorption. Therefore, our results are consistent with the hydrophobic nature of PS nanofibres.[32]

An additional set of the aforementioned experiments could detect the lower concentration of MC-RR and MC-LR in the water. Good linearity of response of both MC-RR and MC-LR was observed in the range of 0.05–0.25 μg/L with $r^2$ values of 0.998 and 0.999, respectively.

3.4. Analysis of in-suit water samples

To evaluate the applicability of our proposed method, three in-suit water samples were analysed. Under the optimized conditions, 20 mL of each sample was extracted by the PS nanofibres. Figure 4 shows a typical chromatogram of an extracted water sample spiked with the appropriate amount of standard MC-LR and MC-RR, as well as the chromatogram of wastewater taken from Taihu Lake. Clearly, all of the compounds could be extracted and separated effectively (Figure 5(a)). Results showed that extracellular MC-RR and total MC-RR were 0.56 and 0.9 μg/L, respectively, in Taihu Lake. For further analysis, three in-suit water samples were detected as the additional set of experiments mentioned. The results indicated that, in Taihu Lake, extracellular LR and total MC-LR were 0.06 and 0.18 μg/L, respectively. Therefore, the concentrations of MC-RR and MC-LR in the other two in-suit water samples may be lower than 0.05 μg/L. Xu et al. [33] reported that the MC concentrations ranged from 0 to 15.6 μg/L from January 2001 to December 2001. Concentrations of MCs were high from July 2001 to October 2001, whereas cyanobacterial blooms often appear in summer and autumn in Taihu Lake.

Table 3. Analytical features and comparison to the literature.

| Adsorbent for SPE | Amount of adsorbent (mg) | Sample volume (mL) | Organic solvent volume (mL) | Evaporating eluate solvent | Drying with nitrogen gas or air | pH | Method |
|------------------|--------------------------|--------------------|-----------------------------|---------------------------|---------------------------------|----|--------|
| Supelclean 500   | 500                      | 1000               | > 22.5                      | Yes                       | Yes                             | 7.5| HPLC   |
| ENVI-18 [34]     |                          |                    |                             |                           |                                  |    |        |
| C-18 [35]        | Unknown                  | 500                | > 31.4                      | Yes                       | Yes                             |    | Unknown HPLC |
| C-18 [36]        | 500                      | 1000               | > 3.5                       | Yes                       | No                              |    | Unknown HPLC-MS/MS |
| PS nanofibre     | 8                        | 20 or 60           | 0.2 or 0.66                 | No                        | No                              | 5  | HPLC   |
3.5. Analytical features and comparative studies

For the comparative studies, a series of parameters were selected as the reference values from the literature; these parameters included the adsorbent used for SPE, sample volume, and the organic solvent volume. The method investigated in this study and the previously reported methods are summarized in Table 3.

Compared with the findings in the literature,[34–36] the volume of organic solvent used in this study did not exceed 1 mL, which obviously illustrates the environment-friendliness of our method. The proposed method apparently required less sample volume and simpler equipment than those of other methods. Moreover, the amount of PS nanofibres was only 8 mg, which was much less than the 500 mg of adsorbent filled in C-18 cartridges. Therefore, our proposed method is a viable technique for extracting MCs from water samples with PS nanofibres as adsorbents for SPE.

4. Conclusions

The use of PS nanofibres as a SPE sorbent for pretreatment of MC-RR and MC-LR was investigated. We successfully extracted and quantified the MCs in water samples, and even the concentrations of MCs were significantly lower than 1 μg/L. The advantages of PS nanofibres as SPE sorbents for the pre-concentration of MCs are as follows: (1) environment-friendliness (only small volumes of organic solvent were needed for the desorption of targets); (2) elimination of the evaporation step; (3) lower volume of water samples; (4) simplicity, low cost, and convenient format. The applicability of the method was further validated by the successful application in determining MCs in in-suit water samples.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental data

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