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RESEARCH PAPER

Determination of Microcystin-LR in Environmental Water by Magnetic Solid Phase Extraction-High Performance Liquid Chromatography

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Abstract: A rapid analytical method was established for the determination of trace amounts of microcystin (MC-LR) in environmental water samples by using magnetic solid phase extraction (MSPE) coupled with HPLC/UV based on a magnetic bentonite sorbent fabricated by solvothermal synthesis method. Several factors influencing the extraction efficiency of MC-LR, such as sorbent amount, pH condition, sample volume, adsorption and desorption time, and desorption solvent, were investigated and optimized. Under the optimal extraction conditions, the limits of detection and quantification for the method were 0.75 and 1.5 ng L^{-1}, respectively, which was far below the guideline recommended by the World Health Organisation. The method showed a good linearity (R^2 = 0.9993) in the concentration ranges of 0.25–250 μg L^{-1} for MC-LR. The MSPE sorbent was simple in preparation, low cost and magnetizable, and the developed MSPE-HPLC method was suitable for the rapid and sensitive determination of MC-LR in nature water samples.

Key Words: Magnetic; Solid phase extraction; Microcystin; High performance liquid chromatography

1 Introduction

Solid phase extraction (SPE), which possesses the attractive features including high enrichment efficiency and ease of operation, is increasingly becoming one of the most frequently applied sample preparation techniques in environmental, food and biological analyses[1,2]. However, the method is relative high-cost and low selectivity. Additionally, it requires large volumes of organic solvent both in the pretreatment and desorption processes[3]. Consequently, a novel sample preparation technique, named magnetic solid phase extraction (MSPE), was developed in this study. Magnetic nanoparticles, as a vital sorbent for MSPE, has unique physical and chemical properties, such as easy modification, high specific surface area, good dispersion and excellent recycling capability. The main advantages of MSPE is that it could selectively obtain high clean-up and enrichment efficiency in the analysis of traces of targets in complex matrices by the simple processes, and avoids the problems of column blocking when dealing with biological and environmental samples in common SPE. Recently, MSPE was used for extraction and determination the organic pollutants and inorganic metal contaminants in water samples coupled with HPLC and GC instruments[4–7].

Microcystins (MCs) are bio-contaminants produced by cyanobacteria. Among the MCs identified to date, microcystin-LR (MC-LR) is one of the most widespread and dangerous toxins[8,9]. The primary target organ of MCs is liver, and long term consumption of MCs-contaminated water may induce liver cancer. MCs are persistent bio-contaminants and may accumulate in the food chain[10]. MCs are fairly stable, even at the high temperature and extreme pH, and the traditional treatment techniques for running water cannot remove MCs effectively. Owing to the strong toxicity and ubiquity of the bio-contaminants, World Health Organization[11] and Standards

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for Drinking Water Quality of China[12] categorized MCs as probable carcinogen for humans and recommends a maximum permissible limit of 1 μg L^{-1} in drinking water and surface water source (MC-LR as represented). Taking into account the low detection limit of the drinking water safety guideline level by WHO for MCs and the complexity of the water sample matrix, the pretreatment techniques to isolate and extract trace amounts of MCs from water samples before the HPLC determination are very important. Till date, MSPE based on magnetic nanoparticles has been widely employed in many fields for the analysis of organic and inorganic pollutants, whereas its application in MSPE-HPLC for analysis of bio-contaminants has been seldom reported. On the basis of our previous work[13], in this study, the noval multifunctional magnetic bentonite materials modified with cetyltrimethylam-monium bromide (CTAB) to extract bio-contaminant MC-LR from water efficiently were fabricated. Significantly, a novel method for analysis of MC-LR in water samples at trace level was developed by investigation the factors influence on extraction and desorption process in MSPE combined with HPLC/UV. The results indicated that the proposed method was simple, reliable and environmentally friendly.

2 Experimental

2.1 Instruments and reagents

LC-20AT HPLC system (Shimadzu, Japan) with a SPD-20A UV detector was used for MC-LR analysis. KQ-500D ultrasonic cleaner (Kunshan ultrasonic instrument Co., Ltd, China) and XW-80A vortex mixer (Qilinbeier Co., Ltd, Haimen, China) was used in the process of extraction and desorption. Fourier transform infrared (FT-IR) spectra were obtained from a FT-IR spectrometer (Vertex 80V, Bruker, Germany). Thermal property was measured by a thermal gravimetric analyzer (TGA, SDT-Q600, TA, USA).

MC-LR was purchased from Algal Science lnc. (Taiwan, China). HPLC grade acetonitrile and methanol were purchased from Damao (Tianjin, China). Chemical pure bentonite was purchased from Guangfu (Tianjin, China). Trifluoroacetic acid (TFA, HPLC grade) was from Aladdin (Shanghai, China). Ultrapure water was prepared through a Milli-Q system from Millipore (Bedford, MA, USA). The other chemicals were of analytical grade.

2.2 Preparation of stock solution

The stock solution of 5 μg mL^{-1} was prepared by dilution of 500 μL of MC-LR standard solution (50 μg mL^{-1}) to fixed volume of 5 mL with Milli-Q water. Then it was stored at a brown screw cap glass vial at 4 ºC.

2.3 Analysis with HPLC

HPLC analysis was performed on a C_{18} analytical column (250 mm × 4.6 mm, 5 μm, Agilent Technologies). The UV detection wavelength was 238 nm. The mobile-phase was a mixture of acetonitrile (A) and 0.1% phosphoric acid buffer (B) (35:65, *V/V)* at mobile-phase flow rates of 1.0 mL min^{-1}. The column was worked at a constant temperature of 30 ºC. All injections were performed manually with a 10-μL sample loop.

2.4 Preparation of MSPE sorbent

2.4.1 Synthesis of magnetic bentonite (Fe_3O_4@B)

Bentonite (0.5 g), $FeCl_3·6H_2O$ (1.35 g), anhydrous sodium acetate (3.60 g) and polyethylene glycol (1.00 g) were homogeneous mixed with 40 mL of ethylene glycol, then the mixture was stirred for 20 min and heated at 190 ºC for 8 h in a 50-mL stainless autoclave. After cooling, the solution was transferred into a 100-mL beaker. The precipitate was aggregated with the aid of a magnet and washed with ethanol and deionized water several times. Next, the magnetic bentonite were aggregated and then diluted by deionized water to 100 mL.

2.4.2 Synthesis of magnetic organic bentonite (Fe_3O_4@B@CTAB)

The Fe_3O_4@B solution was homogeneous dispersion in deionized water by sonication for 10 min and transferred into a 250-mL flask. Subsequently, 0.5 g of CTAB was added to the solution and the mixture was stirred at room temperature for 24 h. Finally, the resultant Fe_3O_4@B@CTAB was separated by an external magnetic field, washed with ethanol and deionized water several times, dried in vacuum at 60 ºC and then store at a screw cap vial.

2.5 MSPE procedures for MC-LR

7.5 μg mL^{-1} of MC-LR solution was prepared by the dilution of 30 μL MC-LR standard solution (5.0 μg mL^{-1}) to 20 mL with Milli-Q water. A certain quality of Fe_3O_4@B@CTAB was dispersed in the solution, and the mixture was fiercely vortexed for 20 min. Then, Fe_3O_4@B@CTAB with adsorbed MC-LR was isolated from the solution by a permanent magnet. After discarding the supernatant, 400 μL of eluate consisted of acetonitrile and 0.1% TFA solution (3:1, *V/V*) was added to elute MC-LR from sorbent under sonication for 20 min. The eluate was separated from the sorbent and matched to 200 μL with Milli-Q water. The samples were injected into the HPLC system for analysis.

2.6 Samples collection and preparation