Marine Pollution Bulletin 111 (2016) 411–417

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Determination of ciprofloxacin in Jiaozhou Bay using molecularly imprinted solid-phase extraction followed by high-performance liquid chromatography with fluorescence detection

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ARTICLE INFO

Article history:
Received 13 May 2016
Received in revised form 22 July 2016
Accepted 24 July 2016
Available online 27 July 2016

Keywords:
Ciprofloxacin
Molecularly imprinted solid-phase extraction
Seawater
Jiaozhou Bay

ABSTRACT

A high selective pre-treatment method for the cleanup and preconcentration of ciprofloxacin in natural seawater samples was developed based on molecularly imprinted solid-phase extraction (MISPE). The ciprofloxacin imprinted polymers were synthesized and the characteristics of obtained polymers were evaluated by scanning electron microscopy, Fourier transform infrared spectroscopy and binding experiments. The imprinted materials showed high adsorption ability for ciprofloxacin and were applied as special solid-phase extraction sorbents for selective separation of ciprofloxacin. An off-line MISPE procedure was optimized and the developed MISPE method allowed direct purification and enrichment of the ciprofloxacin from the aqueous samples prior to high-performance liquid chromatography analysis. The recoveries of spiked seawater on the MISPE cartridges ranged from 75.2 to 112.4% and the relative standard deviations were less than 4.46%. Five seawater samples from Jiaozhou Bay were analyzed and ciprofloxacin was detected in two samples with the concentrations of 0.24 and 0.38 μg L^{-1}, respectively.

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1. Introduction

Antibiotics are more and more a focus point of research due to their high detection frequency in the environment and the increasing bacterial resistance formation. Fluoroquinolones (FQs) are piperazinyl derivatives of quinolones, and are broadly used to treat humans and food-producing animals, due to their broad-spectrum activity against both gram-positive and gram-negative bacteria (Meng et al., 2015; Speltini et al., 2015). Among them, ciprofloxacin (Cip) has been the most widely prescribed fluoroquinolone in the world. These drugs inhibit bacterial replication by blocking the DNA replication pathway. The widespread use of FQs has resulted in the potential risk of theirs residues. Maximum residue limits (MRLs) of FQs for various foodstuffs have been established for safety assessment (Lombardo-Agüí et al., 2010; Yang et al., 2014). Studies have revealed that FQs are excreted unmetabolized up to 70% and, when released in the environment, they can promote resistance formation on microbial populations. The presence of these pseudo- persistent compounds in the environment can induce toxic effects on aquatic organisms (Doorslaer et al., 2014). Besides, the lack of biodegradation and high adsorption affinity results in long residence times in the environment. Up to now, FQs have also been detected in environment water systems in many countries (Chen et al., 2010; Luaces et al., 2013; Sturini et al., 2012; Vázquez et al., 2012). The occurrence of FQs in marine waters is less frequently reported compared to freshwater. In consideration of low concentration and complexity of seawater sample, selective sample preparation methods are necessary to build before chromatographic analysis.

Sample preparation is an extremely important step in chemical analysis. A well- done sample preparation, combined with appropriate instruments, allows the determination of almost all compounds in a sample, even in very low concentrations. The clean-up procedure and preconcentration technique are the critical points for analysis of low concentration analyte (Fonseca et al., 2016). Solid-phase extraction (SPE) has played an important role in purifying and preparation of chemical-sample and biological-sample because of its flexibility, simplicity and low consumption of reagent (Tang et al., 2016). Current research indicates that SPE based on molecularly imprinted polymers (MIPs) is an efficient approach for purification and preconcentration of analytes from complex matrices of the samples (Asiabi et al., 2016; Sarafraz-Yazdi and Razavi, 2015). Molecular imprinting is a developing technique that generates molecular assemblies with chosen structures and properties. MIPs are prepared by the co-polymerization of an adequate monomer and a cross-linker agent in the presence of a target molecule. The synthesized polymers have many cavities complementary to the template molecule in shape, size and chemical functionality making

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http://dx.doi.org/10.1016/j.marpolbul.2016.07.034
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them have a distinctive and predetermined selectivity toward those target molecules (Ji et al., 2016; Saad et al., 2015). Thus, molecularly imprinted solid-phase extraction (MISPE) is able to eliminate complex matrix interferences and preconcentrate analytes from complex matrices, which has been demonstrated more selective than the classical SPE methodology (Bitar et al., 2015; Lian and Wang, 2012; Lulinski et al., 2015). It presents the high specificity, selectivity and sensitivity of the molecular recognition mechanism, and this technique is fast, time-efficient, and easy to use.

Jiaozhou Bay is a typical semi-enclosed bay situated in the southern part of Shandong Peninsula (35°58′–36°18′N, 120°04′–120°23′E), China. Given rapid progresses in industrial and aquaculture development, Jiaozhou Bay is significantly affected by anthropogenic activities and its water quality has deteriorated over the last two decades. Many studies have been conducted on the pollution status of the Bay, including nutrients, heavy metals, petroleum hydrocarbons, and antibiotics such as macrolides, sulfonamides and diaminopyrimidines etc. (Li et al., 2015; Xu et al., 2016; Yuan et al., 2016; Zhang et al., 2013). To our knowledge, there is few report on the FQs antibiotics in Jiaozhou Bay. Additional, there is no application of MISPE for sample preparation and preconcentration of Cip in natural seawater samples. Based on our previous studies of MISPE technology (He et al., 2016; Lian and Wang, 2013a, 2013b; Lian et al., 2015a, 2015b), this method is able to reach the desired results and plays an important role in sample clean-up and preconcentration prior to sample determination.

The aim of the present work was to design a simple and effective method, dedicated to selectively recognize and determinate Cip in seawater samples. We synthesized non-covalent MIPs by bulk polymerization technique and binding affinity was analyzed by static and dynamic adsorption tests. The obtained MIPs showed high affinity to the analyte and were applied as special SPE sorbents for clean-up and preconcentration of Cip in natural seawater samples. Furthermore, an off-line MISPE method was developed and Cip in the Jiaozhou Bay was successfully detected using the method.

2. Experimental

2.1. Materials

Ciprofloxacin and ethylene glycol dimethacrylate (EGDMA) were purchased from Aladdin Chemical Reagent Company (Shanghai, China). Methacrylic acid (MAA) and 2,2-azoisobutyronitrile (AIBN) were obtained from Kermel Chemical Company (Tianjin, China). MAA and EGDMA were purified prior to use to remove the polymerization inhibitor, and AIBN was recrystallized prior to use. Acetonitrile and methanol are all of HPLC grade and from Merck. Unless specified, all reagents were at least HPLC grade or analytical grade. All water used was obtained from a Millipore Milli-Q purification system (Millipore, Bedford, MA, USA). Stock solution of Cip was initially prepared at 200 mg L^{-1} in Milli-Q water and stored at 4 °C in the dark. Working solutions were diluted at various concentrations by Milli-Q water daily.

2.2. HPLC conditions

The chromatographic analyses were performed using a Hitachi L-2000 series HPLC system, equipped with a binary pump, an autosampler, a column compartment and an L-2485 fluorescence detector with excitation set to 280 nm and emission to 452 nm monitoring the effluent for Cip. The analytical column was a 250 mm × 4.6 mm, 5 μm LaChrom C18 column (Hitachi, Japan). The column thermostat was set at 25 °C. The optimized mobile phase consisted of 25 mM orthophosphoric acid (adjusted to pH 2.4 with triethylamine)/acetonitrile (82:18, v/v), and its flow rate was set as 0.8 mL min^{-1}.

2.3. Preparation of the polymers

The MIPs were prepared with a slight modification according to the published procedures (Yan et al., 2008). Briefly, 1 mmol of template molecules (Cip) and 6 mmol of functional monomers (MAA) were dissolved in 30 mL methanol-water (90:10, v:v) in a 50 mL borosilicate glass bottle, equipped with a rubber cap. After oscillating for 30 min at room temperature, 20 mmol of cross-linker (EGDMA) and 100 mg of the initiator (AIBN) were added. Afterwards, the mixture was purged with dry nitrogen gas for 15 min in order to get rid of oxygen. The bottle was sealed and placed in a thermostated water bath at 60 °C for 24 h. After polymerization, the polymer was ground and sieved. The fraction with particle sizes of 75–106 μm was collected and subjected to sedimentation in methanol in order to remove fine particles. The obtained particles were extracted with methanol containing 10% acetic acid using a Soxhlet apparatus until no template molecule was detected. Finally, the products were washed with methanol for three times and dried under vacuum at room temperature.

The corresponding non-imprinted polymers (NIPs) were prepared under the same condition described above but in the absence of Cip.

2.4. Morphology observation and FTIR spectra

The surface morphology of the particles was observed by a Hitachi S-4800 cold field emission scanning electron microscope (Tokyo, Japan). All samples were prepared by wetting the slide glass with a small drop of diluted particle dispersion. Before scanning electron microscopy experiments, the dried specimen was coated with a thin layer of gold under vacuum. FTIR spectra were recorded in powder form in KBr discs in the range of 4000–500 cm^{-1} on an AVATAR360 FTIR spectrophotometer from Nicolet instrument Company.

2.5. Binding experiments

The binding properties of polymers were examined by batch adsorption experiments. Dry polymer particles (10 mg) were weighed and put into a 15 mL test tube. 5 mL of Cip standard solution with known concentration was mixed with the polymer. The mixture was slightly shaken on a horizontal shaker for 24 h at room temperature and then centrifuged at 4000 rpm for 5 min. Final concentrations of Cip were analyzed by HPLC. The amount of bound Cip was calculated by subtracting the amount of free Cip from the initial amount added to the mixture.

A dynamic adsorption test of the MIPs for Cip was performed at different time intervals. In the experiment, 10 mg of the MIPs (or NIPs) was respectively added into 5 mL test tube, and was mixed with 3 mL of a known initial concentration (25 mg L^{-1}) of Cip standard solution. The mixture was shaken at 25 °C for 24 h. Samples were collected at fixed intervals (2 h) and analyzed by HPLC method.

To evaluate the repeatability of the binding protocol, each experiment was repeated in triplicate.

2.6. Preparation of MISPE cartridge

MISPE cartridge was prepared by packing the dry MIP (20 mg) in a 1.0 mL glass syringe (2 cm × 0.9 cm i.d.). The syringe tube was thoroughly cleaned and dried, and attached with two sieve plates at the bottom end and the top end respectively. Prior to loading the sample, the MISPE cartridge was previously conditioned with 2 mL of methanol-water (50:50, v/v) solutions and 2 mL of pure methanol successively.

2.7. MISPE for spiked seawater samples

Five seawater samples were collected from Jiaozhou Bay in Qingdao, China in June 2015 (Fig. 1). Approximately 150 mL of raw seawater was collected at 2 m seawater layer. The seawater samples obtained were immediately filtered through precombusted (450 °C, 3 h) Whatman

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