Journal of Chromatography A, 1443 (2016) 54–61

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Ferrite nanospheres-based magnetic solid-phase extraction for determination of domoic acid in seawater samples using high-performance liquid chromatography with tandem mass spectrometry

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ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form 28 February 2016
Accepted 21 March 2016
Available online 24 March 2016

Keywords:
Domoic acid
Seawater
Ferrite nanospheres
Magnetic solid-phase extraction
HPLC–MS/MS

ABSTRACT

A simple, rapid and sensitive method for determination of trace levels of domoic acid (DA) in seawater was developed, based on a magnetic solid-phase extraction (MSPE) followed by high-performance liquid chromatography with tandem mass spectrometry (HPLC–MS/MS). Five kinds of ferrite magnetic nanospheres (MFe_2O_4; M = Fe, Co, Ni, Cu and Zn) were prepared and first used as sorbents for MSPE of DA and removal of salt interference. Under the same extraction and elution conditions, $CuFe_2O_4$ magnetic nanospheres provided the best pretreatment performance, which were then characterized in detail. After further optimization of conditions, the developed method showed good linearity ($r^2 = 0.9991$) with the range of 5–1000 pg mL^{-1}, low limit of detection (2.5 pg mL^{-1}; S/N = 3:1), low limit of quantification (5.0 pg mL^{-1}; S/N = 10:1), and good recoveries (86.0–98.1%) with acceptable repeatability (RSD ≤ 6.5%; n = 3) in seawater samples. The results demonstrated that the ferrite magnetic nanospheres are promising sorbents for efficient extraction of highly polar analytes from high ionic strength solutions.

1. Introduction

Domoic acid (DA, Fig. 1) is a naturally occurring neurotoxin amino acid produced by several species of marine diatoms from the genus *Pseudo-nitzschia* [1]. It is considered to be the main cause of a human intoxication syndrome known as amnesic shellfish poisoning (ASP), which is characterized by severe gastrointestinal and neurological disorders, and ultimately even death [2–4]. Besides, DA has also caused serious economic losses to the aquaculture industry and massive death of marine fauna worldwide [5–7]. Harmful diatoms species are distributed worldwide in the coastal waters. Measurement of DA in seawater not only is an early alert for potential toxin accumulation in marine organisms, but also may describe its real impact in the environment. Due to extremely low levels of DA in seawater samples, sensitive analytical methods for determination of DA are required.

In recent years, high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC–MS/MS) has become one of the main analytical techniques for monitoring of DA in seawater due to good sensitivity, accuracy, and high selectivity [8–13]. However, seawater contains high levels of salt, which often causes poor spray performance, a decrease in instrumental sensitivity and linear dynamic range, and severe MS contamination, if salts are not removed before HPLC–MS/MS analysis [14,15]. A few studies on sample desalting and concentration of DA from the complicated matrix have been reported. Chan et al. used a sol-gel amorphous titania sorbent for concentration of DA from seawater [16], but the high ionic strength buffer used for desorption of DA from titania sorbent limits its direct injection for HPLC–MS/MS analysis. Though molecularly imprinted polymer (MIP) has been used for selective extraction of DA from seafood, the preparation of MIP required much time and labour [17]. Besides, reverse-phase SPE is the most common method for desalting and concentration of samples. However, DA is a highly polar compound, which makes it difficult for extraction by reversed-phase SPE. Although DA can be retained in reversed-phase SPE after acidification [8], the lower pH would degrade the SPE column, as well as resin-based SPE cartridge [10].

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http://dx.doi.org/10.1016/j.chroma.2016.03.055
0021-9673/

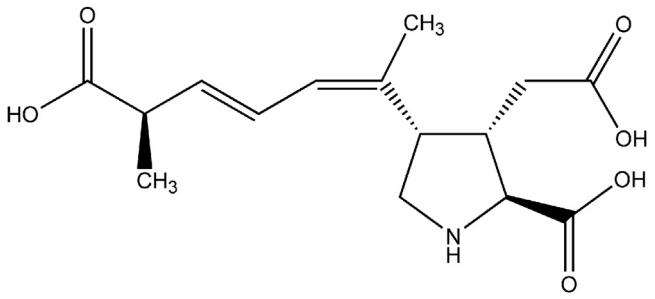

Fig. 1. Chemical structure of domoic acid.

Hence, the development of preparation methods for desalting and concentration of trace levels of DA from seawater samples is still a challenge.

In order to achieve extraction of highly polar algal toxins from complicated seawater matrix, adsorption process cannot be only driven by electrostatic or hydrogen-bonding interaction. Other more powerful interactions have to be explored. Interestingly, numerous researches have demonstrated that certain marine diatom species *P. nitzschia* may produce DA as a chelator to selectively bind trace metals in order to either increase the availability of an essential micronutrient (such as iron), or to decrease the availability of a potentially toxic trace metal (such as copper) [18–22]. In addition, values for the conditional stability constant of DA binding to iron and copper have also been calculated in the previous work [23], indicating that environmental concentrations of DA can compete for these trace metals with natural ligands in seawater. Thus, adsorption mechanisms based on the high affinity of DA towards metal ions could be used for extraction of DA from seawater and removal of salt interference.

Spinel ferrite (MFe_2O_4; M = Fe, Co, Ni, Cu and Zn) magnetic nanospheres are one of the most important magnetic materials and have been widely used in electronic devices, information storage, magnetic resonance imaging, and drug-delivery technology [24,25]. The ferrite magnetic nanospheres not only have a large number of metal sites, but also can be used as the sorbents for magnetic solid-phase extraction (MSPE) that can facilitate the isolation of trapped analytes from sample solution under magnetic fields [26,27]. Owing to these unique properties, the ferrite magnetic nanospheres show great application potential in adsorption and separation. However, up to now, none of the ferrite magnetic nanospheres have been designed as a sorbent for extraction of DA from seawater and removal of salt interference. Herein, five kinds of the ferrite magnetic nanospheres were synthesized and first used for MSPE of DA from seawater. The performances of these magnetic nanospheres were evaluated, and the best one was further characterized in detail. Besides, the potential factors affecting the extraction and desorption of DA were also investigated. Furthermore, the developed method was used for determination of DA in real seawater samples.

2. Experimental

2.1. Materials and chemicals

All solvents used were of analytical grade or better. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), cupric chloride dihydrate ($CuCl_2{\cdot}2H_2O$), sodium acetate (NaAc), trisodium citrate dihydrate ($Na_3Cit{\cdot}2H_2O$) and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and L-histidine (99%) were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). Domoic acid (DA, ≥90%) was purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China). Ultrapure water (18.2 MΩ cm) was obtained with a Milli-Q ultrapure water system (Millipore, USA).

2.2. Instrumentation

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectrometry (EDS) were obtained with an SU8020 SEM instrument (Hitachi, Japan). Transmission electron microscopy (TEM) analyses were performed on a FEI Tecnai G2 F20 (FEI, USA) at 200 kV. Fourier-transform infrared (FT-IR) spectra were measured on a Nicolet 6700 spectrometer (Thermo Fisher, USA). The X-ray diffraction (XRD) patterns were determined using a D8 Advance (Bruker, German). The magnetization curves were obtained at room temperature on an MPMS-XL-7 (Quantum Design, USA) vibrating sample magnetometer (VSM).

The HPLC–MS/MS analysis was carried out using an Accela HPLC system coupled to a TSQ Quantum Access Max^{TM} triple quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source (Thermo Fisher, USA). Chromatography separation was performed on a Hypersil GOLD aQ column (5 μm particle size, 150 × 2.1 mm). Mobile phase consisted of water (A) and acetonitrile (B) in a binary system, both containing 0.1% formic acid. Isocratic chromatography was performed using 20% B for 5 min with a flow rate 200 μL min^{-1}. The column temperature was held at room temperature, and the injection volume of analytical solution was 10 μL. MS analysis was performed using selected reaction monitoring (SRM) mode with the ion source in positive mode. Parameters such as SRM transition (DA, m/z 312 → 266), collision energy (16 eV) and tube lens (96) were obtained by auto tuning. Other parameters were further optimized to achieve the best sensitivity. For instance, the vaporizer temperature and capillary temperature were set at 300 °C and 350 °C, respectively; the ESI source was operated at ion spray voltage of +3000 V; Nitrogen was used as sheath gas and auxiliary gas at flow rates of 35 and 10 arbitrary unit, respectively; Helium (99.999% purity) was employed as collision gas. Data acquisition and processing were performed with LC quan 2.7 software (Thermo Fisher, USA).

2.3. Preparation of MFe_2O_4 (M = Fe, Co, Ni, Cu and Zn) magnetic nanospheres

Fe_3O_4 magnetic nanospheres were prepared by the solvothermal method [28]. Briefly, $FeCl_3{\cdot}6H_2O$ (6.081 g, 22.5 mmol), NaAC (8.203 g, 100 mmol) and $Na_3Cit{\cdot}2H_2O$ (29.4 mg, 0.1 mmol) were dissolved into 100 mL of ethylene glycol by stirring. The mixture was transferred to an autoclave and then heated at 200 °C. After 12 h of reaction, the autoclave was cooled naturally at room temperature. The obtained products were washed with deionized water and ethanol for several times and dried at room temperature.

The above process can be extended to the preparation of other ferrite magnetic nanospheres ($CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$) in a molar ratio (M^{2+}/Fe^{3+}; $M^{2+} = Co^{2+}$, Ni^{2+}, Cu^{2+} and Zn^{2+}) of 1:2 [24,29]. For example, a mixture of $FeCl_3{\cdot}6H_2O$ (4.054 g, 15 mmol), $CuCl_2{\cdot}2H_2O$ (1.278 g, 7.5 mmol) under the same reaction conditions as used for the preparation of Fe_3O_4 nanospheres, produced nanospheres of $CuFe_2O_4$.

2.4. MSPE procedure

The MSPE procedure was carried out as follows. 20 mL of aqueous standard solution or samples solution was added into a 50 mL centrifuge tube. Then, 1.0 mg of $CuFe_2O_4$ magnetic nanospheres was dispersed in the mixture solution. The extraction was performed under vortex for 7 min. Then, an external magnet was