Journal of Chromatography A, 1350 (2014) 23–29

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Double water compatible molecularly imprinted polymers applied as solid-phase extraction sorbent for selective preconcentration and determination of triazines in complicated water samples

Shoufang Xu [a], Hongzhi Lu [a], Lingxin Chen [b,*]

[a] School of Chemistry & Chemical Engineering, Linyi University, Linyi 276005, China
[b] Key Laboratory of Coastal Zone Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

ARTICLE INFO

Article history:
Received 19 March 2014
Received in revised form 7 May 2014
Accepted 11 May 2014
Available online 17 May 2014

Keywords:
Molecularly imprinted polymers
Water-compatible
Triazines
Solid phase extraction
Water sample

ABSTRACT

In the present work, double water compatible molecularly imprinted polymers (DWC-MIPs) with water compatible core and hydrophilic polymer brushes were prepared by reversible addition–fragmentation chain transfer precipitate polymerization (RAFTPP) and applied as solid-phase extraction (SPE) sorbent for selective preconcentration and specific recognition of triazines in water samples. The DWC-MIPs employed as SPE sorbent presented much higher extraction efficiency for four triazines in aqueous media based on the double water compatible property. The validated method was also successfully applied to tap water and river water sample analysis, and satisfactory recoveries were attained, such as 69.2–95.4% with the precision of 1.59–3.94% for four triazines at 100 μg L^{-1}. The DWC-MIPs-SPE proves to be a highly effective cleanup and enrichment method for simultaneous separation and sensitive determination of triazines in complicated water samples.

1. Introduction

Molecular imprinting is known as a technique for creation of tailor-made binding sites with memory of the shape, size and functional groups of the template molecules. Hence, molecularly imprinted polymers (MIPs) are synthetic polymers having a predetermined selectivity for a given analyte, or a group of structurally related compounds [1,2]. In the recent years, MIPs have been widely applied and achieved great progress in many fields, such as solid phase extraction (SPE) [3–7] and chemical sensors [8,9], owing to their desired selectivity, physical robustness, thermal stability, as well as low cost and easy preparation.

Up to date, the most widely used technique for preparing MIPs is non-covalent imprinting, in which the complex of template and functional monomer is formed by non-covalent interactions, such as hydrogen bonding, ionic interactions, van der Waals forces, and π–π interactions. Aprotic and low polar organic solvents are often used for non-covalent imprinting. So, most of produced MIPs can successfully achieve specific recognition in organic solvent-based media. However, they often show poor recognition ability for the target in aqueous environments because the presence of polar solvent can disturb the hydrogen bond formed between template and functional monomer [10]. In addition, the nonspecific hydrophobically binding originated from significant hydrophobic interactions between the MIPs and the template in aqueous media makes the inherent specific recognition ability of MIPs to be obscured [11]. Unfortunately, there are many applications which require MIPs capable of operating in more polar solvents such as methanol, and ultimately water. So, development of water compatible MIPs is urgently desirable.

Initially, two-step extraction method was adopted to solve the problem of water compatibility [12,13]. Typically, liquid–liquid extraction was first applied to transfer analyte from aqueous media to organic phase prior to MIPs based extraction. However, these procedures are complicate, time-consuming and analytes may be partly lost in sample preparation steps. So, aqueous-compatible MIPs were highly needed.

For this purpose, different strategies focusing on development of water compatible MIPs (WC-MIPs) were developed. A representative approach was preparing MIPs in water-containing system [14,15]. Row reported [15] that MIPs prepared in methanol–water system showed better molecular recognition ability in aqueous environment than MIPs prepared in organic solvent. The second approach was using hydrophilic 2-hydroxyethyl

* Corresponding author. Tel.: +86 535 2109130; fax: +86 535 2109130.
E-mail address: lxchen@yic.ac.cn (L. Chen).

http://dx.doi.org/10.1016/j.chroma.2014.05.026
0021-9673/

methacrylate (HEMA) [16,17], acrylamide [18] or β-cyclodextrin [19] as functional monomer in the molecular imprinting process. The third one involved a post-modification procedure for the preformed MIPs. Surface-grafting of hydrophilic polymer brush or chemical bonded hydrophilic functional groups on the surface of the MIP particles were two commonly used methods [20–24]. For example, Zhang's group [22–24] prepared a series of WC-MIPs by grafting of hydrophilic polymer brush, such as poly(N-isopropylacrylamide) (PNIPAM), poly(2-hydrozyethyl methacrylate) (PHEMA) onto the MIP microspheres via surface-initiated reversible addition–fragmentation chain transfer (RAFT) polymerization. The introduction of hydrophilic brushes significantly improved their surface hydrophilicity and led to their pure water compatible binding properties.

However, to the best of our knowledge, integrating those three strategies into one system was few reported. In the present work, three kinds of WC-MIPs were prepared using methanol/water as solvent, HEMA as co-functional monomer, PHEMA as hydrophilic polymer brush, respectively. In addition to the simple WC-MIPs, double water compatible MIPs (DWC-MIPs) were also prepared by integrating two or three of them into one system. In this work, we used atrazine, a well-established template, as a model to study synthesis of hydrophilic MIPs. The obtained DWC-MIPs were characterized by scanning electron microscope. The molecular binding selectivity was tested through equilibrium binding analysis. Ultimately, DWC-MIPs were used as SPE sorbent to extract fours kinds of triazines including atrazine, simetryn, propazine and ametryn from water samples. Under optimal conditions, the DWC-MIPs can be successfully applied to preconcentration and separation of triazines from water samples simultaneously.

2. Experimental

2.1. Materials

Methacrylic acid (MAA), ethyleneglycol dimethacrylate (EGDMA), 2-hydroxyethyl methacrylate (HEMA) were purchased from Sigma–Aldrich (Shanghai, China) and distilled in vacuum prior to use in order to remove stabilizers. 2,2′-Azo-bis-isobutyronitrile (AIBN) were purchased from Shanghai Chemical Reagents Company (Shanghai, China) and recrystallized in methanol prior to use. Atrazine, simetryn, propazine and ametryn were kindly provided by Binzhou Agricultural Technology Co. Ltd. (Shandong, China). Chain transfer agent (CTA) for RAFT polymerization was synthesized as reported [25]. High performance liquid chromatography (HPLC) grade methanol and acetonitrile (ACN) were purchased from Merck (Darmstadt, Germany). Doubly purified deionized water (DDW) was obtained with a Pall Cascada laboratory water system. All other reagents were used as supplied without a further purification step.

2.2. Preparation of water compatible MIPs (WC-MIPs)

In the present work, two kinds of WC-MIPs were prepared. One without polymer brushes were prepared by one spot method, and the other with polymer brushes were prepared by two steps method: MIPs particles were prepared firstly, then polymer brushes were grafted to the MIPs particles. The following was the specific procedure.

For preparation of WC-MIPs without polymer brushes, pre-polymer solution was prepared by dissolving functional monomer (MAA or HEMA, 2 mmol) and template (atrazine, 0.5 mmol) in solvent (methanol or ACN, 60 mL), which was stored at 4 °C in dark for 12 h. Then, cross-linker (EGDMA, 10 mmol), initiator (AIBN, 20 mg), and CTA for RAFT living polymerization (CTA, 60 μL) were added to the pre-polymer solution. The solution was degassed by ultrasonic bath for 5 min, and then purged with nitrogen for 10 min. Polymerization was performed in water bath at 60 °C for 24 h. The resultant polymer particles were washed with methanol/acetic acid solution (9:1, v/v) to remove both the template molecules and residual monomers. Finally, the particles were dried to constant weight under vacuum at 40 °C.

For preparation of WC-MIPs with polymer brushes, MIPs particles were first prepared as above described, then polymer brushes were grafted to MIPs particles according to the following brief procedure as reported: MIP microspheres with dithioester groups (prepared by above method, 150 mg), HEMA (1.76 g, 13.5 mmol), CTA (7.4 mg, 27 μmol), AIBN (1.5 mg, 9 μmol) and methanol (10 mL) were added into a round-bottom flask successively. After being degassed, the grafting polymerization was performed at 70 °C for 24 h. Then the resulting solid products were thoroughly washed with methanol until no white sediment was detected when ether was added into the washing solutions. For the two kinds of MIPs, non-imprinted polymers (NIPs) were also prepared in the same way but omitting the template in the reaction system.

2.3. Characterization of the WC-MIPs

The morphology of the WC-MIPs was evaluated by scanning electron microscope (SEM, Hitachi S-4800, Japan). All samples were sputter-coated with gold before SEM analysis. Molecular recognition properties including rebinding capacity, rebinding kinetics and selectivity experiment were estimated as following: 20 mg WC-MIPs particles were dispersed in 5 mL flask containing 2.0 mL atrazine water solutions of various concentrations. After shaking for 24 h at room temperature, the samples were centrifuged and the supernatant solutions were collected, concentrations of which were determined using HPLC-DAD (Elite, China). The binding amount of atrazine (Q) was determined by subtracting the residual amount of atrazine in solution from the total atrazine amount. Q can be calculated according to the following formula:

$$Q = \frac{(C_0 - C_F)V}{m}$$

where C_0 (mg mL^{-1}) and C_F (mg mL^{-1}) are the initial and final concentration of atrazine solution, respectively. V (mL) is the sample volume and m (g) is the mass of the polymer. Meanwhile, the binding kinetics was tested by monitoring the temporal amount of atrazine in the solutions. And the selectivity experiments were carried out by using simetryn, propazine, ametryn, and pentachlorophenol (PCP) as structural analogs. A C18 column with 250 mm × 4.6 mm i.d. (Waters) was used as the analytical column. HPLC conditions employed for the triazines separation were as follows: mobile phase, acetonitrile:water (40:60, v/v); flow rate, 1.0 mL min^{-1}; room temperature; DAD detection, at 222 nm; injection volume, 20 μL.

2.4. MIPs-SPE procedures

A PTFE column was packed with 400 mg WC-MIPs in 5 mL methanol solution using a wet packing method. Then the cartridge was conditioned with 5 mL methanol. Atrazine or its structural analogs, dissolved in water, was loaded onto the SPE cartridge at a certain flow rate. Subsequently, the cartridge was washed and eluted. The collected column-solution, washing solution and elute were evaporated to dryness under nitrogen and the residues were redissolved in 0.5 mL ACN for HPLC analysis. In order to get the highest SPE recoveries, the variables including the flow rate of loading, loading volume and the elute solvent were studied and optimized.