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Competitive fluorescence assay for specific recognition of atrazine by magnetic molecularly imprinted polymer based on Fe_3O_4-chitosan

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ABSTRACT

A novel fluorescence sensing strategy for determination of atrazine in tap water involving direct competition between atrazine and 5-(4,6-dichlorotriazinyl) aminofluorescein (5-DTAF), and which exploits magnetic molecularly imprinted polymer (MMIP), has been developed. The MMIP, based on Fe_3O_4-chitosan nanoparticles, was synthesized to recognize specific binding sites of atrazine. The recognition capability and selectivity of the MMIP for atrazine and other triazine herbicides was investigated. Under optimal conditions, the competitive reaction between 5-DTAF and atrazine was performed to permit quantitation. Fluorescence intensity changes at 515 nm was linearly related to the logarithm of the atrazine concentration for the range 2.32–185.4 μM. The detection limit for atrazine was 0.86 μM (S/N = 3) and recoveries were 77.6–115% in spiked tap water samples.

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1. Introduction

Molecular imprinting technology (MIT) is a powerful technique for creating tailor-made binding sites within a specific three-dimensional structure of a polymer for selective recognition of target molecules (Chen, Wang, & Tong, 2011). Molecular imprinting polymers (MIP) are novel polymeric materials generated from MIT and designed to chemically recognize the specific template molecule (Altintas et al., 2015). The MIP possesses many outstanding features such as high selectivity, physical and thermal stability, as well as low cost and relative ease of preparation (Chianella et al., 2002). Recently, MIP have attracted considerable interest and have been used successfully in many fields including separation science, solid-phase extraction, sensors, and catalysis (Li et al., 2012). However, the traditional MIP has some disadvantages, such as low binding capacity, poor selectivity, slow mass transfer and incomplete template removal (Xu et al., 2014). In recent years, surface imprinting techniques have been employed to overcome these problems (Martín-Esteban, 2013). Surface imprinted polymers have been synthesized on the surface of silica particles, titanium dioxide particles, carbon materials, polymers, and magnetic materials (Chen, Xu, & Li, 2011).

Chitosan (Luo & Wang, 2014), a natural polysaccharide rich in amino groups, is produced by the deacetylation of chitin and displays hydrophilic, non-toxic, biodegradable, and biocompatible properties (Wan, Wu, Cao, & Dalai, 2008). Because the molecular structure of chitosan contains multiple functional groups such as amino and hydroxyl groups (Gorochovceva & Makuška, 2004), chitosan and its derivatives have been applied in various fields, for instance, the food industry, membranes, cosmetics, and medicine (Yan et al., 2012). Magnetic nanoparticles (e.g., Fe_3O_4) possess favorable characteristics such as small size, superparamagnetism, high surface-to-volume ratio, and functional modification (Lu, Salabas, & Schüth, 2007). According to recent studies (Hola, Markova, Zoppellaro, Tucek, & Zboril, 2015; Wang, Wang, Luo, & Dai, 2008; Zhou, Wang, Liu, & Huang, 2009), magnetic chitosan (Fe_3O_4-chitosan) has great analytical potential in sample pretreatment, magnetic separation, sensors, resonance imaging, drug delivery, and enzyme immobilization. In the past decade, only a few studies concerning the coating of MMIPs onto the surface of

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Fe_3O_4-chitosan have been reported (Chen, Zhang, Luo, & Yao, 2012; Luo et al., 2011; Ou et al., 2015; Zhang, Zhang, Dai, Zhou, & Liu, 2013).

Published articles on the use of MIP in sensors including quartz crystal microbalance sensors (Jha & Hayashi, 2015), electrode-type sensors (Karimian et al., 2015), immunosensors (Feng et al., 2014), and optical sensors (Xu & Lu, 2015) have been increasing in number. Owing to a relatively simple operating procedure, rapid measurement, high sensitivity, and good accuracy (Dai et al., 2014), MIP sensors have become a hot research topic in recent years. However, challenges remain for optical sensors (Song, Xu, Chen, Wei, & Xiong, 2014) based on MIP technology given that the MIP usually needs to contain optical signaling elements such as organic fluorescent materials and quantum dots, or the functional monomer that generates an optical signal or the analyte must be tagged. Such limitations may result in the detection process being relatively complex and time consuming. Consequently, there is the possibility to combine a MIP-Fe_3O_4-chitosan sensor with a direct competitive fluorescence assay, similar to the enzyme-linked immunosorbent assay, and perform fluorescent-type analytical studies. On this basis, therefore, a novel optical sensor system based on a MMIP for direct competitive fluorescence detection of the herbicide atrazine in tap water was developed. The measurement principle of the method is based on competition between the atrazine and 5-(4,6-dichlorotriazinyl) aminofluorescein (5-DTAF), a commercially available fluorescent analog of atrazine, the analyte molecule recognizing the specific binding sites on the surface of the MMIP (Piletsky et al., 1997). By exploiting the unique surface support and magnetic properties of chitosan, a MMIP was prepared via the copolymerization of the functional monomer in the presence of atrazine. The adsorption, selectivity, and analytical characteristics of the MMIP were investigated. Thereafter, a simple fluorescence-based optical sensor was developed for fast and selective measurement of atrazine in tap water samples.

2. Experimental

2.1. Chemicals

Chitosan (100 kD) was purchased from Golden-Shell Biochemical Co., Ltd. (Zhejiang, China). 5-(4,6-Dichlorotriazinyl) aminofluorescein (5-DTAF), atrazine, ametryn, atraton, hexazinone, and metribuzine were all obtained from Sigma–Aldrich (St Louis, MO, USA). Methacrylic acid (MAA), ethyleneglycol dimethacrylate (EGDMA), and 2,2-azobisisobutyronitrile (AIBN) were purchased from Aladdin Industrial Corporation (Shanghai, China). All other reagents were purchased from the Beijing Chemical Reagent Factory (Beijing, China). Standard stock solutions of all pesticides were prepared in Millipore water and stored at 4 °C.

2.2. Preparation of Fe_3O_4-chitosan nanoparticles

First, 0.25 g of chitosan was dissolved in 100 mL of 0.25% acetic acid solution (v/v). Then, Fe_3O_4-chitosan nanoparticles were synthesized according to the reported method (Liu, Xiao, Zhu, & Shi, 2012) as follows: Briefly, 0.7 g of $FeCl_3{\cdot}6H_2O$ and 0.3 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 20 mL of ultrapure water under N_2 in a three-necked flask. After that, 100 mL of chitosan solution were added to the flask under a N_2 atmosphere with mechanical stirring (1000 rpm). After stirring for 1 h at 60 °C, 15 mL of ammonium hydroxide was added to the flask with continuous and vigorous stirring over the next 30 min. Finally, Fe_3O_4-chitosan nanoparticles were collected with the aid of an external magnet. The nanoparticles were then washed with doubly distilled water to remove unreacted chemicals. The precipitate was dried at 50 °C in a vacuum oven.

2.3. Preparation of MMIP

MMIP was synthesized by the surface molecular imprinted method (Xu, Li, & Chen, 2011), with atrazine as the template and Fe_3O_4-chitosan nanoparticles as the core material. Atrazine (0.1 mM) and MAA (0.4 mM) were dispersed in 10 mL methanol by sonication and the mixture was incubated at 4 °C for 1 h. Then, 40 mL of methanol containing 200 mg Fe_3O_4-chitosan nanoparticles were added and the solution was subjected to ultrasound for 30 min. Subsequently, EGDMA (2 mmol), used as the cross-linking monomer and the initiator (AIBN, 90 mg), were added to the solution, respectively. The mixture was deoxygenated with N_2 for 0.5 h and the polymerization reaction proceeded at 55 °C for 24 h. After that, the MMIP was recovered with an external magnet and the product washed with methanol:acetic acid (9:1, v/v) in a Soxhlet extraction unit until atrazine could not be detected by HPLC. As a reference, magnetic molecular non imprinted polymers (MNIP) were prepared under the same conditions but in the absence of atrazine.

2.4. Fluorescence detection

All fluorescence spectra were measured under the same conditions: the excitation wavelength was 380 nm with emission being recorded from 400 nm to 800 nm. The slit widths of the excitation and emission monochromators were both 5 nm. The present method was based on the competition between atrazine and a fluorescent probe DTAF (a commercially available fluorescent analog of atrazine) for the specific binding sites of the MMIP. Forty milligrams of MMIP was mixed with 40 μL 10^{-5} mol/L DTAF and 5 mL of differing concentrations of atrazine in methanol. Then, the mixtures were shaken and incubated at room temperature for 1 h, the suspensions being separated by an external magnetic field. After that, the fluorescence spectra and the intensities of each supernatant were recorded. The excitation and emission slit widths of the fluorimeter were set to 5 nm.

To test for the recoveries of atrazine in the tap water samples, the samples were spiked with different concentrations of atrazine. The spiked water samples were mixed with methanol (1:9, v/v), then analyzed using the competitive fluorescence method.

2.5. Binding studies

To investigate the binding capability of the MMIP, 8 mg of MMIP or MNIP were added to 2 mL of methanol solution containing atrazine at various concentrations (5–200 μM). For the selectivity experiment, 8 mg MMIP or MNIP was added to 2 mL of methanol solutions containing 50 μM of either atrazine, ametryn, atraton, hexazinone, or metribuzine used as the structural analogs, respectively. The static binding capacities of MMIP and MNIP to atrazine were determined and defined by Q (μmol/g), which was calculated based on the following formula: $Q = (C_0 - C_f) \times V/m$ where C_0 (μM) is the initial concentration of atrazine; C_f is the final concentration of atrazine in the supernatant; V (mL) is the total volume of the initial atrazine solution; and m (g) is the mass of MMIP or MNIP. The solutions were incubated for 1 h at room temperature, and after that the suspensions were separated using an external magnet and measured by HPLC with UV detection.

2.6. Characterization of the MMIP

Fourier transform infrared spectra of the Fe_3O_4, Fe_3O_4-chitosan, and MMIP were observed on a FT-IR-8400 spectrometer (Shimadzu,

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