Research Article

Determination of Tributyltin in Seafood Based on Magnetic Molecularly Imprinted Polymers Coupled with High-Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry

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Received 25 August 2016; Accepted 20 December 2016; Published 21 February 2017

Academic Editor: Egidio De Benedetto

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In this study, Fe_3O_4 was adopted as a carrier for surface molecular imprinting with two-stage polymerization. First, the functional monomer (methacrylic acid, MAA) was modified on the surface of Fe_3O_4 , which was then polymerized with the template molecule (tributyltin, TBT), cross linking agent (ethylene glycol dimethacrylate, EGDMA), and porogen (acetonitrile), hereby successfully preparing Fe_3O_4 @MIPs prone to specifically identify TBT. The physical properties of Fe_3O_4 @MIPs were then characterized, and adsorption and selection capacities were also assessed. Compared with conventional imprinting polymers, this magnetic molecular imprinting polymer (MIP) displayed significantly increased and more specific adsorption. Meanwhile, its pretreatment was simpler and faster due to magnetic separation characteristics. Using magnetic MIPs as adsorbents for enrichment and separation, detection limit, recovery rate, and linear range were 1.0 ng g^{-1} , 79.74–95.72%, and $5 \text{ ng g}^{-1} \sim 1000 \text{ ng g}^{-1}$, respectively, for a number of seafood samples. High-performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) was used to analyze *Tegillarca granosa*, mussels, large yellow croaker, and other specimens, with recovery rates of 79.74–95.72% and RSD of 1.3%–4.7%. Overall, this method has a shorter total analysis time, lower detection limit, and wider linear range and can be more effectively applied to determine MAA in seawater and seafood.

1. Introduction

Organic tin compounds show very good reactivity and biological activity and are widely used in various fields of industry and agriculture, for example, as antifoulant additives for naval vessels [1, 2], biocides and bactericides [3], and plastic stabilizers [4]. Due to their widespread application, large amounts of toxic organic tin compounds have entered the environmental ecosystem through various ways, causing damage to the ecosystem [5]. In particular, global water pollution caused by marine antifoulant coatings containing TBT is persistent but also greatly harms marine life and human health through biological accumulation [6]. Thus, TBT is considered one of the most toxic substances introduced into

the marine environment [7]. For example, a TBT content of 1 ng/L in seawater induces sexual aberrations in gastropods [8, 9]; $1 \sim 20 \text{ ng/L}$ TBT is prone to interfere with the breeding of planktons and shellfishes, while $1 \sim 1000 \mu\text{g/L}$ can affect breeding and even cause behavioral disorders in fish [10]. Thus, it is important to develop a highly sensitive and selective detection method to rapidly and efficiently assess microscale organotin.

Currently, various methods have been proposed for organotin detection, including gas chromatography-mass spectrometry (GC-MS) [11], gas chromatography-flame photometric detection (GC-FPD) [12], gas chromatography-atomic adsorption spectroscopy (GC-AAS) [13], and gas

chromatography-microwave induced plasma atomic emission spectroscopy (GC-MIP-AES) [14]. These techniques are irreplaceable in the detection of organic compounds and have been widely used in morphological analysis. However, some of them have low sensitivity and are inappropriate for organotin analysis. Compared to the above methods, HPLC combination technique does not require derivatization procedures. In addition, instrument combination has achieved a great breakthrough in recent years, for example, high-performance liquid chromatography-atomic adsorption spectroscopy (HPLC-AAS) [15, 16], high-performance liquid chromatography-mass spectrometry (HPLC-MS) [15, 16], and high-performance liquid chromatography-induced coupled plasma atomic emission spectrometry (HPLC-ICP-AES) [17]. Nevertheless, some problems remain, including flow rate mismatch and narrow mobile phase. Meanwhile, HPLC-ICP-MS [18, 19] has advantages of liquid chromatography (e.g., no need for derivatization, simplicity and rapidness, and good separation outcome) and also technical superiorities of ICP-MS, including broad application, high sensitivity, low detection limit, low background interference, wide linear range, good stability, as well as long-term resistance to organic mobile phase. Thus, HPLC-ICP-MS is highly sensitive in assessing organic tin compounds and does not require derivatization.

Polymers prepared by the molecular imprinting technique (MIT) [20] are called molecular imprinting polymers (MIPs). MIT can be vividly depicted as a technique to manufacture “artificial lock” for “molecular key” identification [21]. It is a novel affinity separation technique, which provides a new tool to prepare separation medium, with good development potential. It has been widely applied in enrichment and separation, chiral resolution, drug testing, environmental sample analysis, catalysis, sensors, and other fields [22]. Wang et al. [23] utilized MIT products synthesized by non-covalent molecular imprinting in selective solid-phase extraction of organochlorine pesticides in marine biological samples, with recovery rates of 85.8%–101.2%. Meanwhile, Liu et al. [24] applied MIP to preconcentrate serous herbicide, achieving an extraction time of only 30 min. Zhang et al. [25] utilized magnetic MIPs to concentrate and analyze triazine herbicides in vegetables and obtained recovery rates of 71.6%–126.7%, that is, about 100 times their original concentrations.

In-depth analysis of MIP has revealed some deficiencies for conventional molecular imprinting materials, such as difficult binding of template molecules and binding loci, low balance rate, and poor controllability in the grinding process. Therefore, researchers currently focus on developing MIP preparation, using water phase imprinting, electropolymerization, micro-nano imprinting, and magnetic molecular imprinting.

Magnetic adsorption is a newly developed technique, which is applicable to treat pollutants in air and wastewater; it has gained widespread application [26–31]. Adsorbents are easily separated using an external magnetic field and are thus

suitable for large-scale dynamic adsorption. The magnetized adsorbents are permanently magnetic, with the following benefits when applying for separation: (1) fast, efficient, and reusable; (2) simple operation, without requiring expensive equipment; (3) unlikelihood to influence the substances to be separated, especially for biological molecules, which should maintain their physiological activities. According to materials to be separated, particles are usually modified to provide them with active groups or specific antibodies, followed by their input into the solution to be separated, stirring, and ultimately adding an external magnetic field to separate the magnetic particles from the solution, which can be reused [32]. Magnetic MIPs are polymeric microspheres with paramagnetic and MIP properties that combine inorganic magnetic materials and the molecular imprinting technique. Meanwhile, the magnetic separation technique is a relatively new separation tool, where magnetic support bodies are controllable with respect to the imprinting polymers; this tends to provide faster and simpler separation compared with the conventional molecular imprinting centrifugation separation (Ke et al. 2011).

In this study, we attempted to develop a new method to determine TBT in marine products. We first prepared magnetic MIPs and studied their properties. Then, the magnetic MIPs were utilized as the adsorbent to concentrate TBT, which was detected by HPLC-ICP-MS, hereby shortening the analysis time.

2. Materials and Methods

2.1. Main Reagents and Instruments. Main reagents included 96% tributyltin (TBT), 95% monobutyltin (MBT), 97% dibutyltin (DBT), 96% triphenyltin (TPhT), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), 98% azodiisobutyronitrile (AIBN), HPLC-grade methanol, HPLC-grade ethanol, trimethylamine, and acetonitrile (Sigma-Aldrich Co., Shanghai, China). Ultrapure water was produced with the Milli-Q ultrapure water system (resistivity, 18.2 M Ω cm). Main instruments were 1100 high-performance liquid chromatography (Agilent, Palo Alto, United States); 7500ce plasma mass spectrometer (Agilent, Palo Alto, United States); Discovery C18, 150 mm $\times$ 4.6 mm, 5 μ m column (Supelco Co. Ltd., Bellefonte, United States); ZM200 grinder (Retsch, Hanau, Germany); SHA-C stable temperature oscillator (Changzhou Guohua Instrument Factory, Guangzhou, China); BiofugePrimo R 7500 tabletop refrigerated centrifuge (Heraeus, Hanau, Germany); MG-2200 nitrogen blowing instrument (Tokyo Rikakikai Co. Ltd., Bunkyo-ku, Japan); JEM-1011 transmission electron microscope (Jeol Co. Ltd., Akishima, Japan); D8Advande X-ray diffractometer (Bruker-AXS, Karlsruhe, Germany); Nicolet6700 Fourier transform infrared spectroscopy (Thermo, Waltham, United States); and vibrating sample magnetometer (Lake shore, Westerville, United States).

Specimens included *Tegillarca granosa*, mussels, and large yellow croaker that were purchased from Ningbo Lulin Market (500 g, Ningbo, China) and to get rid of internal

organs and other inedible parts, the remaining portion was cleaned, dried, and frozen at -20°C .

2.2. Experimental Methods

2.2.1. Preparation of Magnetic Molecular Imprinting Polymers. Fe_3O_4 nanoparticles were prepared as previously described [32]: briefly, 4.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3.9 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were added to a 500 mL boiling flask-3-neck and mixed with 200 mL 0.1 mol L^{-1} hydrochloride solution, with mechanical stirring. Afterward, the system was rapidly supplemented with 3 mol/L sodium hydroxide to obtain $\text{pH} > 9$, which resulted in immediate color change from yellow to black. Then, the temperature was increased to 80°C for 1 h. When the temperature was restored to room temperature, the products were separated using magnets, collected, rinsed with redistilled water, and dried under vacuum for subsequent experiments.

In two-stage polymerization, MAA (as functional units) was modified onto the surface of Fe_3O_4 nanoparticles: first, 100 mg Fe_3O_4 nanoparticles were dissolved into 150 mL aqueous ethanol solution (v/v, 14 : 1), followed by gradual dripping with 50 μL APTS and stirring at room temperature for 7 h. Then, the products were separated using external magnetic field, followed by 5 ethanol rinses and drying under vacuum to obtain $\text{Fe}_3\text{O}_4\text{@APTS}$ particles [33]. Meanwhile, APTS modified magnetic nanoparticles were reacted with excessive methacrylic acid in methanol at 25°C for 24 h, followed by separation with magnets, rinsing with ethanol, and drying under vacuum, hereby yielding $\text{Fe}_3\text{O}_4\text{@MAA}$ [34].

For molecular imprinting polymerization, magnetic particles coated with a layer of MIP were prepared. $\text{Fe}_3\text{O}_4\text{@MAA}$ particles (100 mg) and TBT (1 mmol) were dissolved into 40 mL acetonitrile, stirred at room temperature for 6 h, and supplemented with EGDMA (22 mmol) and AIBN (15 mg). This was followed by ultrasonication in ice bath bubbled with nitrogen for 5 min, stirring at 50°C for 5 h, polymerization at 65°C for 20 h, and aging at 85°C for 5 h. The particles were ultimately separated, rinsed with methanol dichloromethane solution (v/v, 4 : 1) for 5 times, and extracted with 0.3 mol/L sodium hydroxide methanol as eluent using the Soxhlet method, until no template molecule TBT contained the polymer. Finally, the products were separated and dried under vacuum to obtain TBT coated magnetic MIPs ($\text{Fe}_3\text{O}_4\text{@MIPs}$), which would be used for enrichment and separation analysis.

Magnetic MIP controls ($\text{Fe}_3\text{O}_4\text{@NIPs}$) were prepared using the abovementioned method, except for adding the imprinting molecule TBT.

2.2.2. Determination of Adsorption (Q). 20 mg $\text{Fe}_3\text{O}_4\text{@MIPs}$ or $\text{Fe}_3\text{O}_4\text{@NIPs}$ were added to the TBT solution and incubated with shaking at room temperature for 10 h. Then, the TBT concentration in the supernatant was determined using HPLC-ICP-MS, and adsorption Q was derived by the

FIGURE 1: HPLC-ICP-MS spectrum for TBT standard substance (flow rate 1.2 mL/min).

following formula according to changes of TBT concentration before and after adsorption [34]:

$$Q = \frac{(C_0 - C)V}{W}, \quad (1)$$

where Q is the adsorption ($\mu\text{g g}^{-1}$); C_0 and C are TBT concentrations before and after adsorption, respectively ($\mu\text{g L}^{-1}$); W is dry polymer weight (mg); and V refers to solution volume (L).

2.2.3. Detection of TBT Using HPLC-ICP-MS. SUPELCO Discovery C18 column (15 cm $\times$ 4.6 mm, 5 μm) was adopted and manually tuned using 10 $\mu\text{g L}^{-1}$ tuning liquid to ensure that sensitivity, mass number, oxides, electric double layer, and other indicators met the requirements. Methanol-water equal to 70 : 30 (v/v) was used as mobile phase at a flow rate of 1.2 mL/min; injection volume was 20 μL , and the TBT peak is shown in Figure 1.

2.2.4. $\text{Fe}_3\text{O}_4\text{@MIPs}$ Synthesis Conditions. For eluent selection, 20 mg $\text{Fe}_3\text{O}_4\text{@MIPs}$ were added to 20 $\mu\text{g L}^{-1}$ TBT solution, which was stirred for 10 h. Then, formic acid, acetic acid, sodium hydroxide, and ammonia were mixed to obtain different concentrations of methanol dichloromethane, which was used to eluate TBT adhering to $\text{Fe}_3\text{O}_4\text{@MIPs}$; elution amount was determined. Of all solvents, methanol dichloromethane, with the optimal elution effect, would be selected for subsequent assays.

For elution time selection, 5 shares of 20 mg $\text{Fe}_3\text{O}_4\text{@MIPs}$ were separately added to 20 $\mu\text{g L}^{-1}$ TBT solution, which was stirred to adsorb for 10 h. Then, the eluent selected using the abovementioned method was applied, and the amounts of TBT eluted from $\text{Fe}_3\text{O}_4\text{@MIPs}$ with different times were determined; of these, an elution time yielding an optimal elution effect would be selected for subsequent assays.

2.2.5. Characterization Methods. Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@MIPs}$ dried under vacuum were placed on a microgrid and

TABLE 1: Elution rate of TBT from Fe_3O_4 @MIPs with different pH concentrations of eluents.

Eluent	Formic acid methanol			Acetic acid methanol solution			Sodium hydroxide methanol			Ammonia methanol		
Concentration (M)	0.05	0.1	0.5	0.05	0.1	0.5	0.05	0.1	0.5	0.05	0.1	0.5
Elution rate (%)	56.3	96	83	42	80.6	69.8	41	46	56.7	40	70	79.8

characterized on a JEM-1011 transmission electron microscope (TEM). Then, powder samples (Fe_3O_4 , Fe_3O_4 @MAA, and Fe_3O_4 @MIPs) were dried under vacuum and analyzed for their structure on a Bruker D8 X-ray diffractometer (XRD). For FTIR characterization, powder samples (Fe_3O_4 , Fe_3O_4 @APTS, Fe_3O_4 @MAA, and Fe_3O_4 @MIPs) were dried under vacuum and separately mixed with KBr (mass ratio of 1:4) under an infrared lamp, followed by squashing and characterization with Nicolet6700 Fourier transform infrared spectroscopy. Finally, the magnetic properties of Fe_3O_4 and Fe_3O_4 @MIPs were assessed using a vibrating sample magnetometer (VSM).

2.2.6. Properties of Fe_3O_4 @MIPs

Selection Distinctiveness Test. 20 mg Fe_3O_4 @MIPs and Fe_3O_4 @NIPs were added to four types of $50 \mu\text{g L}^{-1}$ organotin (MBT, DBT, TBT, and TPhT) solutions, respectively, with ethanol as solvent, followed by stirring adsorption for 10 h. Then, the concentrations of residual organotin were assessed by HPLC-ICP-MS, for adsorption calculation.

Adsorption Dynamics Test. 20 mg Fe_3O_4 @MIPs and Fe_3O_4 @NIPs were placed into each of six 10 mL beakers containing $20 \mu\text{g L}^{-1}$ TBT solution, followed by stirring adsorption for 10, 20, 30, 60, 120, and 180 min, respectively. Then, the concentrations of residual TBT were assessed by HPLC-ICP-MS, hereby determining the adsorption rate.

Adsorption Isotherm Test. 20 mg Fe_3O_4 @MIPs and Fe_3O_4 @NIPs were separately added to TBT solutions to yield concentrations of 10, 20, 40, 70, 90, 150, and $300 \mu\text{g L}^{-1}$ and stirred for 10 h. Then, residual TBT concentrations were determined by HPLC-ICP-MS, to calculate adsorption.

Regenerability of Fe_3O_4 @MIPs. 20 mg Fe_3O_4 @MIPs were added to $20 \mu\text{g L}^{-1}$ TBT solution, followed by stirring adsorption for 10 h and elution. Then, residual TBT amounts in the solution were evaluated by HPLC-ICP-MS to calculate the adsorption rate. Afterwards, the eluted MIPs were dried under vacuum and recovered. The above procedures were repeated 5 times.

2.2.7. Preparation of Specimens. Three specimens of 0.1 g frozen marine product tissues (*Tegillarca granosa*, mussels, large yellow croaker) were separately placed into 10 mL centrifuge tubes; in two of them, $100 \mu\text{L}$ standard TBT solutions at concentrations of 50 and $100 \mu\text{g L}^{-1}$, respectively, were added, to yield 5 and 10 ng TBT (adding standard

TABLE 2: Time effect on elution rate of TBT with polymers.

Polymer elution time (h)	0.5	1	2	3	4
Elution rate (%)	46	70.3	88.7	90	91.6

matter amount of 50 ng g^{-1} and 100 ng g^{-1} , resp.). Tissues added with standard matter were oscillated for 1 h and incubated overnight with no shaking. Then, TBT in marine product tissues was extracted by ultrasound for 30 s, with 5 mL acetic acid methanol solution (volume ratio: 1:1) as extract buffer (frequency about 35 KHz). This was followed by centrifugation (4000 rpm, 3 min), and the supernatant was collected. Afterward, the above extraction procedures were repeated once, and supernatants from both extractions (10 mL) were combined and diluted with 50 mL ultrapure water. 20 mg conventional imprinting polymers were added to this mixture and stirred using magnetic force, followed by centrifugation. Finally, 6 mL 0.1 M formic acid methanol solution was used to elute TBT, which was adsorbed on the polymer; the eluent was evaporated using nitrogen blowing instrument and adjusted to 1 mL with aqueous methanol solution (volume ratio 70:30). After filtration with $0.45 \mu\text{m}$ organic filtration membrane, the samples were submitted to subsequent HPLC-ICP-MS analysis.

3. Results and Discussion

3.1. Fe_3O_4 @MIP Synthesis Conditions

3.1.1. Selection of Eluent. Formic acid, acetic acid, sodium hydroxide, and ammonia were used to formulate different concentrations of methanol dichloromethane solution, which was used to eluate TBT adsorbed on Fe_3O_4 @MIPs, hereby deriving elution amounts, as shown in Table 1.

As shown in Table 1, an appropriate pH may make it easier to elute TBT, while an excessively high pH may decrease the elution rate. In addition, acid solutions showed a better elution effect compared with alkaline counterparts, while weakly acidic solutions showed a better elution effect compared to strongly acidic solutions. Therefore, 0.1 M (mol L^{-1}) formic acid methanol solution was selected as eluent.

3.1.2. Selection of Elution Time. After $20 \mu\text{g L}^{-1}$ TBT was adsorbed for 10 h using Fe_3O_4 @MIPs, elution was carried out with 0.1 M (mol L^{-1}) formic acid methanol solution, and results are shown in Table 2.

As shown in Table 2, elution time affected TBT elution volume in Fe_3O_4 @MIPs. Short elution times led to small

FIGURE 2: TEM of Fe₃O₄ nanoparticles (a) and Fe₃O₄@MIPs particles (b).

FIGURE 3: XRD of magnetic particles.

FIGURE 4: The FTIR of magnetic particles.

elution volumes, which may be explained by the fact that the eluent did not fully contact TBT. With increasing elution time, the eluent fully contacts TBT, thereby leading to increased elution volumes. Meanwhile, after 2 h, elution volumes did not change significantly, which indicates that TBT in the Fe₃O₄@MIPs was basically eluted. Therefore, 2 h was selected as elution time for subsequent assays.

3.2. Characterization

3.2.1. TEM Characterization. As shown in Figure 2, the diameters of Fe₃O₄@MIPs nanoparticles were larger than those of Fe₃O₄ nanoparticles, probably because Fe₃O₄@MIPs are coated with an MIP layer. In addition, because the MIP layer has binding sites that can specifically adsorb TBT, Fe₃O₄@MIPs also have specific adsorption capacity.

3.2.2. XRD Characterization. Figure 3 shows the X-ray diffraction patterns of Fe₃O₄, Fe₃O₄@MAA, and Fe₃O₄@MIPs particles. It can be observed that the positions

of their characteristic peaks remained the same, indicating that Fe₃O₄@MIPs are unlikely to alter the crystal structure [35, 36]. Meanwhile, peak intensity of Fe₃O₄@MIPs particles was weaker than those of Fe₃O₄ and Fe₃O₄@MAA particles, likely because Fe₃O₄@MIPs particles are coated with an MIP layer.

3.2.3. FTIR Characterization. Figure 4 displays FTIRs of Fe₃O₄, Fe₃O₄@APTS, Fe₃O₄@MAA, and Fe₃O₄@MIPs particles.

As shown in Figure 4, two strong adsorption peaks appeared at 589 cm⁻¹ and 631 cm⁻¹ for the four samples and are characteristic stretching vibration peaks generated by the group at 570 cm⁻¹ of Fe-O in Fe₃O₄; this indicates the presence of Fe₃O₄ in these four samples. Meanwhile, the peaks at 2856 cm⁻¹ and 2927 cm⁻¹ are stretching vibration peaks of -CH₂, and both appeared in characteristic

FIGURE 5: Hysteresis chart of magnetic particles (a) and reaction to external magnetic fields (b).

plots of $\text{Fe}_3\text{O}_4\text{@APTS}$ and $\text{Fe}_3\text{O}_4\text{@MAA}$ particles, which indicates successful modification with APTS. In addition, both $\text{Fe}_3\text{O}_4\text{@MAA}$ and $\text{Fe}_3\text{O}_4\text{@MIP}$ spectra showed peaks at 1735 cm^{-1} (C=O vibration peak) and 1455 cm^{-1} (C=C vibration peak), which indicates successful modification with MAA monomers. Of these, 1735 cm^{-1} peak intensity in $\text{Fe}_3\text{O}_4\text{@MIPs}$ was significantly stronger than that of $\text{Fe}_3\text{O}_4\text{@MAA}$ particles. This is because $\text{Fe}_3\text{O}_4\text{@MIPs}$ were coated with MIP due to polymerization reaction, which leads to an increase of C=O bonds. Meanwhile, the weak Fe-O vibration peak also provides a certain evidence for nuclear-shell structure of $\text{Fe}_3\text{O}_4\text{@MIPs}$, which indicates successful preparation of nuclear-shell magnetic MIPs.

3.2.4. VSM Characterization. Hysteresis graphs of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@MIPs}$ particles are shown in Figure 5(a), which demonstrated that hysteresis loops of both Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@MIPs}$ pass the origin, with saturation magnetizations of 60 emu g^{-1} and 30 emu g^{-1} , respectively. $\text{Fe}_3\text{O}_4\text{@MIPs}$ ' saturation magnetization declined, which may be due to the coated MIP layer; this would unlikely affect the magnetic separation of $\text{Fe}_3\text{O}_4\text{@MIPs}$. As shown in Figure 5(b), $\text{Fe}_3\text{O}_4\text{@MIPs}$ appeared as yellow suspension particles and were dispersed in the aqueous solution, but quickly concentrating at one side of the external magnetic field upon application of an external magnetic field. Therefore, $\text{Fe}_3\text{O}_4\text{@MIPs}$ have strong separation characteristics.

3.3. $\text{Fe}_3\text{O}_4\text{@MIPs}$ Properties

3.3.1. Selectivity of $\text{Fe}_3\text{O}_4\text{@MIPs}$. MIPs have very high affinity and selectivity and selectively adsorb target molecules from complex samples; indeed, 20 mg of polymers can adsorb four organotins (MBT, DBT, TBT, and TPhT $50\text{ }\mu\text{g L}^{-1}$), as shown in Figure 6.

FIGURE 6: Adsorption capacity of $\text{Fe}_3\text{O}_4\text{@MIP}$ and $\text{Fe}_3\text{O}_4\text{@NIP}$ for the four organic tin compounds.

As shown in Figure 6, $\text{Fe}_3\text{O}_4\text{@MIPs}$ had the highest adsorption capacity to TBT, which was 3 times that of $\text{Fe}_3\text{O}_4\text{@NIPs}$. Meanwhile, $\text{Fe}_3\text{O}_4\text{@MIP}$ adsorption capacities for MBT, DBT, and TPhT were comparable to values obtained for $\text{Fe}_3\text{O}_4\text{@NIPs}$. Thus, $\text{Fe}_3\text{O}_4\text{@MIPs}$ contain three-dimensional voids with highly consistent spatial structure and functional group arrangement similar to TBT, thereby having a very good memory effect for TBT. This might be explained by the following: $\text{Fe}_3\text{O}_4\text{@MIPs}$ are tailored for TBT, and the spatial shape and size of their three-dimensional voids exactly match TBT; the groups on the cavity surface are highly complementary to the electronic characteristics contained in TBT groups. These voids tend to have a very high specific selectivity for TBT, that is, memory function [37].

FIGURE 7: Adsorption kinetics of Fe₃O₄@MIPs and Fe₃O₄@NIPs.

3.3.2. Adsorption Dynamics of Fe₃O₄@MIPs. Figure 7 shows adsorption dynamics curves for Fe₃O₄@MIP and Fe₃O₄@NIPs, which reveal that adsorption volumes of Fe₃O₄@MIP and Fe₃O₄@NIPs to TBT increased with time, and equilibrium could be obtained after 1 h. This is because shallower holes on the surface of Fe₃O₄@MIP and Fe₃O₄@NIPs help quickly adsorb TBT, which results in Fe₃O₄@MIP and Fe₃O₄@NIPs having an initial faster adsorption rate. However, after surface holes achieve adsorption saturation, transmission of TBT to internal holes of Fe₃O₄@MIP and Fe₃O₄@NIPs is hindered, which leads to declined adsorption rate, and adsorption equilibrium is observed after only 1 h.

3.3.3. Adsorption Isotherm of Fe₃O₄@MIPs. Adsorption isotherms of Fe₃O₄@MIP and Fe₃O₄@NIP to TBT are shown in Figure 8.

As shown in Figure 8, the shapes of adsorption isotherms obtained for Fe₃O₄@MIP and the corresponding Fe₃O₄@NIP followed the Langmuir model: adsorption volume of Fe₃O₄@MIP gradually increases with TBT concentration; meanwhile, that of Fe₃O₄@NIP rapidly reaches saturation adsorption. In addition, for the same concentration of TBT solution (regardless the value), adsorption volume of Fe₃O₄@MIP was significantly higher than that of Fe₃O₄@NIP, and these differences increased with the solution concentration. This is due to significant differences in spatial structures of these two polymers. Fe₃O₄@NIP has a weaker adsorption capacity and lacks selectivity, likely because the polar groups on its surface may nonspecifically adsorb TBT. However, Fe₃O₄@MIP contains functional voids that match and are complementary to the spatial structure of TBT. These voids tend to remember TBT molecules and lead to strong selective adsorption capacity. Thus, the difference

FIGURE 8: Adsorption isotherms of Fe₃O₄@MIP and Fe₃O₄@NIP to TBT.

FIGURE 9: Langmuir isotherm plot of Fe₃O₄@MIP adsorption to TBT.

in adsorption capacity of these two polymers mainly derives from the specific adsorption of these voids.

According to Langmuir isotherm equation [38], the results in Figure 9 were generated.

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max}b} + \frac{1}{Q_{\max}}C_e, \quad (2)$$

where C_e is the balance concentration and q_e is the balance adsorption; $Q_{\max}$ represents saturation adsorption, while b is a constant. With respect to C_e , C_e/q_e has a good linear relationship within this concentration range. From Figure 9,

TABLE 3: Relationship between adsorption rate and time of $\text{Fe}_3\text{O}_4\text{@MIP}$ repeated use.

Repeated use time	1	2	3	4	5
Adsorption rate (%)	90	87.5	83	82.1	79.8

TABLE 4: Recovery rates and relative standard deviations ($n = 4$).

Sample	Background value (ng g^{-1})	Detection of TBT		
		Standard addition concentration (ng g^{-1})	Recovery (%)	RSD (%)
Mussels	154	50	87.13	3.5
		100	84.36	2.8
<i>Tegillarca granosa</i>	216	50	95.72	3.2
		100	87.96	2.3
Large yellow croaker	—	50	79.74	4.7
		100	83.25	1.3

the following equation can be obtained: $C_e/q_e = 3.1147 + 0.0423C_e$, where saturation adsorption of $\text{Fe}_3\text{O}_4\text{@MIPs}$ to TBT is $Q_{\max} = 23.6 \mu\text{g g}^{-1}$, $b = 0.0136$.

3.3.4. Regeneration Characteristics of $\text{Fe}_3\text{O}_4\text{@MIPs}$. As shown in Table 3, repeated use may lead to declined adsorption rate of $\text{Fe}_3\text{O}_4\text{@MIPs}$, likely because adsorption capacity of the polymers to TBT is altered after slight swelling. However, these experimental data revealed that $\text{Fe}_3\text{O}_4\text{@MIPs}$ have a high strength and rigidity, with no substantial softening and dissolution during the elution regeneration process, thus presenting good repeatability.

3.4. Linear Range and Detection Limit. Detection was performed under optimal operating conditions. TBT concentration was first assessed by HPLC-ICP-MS, and linear regression equation was obtained with adsorption peak area on the y -axis and TBT concentration ($\mu\text{g L}^{-1}$) on the x -axis. Then, the lowest detection rate of each marine product was calculated with $S/N = 3$ as signal to noise ratio [30]. The results revealed that concentration had a good linear relationship with peak area when TBT amounts in tissue fluid of marine products ranged from 5 ng g^{-1} to 1000 ng g^{-1} , with a correlation coefficient (R_2) of $0.9995\sim 0.9999$ and relative standard deviation equal to or smaller than 5%. Meanwhile, detection rates in tissue fluids of mussels, *Tegillarca granosa*, and large yellow croaker were 1.0 ng g^{-1} , 3.0 ng g^{-1} , and $4.0 \mu\text{g L}^{-1}$, respectively.

3.5. Repeatability. Testing was repeated 6 times by injecting the same concentration of TBT, and a relative standard deviation of 1.3% was obtained, indicating a good repeatability of the analysis method on the instrument used.

3.6. Analysis of Specimens. Marine product specimens were treated using the abovementioned methods, followed by separation and injection. Then, TBT concentrations in the concentrated specimens were tested by HPLC-ICP-MS

under optimal conditions and recovery rates were calculated (Table 4). Indeed, recovery rates for the specimens ranged from 79.74% to 95.72%, with relative standard deviations of 1.3%–4.7%, suggesting that this method has very good accuracy and precision and can be applied for the determination of TBT in marine products.

3.7. Summary of Detection Methods. In terms of molecular imprinting technique based analysis methods for the detection of organic tin compounds, we compared previous ones to that described in this study, and the results are shown in Table 5.

4. Conclusion

Using the surface molecular imprinting technique, we successfully prepared $\text{Fe}_3\text{O}_4\text{@MIPs}$ that specifically identified TBT by employing TBT as template molecules, $\text{Fe}_3\text{O}_4\text{@MAA}$ as functional monomers, EGDMA as the cross linking agent, AIBN as the initiator, and acetonitrile as the porogen. Compared with conventional molecular imprinting polymers, this polymer showed significant selective adsorption and can be rapidly separated by an external magnetic field, with a shortened pretreatment time. In this study, we confirmed that, with magnetic MIP as adsorbent, TBT could be assessed by HPLC-ICP-MS. In addition, with marine products as matrixes, the lowest detection rate and linear range for this method were 1.0 ng g^{-1} and $5.0 \text{ ng g}^{-1}\sim 1000 \text{ ng g}^{-1}$, respectively. Finally, this method was used to analyze mussels, *Tegillarca granosa*, and large yellow croaker, with recovery rates of 79.74–95.72% and RSD values of 1.3%–4.7%.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

TABLE 5: Summary of molecular imprinting technique based methods for detecting organic tin compounds.

Method	Detector	Samples	Analysis range	Detection limit	Analysis time (min)
MISPE [33]	GC-FPD	Seawater	0.05–50.0 ng mL ⁻¹	0.04 ng mL ⁻¹	<20
MISPE [33]	GC-FPD	Mussels, oyster	10–1000 ng g ⁻¹	10.0 ng g ⁻¹	40
MISPE [33]	GC-FPD	Biological and environmental samples	—	10.0 ng g ⁻¹	—
MISPE [33]	LC-ICP/MS	Mussels, oyster	10–50000 ng g ⁻¹	3.0 ng g ⁻¹	20
MIP [33]	LC-MS/MS	Seawater, mussels	0.1–20 µg L ⁻¹ ; 5.0–600.0 ng g ⁻¹	0.05 µg L ⁻¹ ; 3.0 ng g ⁻¹	40
Fe ₃ O ₄ @MIP [33]	LC-MS/MS	Mussels, large yellow croaker	5.0–1000.0 ng g ⁻¹	1.0 ng g ⁻¹	<30
Fe ₃ O ₄ @MIP ^a	HPLC-ICP-MS	Mussels, <i>Tegillarca granosa</i> , large yellow croaker	5.0–1000.0 ng g ⁻¹	1.0 ng g ⁻¹	<15

ICP/MS: inductively coupled plasma mass spectrometry; GC-FPD: gas chromatography flame photometric detector; NaMA: sodium methacrylate; MAA: methacrylic acid; PVA: polyvinyl alcohol; MISPE: molecular imprinting solid phase extraction.
^aMethod described in this study.

Authors' Contributions

Hua Yang and Huien Zhang contributed equally to this work and should be considered co-first authors. Shi Da Chen and Lijun Liu assisted in data processing and production of magnetic molecular imprinting polymers in the paper.

Acknowledgments

This research was funded by the Ministry of Science and Technology of Chinese People's Republic Spark Plan Project (Grant no. 2011GA701001), Zhejiang Province Public Technology Research Projects (Grant no. 2016C32068), and Ningbo City Science Foundation (Grant nos. 2015C10018 and 2016C10009). This work was financially supported by the Projects of Science and Technology Ministry of China (2015BAD17B02-3) and the K.C. Wong Magna Fund in Ningbo University.

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