



A robust electrochemical sensing platform using carbon paste electrode modified with molecularly imprinted microsphere and its application on methyl parathion detection



Yanguang Li^{a,1}, Jiang Liu^{b,1}, Yang Zhang^b, Meng Gu^c, Dongyang Wang^a, Yan-yan Dang^{a,**}, Bang-Ce Ye^{a,d,**}, Yingchun Li^{b,*}

^a Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Shihezi, China

^b College of Science, Harbin Institute of Technology, Shenzhen 518055, China

^c Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China

^d State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

A highly sensitive electrochemical sensor using a carbon paste electrode (CPE) modified with surface molecularly imprinted polymeric microspheres (SMIPMs) was developed for methyl parathion (MP) detection. Molecular imprinting technique based on distillation precipitation polymerization was applied to prepare SMIPMs and non-surface imprinted microspheres (MIPMs). The polymer properties including morphology, size distribution, BET specific surface area and adsorption performance were investigated and compared carefully. Both MIPMs and SMIPMs were adopted to prepare CPE sensors and their electrochemical behaviors were characterized via cyclic voltammetry and electrochemical impedance spectroscopy. Compared with MIPMs packed sensor, SMIPMs/CPE exhibits a higher sensing response towards MP with linear detection range of 1×10^{-12} – 8×10^{-9} mol L⁻¹ and detection limit of 3.4×10^{-13} mol L⁻¹ (S/N = 3). Moreover, SMIPMs/CPE exhibits good selectivity and stability in multiple-cycle usage and after long-time storage. Finally, the developed sensor was used to determine MP in real samples including soil and vegetables and only simple pretreatment is needed. The detection results were consistent with those obtained from liquid chromatography. Collectively, this newly developed sensor system shows significant potential for use in a variety of fields like food safety, drug residue determination and environmental monitoring.

1. Introduction

Electrochemical sensing is a very promising field in analytical chemistry. Analysis of nucleic acid (Tran et al., 2013), protein (Yang et al., 2017), chemical medicine (Elliott et al., 2017), and heavy metal ions (Suherman et al., 2017) have been successfully demonstrated, thanks to its advantage in rapid response, high sensitivity, low cost and simple to operate (Wang et al., 2017b). As one of the electrochemical sensing platforms, carbon paste electrode (CPE) has many other advantages over disk or rod electrodes, in the aspect of economical mass-fabrication and flexible modification (Afkhami et al., 2014; Hočevár et al., 2006; Raoof et al., 2004; Wang et al., 2017a). As the core of electrodes, functional materials are often coated or doped as packing

materials to realize specific sensing response towards targets (Fekry, 2017). As an artificial synthetic material with antibody-like merit, molecularly imprinted polymer (MIP) has been extensively used in electrochemical sensor to achieve specific detection of certain targets (Zhang et al., 2013). Multifaceted features of MIP, including robust structural stability, good environmental adaptability and outstanding reusability, have been also widely demonstrated (Orozco et al., 2013). In our group, a series of high-performance sensors modified with MIP were fabricated and utilized for various chemical molecules detection, such as illegal additives, medicine, environmental pollutants, etc. (Li et al., 2016; Liu et al., 2017a, 2017b; Song et al., 2017). Sensors integrated with granulated MIPs often suffer from unsatisfactory reproducibility and batch-to-batch variation between different electrodes

* Corresponding author at: College of Science, Harbin Institute of Technology, Shenzhen 518055, China.

** Corresponding authors: Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Shihezi, China.

E-mail addresses: dyysz@126.com (Y.-y. Dang), bcye@ecust.edu.cn (B.-C. Ye), liyingchun@hit.edu.cn (Y. Li).

¹ The authors contributed equally to this work.

due to inhomogeneously distributed particle. Even the drawbacks of the modified CPE could be alleviated to some extent by using microspherical MIPs as the packing functional material, the low sensitivity and long assay time are still problems for most non-surface imprinting microspheres due to their low adsorption efficiency and deep location of imprinting sites (Chen et al., 2015; Liu et al., 2017c). Therefore, preparation of MIP microspheres with uniform particle size and their imprinting sites located within surface can be expected to enhance performance of MIP-involved electrochemical sensor effectively.

There are many strategies for synthesis of spherical MIP, including emulsion polymerization, suspension polymerization, precipitation polymerization, multistep swelling polymerization, etc. (Kitayama et al., 2017; Lu et al., 2017; Raouf et al., 2004; Shen and Lei, 2011). However, most of those methods have some ineluctable defects, such as amorphous particle, wide size distribution, surfactant remnant, deep location of imprinting sites (Denderz and Lehotay, 2012; Esfandyarimanesh et al., 2012; Schirhagl, 2014). Recently, we developed a novel method based on distillation precipitation polymerization for preparing spherical MIPs (Liu et al., 2015a, 2015b). By using this tactic, surface or non-surface molecularly imprinted polymeric microspheres (SMIPMs/MIPMs) with narrow size dispersity were synthesized in a facile and controllable manner, and participated in preparing packing material for solid phase extraction and HPLC column (Fang et al., 2012; Qu et al., 2009; Vallano and Remcho, 2000). These microspheres did the job nicely in chromatography, and exhibited good separation and enrichment properties for scheduled targets as well. In our perspective, the polymer prepared by this method will also show great performance and promising applications for CPE sensing.

In this work, both SMIPMs and MIPMs for methyl parathion, an organophosphorus pesticide with lethal toxicity, were synthesized based on one-step and two-step distillation precipitation polymerization. Their adsorption performance and analytical features were carefully evaluated. In comparison to non-surface imprinted microspheres, SMIPMs have shorter adsorption equilibrium time and larger binding capacity in the aspect of sorption and exhibit higher sensitivity when used as a functional material in CPE system. Finally, the proposed SMIPMs/CPE was utilized to detect methyl parathion in soil and vegetables, and the results were confirmed by chromatography. It is also the first report about introducing surface and non-surface imprinting technique to CPE system simultaneously, and the importance of surface imprinted polymer in electrochemical sensing is downright revealed by elaborately comparative study.

2. Experimental section

2.1. Reagents and instruments

Methyl parathion (MP), methamidophos (MAP), parathion (PAR), methylpropenoic acid (MAA) and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Adamas Reagent Co. Ltd (Shanghai, China). Before use, MAA was distilled under vacuum. Divinylbenzene (DVB) was obtained from Sigma Aldrich Co. (Milwaukee, USA) and purified by extraction with 20% NaOH aqueous solution, afterward dried with anhydrous calcium chloride. Other reagents and chemicals, such as $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KNO_3 and methanol, were of analytical grade. All solutions were prepared using double distilled water. Romaine and spinach were obtained from a local market and soil was collected from a local farm.

Electrochemical measurements were performed on a CHI660E electrochemical workstation (Chenhua Instruments Co, Shanghai, China) connected to a PC at room temperature. A three-electrode system was adopted with a carbon paste electrode (CPE) or polymer packed CPE serving as the working electrode, a platinum wire (0.5 mm in diameter, 34 mm in length) as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials given in the article were referred to the SCE. The specific surface area of

polymer was measured by using a Quantachrome NOVA 1000 based on the Brunauer-Emmett-Teller (BET) experiment. Scanning electron microscopy (SEM) images were recorded at 10 kV (Zeiss Supra55VP, Germany). All of adsorption experiments were performed using high-performance liquid chromatography (HPLC) (LC-10A, Shimadzu, Japan) and chromatography conditions followed the reference (Clark et al., 1985; Lin et al., 2006; Paschal et al., 1977; Rung and Schwack, 2005). The particle size distribution was explored by laser scattering particle size analyzer (Zetasizer Nano, Malvern, UK).

2.2. Preparation of polymers

2.2.1. Preparation of SMIPMs by two-step distillation precipitation polymerization

Preparation of SMIPMs was divided into two steps including core fabrication and shell of SMIPMs. The former process was as follows: 0.85 mL functional monomer (MAA), 0.11 g initiator (AIBN) and 9.35 mL cross-linker (DVB) were dissolved sufficiently in 80.00 mL acetonitrile and put in a three-necked flask connected with a condensation recycling installment. Before reaction, the solution was de-gassed by ultrasonication for 5 min and then heated quickly until it boiled. Subsequently, heating temperature was adjusted carefully to maintain distillation rate of the inner solvent at $0.5 \text{ mL} \cdot \text{min}^{-1}$. The reaction was stopped when half volume of solvent was distilled out. In the whole process, the reaction mixture was stirred at the rate of 120 rpm. To get the core particles, the resulting emulsion was filtered and the obtained solid phase was washed three times with methanol and dried to constant weight. The next step is to prepare the shell of SMIPMs, a molecularly imprinted polymeric layer, which is similar to the above step for preparing core with the only difference of the reaction system containing 0.50 g uniformly sized core particles, MP ($3.00 \times 10^{-3} \text{ mol L}^{-1}$), MAA (1.03 mL), DVB (4.12 mL), AIBN (0.11 g) and acetonitrile (80.00 mL). The following work is to remove the template molecules-MP from the polymer, which was realized via Soxhlet extraction with methanol-acetic acid (9:1, v/v) as eluent at the reflux speed of $3.00 \text{ mL} \cdot \text{min}^{-1}$ for 24 h. Finally, the obtained polymer was washed with methanol, dried at room temperature and stored in the oxygen-free environment. Non-imprinted polymeric microspheres (SNIPMs) were prepared following the same above-mentioned procedures except for adding the template MP.

2.2.2. Preparation of MIPMs by one-step distillation precipitation polymerization

$3.00 \times 10^{-3} \text{ mol L}^{-1}$ MP, 4.12 mL DVB and 1.03 mL MAA were added to 80.00 mL of acetonitrile. After addition of 0.11 g AIBN, the system was heated and the subsequent steps were equivalent to that for preparing the shell of SMIPMs. Moreover, the preparation of non-imprinted polymeric microspheres (NIPMs) was performed using the same procedure without adding the template.

2.3. Batch adsorption experiments

In kinetics adsorption experiment, 0.02 g polymer was dispersed in 3.00 mL MP methanol solution at the concentration of $2.50 \times 10^{-3} \text{ mol L}^{-1}$ and the determination was made in different time range (5, 10, 20, 30, 60, 90, 120, 180 and 240 min). For each isotherm adsorption, 0.02 g polymer was placed in 40.00 mL MP methanol solution at different concentrations, which was subsequently placed in a thermostatic water-bath shaker at 25°C for 12 h to ensure equilibrium among the polymer and solution phases is attained. The suspension was centrifuged for 5 min and the concentrations of MP in the supernatant phase were measured by HPLC. For investigating the specificity of imprinted polymer for MP, a number of polymers were dispersed in MP and its structural analogs (MAP and PAR) solution at the same concentration of $1.50 \times 10^{-3} \text{ mol L}^{-1}$ for 12 h, respectively, and the supernatant was assayed by HPLC. The detection wavelength was 273 nm

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