Chemosphere 120 (2015) 615–620

Contents lists available at ScienceDirect

Chemosphere

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

Adsorption kinetics of pesticide in soil assessed by optofluidics-based biosensing platform

Feng Long [a,*], Anna Zhu [b], Hanchang Shi [c], Jianwu Sheng [c], Zhen Zhao [c]

[a] School of Environment and Natural Resources, Renmin University of China, Beijing, China
[b] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA
[c] State Key Joint Laboratory of ESPC, School of Environment, Tsinghua University, Beijing, China

HIGHLIGHTS

- Optofluidic biosensor was firstly used for adsorption kinetics assay of pesticides.
- The platform shows unique advantages for investigation of adsorption kinetics in soil.
- The platform is sensitivity, rapidity, small sample volume, and cost-effective.
- A simple and green method used to investigate transport mechanism of trace analytes.

ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form 19 September 2014
Accepted 20 September 2014

Handling Editor: Tamara S. Galloway

Keywords:
Optofluidics
Biosensor
Adsorption kinetics
Fluorescence immunoassay
Atrazine

ABSTRACT

The adsorption of pesticides in soil is a key process that affects transport, degradation, mobility, and bioaccumulation of these substances. To obtain extensive knowledge regarding the adsorption processes of pesticides in the environment, the new green assay technologies for the rapid, sensitive, field-deployable, and accurate quantification of pesticides are required. In the present study, an evanescent wave-based optofluidics biosensing platform (EWOB) was developed by combining advanced photonics and microfluidics technology for the rapid sensitive immunodetection and adsorption kinetics assay of pesticides. The robustness, reusability, and accuracy of the EWOB allow an enhanced prediction of pesticide adsorption kinetics in soil. Using atrazine (ATZ) as the target model, we found that the adsorption kinetics in soil followed a pseudo-second-order kinetic model. EWOB was compared with liquid chromatography–mass spectrometry/mass spectrometry (LC–MS/MS) method and yielded a good correlation coefficient (r^2 = 0.9968). The underestimated results of LC–MS/MS resulted in a higher adsorption constant of ATZ in soil derived from LC–MS/MS than that of a biosensor. The proposed EWOB system provides a simple, green, and powerful tool to investigate the transport mechanism and fate of pesticide residues.

1. Introduction

Pesticides have been used at increasing amounts to improve agricultural production and yield for 50 years (Hou et al., 2003; Graziano et al., 2006; Katsumata et al., 2006; Zacco et al., 2006; Pichetsurnthorn et al., 2012). The increasing amounts of these contaminants in various natural water systems and in agriculture products have caused increasing concerns because of the adverse effects of these substances on aquatic ecosystems and non-target organisms (Graziano et al., 2006). Previous studies demonstrated that the adsorption processes of pesticides in soil is of great importance because this procedure affects other processes, such as transport, degradation, mobility, and bioaccumulation (Singh et al., 2004; Liu et al., 2010). All of these processes greatly determine the risk of pesticide contaminating surface water and groundwater. Therefore, the extensive knowledge of the adsorption characteristics of pesticides in soil is necessary to predict the transformation and fate of these substances in the environment and protect water bodies from pesticide contamination (Flores et al., 2009; Siripattanakul et al., 2009). Analytical technologies are keys to obtaining accurate information regarding adsorption. Traditional analytical methods such as high-performance liquid chromatography (Katsumata et al., 2006), liquid chromatography–mass spectrometry (LC–MS) (Pichetsurnthorn et al., 2012), and gas chromatography with mass spectrometry identification (Hou et al., 2003) require complicated and time consuming pre-treated procedures (e.g., extraction and concentration). In addition, these

* Corresponding author.
E-mail address: longf04@ruc.edu.cn (F. Long).

http://dx.doi.org/10.1016/j.chemosphere.2014.09.072
0045-6535/

methods are difficult to apply in field investigation. During these pre-treated processes, toxic reagents have to be used (Hou et al., 2003; Katsumata et al., 2006; Pichetsurnthorn et al., 2012). Furthermore, a part of the target that should be measured may be lost and transformed, thereby leading to underestimated results. Hence, new green assay methods should be developed for the rapid, inexpensive, field-deployable, sensitive and accurate pesticide quantification with minimal sample and reagent volumes.

Optofluidics-based biosensing platform is a synergistic integration of photonics, microfluidics, and biosensor technologies; this platform also represents one of the most significant and active advances in biological/chemical analysis that provides numerous unique characteristics to enhance the sensing performance and simplify microsystem design (Psaltis et al., 2006). Many optical properties, such as fluorescence, refractive index, Raman scattering, absorption and polarization, can be exploited individually or in combination to generate sensing signals (Fan and White, 2011). The majority of optical waveguides (e.g., optic fiber) operate based on total internal reflection (TIR); in addition, the evanescent wave generated at optical waveguide surfaces penetrates the surrounding solution of lower refractive index and decays exponentially with distance (Psaltis et al., 2006; Fan and White, 2011). Microfluidics devices can function with small sample and reagent consumption, low unit costs, shorter reaction times, and parallel operation; these advances may possibly lead to the integration a whole laboratory in a chip (Thorsen et al., 2002). Microfluidics is not only an add-on accessory to an optofluidics device, but also an integral part of this system (Harazim et al., 2012). Therefore, optofluidics is suitable for biological/chemical detection in extremely small detection volumes (femtoliters to nanoliters) (Psaltis et al., 2006; Harazim et al., 2012).

In the current study, an evanescent wave-based optofluidics biosensor platform (EWOB) was developed to conduct a rapid on-site determination of pesticides by combining the evanescent wave fiber optic biosensor and microfluidics technology. A microcosm was prepared to investigate pesticide adsorption. Kinetic experiments were performed to provide further insights into pesticide adsorption. Atrazine [6-chloro-N-ethyl-N-1-(1-methylethyl)-1,3,5-triazine-2,4-diamine, ATZ], which is one of the most heavily used herbicides worldwide, was selected as a model target (Katsumata et al., 2006). ATZ is a putative endocrinal disruptor that poses a potential health risk to humans and wildlife even at very low levels (Graziano et al., 2006; Katsumata et al., 2006; Zacco et al., 2006). ATZ is routinely detected in various natural water systems, including groundwater and surface water, because of moderate solubility and relative persistence (Katsumata et al., 2006; Ionescu et al., 2010). The US Environmental Protection Agency (USEPA) has classified ATZ as a possible human carcinogen and mandated a drinking water standard limit of 3 $\mu g\,L^{-1}$ (Stoker et al., 2002). The proposed optofluidics biosensing system shows a considerable promise to conduct an on-site detection of pesticides and investigate the transport mechanism of pesticides by using a simple, fast, and portable technology.

2. Experimental

2.1. Chemicals and reagents

Bovine serum albumin (BSA), 3-aminopropyl triethoxysilane (APTS), glutaraldehyde, N,N′-Dicyclohexylcarbodiimide (DCC), N-hydroxysuccinimide (NHS), Atrazine (ATZ), N,N-Dimethylformamide (DMF), 3-mercaptopropionic acid (MPA), sodium dodecyl sulfate (SDS), 2,4-Dichlorophenoxyacetic acid (2,4-D), Bisphenol A, Diuron, and Simazine were purchased from Sigma–Aldrich (Steinheim, Germany). All other reagents, unless otherwise specified, were supplied by the Beijing Chemical Agents; they were also analytical grade and used without further purification. Distilled deionized water was used throughout the investigation. About 1 mg mL^{-1} atrazine stock solutions were prepared in 0.01 M phosphate-buffered saline (PBS) and stored at 4 °C. Standard concentrations of the analyte were prepared from the stock solution by serial dilutions in 0.01 M PBS.

Anti-ATZ monoclonal antibody (Anti-ATZ-MAb) was produced by our research group and labeled by Cy5.5 as previously described (Long et al., 2009).

2.2. Preparation of mercaptopropionic acid derivative of ATZ (MPAD) and ATZ-BSA

MPAD and the hapten conjugate ATZ-BSA (Fig. S1) was synthesized similar to the procedure proposed by Goodrow et al. (Goodrow et al., 1990). Briefly, 4.6 mmol of ATZ was slowly added into 50 mL of ethanol under constant stirring. Then, 2.0 g KOH was added before 4.7 mmol of MPA in ethanol solution was added. After the mixture was refluxed for 3 h, another 4.7 mmol of MPA was added. The mixture was further refluxed for 3 h, and the solvent was dried under rotary evaporation. The residue was taken up in 25 mL of 5% $NaHCO_3$ and washed thrice with 10 mL of chloroform. The aqueous layer of the solution was acidified (pH 2.0) with 6 N HCl, causing the acidic derivative to precipitate immediately. The supernatant was decanted, and the derivative was dried under rotary evaporation. The precipitate was further dissolved in 1 mL of ethanol and then allowed under reduced pressure at 37 °C to form MPAD crystals. The product was stored in a tightly sealed bottle for further use. To synthesize the hapten conjugate ATZ-BSA, 0.2 mmol of the MPAD derivative of ATZ and 0.2 mmol of NHS were added in 2 mL of DMF. Then, 0.2 mmol DCC in 0.5 mL DMF was added. The mixture was incubated for 18 h at room temperature (RT) and then centrifuged for 5 min at 10,000 rpm to remove the urea precipitate. The reaction mechanism of MPAD protein conjugation is shown in Fig. S1. The supernatant (1 mL) was added dropwise into 5 mL 75 mg BSA solution (PBS, pH 7.4) and stirred for 4 h at 4 °C. The conjugates were passed through P10 gel filtration column (Pharmacia, Sweden). The fractions with maximum protein concentration were collected, pooled, and checked for the final concentration of protein (hapten-protein) using a UV spectrophotometer at 280 nm. The estimated number of hapten molecules attached to the carrier protein (hapten-to-protein molar ratio) BSA was 18.

2.3. Modification of fiber optic sensor

Details on the modification of the combination tapered fiber optic sensor were described previously (Long et al., 2009). The hapten-carrier conjugate ATZ-BSA used as a recognition element was covalently attached onto the sensing surface of the fiber optic sensor by the glutaraldehyde-covalent-coupling strategy to assure the reusability of the sensor surface without affecting the binding properties of the immobilized molecule (Fig. S2) (Hofstetter et al., 1999). Prior to surface modification, the fiber optic sensor surface was cleaned with a piranha solution [H_2SO_4/H_2O_2, 3:1 (v/v)] for 30 min, rinsed with ultrapure water, and then dried in an oven at 105 °C. The immobilization of ATZ-BSA onto the surface of the fiber optic sensor is illustrated in Fig. S2. The fiber optic sensor was first aminated by immersion in 2% (v/v) APTS acetone solution for 1 h to coat a reactive silane layer with an aminated-terminal silane. Excess APTS was eliminated with acetone to ensure order and uniformity of the self-assembled monolayer. The sensor was first immersed in a 5.0% (v/v) glutaraldehyde solution for 1 h at 37 °C, washed with water, and then immersed overnight in 1 mL of a 0.5 μM ATZ-BSA in PBS solution (pH 7.4) at 4 °C to immobilize ATZ-BSA onto the surface of aminated-silanized