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A cyclodextrin polymer membrane-based passive sampler for measuring triclocarban, triclosan and methyl triclosan in rivers

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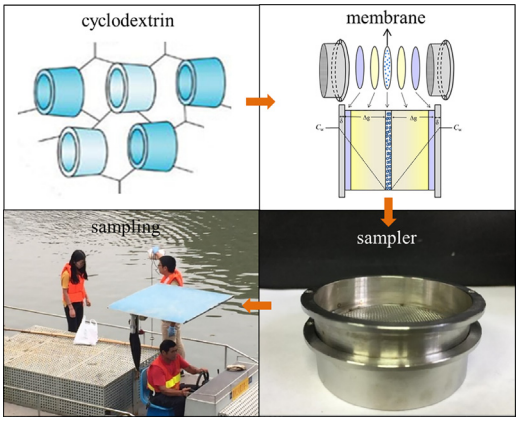
HIGHLIGHTS

- A polymer membrane containing cyclodextrin molecules was prepared.
- A DGT sampler with cyclodextrin polymer membrane as binding phase was designed.
- The sampler had fast uptake rate, enough uptake capacity and stable sampling rate.
- The sampler was successfully applied in the measurement of compounds in rivers.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, extensive attention has been paid to the passive sampling technology of diffusive gradients in thin films (DGT) due to its growing application in the measurement of a widening variety of compounds. Within any DGT device, the binding phase is a key component, and seeking novel binding phases is an issue worth studying. Cyclodextrin polymer, as a green and eco-friendly material, may be a good choice for measuring organic chemicals. In this study, a novel DGT sampler with cyclodextrin polymer membrane (CDPM) as the binding phase was developed for measuring the concentrations of triclosan, triclocarban and methyl triclosan. Firstly, the type and content of cyclodextrin used in CDPM was optimized, and a series of tests showed that CDPM had good hydrophilicity, thermal stability, fast uptake rate and sufficient uptake capacity, thus CDPM was determined to be suitable for use as the binding phase of DGT sampler. Moreover, the sampling rates of this DGT sampler were not influenced by ionic strength and dissolved organic matter, making it feasible for in situ monitoring of compounds in the field. Hence, we deployed the developed DGT sampler in the Qinhuai and Jiuxiang Rivers to measure the concentrations of three compounds. We also collected water samples and processed them with the solid phase extraction (SPE) method. Results indicated that there was no significant difference between the DGT-measured and the SPE-measured concentrations for each compound, which confirmed the reliability of this DGT sampler for monitoring the concentrations of compounds in natural waters.

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1. Introduction

Accurate determination of a compound's concentration is always a prerequisite for further research about its occurrence, effect, and environmental fate. Consequently, developing new sampling technology for measuring the concentrations of compounds has become a hot topic in environmental science. In recent decades, passive sampling technology has had great interest, with its advantages of continuous in-situ monitoring, high sensitivity, low matrix interferences, ease of storage and low solvent consumption (Jonker et al., 2018; Lohmann et al., 2017). Among the current passive sampling technologies, the diffusive gradients in thin films (DGT) technology has drawn particular interest due to its inclusion of a diffusion phase, which can control the molecular diffusion and remain stable against outside interference (e.g., flow rate and concentration fluctuation). This technology has been successfully employed in the measurement of metals and inorganic salts (Huang et al., 2016; Parker et al., 2017), and in recent years DGTs have been extended to measure organic compounds, especially pharmaceuticals and personal care products (PPCPs) (Chen et al., 2012, 2013; Chen et al., 2017).

A DGT consists of a binding phase wrapped in a diffusive phase, which is composed of a diffusive hydrogel and a filter membrane. Over the years, researchers have been working to find various binding phases for measuring organic compounds. The currently available binding phases include HLB binding gel, XAD 18 resin and activated charcoal (Challis et al., 2016; Chen et al., 2012; Zheng et al., 2015). Because different binding phases are suitable for sampling different compounds, developing novel materials as binding phases will continue to be an important research topic in DGT technology. No matter which binding phase is used, the concentrations measured by passive samplers are always the freely dissolved fraction in the water being sampled (Borrelli et al., 2018; Wang et al., 2018), which is the driving force of the diffusion gradient that powers diffusion into the DGT.

Cyclodextrin has the potential of being another binding phase material, because it can include suitably sized compounds into its cavity through host-guest interactions. However, the fixed size of that cavity means that cyclodextrin can only accommodate a suitably sized compound, and only freely dissolved molecules can engage in these interactions. Those sorbed, sequestrated or complexed cannot enter into the cyclodextrin's cavity. Therefore, many studies have reported the applications of cyclodextrin in assessing the bioavailability of compounds. Especially, in soil or sediments, the amounts of compounds extracted by a cyclodextrin solution are well-correlated with those accumulated in organisms (Hartnik et al., 2008; Reid et al., 2000). Based on this work, integrating cyclodextrin into the DGT technique seems feasible, but as far as we know, no studies have been done about this.

Because of the solubility of cyclodextrin in water, before it is used as a DGT binding phase, it should be processed into an insoluble solid form. To this end, numerous insoluble cyclodextrin polymers have been developed to use to remove the organic pollutants from water by means of adsorption (Alsbaiee et al., 2016; Liu et al., 2011; Morin-Crini et al., 2018; Sancey et al., 2011; Xiao et al., 2017). Generally, the available cyclodextrin polymers are usually loose spheres or other granular materials. Containing these loose materials in a shield or housing is an important aspect of passive sampler design, but even if well-designed, this approach can be problematic: polymer particles can still slip out of the housing and the housing itself can slow the uptake of the target compound. Furthermore, most cyclodextrin polymers have high swelling capacity (Huang et al., 2013; Liu et al., 2011), which can prevent the compounds from diffusing freely or distributing evenly. Additionally, after-sampling, regenerating, and extracting the loose materials are solvent-consuming and may not fully restore this type of device to its original performance. All of these deficiencies will result in uncertainty and instability of the monitoring data. However, if the cyclodextrin polymer is made into a coherent membrane material or immobilized onto a solid membrane-support, all the deficiencies mentioned-above may be overcome.

In this study, a cyclodextrin polymer membrane (defined as CDPM) was prepared and characterized. We investigated the uptake kinetics and uptake capacity of the membrane for three target compounds. Then, we designed a novel DGT passive sampler, with the self-prepared CDPM as binding phase. A series of tests were carried out to demonstrate the reliability and robustness of the sampler under the occurrence of ionic strength and dissolved organic matter. Finally, the developed sampler was field-tested in two urban rivers, and by comparing results with those an active sampling technique (i.e., grab sampling with solid-phase extraction), the utility of this passive sampler was assessed and validated.

2. Materials and methods

2.1. Chemicals and reagents

Triclocarban (TCC), triclosan (TCS) and its biodegradation product methyl triclosan (MTCS) are ubiquitous in environmental matrixes and have potential adverse effects (Ding et al., 2018; Hinther et al., 2011). For testing, TCS (97%) and TCC (98%) were purchased from Macklin Inc. (Shanghai, China), and MTCS (99.5%) was purchased from Sigma-Aldrich (Shanghai, China). Cellulose acetate (CA, chemically pure), dibutyltin dilaurate (≥90%) and ethyl acetate (99%) were acquired from Sinopharm Chemical Reagent Co., Ltd., China. Dimethyl formamide (DMF, 99.5%) was obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Ager (99%) was acquired from Adamas Reagent Co. Ltd. (Shanghai, China). Hexamethylene diisocyanate (99%), humic acid (HA) and sodium chloride (NaCl) were purchased from Aladdin (Shanghai, China). β-Cyclodextrin (β-CD, 97%), hydroxypropyl β-cyclodextrin (HPCD, 97%), methanol (≥99.8%) and acetonitrile (≥99.8%) of HPLC grade were obtained from Macklin Inc. (Shanghai, China). Acetone (≥99.5%) was obtained from Jiangsu Yonghua Fine Chemicals Co., Ltd. (Jiangsu, China). Glass-fiber filter membrane, with 50 mm in diameter and 0.7 μm in pore size, was purchased from Taoyuan Medical and Chemical Instrument Factory (Haining, China).

2.2. Preparation and characterization of cyclodextrin polymer membrane

A cyclodextrin polymer (CDP) was prepared using the method proposed by Adams et al. (2012). Briefly, cyclodextrin was dissolved in DMF, and the hexamethylene diisocyanate and dibutyltin dilaurate (used as grafting agent and catalyst, respectively), were added dropwise, successively. The reaction continued for 30 min under inert atmosphere. This was followed by adding acetone to precipitate CDP and then the product CDP was obtained under vacuum drying. After that, an amount of CDP and CA was dissolved in DMF at 40 °C water bath for four hours. Then, the mixture was sat undisturbed for eight hours until it became a homogeneous and semi-transparent solution, and all the air-bubbles were removed. The CDPM was prepared using the phase-inversion method, i.e., a film-casting glass rod was used to cast membranes on a glass plate, and the freshly obtained membrane was immersed in deionized water for 30 min to remove solvent molecules. Finally, the produced membrane with a thickness of 0.5 mm was stored in deionized water, which was changed every day.

The CDPM and cellulose acetate membrane were characterized by a series of technologies, including fourier transform-infrared (FTIR) analysis, thermogravimetric analysis (TGA), and contact angle measurement. Details are presented in the Text S1.

2.3. Design and configuration of the passive sampler

Unlike the common DGT device, our sampler has a symmetric structure with diffusive phase and protecting phase on the both sides of binding phase, so that target compounds can disperse into it evenly from both sides. The passive sampler was designed with CDPM as a binding phase, an agarose gel membrane as a diffusive phase and the