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Diffusive gradients in thin films based on MOF-derived porous carbon binding gel for in-situ measurement of antibiotics in waters

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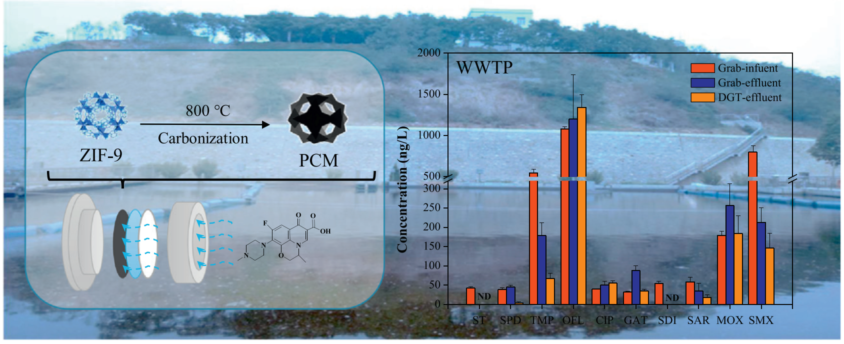
HIGHLIGHTS

- Novel high capacity binding gel based on porous carbon material
- Excellent uptake performance of novel binding gel toward antibiotics
- In-situ measurement of antibiotics in environmental waters with PCM-DGT

GRAPHICAL ABSTRACT



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ABSTRACT

Diffusive gradients in thin films (DGT) can achieve the time-weighted-average (TWA) concentrations of analytes in the period of deployment. Here we developed an approach based on DGT with a novel binding gel using porous carbon material (PCM) derived from metal-organic framework (MOF) for in-situ measurement of antibiotics in water samples. The diffusion coefficients of 20 antibiotics (nine sulfonamides, ten fluoroquinolones, and trimethoprim) in agarose diffusive gel were 1.41×10^{-6} cm^2/s to 4.75×10^{-6} cm^2/s at 25 °C. The capacity of PCM binding gel toward the antibiotics was ~100 μg per gel disc. The masses of the antibiotics accumulated by PCM-based DGT increased linearly with time, and they were almost independent of pH (4.2–8.4) and ionic strength (1–500 mM). The performance of the novel DGT was evaluated using freshwater and synthetic seawater spiked with the antibiotics in laboratory. The results showed good agreement with the theoretical predications except sulfacetamide. The detection limits achieved by the DGT with three devices together for deploying up to seven days were 1.0–18.0 ng/L. Field deployment in municipal wastewater treatment plant effluent and seawater showed that the TWA concentrations of antibiotics were 3.8–1342.5 ng/L and 5.6–43.3 ng/L, respectively, which were comparable to those measured by grab sampling. The proposed DGT was an efficient tool for the measurement of antibiotics in environmental waters.

1. Introduction

Antibiotics are used extensively for the therapy of infectious diseases in human and animals, and the growth promotion of animals in stock breeding and aquaculture (Van Boeckel et al., 2017). The total

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consumption of 36 frequently detected antibiotics in 2013 is 92,700 tons in China (Zhang et al., 2015). Most of antibiotics finally enter natural waters including surface water, groundwater and seawater through municipal wastewater treatment plant (WWTP) effluent and discharge from household sewage and animal manure. In addition, inshore fishery results in direct release of antibiotics into marine environment. The long-term presence of antibiotics in the environment has been increasing the risks of bacterial resistance and antibiotic resistance genes (Cizmas et al., 2015; Gaffney et al., 2015). Therefore, it is of significance to investigate environmental occurrence, fate and behavior of antibiotics and to assess their health risks. These researches highly depend on quantitative measurement and monitoring of antibiotics at environmentally relevant levels (usually μg/L–ng/L).

Till date, active sampling coupled with solid phase extraction is still a predominant strategy for measuring trace organic pollutants in water samples, but it is time-consuming and labor intense. Passive sampling (PS) overcomes the disadvantages and can achieve the time-weighted average (TWA) concentrations of analytes in the long-term period of deployment. Several PS techniques, including the polar organic chemical integrative sampler (POCIS), solid phase microextraction (SPME), and the Chemcatcher, have been developed for sampling polar organic compounds (Ke et al., 2013; Mazzella et al., 2010; Vrana et al., 2007). These techniques require calibration of sampling rates prior to field deployment, however, the observed rates in fields don't always agree with the laboratory-derived rates due to the influences of environmental conditions such as water velocity, temperature and biofouling (Allan et al., 2009; Wille et al., 2011). Although in-situ calibration using performance reference compounds (PRCs) have been used extensively for hydrophobic compounds, the method for polar compounds is still suffered from some limitations such as poor isotropic behavior between absorption and desorption of analytes and PRCs, resulting in large uncertainties (Challis et al., 2016; Harman et al., 2011).

Diffusive gradients in thin films (DGT), first reported by Zhang and co-workers in 1994 (Davison and Zhang, 1994), is an in-situ, passive sampling technique that can quantitatively uptake labile species in aqueous solution through a concentration-dependent dynamic process. The concentration of analytes accumulated by DGT can be calculated by the Eq. (1):

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \tag{1}$$

where M is the mass of analytes in binding gel, Δg is the diffusive gel thickness, δ is the thickness of diffusive boundary layer (DBL), D is the diffusion coefficient of analytes in diffusive gel, t is deployment time, and A is the exposure area of DGT device. The rate of analytes adsorbed on the binding gel must higher than the flux rate of the analyte across the diffusive gel. In addition, the binding gel must not be saturated with analytes at the end of deployment, therefore, a binding gel with a high capacity and relative selectivity is necessary. Previous studies have developed the binding gels, based on Chelex-100, ferrihydrite, Metsorb, and Zr-oxide, for measuring dissolved inorganic substances (Bennett et al., 2010; Ding et al., 2016; Guan et al., 2015; Guan et al., 2016; Zhang and Davison, 1995; Zhang et al., 1998), and their mixed binding gel has been prepared for simultaneous measurements of cations and anions (Wang et al., 2017). Most recently, DGT has attracted increasing attentions in in-situ measurement of organic compounds since several binding gels, based on XAD-18, Oasis-HLB, activated charcoal, and molecularly imprinted polymer, were successfully applied for measuring household and personal care products (HPCPs), pharmaceuticals, pesticides, and phenols (Chen et al., 2013; Chen et al., 2017; Guo et al., 2017; Zheng et al., 2015). Due to complicated structures and extensive species of organic pollutants in environment, novel binding gels are highly desirable for using DGT as an efficient monitoring tool in natural waters.

In principle, the adsorbents with high adsorption capacity and good stability are available for binding gels of DGT. Metal–organic framework (MOF) materials have demonstrated excellent gas adsorption characteristics due to its permanent nano-scale porosity, large surface area up to 10,000 m^2/g, tunable pore structure and high thermal stability (Furukawa et al., 2013; Hasan et al., 2012; Luz et al., 2012). However, using MOF as an adsorbent in water is relatively limited due to its poor stability in aqueous solution (Burtch et al., 2014; Haque et al., 2014). On the other hand, porous carbon material (PCM) derived from MOF not only maintains the specific porous structure and large surface area of MOF but has excellent stability in water (Chaikittisilp et al., 2013; Jiang et al., 2011). For example, Li et al. (2017) have showed efficient adsorption of ciprofloxacin in water using PCM derived from zeolitic imidazolate framework-8 (ZIF-8) achieving a high sorption capacity of 416.7 mg/g.

This work reported an approach based on DGT with a high capacity binding gel containing PCM derived from zeolitic imidazolate framework-9 (ZIF-9) for in-situ measurement of sulfonamides (SAs), fluoroquinolones (FQs), and trimethoprim, frequently detected antibiotics in environmental water. The binding kinetics, capacity and elution efficiency of PCM binding gel, and the effects of pH and ionic strength on the uptake of the antibiotics with PCM-based DGT (PCM-DGT) were studied systematically. The performance of PCM-DGT was evaluated using the freshwater and synthetic seawater spiked with 20 antibiotics in laboratory. Finally, the developed PCM-DGT was validated by field trial in municipal WWTP effluent and seawater for measuring 20 antibiotics.

2. Material and methods

2.1. Reagents and materials

DGT moldings with 3.14 cm^2 exposure window were purchased from DGT Research Ltd., UK. Poly ether sulfone (PES) membrane (2.5 cm in diameter, 0.13 mm thickness, and 0.45 μm pore size) was purchased from Jinteng Co. (Tianjing, China). Antibiotics included sulfamethoxazole (SMX), sulfadiazine (SDI) sulfamerazine (SMZ), sulfadimidine (SDZ), sulfapyridine (SPD), sulfathiazole (ST), sulfacetamide (SCT), sulfadoxine (SD), sulfamethoxypyridazine (SPMZ), trimethoprim (TMP), ofloxacin (OFL), ciprofloxacin (CIP), enrofloxacin (ENR), sarafloxacin (SAR), fleroxacin (FLE), lomefloxacin (LOM), gatifloxacin (GAT), sparfloxacin (SPA), moxifloxacin (MOX) and balofloxacin (BAL) were purchased from Aladdin biological technology LTD. (Shanghai, China). Internal standard compounds including sulfadiazine-d_6 and ciprofloxacin-d_8 were purchased from Dr. Ehrenstorfer GmbH (Germany). Stock solutions of the antibiotics at 1.0 mg/mL were prepared by chromatography-grade methanol and stored in amber glass bottles at −20 °C. Sample solutions for DGT experiments were prepared by Milli-Q high purification water (Millipore, United States). All glass containers were rinsed thoroughly with methanol and deionized water prior to use.

2.2. Synthesis of PCM

ZIF-9 was prepared by a previously described method with minor modifications (Li et al., 2015; Li et al., 2016). Briefly, $Co(NO_3)_2 \cdot 6H_2O$ (0.210 g) and benzimidazole (0.170 g) were dissolved in 36 mL of *N*, *N*-dimethylformamide (DMF) with a 100 mL glass vial. The vial was placed in an oven with a heating rate of 5 °C/min up to 130 °C and maintained for 48 h. After the vial was cooled down to room temperature, purple crystals (ZIF-9) were removed, followed by washing with ethanol three times and dried under vacuum at 60 °C for 12 h. PCM was achieved by carbonizing ZIF-9 at a heating rate of 5 °C/min up to 800 °C for 5 h.

A scanning electron microscope (Nova nanoSEM 450 of FEI; The Netherlands) and a specific surface area analyzer (Quantachrome