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Application of an immobilized ionic liquid for the passive sampling of perfluorinated substances in water

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ABSTRACT

Ionic liquids have been used to efficiently extract a wide range of polar and nonpolar organic contaminants from water. In this study, imidazole ionic liquids immobilized on silica gel were synthesized through a chemical bonding method, and the immobilized dodecylimidazolium ionic liquid was selected as the receiving phase material in a POCIS (polar organic chemical integrative sampler) like passive sampler to monitor five perfluoroalkyl substances (PFASs) in water. Twenty-one days of integrative accumulation was conducted in laboratory scale experiments, and the accumulated PFASs in the samplers were eluted and analyzed by high performance liquid chromatography coupled with tandem mass spectrometry (HPLC–MS/MS). The partitioning coefficients of most PFASs between sampler sorbents and water in the immobilized ionic liquid (IIL)-sampler were higher than those in the HLB-sampler, especially for compounds with shorter alkyl chains. The effects of flow velocity, temperature, dissolved organic matter (DOM) and pH on the uptake of these analytes were also evaluated. Under the experimental conditions, the uptake of PFASs in the IIL-sampler slightly increased with the flow velocity and temperature, while different influences of DOM and pH on the uptake of PFAS homologues with short or long chains were observed. The designed IIL-samplers were applied in the influent and effluent of a wastewater treatment plant. All five PFASs could be accumulated in the samplers, with concentrations ranging from 6.5×10^{-3} – 3.6×10^{-1} nmol/L in the influent and from 1.3×10^{-2} – 2.2×10^{-1} nmol/L in the effluent. The calculated time-weighted average concentrations of most PFASs fit well with the detected concentrations of the active sampling, indicating the applicability of the IIL-sampler in monitoring these compounds in water.

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1. Introduction

Passive sampling has emerged as a useful alternative to conventional spot sampling in monitoring water environments [1,2], as it can provide time weighted average concentrations (TWACs) of pollutants, which compensate for concentration fluctuations by consecutive sampling [3]. Notably, preconcentrations of contaminants are achieved in situ even in complex matrices, and the pretreatments are simplified [4,5]. Semipermeable membrane devices (SPMDs) [6] and the polar organic chemical integrative sampler (POCIS) [7,8] have been developed for sampling non-polar (hydrophobic) organic pollutants and polar organic pollutants, respectively. POCIS proposed by Alvarez et al. in 1999 [9], has

been extensively used for sampling pesticides, pharmaceuticals, hormones and other organic chemicals [10]. To improve its accuracy and expand its application, several new materials, such as Oasis MAX, Oasis MCX [11] and Chromabond HR-X (polystyrene divinylbenzene polymer) [12] have been applied as a substitute for the commercial receiving phase (Oasis HLB, hydrophile-lipophile balance) in the POCIS.

Ionic liquids (ILs) are a class of compounds comprising only ions occurring as liquid at room temperature [13]. ILs can interact with compounds through a variety of interactions, e.g., hydrophobic interaction, ion exchange and electrostatic force [14]. By the optimization and screening of organic cations and inorganic anions, ILs have been successfully used as advanced chemical extractants in liquid-phase microextraction to determine the presence of polycyclic aromatic hydrocarbon (PAHs) [15], pesticides [16,17], phthalate esters [18], UV filters [19] and other organic contaminants [20–23]. In addition, the applications of ILs in immobilized

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stationary phase of solid-phase microextraction (SPME) were well performed [24,25]. ILs with a long alkyl group were successfully used as the receiving phase in SPMDs for the determination of PAHs [26,27] and endocrine-disrupting chemicals [28] in water and sediment. Previous studies have verified the affinity between ILs and polar organic pollutants [29,30]. Caban et al. [31] found that alkylphosphonium ionic liquids showed good selectivity and uptake efficiency to some polar and semi-polar organic chemicals and might be applied as the receiving phase of the passive sampler. However, few studies have reported the application of ILs in the passive sampler for polar organic contaminants, which might be related to the loss of ILs during passive sampling.

The monitoring of perfluoroalkyl substances (PFASs) has attracted increasing interest, due to their ubiquitous distribution and their persistence [32], low concentration [33] and confirmed eco-toxicity [34]. Multiple studies have found low level (a few to several thousand nanogram per liter) concentration in the influent and effluent of the wastewater treatment plant (WWTP) [35]. For water sample, the pretreatments were performed by traditional method, like solid phase extraction (SPE) and liquid–liquid microextraction [36–39]. Perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COO^-$) and perfluoroalkyl sulfonic acids (PFSAs, $C_nF_{2n+1}SO_3^-$) exist as anions in most aquatic environments. Kaserzon et al. [40–42] proposed Strata™ X-AW, a weak anion exchange sorbent, as the receiving phase in modified POCIS to uptake PFASs from water. However, except for anion-exchange resin, receiving phases suitable for PFCAs and PFSAs are still scarce.

To evaluate the availability of ionic liquid material as the receiving phase in passive sampling, the substituted imidazole ionic liquids was immobilized on silica gel and applied as a substitute of the commercial receiving phase material (e.g. HLB sorbent) in a POCIS-like passive sampler. The uptake kinetics of 3 typical PFCAs and 2 PFSAs in the immobilized ionic liquid (IIL)-sampler were studied in the laboratory at the microcosm scale and compared with that in the HLB-sampler (with HLB sorbent as the receiving phase). The impacts of environmental factors, e.g., flow velocity, temperature, DOM (dissolved organic matter) and pH, on the uptake efficiency were discussed. In addition, the developed sampler was applied in the influent and effluent flows of a WWTP for a 7 d passive sampling period.

2. Experimental

2.1. Materials and reagent

3-Chloropropyltriethoxysilane was purchased from Zibo Qiquan Industrial & Trading Co. Ltd., (Shandong, China). *N*-Methylimidazole (MIM, 99%), *N*-(3-aminopropyl) imidazole (APIM, 98%), and *N*-dodecylimidazole (DoDIM, 99%) were purchased from Tiandakewei Chemical Co. Ltd. (Tianjin, China), Alfa Aesar Co. Ltd. (Tianjin, China), and Shanghai Chengjie Chemical Co. Ltd. (Shanghai, China), respectively. Ethylether, methyl *tert*-butyl ether (MTBE), and ammonium acetate (CH_3COONH_4) were of HPLC reagent grade and were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). HPLC-grade methanol and acetonitrile were obtained from Merck KGaA (Darmstadt, Germany). PFHxA (perfluorohexanoic acid, 98%, Matrix Scientific, Columbia, SC, USA), PFOA (perfluorooctanoic acid, 98%, Strem Chemicals, Bischheim, France), PFDoDA (perfluorododecanoic acid, 95%, Sigma-Aldrich Chemical, St. Louis, MO, USA), PFHxS (perfluorohexane sulfonic acid, $\geq 99\%$, Sigma-Aldrich Chemical), and PFOS (perfluorooctane sulfonic acid, 99%, Sigma-Aldrich Chemical) were used as the target analytes.

Silica gel purchased from Qingdao Haiyang Chemical Co., Ltd. (Shangdong, China) was used as the support material in IIL syn-

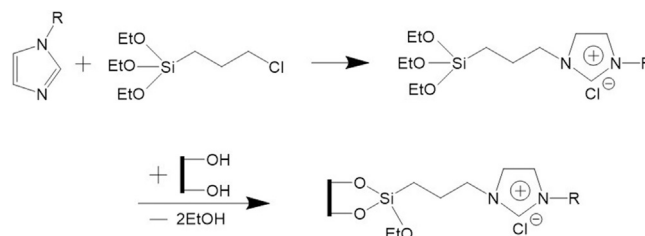


Fig. 1. Synthetic scheme for substituted imidazole ionic liquids immobilized on silica gel. R represented methyl, 3-aminopropyl and dodecyl.

thesis. Before preparation, 20 g of silica gel (100–200 mesh) was activated by immersion in 3.0 mol/L hydrochloric acid (200 mL) for 24 h, washing with Milli-Q water to a neutral pH and then drying under vacuum at 120 °C for 8 h.

2.2. Preparation and comparison of IILs

The synthesis of the IILs in a solid carrier was carried out based on a two-step method with minor modifications (Fig. 1) [43]. Five millilitres of the silane-coupling agent, 3-chloropropyltriethoxysilane, and 50 mmol of the substituent imidazole (MIM, APIM or DoDIM) were placed in a 150 mL round-bottomed flask in the presence of acetonitrile. The suspension was refluxed with stirring at 95 °C for 48 h. When its temperature dropped to the ambient level, activated silica gel (1.0 g) was added, and the mixture was refluxed with stirring over the next 24 h. Then, the product was recovered by a vacuum glass filter and was consecutively washed with ethylether (100 mL), acetonitrile (150 mL), and Milli-Q water (200 mL). The obtained three IILs, i.e., MIM-IIL, APIM-IIL and DoDIM-IIL, were vacuum dried at 80 °C for 8 h.

The sorption experiment was performed as follows, and the distribution coefficients of three target PFASs, i.e., PFHxA, PFDoDA, and PFHxS on the three IILs and the bare silica gel were compared. Fifty milligrams of IIL adsorbents and 5 mL of water solution (containing 1 mmol/L of PFHxA, PFDoDA or PFHxS) were mixed and shaken at 30 °C for 4 h. Then the solution was centrifuged at 4200 r/min for 10 min and the supernatant was analyzed using HPLC–MS/MS. Triplicate samples and control groups without sorbents were set.

2.3. Sampler design and laboratory experiment

POCIS-like samplers were designed and used in this study, using techniques similar to those described by Alvarez et al. [44] with minor modifications. In brief, 30 mg of IIL sorbents was enclosed between two polyethersulfone (PES) membranes and sealed with silica discs and synthetic glass ring flanges to assemble an IIL-sampler. The total exchange surface area of the membrane was 10.75 cm². The surface area per mass of sorbent ratio of the sampler was approximately 358 cm²/g, which was twice as high as the value of the standardized pharmaceutical-POCIS (180 cm²/g). As a control, an HLB-sampler using 30 mg of HLB sorbents (obtained from Waters HLB SPE cartridges) as the receiving phase was also assembled.

Laboratory scale passive sampling experiments were conducted in cylindrical synthetic glass tanks (diameter 65 cm, height 20 cm), with a diving pump and a stainless steel ring (diameter 20 cm, height 20 cm) in the centre (Fig. 2). A punching glass tube (diameter 1 cm, length 20 cm) joins in the pump to achieve circumfluence. Five typical PFASs, including three PFCAs (PFHxA, PFOA, and PFDoDA) and two PFSAs (PFHxS and PFOS) with different alkyl chain lengths, were selected as the target analytes. Fifty litres of effluent water collected from a WWTP was added into each tank, with the background concentrations of approximately 1 nmol/L for PFHxA and 10⁻³–10⁻² nmol/L for other four PFASs analytes. Mixed standard

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