



Preparation of an adsorbent based on polymeric ionic liquid for the simultaneous extraction of acidic, basic and neutral pollutants



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ABSTRACT

In this study, coextraction of acidic, basic and neutral pollutants was realized with a new adsorbent based on polymeric ionic liquid (PIL). In the presence of a porogen solvent containing 1-propanol and 1,4-butanediol, an ionic liquid, 1-vinyl-3-octylimidazolium tetrafluoroborate was used as monomer to copolymerize with dual cross-linkers (divinylbenzene and N,N-methylene-bisacrylamide) to form the adsorbent for stir cake sorptive extraction (SCSE). Phenols, aromatic amines and parabens were selected as acidic, basic and neutral model analytes, respectively. The effects of preparation conditions and extraction parameters on the extraction performance of SCSE/PIL were investigated thoroughly. Under the optimized conditions, the prepared adsorbent showed satisfactory coextraction performance to the selected analytes with multiply interactions. At the same time, simple and sensitive analytical method for simultaneous determination of phenols, aromatic amines and parabens in environmental water samples was developed by the combination of SCSE/PIL with high-performance liquid chromatography with diode array detection. Low limits of detection ($S/N=3$) and quantification limits ($S/N=10$) of the proposed method for the targeted analytes were achieved within the range of 0.064–0.30 $\mu\text{g/L}$ and 0.21–0.99 $\mu\text{g/L}$, respectively. The precision of the proposed method was evaluated in terms of intra- and inter-assay variability calculated as relative standard deviation (RSD), and it was found that the RSD values were all below 10%. Ultimately, the applicability of developed method was successfully confirmed by analyzing lake, reservoir and river water samples. Recoveries obtained for the determination of targeted analytes in spiking samples ranged from 70.0% to 112%, with RSDs within the range of 1.6–9.8%.

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1. Introduction

Sample pretreatment plays a dominant role in whole analytical procedure. Suitable sample preparation can eliminate interfering matrix compounds and preconcentrate up to adequate concentration levels for measurements. Typically, sample pretreatment includes solvent-based and adsorbent-based approach [1]. Adsorbent-based extraction is more popular because less toxic solvent is used than solvent-based extraction. So far, all kinds of adsorbent-based extraction formats such as solid-phase extraction (SPE) [2], magnetic solid-phase extraction [3], solid-phase microextraction (SPME) [4], multiple monolithic fiber solid-phase microextraction (MMF-SPME) [5], stir bar sorptive extraction

(SBSE) [6] and stir cake sorptive extraction (SCSE) [7] have been reported. Undoubtedly, extractive medium (adsorbent) is the core in adsorbent-based extraction because it decides the extraction targets and performance. So far, a great variety of adsorbent materials has been reported and part of them has been commercially available. Surface-modified silicas (C8, C18) [8], macroporous polymeric materials [9], graphene-based materials [10], magnetic nanoparticles (MNPs) [11], carbon nanotubes [12], polymeric ionic liquids (PILs) [13] and metal-organic frameworks (MOFs) [14] et al. have been widely used to extract all kinds of compounds from complicated matrices. However, most of the adsorbents were applied for extraction of the same category compounds, few of them affords coextraction of compounds with obviously different properties such as acidic, basic and neutral pollutants in a single step.

In real environmental water samples, the types and properties of pollutants are very complicated. Acidic, basic and neutral pollutants co-exist in real waters. In most case, acidic and basic pollutants are polar compounds. For example, the $\log K_{OW}$ values for

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2-nitrophenol (acidic compound) and aniline (basic compound) are 1.79 and 0.85, respectively. It is well known that the extraction of polar compounds is difficult due to the strong interactions of these compounds with water molecules in aqueous solutions. Therefore, the coextraction of acidic, basic and neutral pollutants is interesting and challenging. In reported methodologies for the extraction of pollutants, the targeted analytes focus on the same category compounds [8–14]. To comprehensively detect pollutants in real water samples, different category pollutants should be extracted separately under respectively optimal extraction conditions. Hereby, the whole procedure is time consuming and costly. Recently, H. Ebrahimzadeh et al. used different functionalized MNPs to coextract acidic and basic pollutants [3,15,16]. Expected coextraction performance was achieved, but the extraction capacity was limited because a low quantity of extraction media was employed. At the same time, the stability of the functionalized coatings on magnetic cores should be further improved. SPE utilized graphitized carbon black [17] and Oasis HLB [18] was also exploited to coextraction of acidic, basic and neutral pollutants. However, multistep time-consuming processes including extraction, elution, evaporation, and sample reconstitution steps were needed in SPE. Therefore, developing new adsorbent and combining suitable extraction format is highly desired for the simultaneous extraction of acidic, basic and neutral pollutants.

Ionic liquids (ILs) are a class of solvents composed of a co-existing organic cation and organic anion. In comparison to conventional organic solvents, ionic liquids are usually nonvolatile, nonflammable, and generally less toxic. Therefore, ILs are environmentally benign “green” solvents and have been widely used in separation science [19,20]. PILs are synthesized from ILs monomers. It combines the unique properties of ILs together with intrinsic polymer characteristics such as thermal and chemical stability, improved processability, durability and spatial controllability [21]. These advantages make PILs favorable materials for adsorbents in sample preparation [22,23]. In this study, according to the in-situ polymerization method of monolith, we tried to develop a new PIL-based adsorbent and used it as SCSE extractive medium for the coextraction of acidic, basic and neutral pollutants in environmental water samples. SCSE using porous monolithic materials is an environmentally friendly extraction format which developed in our group [24,25]. SCSE combines the processes of extraction, concentration and clean-up as one single step. There are some distinct advantages for SCSE including simple operation, high extractive capacity, good flexibility, cost-effectiveness, and satisfactory lifespan. Furthermore, the extraction medium (monolithic cake) is flexible. According to the character of targeted analytes, the monolithic cake can be easily designed and prepared to realize effective extraction of analytes.

Aromatic amines and phenols are serious environmental pollutants and they are classified as the hazardous wastes and priority toxic pollutants by Environmental Protection Agency of America [26]. Parabens are widely used as preservatives in personal care products, and they are considered as possible endocrine disruptors [27]. Because aromatic amines, phenols and parabens have a very wide range of application, their consumption revealed a trend of dramatic increase in many countries. However, these compounds can enter into the environment waters through all kinds of ways such as industrial waste, the excretion of human and animals and the aquaculture wastewater. Therefore, coextraction of these pollutants is highly desired. In present work, phenols, aromatic amines and parabens were selected as acidic, basic and neutral targeted analytes, respectively. According to the structural characteristics and chemical properties of these compounds (Supporting information, Table S1), a new PIL was synthesized. The PIL was obtained by in situ copolymerization of 1-vinyl-3-octylimidazolium tetrafluoroborate (VOI) and dual

cross-linkers (divinylbenzene and N,N-methylene-bisacrylamide). Because there are abundant groups including imidazole, amino, phenyl and alkyl groups in the new adsorbent, it is reasonable to expect that the new PIL can coextract the above-mentioned compounds effectively because multi-interactions including π - π , hydrophobic, hydrogen-bonding and dipole-dipole interactions will involve the extraction procedure. After the optimization of preparation conditions and coextraction parameters, a simple and sensitive methodology combining the SCSE/PIL and liquid desorption (LD), followed by high performance liquid chromatography with diode array detection (SCSE/PIL-LD-HPLC/DAD) for the direct analysis of trace phenols, aromatic amines and parabens in lake, river and reservoir waters was developed.

2. Experimental

2.1. Chemicals

VOI (99%) was purchased from Lanzhou Zhongke Kaite Chemical Co. LTD (Lanzhou, China); divinylbenzene (DB) (80%) and N,N-methylene-bisacrylamide (MB) (98%) were supplied by Sigma-Aldrich Ltd. (Shanghai, China); 1-propanol (97%), 1,4-butanediol (98%) (distilled before use), formic acid (FA) ($\geq 88\%$) and azobisisobutyronitrile (AIBN) (97%, re-crystallized before use) were purchased from Shanghai Chemical Co. (China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, Ohio, USA). Water used throughout the study was purified using a Milli-Q water-purification system (Millipore Corp, Billerica, MA, USA). Aniline (A), 2-nitroaniline (2-NA), 2-nitrophenol (2-NP) and 5-methyl-2-nitrophenol (5-M-2-NP) were supplied by Alfa Aesar Ltd. (Tianjin, China). Heptyl 4-hydroxybenzoate (HHB) and 2-octyl-4-hydroxybenzoate (OHB) were supplied by National Institute for the Control of Pharmaceutical and Biological Products. The chemical properties of the above analytes are shown in Table S1. Water samples were collected from Xiamen and Zhangzhou cities, and filtrated through 0.45 μm membranes. All samples were stored at -4°C before use. Individual stock solutions of analytes were prepared at a concentration of 10.0 mg/L by dissolving methanol and renewed monthly. The standard mixtures of phenols, aromatic amines and parabens were prepared by dissolving 2.00 mg of each compound in methanol in 100 mL volumetric flask. The stock solutions were stored at 4°C and diluted with ultrapure water to give the required concentration.

2.2. Equipments and materials

HPLC analyses were carried out on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A). Sample injection was carried out using a RE3725i auto sample injector with a 20 μL loop (Rheodyne, Cotati, CA, USA), all experiments were performed at 25°C .

The morphologies of PIL were examined by a Model XL30 scanning electron microscopy (SEM) instrument (Philips, Eindhoven, The Netherlands). The pore size distribution of the adsorbent was measured on mercury intrusion porosimeter (MIP) Model PoreMaster-60 (Quantachrome Instruments, Florida, USA). Elemental analysis (EA) was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400. FT-IR was performed on an Avatar-360 FT-IR instrument (Thermo Nicolet, Madison, WI, USA).

2.3. Chromatographic conditions

The separation of targeted analytes was performed on a Kromasil C18 column (5 μm particle size, 250 mm \times 4.6 mm I.D.). Optimum separation was obtained with a binary mobile phase composed of ultrapure water (solvent A) and ACN (solvent B).

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