Talanta 172 (2017) 186–198

Contents lists available at ScienceDirect

Talanta

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

Probing the specificity of polyurethane foam as a ‘solid-phase extractant’: Extractability-governing molecular attributes of lipophilic phenolic compounds

Jie Han[a,b,*], Zhi Cao[c], Wei Qiu[a,b], Wei Gao[b], Jiangyong Hu[d], Baoshan Xing[a,**]

[a] *Paige Laboratory, Stockbridge School of Agriculture, University of Massachusetts Amherst, MA 01003, United States*
[b] *Department of Chemical and Materials Engineering, The University of Auckland, Auckland 1010, New Zealand*
[c] *Department of Chemistry, University of California Berkeley, CA 94720, United States*
[d] *Center for Water Research, Department of Civil and Environmental Engineering, National University of Singapore, Singapore 117576, Singapore*

ARTICLE INFO

Keywords:
Polyurethane foam
Extraction
Sampling
Bisphenol
Alkylphenol
Chlorophenol

ABSTRACT

The long-proposed use of open-cell polyurethane foam (PUF) as a convenient ‘solid-phase extractant’ for aqueous organic compounds has been hindered by a critical lack of understanding on the underlying specificity of its extraction mechanism. In this work, we tasked ourselves to understand the hierarchy of molecular structure, properties, and partitioning characteristics of compounds in PUF and aqueous phase by targeting lipophilic phenolic compounds (LPCs) as a group of primary targets for PUF extraction. Using six structurally related bisphenol analogs as comparative probes, we identified molecular lipophilicity and H-bond acidity as key molecular attributes that governed their extractability by PUF. Molecular modeling study on H-bonding interactions between PUF surrogates, bisphenols, and water molecules elucidated the governing effect of H-bond acidity in the binding affinity of guest molecules onto PUF lone-pair donors. A holistic view must be adopted when assessing the extractability of LPCs with reactive lone-pair donors *e.g.* bisphenol S which forms multidentate H-bond adducts with water molecules. We validated our theory on two model groups of monofunctional LPCs, alkylphenols and chlorophenols, with the observation that the presence of a second proton-donating moiety dramatically enhanced the extractability of bisphenol molecules. The specificity of PUF rendered it selective towards compounds with correlating molecular attributes against other structural analogs and co-existing matrix organics. For LPCs, the PUF macromolecular structure can be conceptualized as a flexible 'molecular zipper network' that is most affinitive towards nonionic, permeable, and lipophilic guest molecules with multiple reactive proton donors.

1. Introduction

A light-weight, flexible, abundant, and widely accessible material, open-cell polyurethane foam (PUF) has many desired material attributes which make it an appealing extraction medium for large-scale environmental sampling [1–3]. Apart from its routine use in passive air sampling, the material is lesser known for its ability to retain organic and inorganic species by functioning as a ‘solid-phase extractant’ in aqueous media [4,5]. Ether-type PUF, in particular, can extract aqueous organic compounds *via* an analogized etheric solvent-extraction mechanism [6]. Early reports on this phenomenon date back to the 1970s [6,7], and research interests on its applications continued into the 2000s [5,8–10].

Despite the long course of studies, the material has not attained widespread usage to date as a practical extraction or sampling medium for organic compounds in aqueous matrices. A seemingly drawback of PUF – compared with other extraction media commonly used in environmental water sampling [11–15] – is its wildly variable and often low extractability towards its target compounds [7,16–18]. Partitioning coefficient (K_{PW}), a key metric for measuring the efficacy of extraction media, was reported at mixed or low levels (*e.g.* below 10^3 L kg^{-1}) in earlier studies [18–22].

The problem does not seem to lie in the material itself but in how we understand its material chemistry. Previous studies, including an early assessment conducted by US EPA [7], inadvertently considered PUF as a versatile extraction medium by pairing it with an arbitrary range of target compounds selected on the basis of their industrial usage and environmental toxicity, without assessing their potential

---

[*] Corresponding author at: Paige Laboratory, Stockbridge School of Agriculture, University of Massachusetts Amherst, MA 01003, United States.
[**] Corresponding author.
E-mail addresses: jiehan@umass.edu (J. Han), bx@umass.edu (B. Xing).

http://dx.doi.org/10.1016/j.talanta.2017.05.020
Received 25 March 2017; Received in revised form 8 May 2017; Accepted 9 May 2017

extractability by PUF. This arbitrary approach has been widely adopted in previous studies and has resulted in mixed outcomes reported on PUF-based extraction and sampling techniques (Table S1). To overcome this, various techniques have been employed to alter the surface and structural properties of PUF [23–25]. Although improvements were generally achieved by those efforts, the custom material synthesis or additional treatment can diminish some key advantages of raw, unmodified PUF as an originally low-cost and widely accessible material.

The arbitrary compound targeting stemmed from a critical lack of understanding of its extraction mechanism and particularly, the underlying specificity of its affinity to aqueous organic compounds. Widely exploited as a versatile extraction medium, a key overlooked aspect of PUF is the lipophilic and nucleophilic nature of its macromolecular chains, which render it intrinsically affinitive to lipophilic and electrophilic penetrants once molecular contact is effected. In his first study, Bowen proposed the etheric solvent extraction analogy to rationalize the apparent sorption properties of PUF for several aqueous organic and inorganic species [6]. This analogy, while widely accepted in later studies [16,18,20,25], was not rigorously validated until recently where we demonstrated a remarkable case of bisphenol A (BPA) retention by several consumer-grade PUFs [26]. The retention was found to proceed *via* solid-phase partitioning which effectively rendered the material an absorptive sink in aqueous media.

The key question, however, remains as to which molecular attributes govern the extractability of aqueous organic compounds and further, how we might use this understanding to guide future applications of PUF-based extraction and sampling techniques. To answer these questions, we must first gain a fundamental understanding on the hierarchy of molecular structure, properties, and partitioning characteristics of compounds in PUF and aqueous phase. To this end, we focused on lipophilic phenolic compounds (LPCs) as a primary group of target compounds for PUF and further selected six bisphenol structural analogs as our initial probing compounds. These not only offered a group of comparative targets for the initial correlation analysis but, given the nucleophilic nature of PUF macromolecular chains, served as molecular probes to examine their interactions with various types of functional groups in PUF. Molecular modeling was found to be an invaluable tool in elucidating differences in molecular H-bond acidity and their governing effect on the affinity of probing molecules to PUF nucleophilic groups. As the competing solvation medium, we examined the role of water molecules and their complicating effect in the extractability of a compound with lone-pair donors. We conclude the study by validating our theories on two model groups of monofunctional LPCs and demonstrating the compound selectivity of PUF extraction in multi-component solutions and simulated water matrices.

2. Material and methods (see Supplementary Methods and QA/QC in the Supplementary Material)

2.1. Materials and reagents

Laboratory-grade PUF was supplied by Restek (Bellefonte, PA) as cylindrical blocks of 60 mm in diameter and 76 mm in length. The material is free of organophosphate or halogenated flame retardant (Fig. S1). Prior to use, PUF blocks were cut and washed briefly with hexane, acetone, methanol, deionized water, and dried at 50 °C. Activated carbon (AC, Darco®, Carbot Noirt), macroreticular divinylbenzene-crosslinked polystyrene resin (dvb-PS, Amberlite™ XAD4, Dow Chemical), single-walled carbon nanotubes (SWCNTs, > 90%, NTP), and octadecyl-bonded silica (Hypersep™ C18 SPE, 40–60 µm) were obtained as benchmark materials (Table S2). Six bisphenols (BPs) and nine monofunctional LPCs including phenol, four alkylphenols, and four chlorophenols were supplied by Sigma-Aldrich and TCI America. Ionic salts, acetic acid (glacial), sodium hydroxide, and humic acids (technical) were supplied by Fisher Chemical for preparing synthetic leachates (Table S3). All chemicals were of reagent grade unless otherwise specified.

2.2. Partitioning and adsorption isotherms

Stock solutions of LPCs were prepared by saturating compounds in deionized water with 5–7 days of magnetic stirring under a controlled lab temperature (20 °C). The solutions were settled for 24 h and filtered by 0.2-µm regenerated cellulose (RC) membranes on a Millipore™ vacuum filtration apparatus. Filtrates were sampled to measure the aqueous solubilities of LPCs at 20 °C. Isotherm experiments were conducted by transferring aliquots of LPC working solutions (1.5–900 µM) into 200-mL Qorpak™ wide-mouth glass jars and mixing with varied weights of PUF (1.2–650 mg) or benchmark materials (20–670 mg) to attain a wide span of solute:solid ratios in solutions. Weighed PUF blocks were squeezed to release air trapped inside after immersing them into the solutions. After the initial mixing, the Qorpak™ jars were sealed with Teflon-lined caps and agitated in a thermostated incubator shaker (New Brunswick Scientific, G25, NJ) at 225 rpm. Kinetic data were acquired in three BP solutions under the same equilibrating conditions. An equal initial molar concentration (4.4 µM, or 1.0–1.5 mg L^{-1}) and material dosage (100 mg, dry weight basis) were applied in each experiment. All PUF blocks were pre-wetted with 2–3 mL deionized water before adding them into the solutions. For dvb-PS and AC, a short period (10–15 s) of hand mixing was also applied to ensure thorough mixing with the solution before shaker agitation was applied. Samples (2 mL) were collected at pre-set time intervals and immediately passed through Phenex™ 0.2-µm RC syringe filters with the first 0.5 mL filtrate discarded. Given its rapid compound uptake, the equilibrating period was set as 24 h for PUF partitioning isotherm experiments and prolonged to 5 days for dvb-PS and AC to attain true equillibria due to their large porosities and surface areas (Table S2).

2.3. Selective extraction in mixed solutions and simulated water matrices

Four sets of mixed BP solutions, each containing 5–6 BPs at an equal molar concentration (*ca.* 0.5, 4.0, 40, or 90 µM), were prepared. The solutions were mixed with PUF at varied dosages (0.05–0.5 g L^{-1}) and equilibrated by 24-h shaker agitation to examine its compound selectivity. Control experiments were conducted separately in pure BP solutions to examine the competitive partitioning effect of BPs. The extraction of BPs was further studied in simulated water matrices to examine the effect of water chemistry and co-extraction of matrix organics by PUF. Solutions containing *ca.* 0.5 µM of all six BPs were spiked with 1.0 or 10 mg L^{-1} humic acids to simulate surface water containing elevated levels of BPs (Table S4). Two synthetic leachates, representing the acetogenic and methanogenic phases of leachates in municipal solid waste landfills, were prepared as described in Table S3 and spiked with *ca.* 90 µM BPs to simulate landfill leachates containing high levels of BPs (Table S4).

2.4. Analytical methods

Samples were analyzed on a Shimadzu Prominence® liquid chromatography system after filtered by Phenex™ 0.2-µm RC syringe filters. For analyte quantification, samples and standards were injected (2–50 µL) into a reverse-phase C18 column (Phenomenex™ Gemini®-NX, 5 µm, 250 × 4.6 mm) and analyzed by a diode array detector. Acetonitrile was mixed with deionized water or 20 mM H_3PO_4 buffer as the mobile phase and pumped isocratically at 1.0 mL min^{-1}. Under these operating conditions, the system recorded a retention time of 4.3–21.3 min for the six BPs and nine monofunctional LPCs with detection limits of 1.0–8.0 µg L^{-1} (Table S5). Concentrations of humic acids were measured on a Shimadzu UV2550 UV/Vis spectrophot-