



Contents lists available at ScienceDirect

Journal of Hazardous Materials

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



Use of fluorescence quenching method to measure sorption constants of phenolic xenoestrogens onto humic fractions from sediment

Yi-Lung Yeh^{a,b}, Kuei-Jyum Yeh^{b,c}, Liang-Fong Hsu^d, Wu-Chou Yu^c,
Ming-His Lee^e, Ting-Chien Chen^{b,c,*}

^a Department of Civil Engineering, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan

^b Emerging Compounds Research Center, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan

^c Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan

^d Department of Applied English, Tainan University of Technology, Tainan City 71002, Taiwan

^e Department of Soil and Water Conservation, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan

HIGHLIGHTS

- Range of log K_{HS} values are 4.59–5.09 (NP), 4.74–5.07 (OP), and 4.80–5.09 (BPA).
- Range of log K_{HS} values are 4.74–5.09 and 4.59–5.09 for BKHS and HMHS.
- LMHS did not show significant sorption ability to phenolic estrogens.
- SUVA₂₅₄ values are 4.29 (HMHS) and 1.31 (LMHS) L m⁻¹ mg-C⁻¹.
- HMHS (1 kDa–0.45 μm) had higher a humification degree than LMHS (<1 kDa).

ARTICLE INFO

Article history:

Received 20 September 2013

Received in revised form 22 March 2014

Accepted 27 March 2014

Available online xxx

Keywords:

Phenolic xenoestrogens

Fluorescence quenching

Humic substances

UV/vis indicators

Excitation–emission matrix (EEM)

ABSTRACT

Humic substance (HS) in sediment can affect hydrophobic organic compound distribution, transportation, bioavailability, and toxicity. This study investigated the HS (BKHS) extracted from sediment and separated it into low molecular humic (LMHS, <1 kDa) and high molecular humic substances (HMHS, 1 kDa–0.45 μm). Nonylphenol (NP), octylphenol (OP), and bisphenol A (BPA) have a significant sorption capacity for HMHS and BKHS solutions. They are xenoestrogenic endocrine-disrupting compounds that are widely produced and discharged to the environment. The log K_{HS} values of the BKHS and HMHS solutions were between 4.74–5.09 L kg-C⁻¹ and 4.57–5.09 L kg-C⁻¹, respectively. However, the three compounds were not sorbed by the LMHS solution. The average values of SUVA₂₅₄ for HMHS and LMHS were 4.29 and 1.31 L m⁻¹ mg-C⁻¹ and the average values of $A_{250-400}$ for HMHS and LMHS were 18.1 and 4.51 nm cm⁻¹, respectively. The HMHS peak position in the fluorescence excitation/emission matrix at longer wavelengths corresponded to the peak position of LMHS, which indicates that the HMHS had a higher degree of humification than the LMHS. The results suggested that the K_{HS} value's dominant factor was the degree of HS humification.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Endocrine disrupting compounds (EDCs) that interfere with the endocrine systems of humans and wild animals have been a

concern worldwide. Phenolic xenoestrogenic compounds such as nonylphenol (NP), octylphenol (OP), and bisphenol A (BPA) are moderately estrogenic compounds. They mimic natural hormones that bind to the estrogen receptor of organisms [1–3], and interrupt the endocrine system. These compounds are heavily produced; the global annual production is more than a half million metric tons for NP and BPA. Furthermore, a high proportion of these compounds are released into the environment [2–4]. These compounds have been found at high concentrations in sediment, even up to the mg kg⁻¹ level [5,6]. Due to anaerobic conditions, such as in

* Corresponding author at: National Pingtung University of Science and Technology, Environmental Science and Engineering, 1, Hsueh Fu Road, Nei-Pu, Pingtung 91201, Taiwan. Tel.: +886 8 7740333; fax: +886 8 7740244.

E-mail address: chen5637@mail.npust.edu.tw (T.-C. Chen).

sediment, they are not easily degraded [2,7] and can last a long time in the environment. When these compounds are released in re-suspension conditions, the benthic systems may cause long-term harm in the environment [2].

These phenolic estrogenic compounds are moderately hydrophobic compounds and the log K_{OW} values are between 3.32 and 4.48 [1,2,8]. They are favored in sorption and distribution in sediment humic substances (HSs). HS affects hydrophobic organic compound (HOC) sorption, distribution, transport, degradation, bioavailability, and toxicity in soil and sediment environments [9–13]. Studies have found that phenolic estrogenic compounds can be adsorbed on sediment, soil, and suspended particulate matter (SPM) [5–8,14–16]. They can bind with colloidal dissolved organic matter (DOM) isolated from river and seawater [17,18]. A few studies have concentrated on the sorption behavior on HS extracted from sediment [11–13].

Fluorescence spectroscopy is a very sensitive technique, which is often used to track the dynamics of marine and freshwater DOM. It is a useful monitoring tool for river water quality, compost, and solid waste landfill leaching water [19–27]. The fluorescence-quenching (FQ) method is widely used to study the sorption behavior of hydrophobic compounds and colloidal DOM and HS. Previous research has focused on the highly hydrophobic compounds such as polychlorinated biphenyls (PCBs), Polycyclic aromatic hydrocarbons (PAHs), and pesticides [9,28–30], but little attention has been applied to moderately hydrophobic compounds [11].

The degree of HS humification in sediment is the most important factor that influences the sorption ability of HOC's sorption on HS. The sorption extent of HOCs on HS is related to the degree of aromatic content, molecular weight, and hydrophobicity of HS [31–34]. River sources receiving livestock animals' wastewater discharge often contain high concentrations of particulate organic matter, which when deposited on sediment may cause a high level of HS in sediment. In addition, these sediments also contain high concentrations of phenolic estrogen compounds [35–38].

This study investigated sorption constants of phenolic xenoestrogens onto humic fractions from river sediment. The extracted alkaline HS solution was separated into HMHS (1 kDa–0.45 μ m) and LMHS (<1 kDa). The HS characteristics were defined via UV/vis and fluorescence methods. Sorption constants between phenolic xenoestrogenic compounds (NP, OP, and BPA) and HS solutions (BKHS, HMHS, and LMHS) were measured with a fluorescence-quenching method. The comparison of sorption capacity of phenolic xenoestrogenic compounds onto individual HS fraction was examined by indicators of UV/vis and fluorescence spectrum.

2. Methods and materials

2.1. Sediment collection and treatment

The studied sediment was collected from Wulo Creek, which is one of the major sources of pollution for Kaoping River, an important river in southern Taiwan. The creek receives a large amount of wastewater discharged from livestock. Water containing high concentrations of organic matter has been reported [38]. Sediment taken back to the laboratory was air dried, then passed through a 0.841 mm sieve, and stored in sealed plastic cans for subsequent tests. The extraction and purification of HS was carried out in accordance with the procedure recommended by IHSS [39]. A 0.1 N HCl solution was added to the sieved sediment to remove the alkaline earth metals and carbonate. The treated sediment was centrifuged (4500 rpm, 20 min) to remove the acid solution and the residual sediment was adjusted to neutral pH with 1 N NaOH. The residual sediment was mixed with a 0.1 N NaOH solution at a ratio of 1/20

(w/v). The HS was extracted from a reciprocating shaker (150 rpm, 24 h). The extracted NaOH solution was centrifuged (4500 rpm, 20 min) to separate HS, and then passed through a 0.45 μ m filter (Pall) to collect the HS (BKHS) solution, which was at an alkaline pH. Sodium azide (0.5%) was added to the BKHS solution to prevent the effect of bacteria on HS, and stored in a 4 °C refrigerator. To avoid contamination, the containers were previously washed with ultrapure water.

2.2. HMHS and LMHS separation

The extracted BKHS solution was separated into HMHS and LMHS solutions using tangential ultrafiltration equipment (Long-Whor, Taiwan) with the ceramic membranes tube (TAMI, France, pore size 1 kDa, membrane area of 320 cm²), operating at a flow rate of 1.67–2.0 L h⁻¹ and a pressure of 5 kg cm⁻². The BKHS solution separated into high and low molecular weight humic substance solutions (1 kDa < HMHS < 0.45 μ m and 1 kDa > LMHS). Three different HS filtrates were measured with dissolved organic carbon (DOC), UV/vis, and fluorescence spectroscopy.

2.3. UV/vis measurements

An aliquot of 5 mg-DOCL⁻¹ from each of the three filtered HS solutions was measured with a UV/vis spectrophotometer (Hitachi, U-2900) for absorbance measurement, on a scanning wavelength of 800–200 nm. Background was corrected according to the Helms et al. [21] method. The average absorbance value of 700–800 nm was adopted as the background value, which was subtracted from the sample value. $SUVA_{254}$ (L m⁻¹ mg-C⁻¹) = (UV₂₅₄/[HS]) × 100, UV₂₅₄ was the UV/vis absorbance at 254 nm (cm⁻¹) of the sample, and [HS] was the DOC concentration (mg-CL⁻¹) of the HS solution [40]. UV/vis indicator A_{250} (nm cm⁻¹) was the integration area of absorbance at a wavelength interval of 250–400 nm [21].

2.4. Fluorescence spectroscopy

In this study, three-dimensional fluorescence excitation/emission matrix spectroscopy (EEM) was recorded. The emission wavelength (E_m) was the EEM X-axis. The Y-axis was the excitation wavelength (E_x) and the Z-axis was the fluorescence intensity. The peak position in EEM evaluated the HS species. An aliquot of 5 mg-DOCL⁻¹ for each of the three HS solutions was measured by fluorescence spectrophotometer (Hitachi, F-7000). Before measurement, the HS solution was adjusted to pH = 3 with 0.3 N H₂SO₄. Fluorescent scanning conditions were: excitation wavelength 200–450 nm, 5 nm increase, emission wavelength 250–550 nm, 2 nm increase, the scan rate 2400 nm min⁻¹, the slit width 5 nm, and the voltage amplifying of 700 V. The spectra were obtained by subtracting an ultrapure water blank spectrum, recorded in the same condition, to eliminate the Raman scatter peaks.

Fluorescent indicators included the FIX, with an excitation at wavelength 370 nm, and the fluorescence intensity ratio of emission wavelengths at 450 nm and 500 nm [41,42]. The BIX calculated the fluorescence intensity ratio of the emission wavelength at 380 nm/430 nm and the excitation wavelength at 310 nm [43]. The HIX was calculated when the excitation wavelength was 254 nm. The sum of the emission wavelength at 435–480 nm was divided by the sum of the emission wavelength at 300–345 nm [44].

2.5. Fluorescence quenching

Seven different HS concentrations were prepared (1–20 mg-CL⁻¹). Next, 1 mg L⁻¹ standard solution (NP, OP, and BPA) was

Download English Version:

<https://daneshyari.com/en/article/576651>

Download Persian Version:

<https://daneshyari.com/article/576651>

[Daneshyari.com](https://daneshyari.com)