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Biosorption of nonylphenol by pure algae, field-collected planktons and their fractions

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ABSTRACT

Algal samples were fractionated into lipid (LP), lipid free (LF), alkaline nonhydrolyzable carbon (ANHC), and acid nonhydrolyzable carbon (NHC) fractions, and were characterized by the quantitative ^{13}C multiCP NMR technique. The biosorption isotherms for nonylphenol (NP) were established and compared with previously published data for phenanthrene (Phen). The log K_{OC} values are significantly higher for the field-collected plankton samples than for the commercial algae and cultured algae samples, correlating with their lipid contents and aliphatic carbon structure. As the NHC fraction contains more poly(methylene) carbon, it exhibits a higher biosorption capacity. The sorption capacities are negatively related to the polarity index, COO/N–C=O, polar C and O-alkyl C concentrations, but are positively related to the H/O atomic ratios and poly(methylene) carbon. The higher sorption capacities observed for NP than for Phen on the investigated samples are explained by specific interactions such as hydrogen bonding and π–π interaction.

1. Introduction

Nonylphenol (NP) is one of endocrine disrupting chemicals (EDCs) since it is able to mimic natural estrogens and disrupts the endocrine systems of higher organisms by interacting with the estrogen receptor (Soares et al., 2008; Vazquez-Duhalt et al., 2005). NP can also affect plankton community structure when released into an aquatic environment (Gao et al., 2011a). Traditional techniques for NP removal such as adsorption on activated carbon, photo-oxidation, and ozone treatments have been studied and found to be effective, but cost-effectiveness is relatively low and limits widespread practical use (Nakada et al., 2006; Kawasaki et al., 2001). Biosorption is a physicochemical process that utilizes inexpensive live or dead biomass to remove contaminants and deals with the sorption of a chemical substance in/on a biological matrix/surface (Kratochvil and Volesky, 1998; Chen et al., 2010). Biosorbents are prepared from the naturally abundant and/or waste biomass of algae, moss, fungi or bacteria that has been sterilized by washing with acids and/or bases before final drying and granulation (Kratochvil and Volesky, 1998). Moreover, algae are found to be highly effective, reliable, and economic in the removal of contaminants from aqueous solutions (Kratochvil and Volesky, 1998; Navarro et al., 2008).

The coupling between primary producer biomass dynamics and the distribution and fate of persistent organic pollutants in a lake pelagic ecosystem has been reported (Nizzetto et al., 2012). Algae are the important primary producers in aquatic ecosystems, and play an important role in determining the transport and fate of NP in aquatic systems. Due to their substantial biomass and extensive range of habitat and diversity, algae constitute the largest and most widely distributed group of photosynthetic organisms in aquatic ecosystems. Algae act as precursors of natural organic matter (NOM) in sediment organic matter through selective preservation, which is based on the presence of highly aliphatic biomacromolecules, termed algaenans (Gelin et al., 1999).

Investigation on biosorption of toxic organic compounds with biomass showed that better removal was obtained with dead biomass than with live biomass (Aksu, 2005). Most studies reported that structural components of biomass affect the biosorption of

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hydrophobic organic compounds (Chen et al., 2005; Chen and Schnoor, 2009; Kwon et al., 2007; Li et al., 2010; Wang et al., 2007; Wang and Xing, 2007). In recent studies, the sorption mechanisms of EDCs by activated sludge biomass, stream biofilms, synthetic membrane vesicles and condensed SOM of soils and sediments have been investigated (Kwon et al., 2007; Sun et al., 2010; Writer et al., 2011; Xu et al., 2008). Other investigation reported that the molecular interactions such as hydrogen bonding and hydrophobic interaction could play an important role for the NP biosorption on biomass (Lang et al., 2009). However, few investigations are available about biosorption mechanisms of NP by algae (Gao et al., 2011a, 2011b).

This study investigates the biosorption of NP on three field-collected plankton samples, two cultured algal species, and three commercial algal species and their algal fractions. In our previous study (Zhang et al., 2013a), acid nonhydrolyzable carbon (NHC) is considered to be organic carbon in algae not soluble in acid, base, and organic solvents. We hypothesize that some of the algal fractions such as NHC and lipid (LP) are very important to the biosorption of NP. We examine the biosorption behaviors of NP on the bulk algal samples (OS) and their isolated organic matter fractions, relate the biosorption behaviors of NP to the compositions of the algal samples determined by elemental analysis and quantitative solid-state NMR, and compare biosorption behaviors of NP with those of phenanthrene (Phen) to infer the possible biosorption mechanism.

2. Material and methods

2.1. Algal samples and isolation of algal fractions

The sample set included the following algae: two cultured algal species (*Chlorella, Sphaerellopsis*) cultured in lab conditions, three commercial algal species (*Spirulina, Seaweed, Porphyra*) purchased in a supermarket, and three field-collected plankton samples from two eutrophication lakes. The LHH25 sample was collected by using 25 size plankton net in August 2011 from the Liuhuahu park in Guangzhou city, China. The LHHPOM sample was separated from the large volume of water sample collected in the Liuhuahu park by using a continuous flow centrifuge at 8000 rpm. The YTDQ algal sample was collected by using 25 size plankton net in September 2011 from the Yanta Bridge reservoir in Zengcheng city, China. The sample details were described elsewhere (Zhang et al., 2013a).

The three commercial algae were fractionated into the lipid (LP), lipid free (LF), alkaline nonhydrolyzable carbon (ANHC), and acid nonhydrolyzable carbon (NHC). The flow chart in Fig. S1 in Supplemental data summarizes the major steps for isolation of the algal fractions, as described elsewhere (Zhang et al., 2013a). Briefly, the OS samples were extracted to separate lipids by using Soxhlet extraction with 2:1 $CHCl_3/CH_3OH$ (v/v) for 24 h. The lipid fractions (LP) were dried at 100 °C. Subsamples of the lipid-free fractions (LF) were saponified for 1 h in 1 M KOH in 85:15 methanol/H_2O (v/v). The alkaline nonhydrolyzable carbon (ANHC) fractions were hydrolyzed twice with 2 M trifluoroacetic acid (TFA, Acros) at 100 °C for 3 h. Subsequently subsamples of ANHC fractions were hydrolyzed in 4 and 6 M TFA at 100 °C for 18 h. Finally, the residual hydrolyzable organic matter was removed with 6 M HCl at 110 °C for 24 h.

2.2. Characterization of algae and algal fractions

The algal and zooplankton samples were then analyzed for C, H, N, and O using an Elementar Vario ELIII or a Heraeus CHN-O-RAPID elemental analyzer. The elemental compositions of the investigated samples are summarized in Table 1 and Table S1 in Supplemental data.

Solid-state NMR experiments were performed on a Bruker DSX400 spectrometer operating at 400-MHz ^1H and 100-MHz ^{13}C frequencies. The ^{13}C chemical shifts were referenced to tetramethylsilane, using the COO resonance of glycine in the α-modification at 176.46 ppm as a secondary reference. The high-spinning speed multi-ramped amplitude cross polarization/magic angle spinning technique was applied for acquiring quantitative ^{13}C NMR spectra (Johnson and Schmidt-Rohr, 2014). This multiple-cross polarization (multiCP) technique provides a simple, robust way to obtain quantitative solid-state ^{13}C NMR spectra of organic materials, with

Table 1
Elemental compositions of the original algal samples and their fractions.

Sample	N %	C %	H %	O %	CHNO %	C/N	H/C	H/O	O/C	(O + N)/C
OS										
Spirulina	3.72	33.9	4.97	38.0	80.6	10.6	1.76	2.09	0.84	0.93
Seaweed	2.17	28.8	4.29	33.3	68.6	15.5	1.79	2.06	0.87	0.93
Porphyra	5.43	42.7	6.45	42.7	97.3	9.17	1.81	2.42	0.75	0.86
Chlorella	4.32	25.5	4.85	30.9	65.5	6.89	2.28	2.51	0.91	1.05
Sphaerellopsis	4.06	26.0	4.91	31.2	66.2	7.47	2.27	2.52	0.9	1.03
LHH25	3.07	20.2	3.59	18.4	45.3	7.68	2.13	3.12	0.68	0.81
LHHPOM	5.87	31.9	5.11	26.9	69.8	6.34	1.92	3.04	0.63	0.79
YTDQ	7.42	41.8	6.56	34.9	90.7	6.57	1.88	3.01	0.63	0.78
LP										
Spirulina	0.83	66.1	9.09	21.6	97.6	92.9	1.65	6.73	0.25	0.26
Seaweed	0.92	68.2	8.84	21.4	99.4	86.5	1.56	6.61	0.24	0.25
Porphyra	1.59	62.4	8.86	29.7	102	45.8	1.7	4.77	0.36	0.38
LF										
Spirulina	4.59	28.6	4.26	31.5	69	7.27	1.79	2.16	0.83	0.96
Seaweed	2.74	25.4	4.05	29.9	62.1	10.8	1.91	2.17	0.88	0.97
Porphyra	5.73	42.9	6.5	42.3	97.3	8.73	1.82	2.46	0.74	0.85
ANHC										
Spirulina	0.87	30.0	4.21	44.2	79.3	40.2	1.69	1.52	1.11	1.13
Seaweed	1.2	31.4	4.2	40.6	77.4	30.5	1.61	1.66	0.97	1.00
Porphyra	0.61	40.5	6.18	51.0	98.3	77.5	1.83	1.94	0.94	0.96
NHC										
Spirulina	0.71	36.1	3.40	34.2	74.4	59.32	1.13	1.59	0.71	0.73
Seaweed	0.81	38.4	3.21	32.7	75.1	55.31	1.00	1.57	0.64	0.66
Porphyra	0.92	43.1	4.19	32.9	81.1	54.66	1.17	2.04	0.57	0.59