Chemosphere 174 (2017) 739–746

Contents lists available at ScienceDirect

Chemosphere

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

Effects of molecular size fraction of DOM on photodegradation of aqueous methylmercury

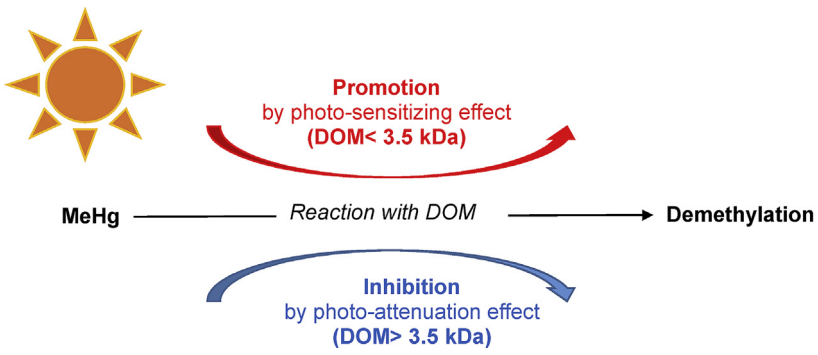
Moon-Kyung Kim [a, b], A-Young Won [a], Kyung-Duk Zoh [a, b, *]

[a] Department of Environmental Health Sciences, School of Public Health, Seoul National University, Seoul 08826, South Korea
[b] Institute of Health & Environment, Seoul National University, Seoul 08826, South Korea

HIGHLIGHTS

- We examined the effect of DOM in humic substances on the photo-degradation of MeHg.
- DOM fraction of MW < 3.5 kDa showed the highest photo-degradation rate of MeHg.
- MeHg photodegradation increased at alkaline pH due to OH radical production.
- Photo-degradation of MeHg increased with increasing DOM concentration.
- Radicals produced by DOM under MW < 3.5 kDa increased photo-degradation of MeHg.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 October 2016
Received in revised form
26 January 2017
Accepted 5 February 2017
Available online 6 February 2017

Keywords:
Methylmercury
Size fraction
Dialysis
DOM
Photo-attenuation
Radical scavenger

ABSTRACT

This study investigated the photodegradation kinetics of MeHg in the presence of various size fractions of dissolved organic matter (DOM) with MW < 3.5 kDa, 3.5 < MW < 10 kDa, and MW > 10 kDa. The DOM fraction with MW < 3.5 kDa was most effective in MeHg photodegradation. Increasing UV intensity resulted in the increase of photodegradation rate of the MeHg in all size of DOM fractions. Higher rates of MeHg degradation was observed at higher pH. For the portion of MW < 3.5 kDa, the photodegradation rate of MeHg increased with increasing DOM concentration, indicating that radicals such as singlet oxygen ($^1O_2$) radicals can be effectively produced by DOM. At higher portion of MW > 3.5 kDa, the inhibition of MeHg degradation was observed due to the effect of DOM photo-attenuation. Our result indicates that radical mediated reaction is the main mechanism of photodegradation of MeHg especially in the presence of MW < 3.5 kDa. Our results imply that the smaller molecular weight fraction (MW < 3.5 kDa) of DOM mainly increased the photodegradation rate of MeHg.

1. Introduction

Dissolved organic matter (DOM) is ubiquitous in the aquatic environment, formed by abiotic and microbial transformations of plants and animal materials. DOM originates from different sources such as organism residues, soil humus or other organic wastes (Kalbitz et al., 2000). DOM is a diverse and complex mixture with a

* Corresponding author. Department of Environmental Health Sciences, School of Public Health, Seoul National University, Seoul 08826, South Korea.
E-mail address: zohkd@snu.ac.kr (K.-D. Zoh).

http://dx.doi.org/10.1016/j.chemosphere.2017.02.033
0045-6535/

wide range of molecular weights and chemical structures that may exert multiple functions in natural environments (Frimmel, 1998).

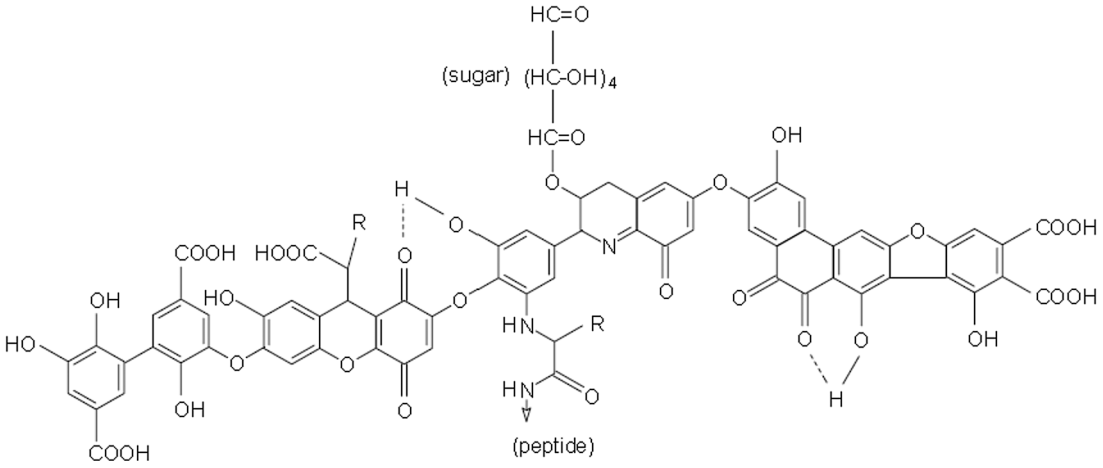
Among the DOM, humic acid is known to be the fraction of DOM with an average molecular weight (MW) between 2000 and 3000 Da, and is known to be the major extractable component of DOM in soil (Peuravuori et al., 2002). Fulvic acid is the fraction of DOM with average MW less than 1000 Da. DOM has a high portion of oxygen-containing functional groups, such as OH and COOH groups. The low MW fulvic acids have higher oxygen but lower carbon contents than the high MW humic acids. While the oxygen in fulvic acids can be accounted for largely in known functional groups (COOH, OH, C═O), a high portion of the oxygen in humic acids seems to occur as a structural component of the nucleus (Peña-Méndez et al., 2005; Alvarez-Puebla et al., 2006) (Table 1). Theses functional groups absorb solar radiation between 300 and 500 nm to reach an excited state, hence generating free radicals that cause photo-oxidation of organic contaminants (Vaughan and Blough, 1998; Chen et al., 2003; Chin et al., 2004; Chowdhury et al., 2011; Jacobs et al., 2011). DOM interacts with other radical forming constituents potentially making it a dominant variable in photolysis (Gerecke et al., 2001; Gu et al., 2011).

These DOM can also plays an important role in the speciation and bioavailability of mercury (Hg) (Amon and Benner, 1996; Benoit et al., 1999, 2001) and MeHg (O'Driscoll and Evans, 2000) in aqueous systems. DOM can strongly interact with Hg, thus affecting fate, transformation, and bioavailability of Hg in water systems (Haitzer et al., 2002; Ravichandran, 2004). DOM is known to directly bind Hg(II) (Ravichandran, 2004; Han et al., 2007) and methylmercury (MeHg) (Hintelmann et al., 1995; Khwaja et al., 2010).

Recent studies have shown that DOM plays a direct role in photodegradation of MeHg. Li et al. (2010) showed that MeHg degradation rates decreased with increasing bulk DOM concentration due to the reduced penetration of UV light. In our previous research, the presence of DOM such as humic acid lowered the photodegradation rate of MeHg by the radical scavenging effect (Kim and Zoh, 2013). In contrast, Zhang and Hsu-Kim (2010) reported that the binding of MeHg to thiol groups within DOM increased the photo reactivity of the MeHg and thus its degradation rate. Another study showed that, as further complicating the role of DOM in MeHg cycling, the binding of Hg to DOM decreased photolytic Hg reduction from Hg(II) to Hg(0), keeping the Hg(II) available for re-methylation in the system (O'Driscoll et al., 2006). This complexity of the MeHg-DOM interactions highlights the need for a more complete understanding of the DOM in a particular system to predict photodegradation of MeHg in water. Recently, according to Qian et al. (2014), DOM containing both thiol and aromatic moieties within the same molecule increased MeHg

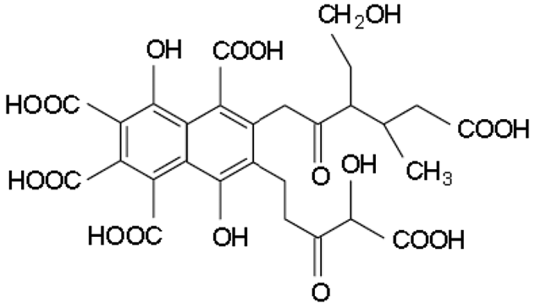
Table 1
Physicochemical properties of humic acid and fulvic acid.

Molecular structure of humic acid



*R can be alkyl, aryl or aralkyl.

Molecular structure of fulvic acid



Substances	% dry ash-free basis			
	C	H	O	N
Elemental composition of humic and fulvic acid				
Fulvic acid	44–49	3.5–5.0	44–49	2.0–4.0
Humic acid	52–62	3.0–5.5	30–33	3.5–5.0