



Dissolved organic matter affects the bioaccumulation of copper and lead in *Chlorella pyrenoidosa*: A case of long-term exposure



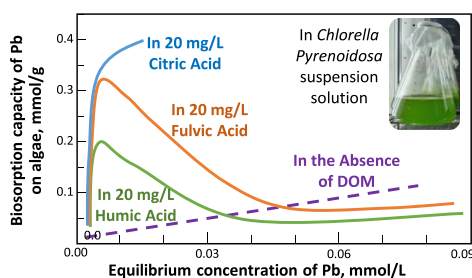
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HIGHLIGHTS

- Metal biosorption by *algae* was studied in 10-day tests in the presence of DOM.
- DOM inhibited Cu's bioavailability to *C. pyrenoidosa* by increasing its MAC.
- DOM greatly increased Pb biosorption capacity on algae.
- Pb maximum biosorption capacity changed as DOM concentration and MW increased.
- Stoichiometry relationships verified the ternary complex of Pb-DOM-alga formed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 December 2016

Received in revised form

21 January 2017

Accepted 23 January 2017

Available online 2 February 2017

Handling Editor: Jim Lazorchak

Keywords:

Citric acid

Fulvic acid

Humic acid

Freshwater alga

Heavy metal

ABSTRACT

This study evaluated the impact of dissolved organic matter (DOM) of varying molecule weights (MWs) on long-term exposure to Cu and Pb in *Chlorella pyrenoidosa*. Citric acid, fulvic acid, and humic acid, in the order of increasing MWs, were selected to represent DOM. The results showed that DOM with larger MWs had stronger inhibitory effects on the bioavailability of Cu to algae. However, the biosorption isotherm of Pb in the presence of DOM was different: as Pb equilibrium concentration increased, the biosorption capacity increased sharply to a maximum, then decreased. The maximum values ranged between 0.186 and 0.398 mmol g⁻¹, as the solution DOM concentration and MW changed, exhibiting a stoichiometric relationship between DOM, Pb and algae. The ternary complex of Pb-DOM-alga formed in a limited Pb concentration range, and increased the percentage of internalized Pb. This research helps to understand the role of DOM in metal uptake in phytoplankton.

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1. Introduction

Heavy metal contaminants that enter the aquatic ecosystem are not biodegradable and tend to accumulate in living organisms, causing various disorders (Horvat et al., 2007). Heavy

metals could be accumulated in living freshwater algae in aqueous solution (Atici et al., 2010), and the process of bioaccumulation by freshwater algae has been used to remove metals from aquatic solution and wastewater (Wang et al., 2016). The removal efficiency by algae can be very high even under very low heavy metal concentrations in aqueous solutions (Shamshad et al., 2015). Peat treated with microalga was proved be useful for the purification of water contaminated by heavy metals (Lourie and Gjengedal, 2011). Much research has focused on

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Abbreviations

DOM	dissolved organic matter
MW	molecule weights
CA	citric acid
FA	fulvic acid
HA	humic acid
OD	optical density
EDTA	ethylenediaminetetraacetic acid
MAC	maximum allowable concentration

bioaccumulation in binary mixtures of algae and heavy metals (Arief et al., 2008). Established models, such as the free-ion model and the biotic ligand model, have been employed to predict the bioavailability or toxicity of heavy metals (Gao et al., 2016). However, the efficacy of these models is called into question when dissolved organic matter (DOM) is present. For example, Pb biouptake by green microalgae in the presence of humic acid was higher than predicted from the measured free metal concentration (Parent et al., 1996). However, it is difficult to quantitate the contribution of DOM to the bioavailability and toxicity of heavy metals in aquatic systems because DOM is a complex mixture of ill-defined components.

DOM from various sources and with different molar weights exhibit different binding capacities to heavy metals. For example, the binding ability of exogenous DOM was higher than endogenous DOM in Tai Lake, and the binding ability of DOM derived from aquatic macrophytes was higher than DOM derived from algae (Zhang et al., 2014). Humic and fulvic acids contributed more DOM-binding Pb to cellular Pb, while alginate contributed very little (Lamelas and Slaveykova, 2008). Colloidal organic matter separated from wastewater treatment plants was found to associate with Ag, Cd, Cu, Cr, Mn and Zn in the low molar mass fraction, while a comparable association with Al, Fe and Pb was observed with the low and high molar mass fractions (Worms et al., 2010). DOM of molar weight greater than 1 kDa decreased the concentration of free Cu²⁺, as well as its availability and toxicity to lettuce (Wang et al., 2010). The physical properties and reactivity of DOM may depend on the nature of the heavy metals present (Zhao and Wilkinson, 2015). DOM of high molecular weight (>1 kDa) generally had higher log *K* and binding fluorophore abundance compared to low molecular weight (<1 kDa) DOM in the presence of Cu and Ca, but not Hg (Chen et al., 2013). Slaveykova reported that the uptake of Pb by *C. kesslerii* in the presence of colloidal organic matter was quite higher than that of Cd (Slaveykova and Wilkinson, 2002).

In contrast to the substantial work on binary systems of algae and metals, the role of DOM in metal uptake by algae in ternary systems is not well understood. Only a few works examining Pb, Cd and rare earth elements have been published (Lamelas and Slaveykova, 2007; Slaveykova, 2007). Pb and rare earth elements showed enhanced biouptake than was predicted by BLM, which was attributed to the formation of a ternary complex {L-HM-R} (Zhao and Wilkinson, 2015). The interactions between DOM, heavy metals and algae in the ternary system are complicated, as each pair is also known to interact in a binary fashion. The average time required for algae to adsorb heavy metal was approximately 30 min to 2 h; in the case of DOM, the time was shortened to less than 10 s (Lamelas et al., 2009). On the other hand, heavy metal biosorption in algae in the presence of DOM was far from equilibrium after a short-term exposure of 30-min (Praveen and Vijayaraghavan, 2015). The objective of this work was therefore to study the role

of DOM of varying molar weights on the biosorption of Cu and Pb by *C. pyrenoidosa* in long-term experiments.

Citric acid (CA) purchased from a chemical supplier, as well as fulvic acid (FA) and humic acid (HA) isolated from the Suwannee River, were selected to represent DOM of different molar weights because they are well-characterized in the literature (Lamelas et al., 2009). CA, FA, and HA represent low, medium and high molar weight DOM, respectively. Cu and Pb were selected due to their environmental relevance as well as their contrasting chemical properties. Cu is an essential nutrient that can be toxic when the concentration rises above nutritional requirements. Pb is generally considered to be a nonessential and toxic element to cells; however, it has a pronounced affinity for algae and can form a ternary complex between Pb(II), algae and DOM, although there is little evidence for the latter (Slaveykova, 2007; Lamelas et al., 2009). Adsorbed and intracellular metals in algae were separated by duplicate extraction with 4 mL 0.01 mol L⁻¹ EDTA solution.

2. Material and methods

2.1. Experimental materials and standard solution

C. pyrenoidosa, obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, was cultured in SE (Bristol's solution) in an incubator (Hengyi MGC-450HP-2, Shanghai, China) at a constant temperature of 25 °C and a 12:12 h light: dark regime, with shaking twice a day. Algal cells were harvested when algal optical density (OD) was increased from 0.1 to 0.6 by gentle filtration, washed with a metal-free medium and re-suspended to an experimental density.

Algal density was expressed as an OD value measured at 660 nm with a spectrophotometer (AoxiUV754N, Shanghai, China) at pre- and post-test, and algal mass concentration and cell density were calculated as the linear equations established in our laboratory, as follows:

$$C_{\text{alga}}, \text{mg/L} = 349 \times OD_{660} + 0.004, R^2 = 0.9997 \quad (1)$$

$$N_{\text{alga}} \times 10^4 \text{cell/mL} = 3945 \times OD_{660} - 46.6, R^2 = 0.9991 \quad (2)$$

where C_{alga} is the freeze-dried algal mass per unit volume of algal solution, mg L⁻¹ and N_{alga} is the cell number measured with a Coulter Counter equipped with a 50 μm sensor orifice (Multisizer 3, Beckman Coulter, Miami FL). All experiments reported herein were conducted with an initial cell concentration of 0.1 OD if not otherwise specified. This is equivalent to a 34.9 mg L⁻¹ dried algal mass concentration or 3.48 × 10⁶ cell number concentration, and algae were at mid-exponential growth state.

FA and HA, which were isolated from the Suwannee River, were obtained from the International Humic Substances Society (IHSS). CA (analytical reagent, AR) was obtained from Zhejiang Changqing Chemical Co., Ltd. (Hangzhou, China) Stock solutions of CA, FA and HA (1000 mg L⁻¹) were prepared in Milli-Q (Millipore, USA) water and stored at 4 °C for a maximum of 20 days.

Standard solutions of metals (1000 mg L⁻¹, National Institute of Metrology, Beijing, China) for experiments and the calibration of atomic absorption spectroscopy determinations were diluted to appropriate concentrations using 2% HNO₃ (Lingfeng Chemical Co. Ltd., Shanghai, China).

2.2. Biosorption in binary systems

The kinetics of metal uptake were determined by measuring the amount of metal biouptake (including adsorbed and internalized)

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