

Marine Macroalgae: Effect of Synthetic Aminopolycarboxylate Ligand on Metal (Cd and Cu) Uptake Mechanism

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INTRODUCTION

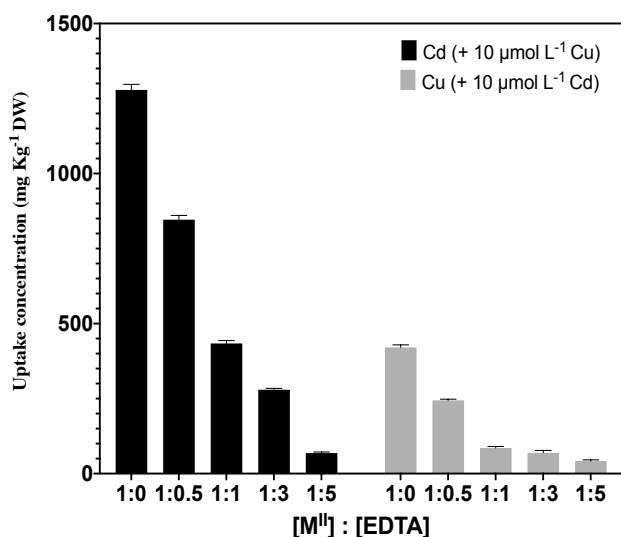
Metal uptake by macroalgal species largely depends on supplied elements, chemical affinities for ionic-binding sites of extracellular and biological demand of algae itself (Paoli L., Vannini A. et al., 2018). Conversely, excessive amount of strong chelating agents such as ethylenediaminetetraacetic acid (EDTA) in environmental system possibly has negative impacts on metal uptake (Pascual G., Sano D. et al., 2020) and growth inhibition (Hasegawa H., Nozawa A. et al., 2018) of algal species. The effects of synthetic and biodegradable chelating ligands on metal uptake and mobility in growth medium by plant and marine microalgae have been extensively studied (Hasegawa H., Rahman M A. et al. 2010). However, to date, limited information is available on the metal uptake mechanism by marine macroalgae in the presence of chelating ligand like EDTA. Therefore, the present study aims to breach the research gap by investigating the uptake mechanisms of two divalent metals (Cd^{II} and Cu^{II}) in growth medium, acclimatized with synthetic aminopolycarboxylates: EDTA, by a marine macroalga: *S. hemiphyllum*. The study also determines the optimum environmental conditions for metal uptake process when exposed to single (Cd^{II} or Cu^{II}) and double (Cd^{II} and Cu^{II}) metals in EDTA adjusted culture medium.

MATERIALS AND METHODS

In this study, two different experimental conditions were employed in culture media preparation: single metal (Cd^{II} or Cu^{II}) exposure and double (Cd^{II} and Cu^{II}) metal exposure. In addition, various ratios of metal and EDTA ([M^{II}]: [EDTA]) such as 1:0, 1:0.5, 1:1, 1:3, 1:5 was applied to evaluate the uptake concentration and stress level of *S. hemiphyllum*. EDTA was added into the 250 mL of culture medium (natural seawater enriched with 1% PES medium). For single metal exposure, 10 µmol L⁻¹ of Cd^{II} or Cu^{II} and for double metal exposure, 10 µmol L⁻¹ of Cd^{II} and 10 µmol L⁻¹ of Cu^{II} was used. The algal cultivation was maintained in an incubator room at constant temperature (20 °C) at irradiation of 90 µmol photons m⁻² S⁻¹ with 12/12 h light and dark cycle for 7 days.

RESULTS AND DISCUSSION

Based on uptake concentration and photosynthetic efficiency, the optimum condition was observed at 1:0.5 $[M^{II}]:[EDTA]$ concentration ratio (Figure 1). In single metal exposure experiment, the uptake concentration of divalent metals were 600.23 ± 12 and 282.71 ± 8 $mg\ Kg^{-1}$ DW for Cd^{II} and Cu^{II} , respectively. In double metals exposure, the uptake concentrations were 846.13 ± 14 $mg\ Kg^{-1}$ DW of Cd^{II} and 244.23 ± 3 $mg\ Kg^{-1}$ DW of Cu^{II} . Photosynthetic activities for single metal exposure conditions were 0.75 ± 0.02 and 0.73 ± 0.03 for Cd^{II} and Cu^{II} , respectively, while for double metal exposure were 0.74 ± 0.03 , which was not



significantly different compared to control ($p > 0.05$). Uptake inhibition started at 1:1 $[M^{II}]:[EDTA]$ in both the metal exposure condition when uptake concentration of Cd^{II} and Cu^{II} was reduced to more than 2-fold. Meanwhile, the higher concentration of metal was accumulated in *S. hemiphyllum* in the absence of EDTA (1:0). But photosynthetic activity was not detected at this level, indicated that sufficient EDTA was required to mitigate stress level by *S. hemiphyllum* on metal exposure condition.

Figure 1. Effect of metal:EDTA concentration ratio on metal uptake by *S. hemiphyllum*

CONCLUSION

In this study, various ratios of divalent metal and EDTA were taken into consideration to evaluate the optimum condition for metal uptake by *S. hemiphyllum*. Ratio 1:0.5 of $[M^{II}]:[EDTA]$, where EDTA concentration was sufficient to increase the uptake tendency and elevates stress level of macroalgae on metal exposure during algal cultivation for 7 days. The higher concentration of EDTA could inhibit the accumulation of metal, however, in the absence of EDTA may also cause negative impacts on *S. hemiphyllum* in terms of growth performance and metabolic activities.

REFERENCES

- Hasegawa, H., Rahman, MA. et al., Effect of biodegradable chelating ligand on iron bioavailability and radish growth, *Journal of Plant Nutrition*, 33, 933–942, 2010.
- Hasegawa, H., Nozawa, A. et al., Effect of biodegradable chelating ligands on Fe uptake in and growth of marine microalgae, *Journal of Applied Phycology*, 30, 2215–2225, 2018.
- Paoli, L., Vannini, A. et al., Competition between heavy metal ions for binding sites in lichens: Implications for biomonitoring studies, *Chemosphere*, 199, 655–660, 2018.
- Pascual, G., Sano, D. et al., Effects of chemical interaction of nutrients and EDTA on metals toxicity to *Pseudokirchneriella subcapitata*, *Ecotoxicology and Environmental Safety*, 203, 110966, 2020.