Supporting information for "Ammonium interference reduced copper uptake by formaldehyde crosslinked *Sargassum* sp. seaweed"

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Effectiveness of formaldehyde crosslinking in reducing organic leaching

Given the diversity of *Sargassum* species present, subtle differences in the cell wall structure of specific species and strains, and small (but noticeable) differences in how formaldehyde interacts with chemical moieties on algal surface, the effectiveness of formaldehyde crosslinking, as measured by leaching of organics from seaweed upon solution contact, would need to be assessed in each pretreatment. While the types and relative abundances of individual organic compounds leached can be determined via high performance liquid chromatography mass spectrometry (HPLC-MS), the high cost and lengthy analytical runs meant that the approach is not economical. On the other hand, if the objective is to gain a holistic understanding of treated SW (i.e., formaldehyde crosslinked) stability across a pH range, a variable amenable to facile measurement (at sufficient throughput) via instrumented techniques would be desirable. To this end, total organic carbon (TOC), defined as the subtraction of inorganic carbon (IC) from total carbon (TC), satisfy all aforementioned analytical criteria. Thus, using TOC as a lumped proxy parameter for the ensemble of organic compounds solubilized from seaweed [1], batch experiments were performed to quantify organic leaching at various initial pH with biomass concentration identical to that in subsequent batch kinetic and equilibrium sorption experiments.

Within the pH range of 3 to 9, organic leaching was ~ 4 ppm, but there was a significant increase in TOC beyond pH 9 (Fig. S1), which suggested disintegration of the extracellular cell wall matrix in highly alkaline solution. Visual observation of the solutions after biomass contact revealed no substantial yellow discoloration, which corroborated with the low TOC detected. In contrast, higher TOC values (~ 20 ppm after filtration) were observed for unmodified *Sargassum* sp. [2]. Application of the treated SW to Cu^{2+} removal at trace concentration (1000 ppb) revealed a biphasic TOC time profile with an initial rapid phase followed by more gradual increase in TOC (Fig. S2). Essentially, time course evolution of TOC was similar to that of Cu^{2+} uptake by *Sargassum* sp. (i.e., a rapid initial phase followed by a more gradual secondary phase); suggesting that organics leached from seaweed (modified or pristine) might be related to metal uptake [3]. The equilibrium TOC observed was ~ 4 to 4.5 ppm, which was in good agreement with that observed in batch equilibrium tests described earlier. However, the observed results should be understood in the context that the solutions used in both sets of experiment (i.e., ultrapure water and 1000 ppb copper solution) did not differ significantly in ionic strength and composition. Thus, the low copper concentration solution did not result in greater organic leaching, which precluded the discrimination of background organic leaching from that induced by metal uptake. Collectively, the experiment data revealed that formaldehyde crosslinking stabilized seaweed's cell wall structure and reduced organic leaching. Furthermore, the treated SW showed good structural stability across a wide pH range from 3 to 9; thereby, opening up its application in remediating a variety of industrial effluents and natural waters. Finally, greater stability of treated SW at pH 3 relative to pH 10 raise interesting questions concerning the structural characteristics, biochemical composition (lipid, proteins, etc.) and functional groups, that together, accounts for the observed stability trend.

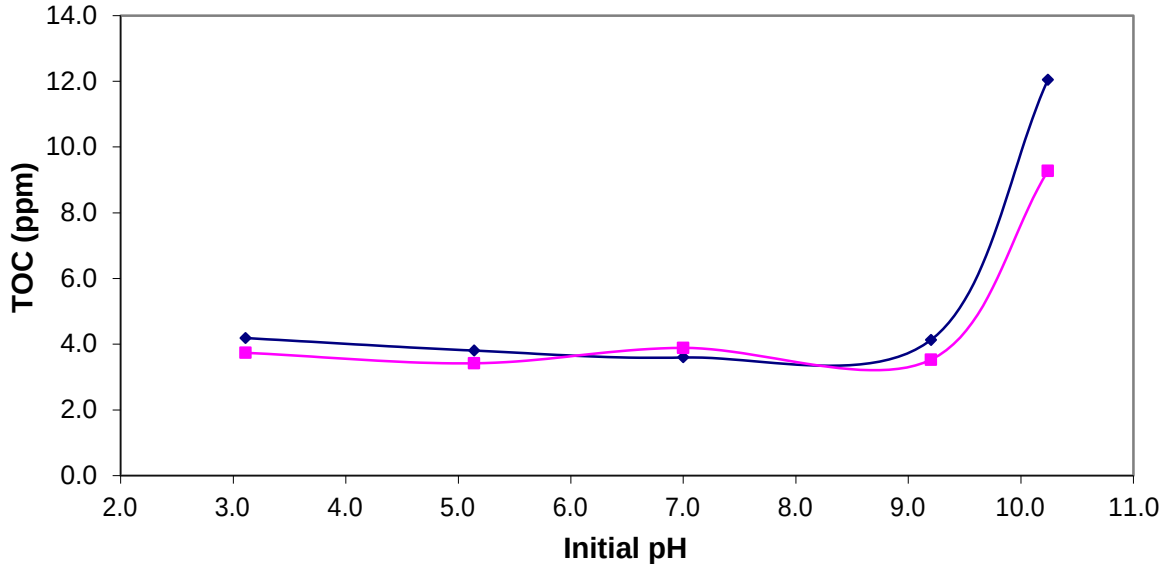

FIG. S1: Influence of initial pH on organic leaching from treated SW. Data points were from individual runs of the same experiment.

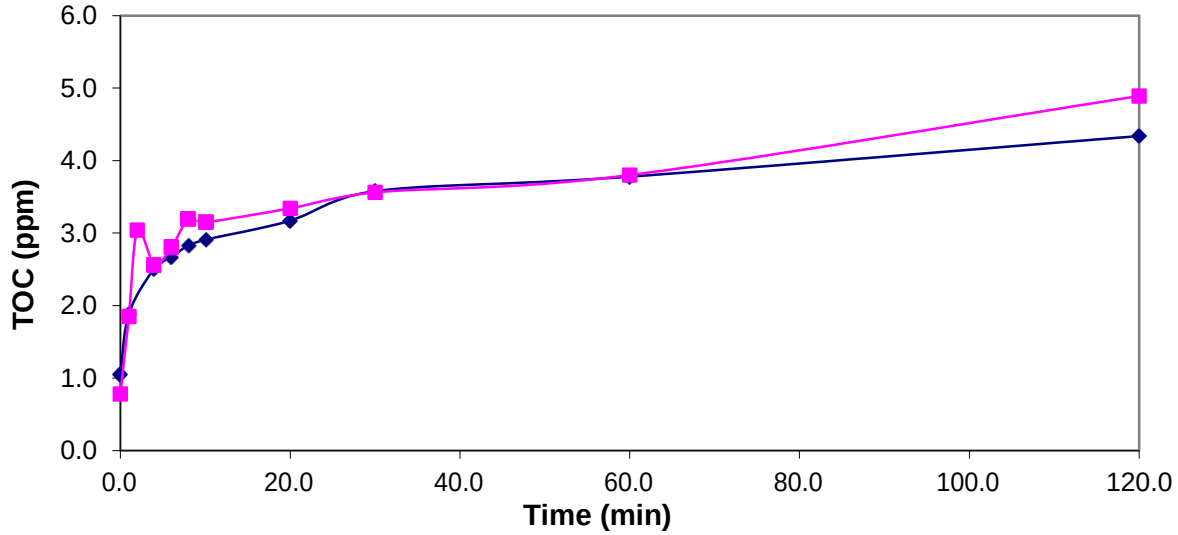

FIG. S2: Time course evolution of TOC from treated SW in contact with 1000 ppb (parts per billion) copper solution (without added ammonium). Data points were individual runs of the same experiment.

Experimental method

Effect of initial solution pH on organics leaching from treated SW

100 mL of ultrapure water (18.2 MΩ) in 125 mL polypropylene Azlon bottles served as the contact solution. 10 mL aliquot was withdrawn before and after equilibration to determine the total organic carbon (TOC) concentration using Shimadzu TOC-5000A. Biosorbent concentration used was 1 g/L. The sorbent water mixtures were continuously mixed on an orbital shaker for 24 hours at 200 rpm. Solution pH was measured using an Orion 525A pH/ISE meter and was adjusted to the required value with either 0.1M HNO_3 or

0.1M NaOH prior to the experiment, but not controlled thereafter since addition of acids would introduce volume changes that reduce the reliability of TOC concentration measurement. All aliquots were filtered through 0.45 μm PTFE membrane filters (Whatman Autovial, USA), acidified with 2% HNO_3 and stored at 4 ^oC prior to analysis. Duplicate experiments were conducted at 22 to 25 ^oC.

References

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[2] Chen, J. P., Yang, L. (2005) Chemical Modification of *Sargassum* sp. for Prevention of Organic Leaching and Enhancement of Uptake during Metal Biosorption. *Ind. Chem. Eng.* **44**, 9931-9942.

[3] Davis, T. A., Ali, F. E. C., Giannitti, E., Volesky, B., Mucci, A. (2004) Cadmium Biosorption by *S. fluitans*: Treatment, Resilience and Uptake Relative to Other *Sargassum* spp. and Brown Algae. *Water Quality Research Journal of Canada* **39**, 183-189.