Ammonium interference reduced copper uptake by formaldehyde crosslinked *Sargassum* sp. seaweed

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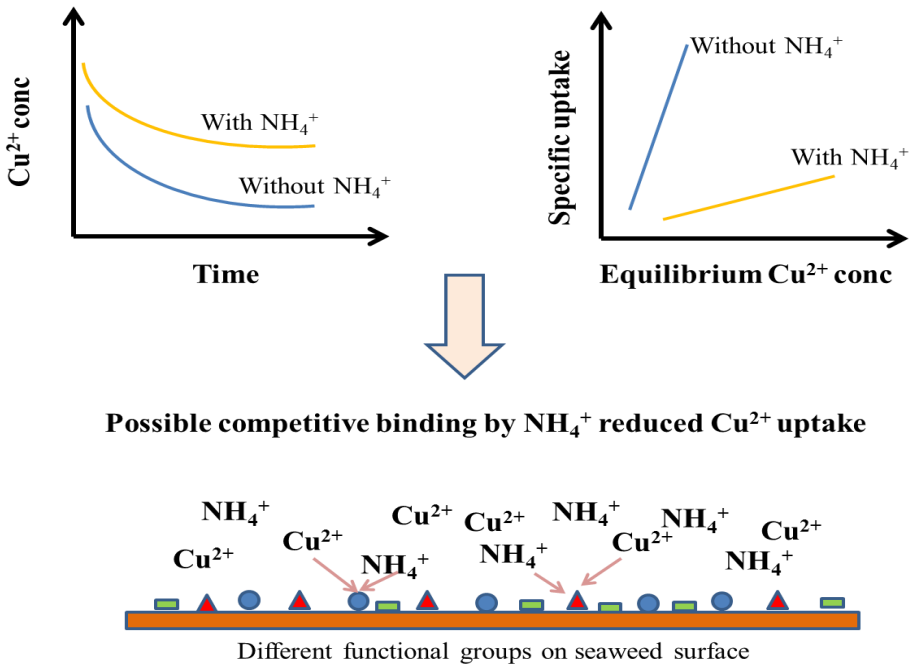
Graphical abstract



Short description

Reduced kinetic and equilibrium uptake of copper on formaldehyde crosslinked *Sargassum* sp. seaweed from low concentration solutions revealed interference effect from ammonium ion co-solute

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Abstract

Sargassum sp., a marine brown macroalgae, is an efficient sorbent for various heavy metals at high concentrations. Nevertheless, the efficiency at which seaweed removes heavy metals from dilute solutions and the effect of ammonium on metal removal is not well understood; an issue of importance given the ubiquity of nitrogenous compounds in the environment arising from various surface run-offs. Herein, the effect of ammonium on copper removal (at trace to low concentration) by formaldehyde crosslinked *Sargassum* sp. (treated SW) was studied. Due to high copper background, equilibrium sorption experiments was inconclusive concerning treated SW's ability in removing copper (<1000 ppb), but rapid copper sorption observed in kinetic experiments suggested potential feasibility of the process. Within initial copper concentration of 4 to 20 ppm and pH 2 to 5, experiments revealed that, above a threshold concentration of [NH_4^+-N] of 50 ppm, ammonium impeded copper uptake on treated SW in a concentration-dependent manner. Specifically, sorption kinetics slowed and uptake capacity decreased with increase in [NH_4^+-N] from 0 to 2500 ppm. Collectively, beyond demonstrating that treated SW could remove copper from dilute solutions, revelations that ammonium reduced copper sorption highlighted the importance of accounting for the effect in data interpretation and modelling.

Keywords: metal adsorption; trace concentration; chemical pretreatment;

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1. Introduction

Multiple useful properties such as high conductivity and malleability afford the use of metals in diverse applications. Metal production, either from pristine ores or recycled electronic waste, would inevitably generate fugitive emissions to the environment. Similarly, secondary processing of metals (such as in electroplating and semiconductor manufacturing) would also result in metal release, for example, as soluble ions in industrial effluents. Well-documented toxicity of metals on humans in combination with increasingly stringent environmental regulations motivates the development of new technologies for remediating metal impacted waters. Biosorption, a surface-mediated passive uptake of heavy metals by dead biomass, is one such example, and offers a couple of key advantages relative to commercial metal removal techniques based on ion-exchange resins [1, 2]. Specifically, in utilizing dead biomass – often with minimal processing – waste resources receive a second lease of life in helping remediate environmental pollution; generating cost-savings while simultaneously solving a waste disposal problem. Various bacteria, yeast, fungi, micro- and macro-algae, and agricultural waste products are shown to be useful in removing metal ions [3-9]. Nevertheless, the uptake capacities differ between biosorbents given different cell wall organization as well as availability and accessibility of functional groups for metal uptake [10].

The brown marine marcoalgae, *Sargassum* sp., is an efficient sorbent (up to 20% of the biomass dry weight) for a variety of heavy metal ions [10-12]. Commonly found in the inter-tidal zones of coastal areas in tropical and sub-tropical climes, the seaweed is a plentiful and inexpensive resource. More important, evolutionary pressure unique to the marine environment (i.e., the relatively high Ca^{2+} and Mg^{2+} content of seawater relative to freshwater) has endowed *Sargassum* sp. with unique capabilities in metal sorption through the evolution of cell wall structures comprising specific functional groups.

Copper is intermediate in toxicity relative to more toxic metals such as cadmium, chromium and mercury, but its utility in a variety of applications, particularly as wires in new homes and commercial buildings or as interconnects in silicon chips meant that it is an important element from the environmental remediation perspective. With a demonstrated propensity to bioaccumulate in the kidney, liver and other organs, chronic exposure to copper via ingestion is known to cause Wilson's disease, even though it is an essential micronutrient with diverse physiological functions – chief amongst which is its role as cofactors in enzymes [1, 13]. Since industry is the major source of metal release into the environment, studies in the literature have predominantly focused on remediating high copper concentration wastewater [14]. From the environmental protection perspective, trace to low concentration is defined in this study to be less than 20 ppm (parts per million); a concentration range where metals have been detected in environmental water samples [15]. Given that many water-scarce regions rely on untreated surface waters for drinking and domestic uses, a need exist for understanding the efficacy of biosorption technology as a possible low-cost and point-of-use treatment technique for removing low concentration metal contaminants in source waters.

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Increasing population and demand for higher food production necessitates increased application of fertilizers on fields. This, together with suboptimal application techniques lead to substantial run-offs of nitrogen-rich fertilizers into the natural environment. Hence, many surface water bodies would likely contain elevated concentrations of ammonium and other nitrogenous compounds. At the circumneutral pH typical of most environmental waters, ammonia exists in the soluble, positively charged, ammonium ion form (i.e., NH_4^+), which, in addition to competing with other cations for binding sites in environmental matrices such as river sediments and clays, also substitutes for water molecules in the hydration shells of cations when present at high concentrations (i.e., ammoniacal solutions) [16]. Thus, co-occurrence of metals in waters at trace concentration with elevated concentrations of ammonium compounds is possible and poses a relevant research question concerning ammonium's effect on trace metal biosorption.

Collectively, a knowledge gap exists in our understanding of both the utility of seaweed in removing copper at trace and low concentrations, and the roles of ammonium ion in affecting metal removal from dilute solutions. More specifically, removing metal at the trace/low concentration range requires strong affinity between seaweed functional groups and metal, which could not be directly assessed in sorption experiments conducted at high metal concentrations typical of industrial effluents. Thus, using batch kinetic and equilibrium experiments, the present study aimed to (i) assess the feasibility of adsorbing copper from water at trace and low concentrations and quantitating the speed and extent of such an uptake, and (ii) investigating possible interference effect of NH_4^+ ion on Cu^{2+} biosorption by formaldehyde crosslinked *Sargassum* sp. (treated SW). Formaldehyde crosslinking was chosen for chemically modifying *Sargassum* sp. since pristine seaweed is known to leach significant amounts of organics during biosorption, which translates into progressive reduction of sorption capacity and deterioration of mechanical properties in cycles od sorption/desorption [17]. More intriguingly, the crosslinking technique has also been reported to increase sorption capacity [18].

Results were inconclusive concerning the feasibility of removing copper at trace concentrations (<1000 ppb) in batch equilibrium studies. Nevertheless, kinetic experiments revealed a consistent trend of exceptionally rapid copper uptake. The preliminary data highlighted the need of extra precautions in removing seaweed and apparatus bound copper in trace concentration studies. The focus of the study subsequently shifted to higher [Cu^{2+}] of 4 to 20 ppm, where experimental data revealed rapid uptake of Cu^{2+}, even under NH_4^+ interference. Nevertheless, speed of Cu^{2+} sorption on treated SW decreased, in a concentration-dependent manner, with increase in [NH_4^+-N], with a threshold concentration of 50 ppm (or 3.57 mM) below which interference effect was not observed. Batch equilibrium experiments revealed similar trends, which together with kinetic sorption data, suggested that within the pH range investigated (i.e., pH 2 to 5), NH_4^+ reduced Cu^{2+} sorption. Collectively, experimental data revealed that ammonium ion impeded copper sorption on treated SW in a concentration-dependent manner; thereby, highlighting the importance of factoring this effect in modelling metal biosorption processes and interpreting experimental results.

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2. Materials and methods

2.1 Chemicals

Copper and ammonium stock solutions were prepared by dissolving crystalline $Cu(NO_3)_2.3H_2O$ salts and amorphous NH_4Cl (Merck, min purity 99.5%) in deionized water. Formaldehyde (37 wt%) for crosslinking seaweed was from Riedel-deHaen.

2.2 Collection and pre-treatment of seaweed

Sargassum sp. was harvested at Labrador Nature Reserve, Singapore. The seaweed was washed with copious quantities of deionised water, sun dried for a couple of days, and further dried at 60 ^oC for 8 to 10 hours in an oven. The seaweed was then grounded into a heterogeneous mixture and sieved by a granulated separator into different size fractions. Only one particle size fraction (500-850 μm) was used to prepare formaldehyde crosslinked seaweed since uptake capacity of seaweed is independent of particle size [19].

2.3 Preparation of formaldehyde crosslinked seaweed

10 g of seaweed prepared above was added to 1 L of 0.2 mol% formaldehyde solution in a glass beaker and continuously stirred for 24 hours at 350 rpm [17]. The reaction mixture was allowed to settle to facilitate the collection of formaldehyde crosslinked seaweed (treated SW). The supernatant was decanted and the treated SW washed with copious quantities of ultrapure water and dried at 60 ^oC for 24 hours. The treated SW was subsequently cooled and kept in a plastic container before use. Effectiveness of formaldehyde crosslinking in reducing organic leaching from seaweed is depicted in Figure S1 of the Supporting information. The materials and methods associated with the experiment are also detailed in the supplementary file.

2.4 Kinetic biosorption experiments

Solution chemistry modelling, via the chemical equilibrium software MINEQL$^+$ 4.5, revealed that at pH 5.0, about 99% of the total copper exists as Cu^{2+} and ammonia as NH_4^+. Copper nitrate and ammoniacal copper solution (2L volume) was prepared in 2L borosilicate glass beaker. Solution pH was measured with an Orion 525A pH/ISE meter and maintained at 5.0 ± 0.1 with 0.1M HNO_3 or 0.1M NaOH throughout the experiment to prevent copper precipitation. Biosorbent concentration was 1 g/L. In ammonium effect experiments, solutions were constituted by adding an aliquot (volume depending on target concentration) of NH_4Cl stock solution to copper nitrate solution. The solution was stirred at 400 rpm on a stirring hotplate to ensure solution homogeneity (Fisher Scientific, USA). 10 mL of solution was withdrawn at stipulated time-points, filtered through a 0.45 μm PTFE membrane filter into 20 mL plastic sample bottles. All samples were acidified with 2% HNO_3 and stored at 4 ^oC prior to analysis of metal concentrations by ICP-OES (Perkin Elmer Optima 3000DV) when $[Cu^{2+}] > 1$ ppm, and ICP-MS (Perkin Elmer Elan 6100, upper detection limit, 200 ppb) when $[Cu^{2+}] < 1$ ppm.

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2.5 Equilibrium biosorption experiments

Copper nitrate or ammoniacal copper solutions (100 mL) were prepared in 125 mL polypropylene Azlon bottles. Ammoniacal copper solutions were constituted by adding an aliquot from a stock solution of NH_4Cl into copper nitrate solutions of differing concentrations within the investigated range. 10 mL of solution was withdrawn before and after equilibration for determining the copper concentration either via ICP-MS or ICP-OES. The biosorbent concentration used was 1 g/L. The sorption mixtures were equilibrated on an orbital shaker for 24 hours at 200 rpm. All aliquots were filtered through 0.45 μm PTFE membrane filter into 20 mL plastic sample bottles, followed by acidification with 2 % HNO_3, and stored at 4 ºC before metal analysis. The initial and final solution pH was measured with an Orion 525A pH/ISE meter but not controlled during the experiment. Duplicate experiments were conducted at 22 ºC.

2.6 Data analysis

The copper uptake per gram of dry treated SW was calculated by Eq. 1.

$$q = \frac{V(C_i - C_f)}{m} \quad (1)$$

where q is specific uptake (mg/g), V is volume of solution (mL), C_i and C_f are the initial and final concentrations, respectively, and m is the mass of dry treated SW added (mg).

3. Results and discussion

3.1 Biosorption of copper at trace concentration

Kinetic experiments with initial [Cu^{2+}] of 1000 ppb were performed and revealed rapid uptake of Cu^{2+}; with ~90% of uptake occurring within the first 10 seconds (Fig. 1a). This fine-grained snapshot of copper sorption was enabled by high temporal resolution sampling within the first 2 mins of the kinetic experiment. In contrast, typical kinetic experiments tend to have lower sampling resolution within the first few minutes since, depending on the metal concentration tens of minutes to hours would be needed for the system to reach equilibrium. Over the entire kinetic run, there was a transient increase in [Cu^{2+}] after initial rapid sorption, which was followed by a gradual decrease in [Cu^{2+}] till the end of experiment at 120 mins (Fig. 1b). Focusing on Figure 1a, which depicted rapid decrease in [Cu^{2+}] within the first 2 mins of sorption, it can be seen that almost all copper uptake occurred within 10 seconds, with the [Cu^{2+}] essentially constant thereafter – albeit with a slight upward trend. A more holistic view of the phenomenon in Figure 1b, however, showed that there was slow decline in [Cu^{2+}] up to 120 mins. Besides metal analysis, the TOC of samples were also analyzed in experiments designed to investigate possible correlation between organic release and copper sorption (Supporting information). Nevertheless, the trace concentration used (1000 ppb Cu^{2+}) was not sufficient to afford the discrimination of the relative contribution of *de novo* (i.e., without metal influence) and metal uptake mediated organic leaching, since amount of organics leached was similar to background levels observed when ultrapure water was the contact solution.

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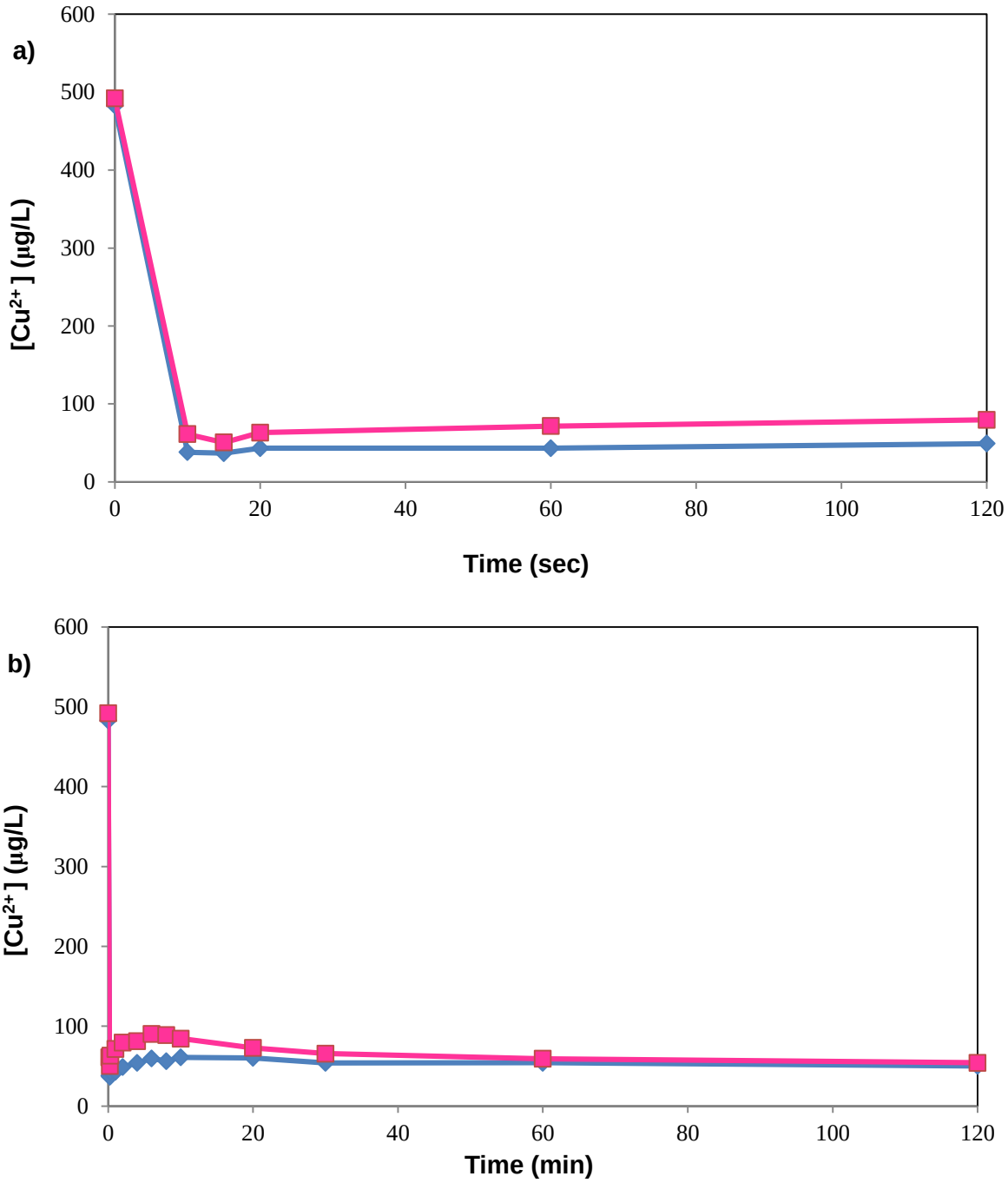

FIG. 1 Rapid decrease in copper concentration upon contact with treated SW, a) evolution of $[Cu^{2+}]$ in first 2 minutes of sorption; b) over the entire sorption run. Biomass concentration = 1 g/L, pH not controlled after initial adjustment, data points were of individual runs of the same experiment.

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Batch equilibrium experiments (initial [Cu^{2+}] between 1 and 1000 ppb, data not shown), however, were inconclusive; specifically, large data scatter with no discernible trends. The effect was especially pronounced at the lower end of [Cu^{2+}] (1 to 100 ppb), possibly due to the high background residual on polypropylene bottles, and the trace amount of metal ions present on treated SW. Preliminary results suggested net desorption of copper ions from the treated SW into the bulk solution. Further work in the trace concentration regime would likely require the use of Teflon bottles, and ultrapure acids for preserving the samples prior to ICP-MS analysis. In view of the inconclusive results obtained, the experimental focus shifted to higher initial [Cu^{2+}] of 4 to 20 ppm.

3.2 Low concentration kinetic biosorption experiment

Uptake of Cu^{2+} from low concentration solutions onto treated seaweed was biphasic, with a fast initial phase and a slower secondary phase - similar to sorption of other metals to seaweed (Fig. 2). The fast initial phase could be attributed to Cu^{2+} sorption onto treated SW's exterior surfaces, while diffusion of Cu^{2+} into the seaweed's interior accounted for the observed slower secondary phase [10]. From the relative amount of copper sorption that occurred in each phase, it could be inferred qualitatively, that surface sorption played a more important role in Cu^{2+} uptake relative to sorption on intra-particle binding sites, since the gelatinous nature of alginate severely retarded the microporous diffusion of metal ions into the seaweed interior [17]. From another perspective, the extracellular alginate matrix is akin to a thin polyelectrolyte film through which the metal ions diffuse into the seaweed's interior during the slower secondary sorption phase [11]. Finally, independent of ammonium interference, a higher initial [Cu^{2+}] used would result in corresponding higher equilibrium [Cu^{2+}], consistent with trends reported in the literature [20].

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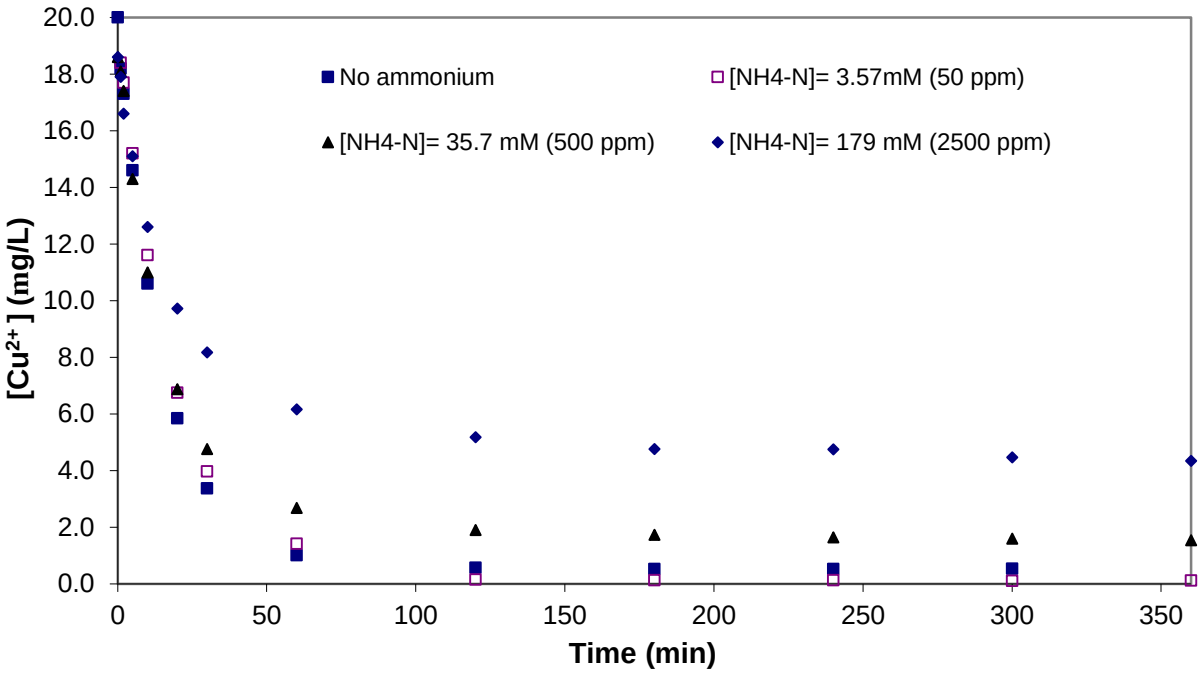

FIG 2 Kinetics of copper biosorption by treated SW with and without added ammonium (0-179 mM), biomass concentration = 1 g/L, pH = 5.0 (controlled) and initial copper concentration of 20 ppm

The data for NH_4^+ effect experiments revealed higher residual $[Cu^{2+}]$ (i.e., poorer uptake) with increase in $[NH_4^+\text{-N}]$. Specifically, NH_4^+ impeded Cu^{2+} uptake in a concentration-dependent manner, with $[NH_4^+\text{-N}]$ of 179 mM severely affecting Cu^{2+} uptake (equilibrium $[Cu^{2+}]$ ~5 ppm relative to ~0.5 ppm in experiments without added NH_4^+). Nevertheless, there was no appreciable effect on Cu^{2+} sorption at $[NH_4^+\text{-N}]$ = 3.57 mM, which suggested a threshold concentration existed beyond which NH_4^+ would impede Cu^{2+} sorption on treated SW. Besides higher $[Cu^{2+}]$ residuals, longer equilibration times were also observed with increasing $[NH_4^+\text{-N}]$. Further evidence of the threshold effect could be seen in the similar equilibration time observed in systems with $[NH_4^+\text{-N}]$ of 0 and 3.57 mM (50 ppm). Specifically, 120 mins was required for the system to reach equilibrium at $[NH_4^+\text{-N}]$ of 0 mM and 3.57 mM, while longer equilibration times (~240 mins and > 360 mins) were needed at $[NH_4^+\text{-N}]$ of 35.7 mM and 179 mM, respectively. One possible explanation for the decreased uptake capacity might be the direct binding of NH_4^+ on treated SW; although questions on the type of functional groups mediating the binding and whether they were the same ones that bind Cu^{2+} remain to be elucidated. Alternatively, ammonium-copper complexation could also hinder copper binding to seaweed.

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3.3 Equilibrium biosorption experiments

The equilibrium specific uptake of copper increased with pH, independent of ammonium interference (Fig. 3). Specifically, the gradient of the linearized lines at pH 3 and 4.5 were larger than that at pH 2, indicating that biosorption was more favourable at higher pH, which broadly agreed with other studies in the literature [10, 17, 21]. At initial pH = 2, there was almost no uptake of Cu^{2+}, most likely due to the competitive binding effect from the high concentration of protons [10]. Possible explanations of the enhanced copper uptake at higher pH include: (i) deprotonation of the carboxyl sites (of alginate) and sulfated polysaccharides sites (of fucoidan) in the treated SW cell wall matrix at high pH, which increased the number of negatively charged sites available for binding Cu^{2+} ions, and (ii) reduced competition from solution H^{+} ions for the same binding sites at high pH [17, 22].

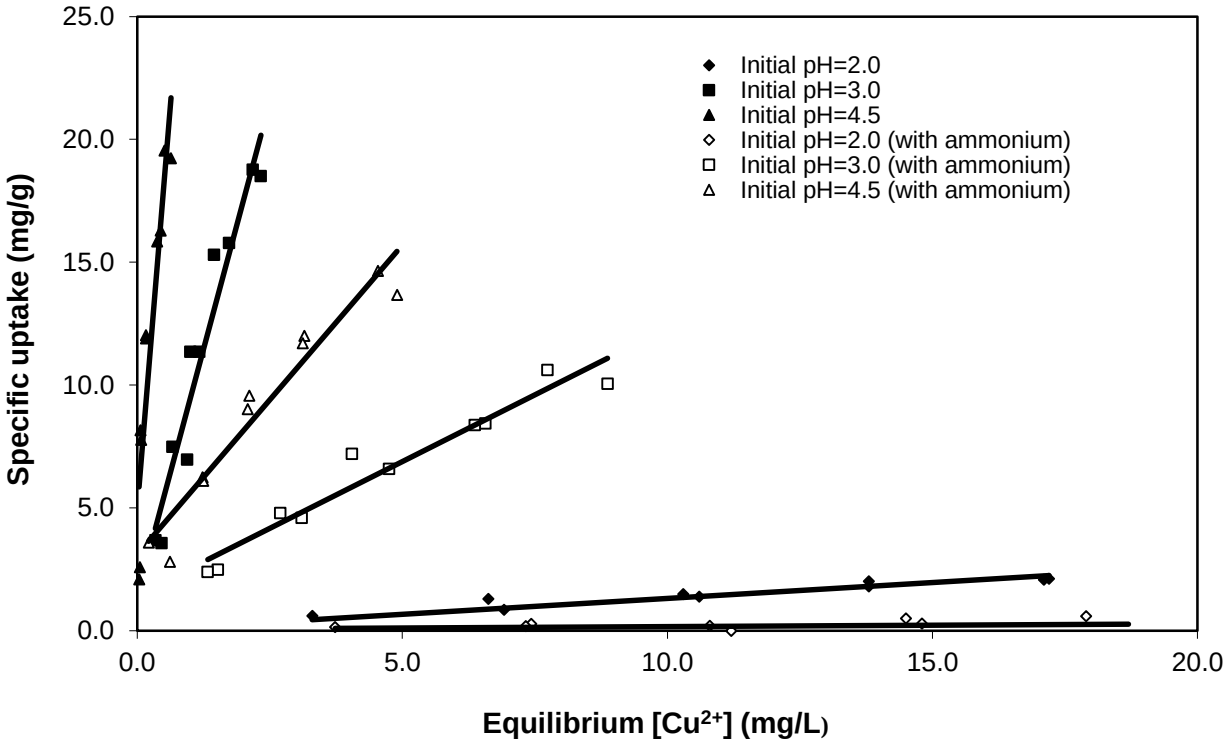

FIG 3. Batch equilibrium studies with and without ammonium interference. Biosorbent concentration = 1 g/L, no pH control, $[NH_4^{+}\text{-N}]$ = 179 mM. Data points were of individual experiment runs.

The specific uptake and equilibrium $[Cu^{2+}]$ showed a positive linear relationship for $[Cu^{2+}]$ of 0.1 to 20 ppm, which indicated that initial $[Cu^{2+}]$ was positively correlated with equilibrium specific uptake. Such a linear relationship concurred with predictions from various isotherm models such as Langmuir and Freundlich, and is typical of metal sorption from low concentration solutions.

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At the same initial pH, the presence of NH_4^+ reduced the equilibrium specific uptake for [Cu^{2+}] within 0.1 to 20 ppm.

4. Conclusions

Taken together, the feasibility of removing copper (at trace concentration) by formaldehyde crosslinked *Sargassum* sp., was equivocal, even though rapid sorption was observed in kinetic experiments. Future research in this concentration regime should adopt better contaminant control practices. Kinetic and equilibrium experiments in the low copper concentration regime (i.e., 4 to 20 ppm), however, provided strong evidence of Cu^{2+} uptake by treated SW - even under NH_4^+ interference, where NH_4^+ reduced Cu^{2+} sorption in a concentration-dependent manner beyond a threshold concentration of 50 ppm NH_4^+-N.

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Conflicts of interest
The author declares no conflict of interest.

Author contribution
The author performed the experiments, analyzed the data and wrote the manuscript. Dr. Yang Lei designed the experiments and helped with operation of analytical instruments.

Supporting information
The supplementary material discusses an experiment designed to examine the effectiveness of formaldehyde crosslinking in reducing organic leaching from seaweed.

6. References

[1] Volesky, B. (1990) Biosorption of Heavy Metals, CRC Press.
[2] Raize, O., Argaman, Y., Yannai, S. (2004) Mechanisms of biosorption of different heavy metals by brown marine macroalgae. *Biotechnol. Bioeng.* **87**, 451-458.

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[3] Vijayaraghavan, K., Yun, Y.-S. (2008) Bacterial biosorbents and biosorption. *Biotechnol. Adv.* **26**, 266-291.
[4] Dhankhar, R., Hooda, A. (2011) Fungal biosorption – an alternative to meet the challenges of heavy metal pollution in aqueous solutions. *Environ. Technol.* **32**, 467-491.
[5] Kordialik-Bogacka, E. (2011) Surface properties of yeast cells during heavy metal biosorption. *Cent. Eur. J. Chem.* **9**, 348-351.
[6] Kuroda, K., Ueda, M., in Kotrba, P., Mackova, M., Macek, T. Eds. (2011) Yeast Biosorption and Recycling of Metal Ions by Cell Surface Engineering Cell Surface Engineering, Springer Netherlands, pp. 235-247.
[7] Hanbali, M., Holail, H., Hammud, H. (2014) Remediation of lead by pretreated red algae: adsorption isotherm, kinetic, column modeling and simulation studies. *Green Chemistry Letters and Reviews* **7**, 342-358.
[8] Rodrigues, M. S., Ferreira, L. S., Carvalho, J. C. M. d., Lodi, A., Finocchio, E., Converti, A. (2012) Metal biosorption onto dry biomass of *Arthrospira (Spirulina)* platensis and *Chlorella vulgaris*: Multi-metal systems. *J. Hazard. Mater.* **217–218**, 246-255.
[9] Hossain, M. A., Ngo, H. H., Guo, W. S., Nguyen, T. V. (2012) Biosorption of Cu (II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption. *Journal of Water Sustainability* **2**, 87-104.
[10] Volesky, B. (2003) Sorption and Biosorption, BV Sorbex, Inc.
[11] Fourest, E., Volesky, B. (1995) Contribution of Sulfonate Groups and Alginate to Heavy Metal Biosorption by the Dry Biomass of *Sargassum fluitans*. *Environ. Sci. Technol.* **30**, 277-282.
[12] Davis, T. A., Volesky, B., Mucci, A. (2003) A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* **37**, 4311-4330.
[13] U.S. National Research Council, (2000) Physiological Role of Copper, National Academies Press.
[14] Niad, M., Rasoolzadeh, L., Zarei, F. (2014) Biosorption of copper (II) on *Sargassum angostifolium* C.Agardh phaeophyceae biomass. *Chem. Spec. Bioavailab.* **26**, 176-183.
[15] Ada, F. B., Ayotunde, E. O., Offem, B. O. (2012) Surface and Ground Waters Concentrations of Metal Elements in Central Cross River State, Nigeria, and their Suitability for Fish Culture. *International Journal of Environment and Sustainability* **1**, 9-20.
[16] Copcia, V., Hristodor, C., Luchian, C., Bilba, N., Sandu, I. (2010) Ammonium nitrogen removal from aqueous solution by natural clay. *Revista de Chimie (Bucharest)* **61**, 1192-1196.
[17] 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.
[18] Veit, M. T., Gonçalves, G. d. C., Fagundes-Klen, Regina, M., Da Silva, E. A., Granhen Tavares, C. R., Honorio, J. F. (2014) Organic leaching and metal removal with *Sargassum filipendula*. *Acta Scientiarum: Technology* **36**, 429-435.
[19] 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.

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[20] Tsui, M. T. K., Cheung, K. C., Tam, N. F. Y., Wong, M. H. (2006) A comparative study on metal sorption by brown seaweed. *Chemosphere* **65**, 51-57.
[21] Sheng, P. X., Ting, Y.-P., Chen, J. P., Hong, L. (2004) Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid Interf. Sci.* **275**, 131-141.
[22] Carsky, M., Mbhele, F. N. (2013) Adsorption of heavy metals using marine algae. *South African Journal of Chemical Engineering* **18**, 40-51.

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