Inability to completely remove trace contaminants from drinking water by adsorption

Wenfa Ng

Unaffiliated researcher, Singapore, Email: ngwenfa771@hotmail.com

Abstract

Trace contaminant removal is of contemporary concern in drinking water and wastewater treatment, given increasing evidence of potential toxicity of various heavy metals and metalloids in water at parts per billion (ppb) concentration levels. Currently, only high pressure reverse osmosis is able to reliably remove trace concentration contaminants from water but with high energy cost. Thus, the search is on for techniques and methods able to remove trace concentration contaminants with a lower energy footprint. Adsorption, a low energy technique for water and wastewater treatment is one possibility, which when coupled with the use of low cost biomass as adsorbent, would further improve process efficiency. This synopsis describes work done on examining the use of local marine seaweed, *Sargassum* sp. for removing copper at low (4 to 20 ppm, parts per million) and trace concentration (< 1000 ppb), with and without ammonium ion interference at different solution pH. Specifically, to reduce organic leaching and improve mechanical stability, formaldehyde crosslinking was used and was effective in enhancing stability of seaweed between pH 3 and 9. But, residual organic leaching of ~ 4 ppm meant that modified seaweed was not suitable for drinking water treatment. Batch kinetic and equilibrium studies revealed that up to a threshold ammonium concentration of 50 ppm [NH_4^+-N], there was good sorption of copper on formaldehyde crosslinked seaweed (treated seaweed), with residual copper concentration of 0.5 ppm. Residual copper concentration increased with increase in ammonium concentration (up to 2500 ppm [NH_4^+-N]); thereby, highlighting a competitive binding effect for treated seaweed's surface functional groups. Attempts to remove trace concentration copper highlighted feasibility of the approach. However, significant residual equilibrium concentration of copper remained in the solution. More importantly, thermodynamic considerations point to the existence of a finite residual equilibrium concentration for copper in water; thereby, making adsorption not feasible as a method for completely removing trace concentration copper. Additionally, surface concentration of copper at the adsorbent might, in some cases, be higher than the bulk solution; thus, leading to desorption of copper from the seaweed surface back to the solution. Collectively, adsorption is not capable of completely removing a contaminant such as is the case for reverse osmosis where the non-porous membrane serves as barrier separating treated water from raw influent.

Synopsis

The goal in water treatment has always been the search for cost effective techniques and methodologies for removing various contaminants from water. To this end, adsorption of heavy metals and other ionic contaminants onto adsorbents derived from biomass is one attractive option for reducing the cost of treating water, enabling reuse of waste biomass materials, as well as tap on a low energy water treatment technique. Indeed, compared to high pressure reverse osmosis treatment of drinking water which effectively remove all ionic and non-ionic contaminants through a non-porous water permeable membrane, adsorption is lower in energy consumption given the relatively low pressure at which water flow through the adsorbent column. However, the technique's most significant drawback comes from the inability to remove all contaminants given the dependence on thermodynamic equilibration between the water and adsorbent. Thus, adsorption is effective in removing significant fraction of the pollutant load from water, but ineffective in realizing zero pollutant in drinking water. Nevertheless, the technique remains highly useful in applications not requiring the removal of trace contaminants in the parts per billion (ppb) range.

Realization of potential carcinogenic effects of many heavy metal contaminants and non-ionic pollutants has driven the search for more effective methods for removing trace contaminants from drinking water, with the goal of producing reverse osmosis grade water with lower cost and energy consumption. To this end, optimization of reverse osmosis processes has helped improved process efficiencies and cost of energy usage relative to contaminant removal level. But, the inherent high energy consuming nature of reverse osmosis placed the technique at the upper end of energy consumption for water and wastewater treatment.

Adsorption has drawn attention due to its lower energy requirement. Coupled with the use of plant biomass found to be useful in high capacity adsorption of various heavy metals such as copper, cadmium and lead, the technique of biosorption was intensively researched for its possible use in treating various wastewaters.[1] To this end, a study[2] attempted to remove copper at low concentration level of 4 to 20 ppm from water under the competition of ammonium cations at high concentrations of up to 2500 ppm [NH_4^+-N], via formaldehyde treated local marine seaweed (treated seaweed).

Specifically, marine seaweed was harvested from the local coastline, washed with copious amounts of tap water, dried and ground into small size fraction suitable for adsorption: 500 to 850 m size range. Due to the phenomenon of leaching of organics from unmodified seaweed during adsorption experiments, 0.2 wt% formaldehyde solution was contacted with seaweed for crosslinking the seaweed surface, which helped improved mechanical stability of the seaweed, *Sargassum* sp. After formaldehyde crosslinking, organic leaching from the treated seaweed significantly decreased to ~ 4 ppm; thereby, making it suitable for use in treating wastewater. However, use of formaldehyde crosslinked seaweed in drinking water treatment would pose a secondary pollution problem due to the organics leached from the modified seaweed.

2

Experiment results revealed that, up to an ammonium concentration of 50 ppm [NH_4^+-N], adsorption by treated seaweed was effective in removing copper at low concentration range of 4 to 20 ppm. Specifically, residual copper concentration after adsorption on treated seaweed was ~ 0.5 ppm for ammonium concentration less than 50 ppm [NH_4^+-N]. With increase in ammonium concentration from 50 ppm to 2500 ppm [NH_4^+-N], time taken for the system to reach equilibrium increased. Similarly, the concentration of residual copper in the solution also increased. Thus, ammonium, as a cation, likely interfered with the adsorption of Cu^{2+} by treated seaweed through a competitive binding mechanism, where ammonium competed with Cu^{2+} for the same functional groups.

Investigating the speed at which copper was adsorbed by treated seaweed revealed that sorption was fast and could be depicted as a two phase process. Specifically, the initial phase of fast sorption most likely occurred due to adsorption of copper onto surface functional groups of treated seaweed. On the other hand, the slower second phase of sorption could be accounted for by the diffusion of copper ions into the pores of treated seaweed, where they are adsorbed by functional groups within the pores. Similar to the case with batch equilibrium studies, ammonium ion interfered with the sorption of copper most likely through a competitive mechanism, where the time taken for the process to reach equilibrium increased with increase in ammonium ion concentration.

Solution pH is a critical variable in wastewater and water chemistry, and plays a significant role in influencing sorption speed and capacity. Specifically, adsorption of copper from low concentration solutions (4 – 20 ppm copper) on treated seaweed was substantially lower at pH 2 and 3 compared to pH 4.5. This highlighted that treated seaweed's application potential at treating acidic wastewater is limited, even though it has good mechanical stability with respect to organic leaching between pH 3 and 9. Broadly speaking, significant competitive effect from H^+ ions as well as changes in the polarity of surface functional groups at low pH reduced the biosorption capacity of treated seaweed for positively charged copper ions at acidic pH.

To understand the feasibility of treated seaweed in removing copper at the trace concentration level (i.e., [Cu^{2+}] < 1000 ppb, parts per billion), both batch kinetic and equilibrium studies were conducted. Specifically, kinetic experiments revealed that about 90% of copper was removed from the solution within 10 seconds; thereby, highlighting the possibility of using biosorption for removing trace copper contamination. Importantly, the residual copper concentration was about 50 ppb, which reaffirmed that adsorption could not remove a contaminant completely. Batch equilibrium experiments, on the other hand, were equivocal on the ability of treated seaweed in removing copper at trace concentration. Specifically, significant scatter in the data points revealed that more care must be taken in removing background copper adsorption to the walls of the polyethylene bottles used as adsorption and sample bottles.

3

Hence, while possibility exists for adsorption of copper by treated seaweed at the trace concentration range (i.e., $[Cu^{2+}] < 1000$ ppb), adsorption as a technique could not completely remove the contaminant due to thermodynamic equilibrium considerations, where the driving force for adsorption comes from the concentration difference between the solution and the seaweed surface (Figure 1). Specifically, given that adsorption is an affinity based process aided by a concentration gradient between the solution and the adsorbent surface, the smaller the concentration difference, the smaller would be the amount of adsorption of the contaminant on the adsorbent surface. Thus, it is theoretically impossible to completely remove a contaminant from water by adsorption as a finite concentration would exist as residual equilibrium concentration in solution. Hence, deployment of adsorption as a water and wastewater treatment technique is based on the removal of contaminant to a level where the residual equilibrium concentration is lower than the water quality standard for drinking or for discharge, respectively.
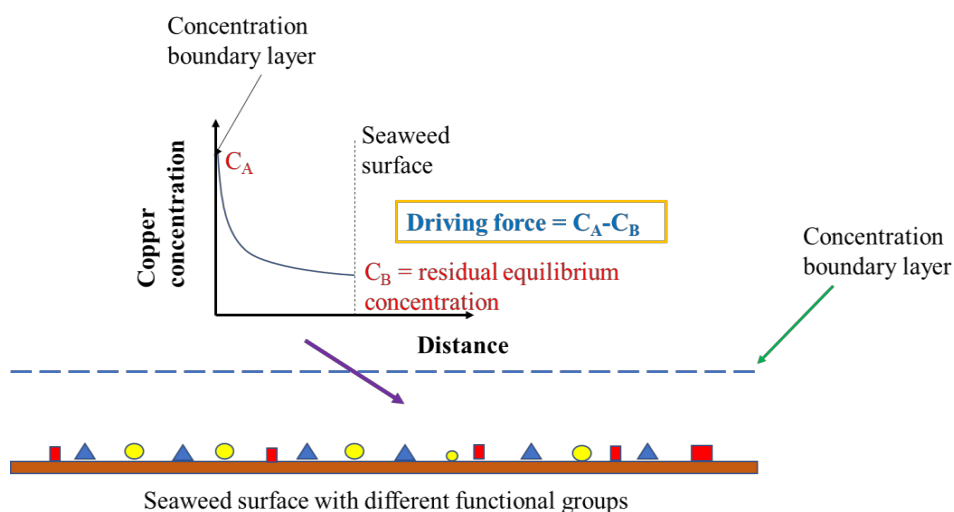

Figure 1: Thermodynamic driving force accounts for the adsorption of solute to a surface, where the residual equilibrium concentration of a solute at the seaweed surface could be higher than that at the concentration boundary layer for a trace concentration contaminant.

More importantly, in treating water with trace contaminants, the adsorbent surface may have a higher concentration of contaminants compared to the bulk water; thus, a reverse concentration gradient exists between the adsorbent surface and the solution, where thermodynamic driving force may drive the desorption of the contaminant from the adsorbent back into solution. Thus, desorption of previously sorbed contaminants provide a residual contaminant concentration in solution that preclude the use of adsorption as a method for completely removing trace contaminants from water.

Collectively, batch kinetic and equilibrium studies have affirmed treated seaweed's ability at removing copper from low concentration solutions (4 to 20 ppm). However, presence of ammonium co-solute would severely reduce adsorption of copper beyond a threshold concentration of 50 ppm $[NH_4^+-N]$, where residual copper concentration would be significantly

4

higher than without ammonium interference. Possible competitive effect from ammonium ions at circumneutral pH of 5 meant that ammonium co-solute is an important factor affecting biosorption processes for both drinking water and wastewater treatment applications, and should be factored in modelling studies. Additionally, presence of significant organic leaching from treated seaweed (i.e., total organic carbon concentration of 4 ppm) during biosorption meant that the biosorbent was not suitable for use in drinking water treatment. More importantly, given that adsorption processes are guided by fundamental thermodynamic equilibrium considerations where a residual equilibrium concentration exists for the solute in water, it is thus impossible to completely remove a contaminant from water through adsorption processes. Thus, unlike reverse osmosis process where a barrier (i.e., non-porous membrane) prevents the mixing of the influent and treated water, the lack of a barrier in adsorption processes meant that a residual equilibrium concentration of the contaminant exists; thereby, preventing removal of the trace contaminant.

References

1. De Gisi, S., Lofrano, G., Grassi, M. & Notarnicola, M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustain. Mater. Technol.* **9,** 10–40 (2016).

2. Ng, W. Ammonium interference reduced copper uptake by formaldehyde-crosslinked Sargassum sp. seaweed. *PeerJ Prepr.* **5,** e1228v2 (2017).

Conflicts of interest

The author declares no conflicts of interest.

Author's contribution

The author thought about the possibility of removing trace contaminants using the low energy technique of adsorption and realized that adsorption would most likely not be able to completely remove trace contaminants. He wrote the synopsis to put a preprint manuscript he published into contemporary perspective, where the focus is on exploring methods for removing trace contaminants such as heavy metals from drinking water cost-effectively.

Funding