



Application of *Sargassum* biomass to remove heavy metal ions from synthetic multi-metal solutions and urban storm water runoff

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ABSTRACT

The ability of *Sargassum* sp. to biosorb four metal ions, namely lead, copper, zinc, and manganese from a synthetic multi-solute system and real storm water runoff has been investigated for the first time. Experiments on synthetic multi-solute systems revealed that *Sargassum* performed well in the biosorption of all four metal ions, with preference towards Pb, followed by Cu, Zn, and Mn. The solution pH strongly affected the metal biosorption, with pH 6 being identified as the optimal condition for achieving maximum biosorption. Experiments at different biosorbent dosages revealed that good biosorption capacity as well as high metal removal efficiency was observed at 3 g/L. The biosorption kinetics was found to be fast with equilibrium being attained within 50 min. According to the Langmuir isotherm model, *Sargassum* exhibited maximum uptakes of 214, 67.5, 24.2 and 20.2 mg/g for lead, copper, zinc, and manganese, respectively in single-solute systems. In multi-metal systems, strong competition between four metal ions in terms of occupancy binding sites was observed, and *Sargassum* showed preference in the order of Pb > Cu > Zn > Mn. The application of *Sargassum* to remove four heavy metal ions in real storm water runoff revealed that the biomass was capable of removing the heavy metal ions. However, the biosorption performance was slightly lower compared to that of synthetic metal solutions. Several factors were responsible for this difference, and the most important factor is the presence of other contaminants such as anions, organics, and other trace metals in the runoff.

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1. Introduction

Among the various non-point sources, storm water runoff from urban areas has been recognized as a major contributor to a variety of water pollution problems in adjacent receiving bodies of water [1]. Urban storm water runoff contains pollutants which can impact the quality of surface, seepage, and ground waters. Heavy metals, polycyclic aromatic hydrocarbons, and mineral oil hydrocarbons are generally regarded as hazardous to water [2,3]. In particular, heavy metals are of great concern in such runoff due to their non-biodegradability. These metals are either dissolved in the storm water, or are bound to particulates [4]. However, their presence is strongly site-specific. Studies done in Ashdod, Israel [5] showed that the trace metal concentrations in storm water runoff were in the following ranges: manganese (0.001–0.516 mg/L), zinc (0.008–0.720 mg/L), copper

(0.001–0.079 mg/L), and lead (0.003–0.010 mg/L). In another characterization study, Walker et al. [6] summarized the concentrations of heavy metals in urban runoff in the following concentration ranges: zinc (0.0007–22.0 mg/L), copper (0.00006–1.41 mg/L), and lead (0.00057–26.0 mg/L).

To reduce the heavy metal concentrations in storm water to acceptable limits, simple and cost-effective treatment techniques are necessary. In addition, several other factors including physical and chemical characteristics of polluted water should also be considered. Several conventional techniques such as electro-dialysis, precipitation, and reverse osmosis could be applied to treat storm water runoff. However, most of these techniques either strongly depend on concentrations of pollutants, or lack practical applications because of economic constraints. Biosorption has been portrayed as an efficient technique for the remediation of inorganic pollutants, with many biosorbents showing excellent binding ability towards a variety of heavy metal ions [7,8]. However, most of the published results used synthetic metal solutions to explore the binding ability of biosorbents. The application of biosorption techniques to real-world conditions was seldom reported in Ref. [9]. In particular, there has been no report on studying the feasibility of

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using biosorbents to treat urban runoff, which comprises very low to moderate metal ion concentrations.

Marine algae, popularly known as seaweeds, are biological resources, which are available in many parts of the world. Algal divisions include red, green, and brown seaweed, of which brown seaweeds are found to be excellent biosorbents [10]. *Sargassum*, brown marine algae, is a well-established biosorbent for a variety of metal ions [11]. It is also one of the most abundantly available marine algae along the coast of several beaches in Singapore. Thus, this work explores the possibility of removing a variety of metal ions from storm water runoff using *Sargassum*. Initially, efforts were made to study the multi-component biosorption of four commonly present metal ions (Pb, Cu, Zn, and Mn) from a synthetic solution onto *Sargassum*.

2. Materials and methods

2.1. Biomass preparation

Fresh biomass of *Sargassum* sp. was collected from the beaches of Labrador Park in Singapore. The biomass was extensively washed with deionized water and sun-dried. The dried biomass was then grounded in a blender. The grounded seaweed was analyzed using LS Particle Size Analyzer and the mean size was found to be 722 μm .

2.2. Storm water collection and characterization

Two samples of storm water were collected at different periods from a drain near a residential area in Singapore and stored in plastic bottles. These samples were filtered to remove any solid sediment present. The samples of storm water were analyzed for metal content by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The storm water samples collected in the month of August and November were designated as storm water-1 and storm water-2, respectively. The concentrations of metals and anions of two storm water samples are presented in Table 1.

2.3. Metal biosorption experiments

Batch biosorption experiments were conducted as a function of pH, biomass dosage, and equilibrium time using 250 mL Erlenmeyer flasks as reaction vessels. To a mixed metal synthetic solution consisting of Mn, Pb, Cu and Zn at ca. 10 mg/L each, a known quantity of seaweed was added. The pH of the suspension was adjusted to desired values (pH 2–6) using 0.1 M HCl and 0.1 M NaOH. The reaction vessels were placed on a rotary shaker at 150 rpm for 3 h at 23 °C. After 3 h, the reaction mixture was filtered through a 0.45 μm PTFE membrane filter. Each filtrate was acidified and analyzed for aqueous metal content by ICP-AES.

Table 1
Composition of two storm water samples

Metal/anion (mg/L)	Storm water-1	Storm water-2
Pb	0.076	0.056
Cu	0.134	0.014
Zn	0.181	0.143
Mn	0.155	0.128
Na	6.56	3.31
K	3.92	1.39
Mg	8.81	6.92
Ca	0.74	0.54
Cl	1.94	0.86
NO ₃	5.42	1.74
NO ₂	1.60	0.95
SO ₄	12.91	5.81
PO ₃	0.16	0.05

The amount of metal sorbed by biomass was calculated from the differences between the metal quantity added to the biomass and the metal content of the supernatant using the following equation:

$$Q = \frac{V(C_0 - C_f)}{M} \quad (1)$$

where Q is the metal uptake (mg/g); C_0 and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biosorbent (g).

All experiments were done in duplicates and the reported data were the mean values of two replicated experiments. Isotherm model parameters were evaluated by non-linear regression using the Sigma-plot (Version 4.0, SPSS, USA).

3. Results and discussion

3.1. Biosorption of four metal ions from synthetic solutions

3.1.1. Influence of solution pH

In the first series of batch biosorption experiments, the influence of solution pH on the biosorption capacity of *Sargassum* biomass was studied (Fig. 1). The solution pH was found to severely affect the metal uptake capacity of *Sargassum* biomass, with pH values above 4.0 resulting in maximum uptakes. Brown algae mainly consist of alginic acid, which constitutes 10–40% of the dry weight of the algae [10]. The alginic acids are linear carboxylated copolymers constituted by different proportions of 1,4-linked β -D-mannuronic acid (M-block) and α -L-guluronic acid (G-block) [12]. The M- and G-block sequences display significantly different structures and their proportions in the alginate determine the physical properties and reactivity of the polysaccharide [13]. The most abundant carboxyl groups of alginate, the second abundant sulfonate groups of fucoidan, and hydroxyl groups in other polysaccharides are found to play an important role in metal binding at different pH conditions [10]. At lower pH values, the functional groups are protonated with H^+ , or other light metal ions which imply that majority of the binding sites were occupied. As the pH increases, the concentration of H^+ ions decrease and negatively charged biomass surface can interact with the positively charged metal ions.

The pH also influences the chemical speciation of metals in the solution. For instance, Pb(II) exists as Pb^{2+} and PbOH^+ at $\text{pH} \leq 6$, beyond which $\text{Pb}(\text{OH})_2$ tends to dominate [14]. On the other hand, Zn(II) is present mainly as Zn^{2+} at $\text{pH} < 7$; and at pH 8–9, it exists mainly as Zn^{2+} and $\text{Zn}(\text{OH})_2$, and in small quantities as $\text{Zn}(\text{OH})^+$ [15]. In the cases of Cu and Mn, the predominant species were Cu^{2+}

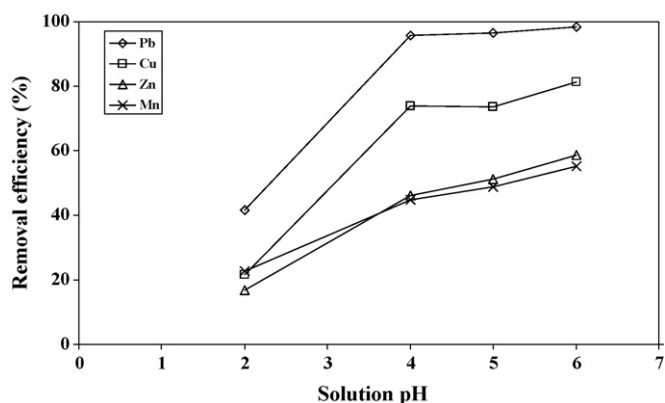


Fig. 1. Effect of solution pH on the biosorption of Pb, Cu, Zn and Mn in multi-solute system by *Sargassum* biomass (biosorbent dosage = 3 g/L; temperature = 23 °C; agitation rate = 150 rpm).

and Mn^{2+} , respectively at $pH \leq 6$ [16,17]. Therefore at $pH 6$, the predominant species of lead, copper, zinc and manganese were Pb^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} , respectively. These cations can interact with negatively charged groups of *Sargassum* biomass.

From Fig. 1, it was clear that *Sargassum* biomass performed well in the case of Pb compared to other metal ions. The lead removal efficiency reached almost 100% at $pH 6$, followed by Cu, Zn, and Mn removal efficiencies of 81.4, 58.6 and 55.1%, respectively. This order may be related to the differences in electronegativity and ionic radius of the atoms. The electronegativity decreases in the following order: $Pb (2.33) > Cu (1.90) > Zn (1.65) > Mn (1.55)$. Similarly the ionic radius of Pb was found to be relatively high (133 pm), compared to copper (87 pm), zinc (88 pm), and Mn (89 pm). Thus, it can be confirmed that both electronegativity and ionic radii determine the order of preference of metal binding onto alginate.

3.1.2. Influence of biomass dosage

The influence of biomass dosage on the adsorption of metal ions in multi-component systems was examined by varying dosages from 0.1 to 5 g/L. Fig. 2 presents the typical set of results obtained by varying *Sargassum* dosages during biosorption. On analysis, it was observed that removal efficiency increased with increase in biomass dosage. An increase in biomass concentration generally increases the degree of biosorption of metal ions because of an increase in overall surface area of the biosorbent, which in turn increases the number of binding sites [18]. On the contrary, the metal uptake decreases by increasing the biosorbent dosage, this may be due to complex interactions of several factors. The important factor is that at high sorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low metal uptake. Also, the interference between binding sites due to increased biosorbent dosages cannot be overruled, as this may result in a low specific uptake [19]. Several

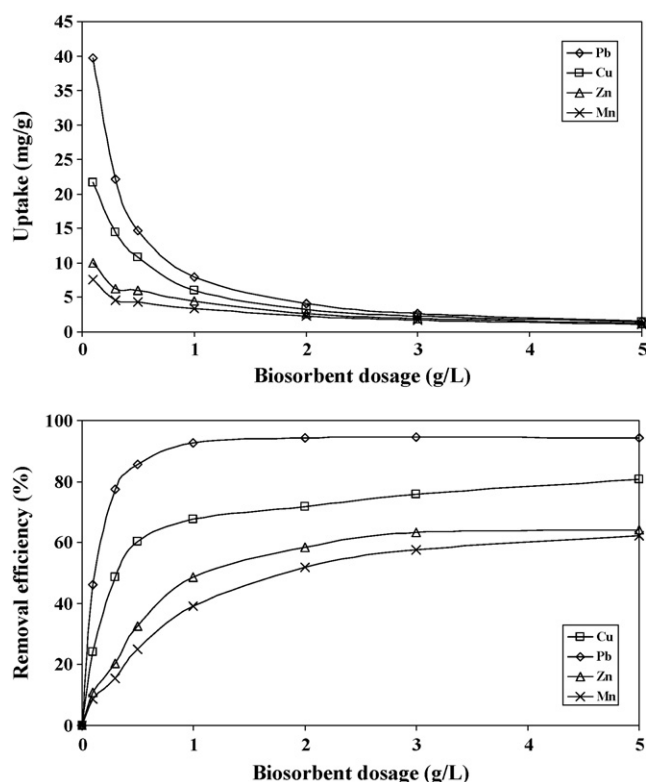


Fig. 2. Effect of *Sargassum* dosage on biosorption of Pb, Cu, Zn and Mn (solution $pH 6$; temperature = $23^\circ C$; agitation rate = 150 rpm).

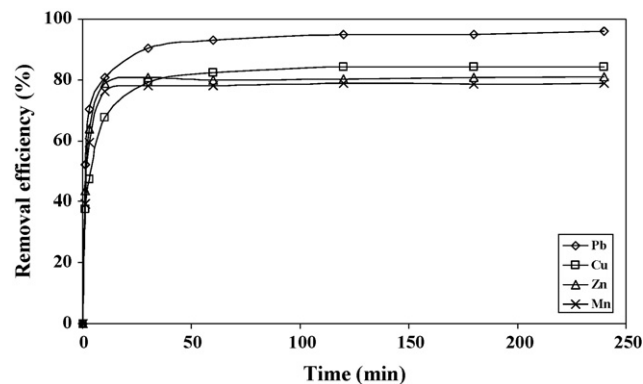


Fig. 3. Biosorption kinetics of multi-metal system (solution $pH 6$; biosorbent dosage = 3 g/L; temperature = $23^\circ C$; agitation rate = 150 rpm).

investigators observed this trend during their biosorption experiments. For instance, Vijayaraghavan et al. [20] observed that copper removal efficiency of crab shell increased with increasing biosorbent concentration, whereas copper uptake capacity decreased at higher biosorbent concentrations. From Fig. 2, it was clear that maximum removal efficiencies were observed at biomass dosages above 3 g/L. On the other hand, maximum biosorption capacities were observed at dosages below 1 g/L. The metal uptake capacity and removal efficiency are equally important in sorption experiments as both usually take part in deciding the sorption performance of a given biosorbent. Taking these two factors into consideration, the biosorbent dosage of 3 g/L was selected for further studies, as it shown relatively good removal efficiencies and uptake capacities.

3.1.3. Effect of contact time

In next series of experiments, efforts were made to understand the biosorption kinetics. Sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions [21]. Therefore, the concentration–time profile during interaction of *Sargassum*–multi-metal system was recorded (Fig. 3). For all the metal ions, the biosorption rate was fast and most of the process was completed within 20 min, followed by slow attainment of equilibrium around 50 min. The very fast sorption kinetics observed with *Sargassum* represents an advantageous aspect when water treatment systems are designed.

3.1.4. Biosorption isotherms

To explore and compare the performance of *Sargassum* on different metal ions, single metal biosorption isotherms were derived. Fig. 4 shows the representation of metal biosorption isotherms, the capacity (Q) of *Sargassum* (in mg/g) against the equilibrium concentration (C_f) at $pH 6$. The uptake of all four metal ions increased with increase in their corresponding metal concentrations and reached saturation at higher equilibrium concentrations. Among the metal ions, *Sargassum* recorded the highest uptake of 168.7 mg Pb/g, followed by copper (45.2 mg/g), zinc (20.3 mg/g), and manganese (16 mg/g).

Attempts were made to model the metal biosorption isotherms using the non-linear forms of the Langmuir and Freundlich, which can be represented as follows:

$$\text{Langmuir model : } Q = \frac{Q_{\max} b_L C_f}{1 + b_L C_f} \quad (2)$$

$$\text{Freundlich model : } Q = K_F C_f^{1/n} \quad (3)$$

where Q_{\max} is the maximum metal uptake (mg/g), b_L the Langmuir equilibrium constant (L/mg), K_F is the Freundlich constant (L/g) $^{1/n}$,

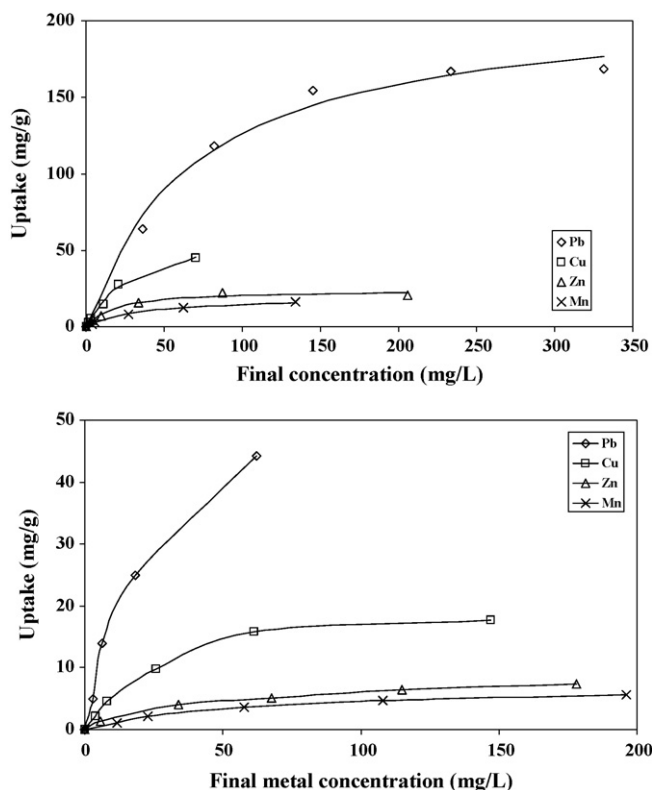


Fig. 4. Biosorption isotherms at pH 6 for single- and multi-metal solutions (biosorbent dosage = 3 g/L; temperature = 23 °C; agitation rate = 150 rpm). Single-component isotherm curves were predicted by the Langmuir model.

and n is the Freundlich constant. The main reason for the extended use of these isotherm models is that they incorporate constants that are easily interpretable. The constants along with correlation coefficients obtained from the isotherm models are listed in Table 2. The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different sorbents. The Langmuir model served to estimate the maximum metal uptake values where they could not be reached in the experiments. The constant b represents affinity between the sorbent and sorbate. The Langmuir constant, Q_{\max} , revealed that *Sargassum* biomass performed well in the case of lead, followed by Cu, Zn, and Mn. For favorable biosorption, high Q_{\max} and a steep initial isotherm slope (i.e., high b) are desirable.

The Freundlich isotherm is originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces, or surfaces supporting sites of varied affinities. From Table 2, considering the R^2 values, it was obvious that the Freundlich model

Table 2
Biosorption isotherm constants for metal biosorption by *Sargassum* biomass

Isotherm models	Metal ions			
	Lead	Copper	Zinc	Manganese
Langmuir				
Q_{\max} (mg/g)	214.0	67.5	24.2	20.2
b (L/mg)	0.014	0.0296	0.0534	0.0268
R^2	0.997	0.999	0.995	0.999
ε (%)	1.85	2.58	2.52	3.40
Freundlich				
K_F (L/g)	22.9	3.9	4.5	1.6
n	3.79	1.73	3.22	2.06
R^2	0.990	0.994	0.850	0.994
ε (%)	3.40	22.10	13.67	12.09

well described the isotherm data in all cases. High values of K_F and n were observed for lead, which implies that the binding capacity reaches the highest value and the affinity between the biomass and metal ions was also higher. Considering the percentage error values, the Langmuir model was found to describe the isotherm data well for all four metal ions.

Thus, *Sargassum* biomass can be competent for the single-component biosorption of Pb, Cu, Zn, and Mn at pH 6 and biosorbent dosage of 3 g/L. Next, isotherm experiments were conducted to study the multi-component biosorption potential of the biomass (Fig. 4). Typical biosorption isotherms were observed in the case of all four metal ions. The isotherms obtained for *Sargassum* biomass were close to “L-isotherms” [22]. This means that the ratio between the concentration of the solute remaining in the solution and those biosorbed on the sorbent decreases when the solute concentration increases, providing a concave curve. However, it should be noted that isotherm curves of all four metal ions do not reach any plateau which clearly indicates the further sorption potential of *Sargassum*. As expected, *Sargassum* biosorbed more Pb, followed by Cu, Zn, and Mn. The highest uptake capacity was observed as 44.2, 17.7, 7.3, and 5.7 mg/g for Pb, Cu, Zn, and Mn, respectively.

Comparing the single- and multi-metal solutions, a clear decrease in biosorption capacity was observed. This may be attributed to the competition between the metal ions in occupying the active binding sites. While comparing the metal uptakes observed in single solutions to those of multi-metal solutions, lead uptake was decreased to a maximum of 3.8 times; while the decrease of other three metal ions was in the range of 2.5–2.8 times. This clearly implies that four metal ions compete for the same binding sites and thus decrease the overall biosorption capacity of the *Sargassum* biomass.

3.2. Application of *Sargassum* to storm water runoff

As *Sargassum* performed well in synthetic multi-metal solutions, further experiments were conducted to study the potential of the biomass for decontamination of real storm water runoff. The characterization of the storm water samples revealed that the metal concentrations were within the allowable limit [23]. Also, it is worth noting that there was not much variation in the two samples taken at different periods. The reason for these results could be attributed to the light activities carried out near the sampling spot and no drastic change in the intensity of activities was observed during the sampling period. However, the metal concentrations were expected to increase in highly trafficked and industrial areas [3]. To account for these likely variations, the storm water samples were spiked with 10 mg/L each of four metal ions. The performance of *Sargassum* in the removal of four metal ions from storm water sample was slightly less when compared with synthetic multi-solute solution (Fig. 5). This loss in biosorption performance could be due to the inherent characteristics of the water sample. The storm water contained contaminants other than these four metal ions including a number of light metal ions and anions (Table 1). It is known that light metal ions such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} can compete with heavy metal ions in occupying carboxyl sites of marine algal biomass [24–26]. However, the presence of monovalent ions, such as Na^+ and K^+ , which can be bound weakly through mostly electrostatic attraction, are effective in competing only with other weakly bound ions. Since deprotonated negatively charged groups in algal biomass can electrostatically attract any cation, the presence of significant Na^+ and K^+ ions can pose competition to Pb, Cu, Zn and Mn during biosorption. On the other hand, the presence of divalent cations such as Ca^{2+} and Mg^{2+} may exert a stronger influence on metal uptake than that of monovalent ions. This is because of their high electrostatic accumulation and greater

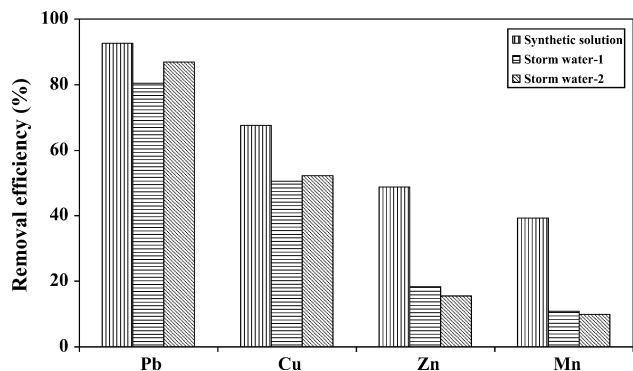


Fig. 5. Comparison of biosorption performance on synthetic multi-metal solutions and storm water runoffs (solution pH 6; biosorbent dosage = 3 g/L; temperature = 23 °C; agitation rate = 150 rpm).

affinity towards the algal binding sites [26,27]. The presence of anions can lead to the following: (1) formation of complexes with higher affinity for the sorbent than the free metal ions (i.e., an enhancement of sorption) and (2) formation of complexes with lower affinity for the sorbent than free metal ions (i.e., a reduction of sorption) [28]. In many instances, the presence of anions such as nitrate, chloride and sulfate decreased metal biosorption [29,30].

4. Conclusions

The following conclusions can be drawn from the present study:

1. *Sargassum* sp. was found to be an effective biosorbent for the removal of lead, copper, zinc, and manganese from synthetic multi-solute solutions and real storm water runoff.
2. Preliminary experiments using synthetic multi-metal solutions revealed that optimal experimental conditions of pH 6, biosorbent dosage of 3 g/L, and equilibrium time of 50 min were required to obtain high biosorption performance of *Sargassum* sp.
3. Isotherm experiments revealed that *Sargassum* can accommodate 168.7 mg Pb/g, 45.2 mg Cu/g, 20.3 mg Zn/g, and 16 mg Mn/g from single solute systems. In the case of multi-solute system, *Sargassum* exhibited 44.2 mg Pb/g, 17.7 mg Cu/g, 7.3 mg Zn/g, and 5.7 mg Mn/g.
4. The potential of *Sargassum* to decontaminate storm water runoff was examined. The results revealed that the seaweed performance on the removal of four metal ions was satisfactory. Even though slightly inferior to those of synthetic metal solutions, which was expected due to the competition of other ions and organics, the seaweed showed promise for the removal of metal ions present in low concentrations.
5. Overall, this study demonstrated the possible application of biosorption to decontaminate storm water runoff and further study is required to investigate the influence of other ions, organics and water characteristics on the biosorption of metal ions onto seaweeds such as *Sargassum*.

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