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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.

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 pH ≤ 6, beyond which $Pb(OH)_2$ tends to dominate [14]. On the other hand, Zn(II) is present mainly as Zn^{2+} at pH < 7; and at pH 8–9, it exists mainly as Zn^{2+} and $Zn(OH)_2$, and in small quantities as $Zn(OH)^+$ [15]. In the cases of Cu and Mn, the predominant species were Cu^{2+}

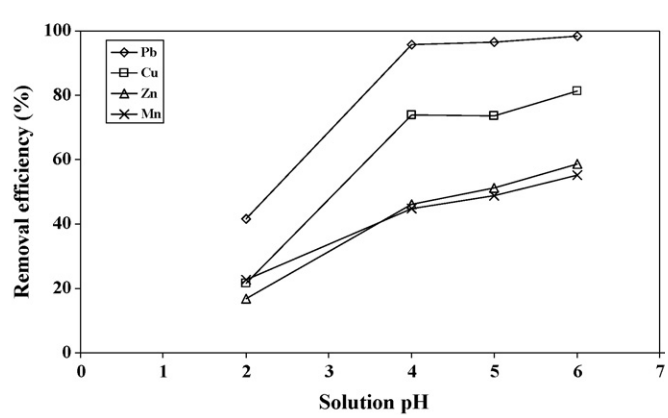

Fig. 1. Effect of solution pH on the biosorption of Pb, Cu, Zn and Mn in multi-solute system by *Sargassum* biomass (biosorbent dosage = 3 g/L; temperature = 23 °C; agitation rate = 150 rpm).