Hybrid Sargassum-sand sorbent: A novel adsorbent in packed column to treat metal-bearing wastewaters from inductively coupled plasma-optical emission spectrometry

K. Vijayaraghavan $^{a,b}$ & U.M. Joshi $^a$

$^a$ Singapore-Delft Water Alliance, National University of Singapore, Singapore

$^b$ Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India

Published online: 15 Aug 2013.


To link to this article: http://dx.doi.org/10.1080/10934529.2013.815503
Hybrid *Sargassum*-sand sorbent: A novel adsorbent in packed column to treat metal-bearing wastewaters from inductively coupled plasma-optical emission spectrometry

K. VIJAYARAGHAVAN\(^1,2\) and U.M. JOSHI\(^1\)

\(^1\)Singapore-Delft Water Alliance, National University of Singapore, Singapore
\(^2\)Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India

Laboratory batch and column experiments were carried out to examine the efficiency of algal-based treatment technique to clean-up wastewaters emanating from inductively coupled plasma-optical emission spectrometry (ICP-OES). Chemical characterization revealed the extreme complexity of the wastewater, with the presence of 14 different metals under very low pH (pH = 1.1), high conductivity (6.98 mS/cm), total dissolved solid (4.46 g/L) and salinity (3.77). Batch experiments using *Sargassum* biomass indicated that it was possible to attain high removal efficiencies at optimum pH of 4.0. Efforts were also made to continuously treat ICP-OES wastewater using up-flow packed column. However, swelling of *Sargassum* biomass leads to stoppage of column. To address the problem, *Sargassum* was mixed with sand at a ratio of 40: 60 on volume basis. Remarkably, the hybrid *Sargassum*-sand sorbent showed very high removal efficiency towards multiple metal ions with the column able to operate for 11 h at a flow rate of 10 mL/min. Metal ions such as Cu, Cd, and Pb were only under trace levels in the treated water until 11 h. The results of the treatment process were compared with trade effluent discharge standards. Further the process evaluation and cost analysis were presented.

**Keywords:** Wastewater treatment, algae, bioremediation, packed column, biosorption, separation.

**Introduction**

Marine algae (seaweeds), a renewable natural biomass, proliferate ubiquitously and abundantly in the littoral zones of world oceans. Seaweeds have many applications which include production of agar, alginate and carrageenan.\(^1\) In recent years, seaweeds are also identified as good biosorbents for various heavy metal ions.\(^2,3\) Seaweeds are usually found in three basic colours (divisions): brown (Phaeophyta), red (Rhodophyta) and green (Chlorophyta). Among these types, brown seaweeds are proved to be efficient in metal biosorption\(^4\) because of their polysaccharide content. The acid polysaccharides are mainly composed of alginic acids and sulfated fucans; and these components are often associated with excellent biosorption capacity of brown seaweeds.

In biosorption schemes, seaweeds possess several advantages such as being inexpensive, and they possess excellent metal binding ability, high mechanical stability and easily available.\(^3\) However, previous studies have revealed that seaweeds suffer from few drawbacks such as swelling\(^6,7\) and poor performance in multi-component solutions.\(^8\) These shortcomings hinder the usage of seaweeds in real-scale applications. Fixed bed sorption columns are often used in industrial wastewater treatment scheme to remove dissolved contaminants. On loading seaweeds in packed column, they block the liquid flow because of swelling characteristics which leads to stoppage of column. Some investigators worked on this issue through techniques such as immobilization or chemical modification of seaweed biomass.\(^9,10\) These techniques are often costly and involve usage of chemicals. Hence, cheap and environmental friendly techniques to successfully operate seaweed-biosorption columns are on the horizon to make the process successful in real applications.

Studies on application of biosorption techniques to real wastewaters are seldom found in literature. Most of the published results were based on exploring the efficiency of biosorbents in single-solute systems.\(^11\) However, real wastewaters often comprise of multiple ions and their presence strongly influences the removal capacity of the biosorbent towards a particular solute.\(^12,13\) Since biosorption is a passive process in which several chemical groups or chemical components of the same biomass play a vital role in metal biosorption, one can expect a complicated...
interaction in the presence of many ions.\cite{8} Hence, more research is needed to explore the suitability of biosorption technique to treat different metal-bearing wastewaters.

Thus, the present article utilizes the well established seaweed biosorbent, \textit{Sargassum} biomass, for the decontamination of wastewaters emanating from Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). These wastewaters are usually very complicated and difficult to treat owing to the presence of multiple metal ions, very low pH and complex metal speciation due to extended storage periods. It is very common for research laboratories to send ICP-OES wastewater directly to waste collectors, who decide the treatment scheme. Considering that many industries approach research laboratories to solve their wastewater disposal problems, it is regretful to know that research laboratories have no solution for their own wastewaters. Understanding this major problem, this article intended to utilize \textit{Sargassum}-loaded packed column for the removal of heavy metal ions from ICP-OES wastewaters. Also, this study has developed a technique to overcome the problem of seaweed swelling during operation of a packed column.

Materials and methods

\textbf{Collection of seaweeds and effluent}

\textit{Sargassum} biomass was collected from beaches of Sentosa Island, Singapore. The biomass was extensively washed with deionized water in laboratory to remove sand, and other dirt particles. The biomass were then dried in an oven at 60°C and subsequently grounded to obtain particles with an average size of 0.75 mm. Sand (0.8–1.8 mm), purchased locally, was washed extensively with deionized water and subsequently dried naturally for usage in sorption experiments.

The wastewater generated by ICP-OES (Perkin Elmer Optima 3000 DV, USA), located in Temasek Laboratories (Level 7) of National University of Singapore (Singapore), was collected from July 2011 to August 2011. The wastewater generated every week was stored in plastic containers and kept in cold room (4°C). After the collection period, the composite samples were analyzed for pH, conductivity, total dissolved solids (TDS), salinity, light metal and heavy metal concentrations.

\textbf{Batch experiments}

The batch sorption experiments were conducted in 250 mL Erlenmeyer flasks at 22 ± 1°C. Two hundred milligrams of \textit{Sargassum} biomass were mixed with 100 mL of effluent in Erlenmeyer flask, and the contents were agitated on a rotary shaker at 160 rpm. After agitation for 1 h, the mixture was filtered using 0.45-\(\mu\)m PTFE membrane filter and the filtrate was analyzed for metal concentrations in ICP-OES (PerkinElmer Optima 3000 DV). For pH edge studies, the effluent pH was adjusted using 1 M NaOH from 1.1 to 4.0.

For kinetic studies, experiments were conducted at pH 4 and samples were withdrawn at regular time intervals. For desorption experiments, the \textit{Sargassum} biomass that was previously exposed to ICP-OES wastewater at pH 4 was separated from the solution by filtration. The metal-loaded \textit{Sargassum} was then contacted with 50 mL of HCl at different strengths in Erlenmeyer flasks on a rotary shaker at 160 rpm for 3 h. The remaining analysis procedure was same as stated earlier. The metal-free \textit{Sargassum} biomass obtained after desorption was washed extensively with deionized water and subsequently reused for next sorption cycle to evaluate the reuse capacity of the biosorbent.

\textbf{Column experiments}

For fixed bed column studies, a glass column (ID = 2.4 cm and height = 35 cm) was fabricated with L/D ratio greater than 10. At the top of column an adjustable plunger was attached to fix the bed height at 25 cm. There was a 3-cm layer of glass beads at the bottom of column to distribute the effluent uniformly. Different sorbents were tested in the column, which include \textit{Sargassum}, sand and hybrid \textit{Sargassum}-sand sorbent. The hybrid \textit{Sargassum}-sand sorbent was prepared as follows: a known quantity of \textit{Sargassum} biomass was soaked in DI water for 2 h. Once completely swelled, water was decanted and known quantity of sand was mixed uniformly with the wet biomass to obtain the desired sorbent mix. After loading the sorbent in packed column, the ICP-OES effluent at pH 4 was pumped upwards through the column using a peristaltic pump at a flow rate of 10 mL/min. Treated effluent samples were collected at the top of the column at regular time intervals and analysed for metal concentrations. Once the column was exhausted, desorption process was started using 0.01 M HCl as an influent at flow rate of 10 mL/min.

\textbf{Results and discussion}

\textbf{Characterization of ICP-OES wastewater}

The physicochemical characteristics of ICP-OES wastewater are shown in Table 1. In general, the ICP-OES wastewater showed relatively high values for pollution indicating parameters such as conductivity, TDS and salinity. In contrary, the pH of wastewater was extremely low, on the order of 1.1. Since the experimental protocol for sample preparation for ICP-OES is to digest the samples in acid, the wastewaters emanating from ICP-OES usually have low pH value. Owing to the presence of high dissolved fractions, the wastewater was found to have high conductivity, TDS and salinity. Further efforts were made to identify the presence of metal ions in the wastewater by examining the
Sargassum-sand sorbent to treat metal-bearing wastewaters

Table 1. Characteristics of ICP-OES wastewater, treated wastewater and trade effluent discharge standards.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ICP-OES wastewater</th>
<th>NEA discharge limit$^{[14]}$</th>
<th>Treated ICP-OES wastewater by Sargassum-sand column$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.1</td>
<td>6–9</td>
<td>5.1–5.7 (5.5)</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>6.98 ± 0.05</td>
<td>—</td>
<td>6.60–6.70 (6.63)</td>
</tr>
<tr>
<td>Salinity</td>
<td>4.46 ± 0.02</td>
<td>—</td>
<td>3.81–3.84 (3.82)</td>
</tr>
<tr>
<td>Total dissolved solids (g/L)</td>
<td>3.77 ± 0.03</td>
<td>1.0</td>
<td>4.51–4.56 (4.53)</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>118 ± 1.5</td>
<td>—</td>
<td>&gt; 1000 (&gt;1000)</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>17.2 ± 0.3</td>
<td>—</td>
<td>46.9–153.5 (61.2)</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>7.84 ± 0.23</td>
<td>200</td>
<td>16.5–65.3 (28.1)</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>4.55 ± 0.09</td>
<td>200</td>
<td>5.01–98.3 (25.5)</td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>0.36 ± 0.11</td>
<td>1.0</td>
<td>0–0.318 (0.171)</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>2.08 ± 0.07</td>
<td>5.0</td>
<td>0–2.02 (0.96)</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.43 ± 0.17</td>
<td>10.0</td>
<td>0–0.298 (0.134)</td>
</tr>
<tr>
<td>Co (mg/L)</td>
<td>0.26 ± 0.04</td>
<td>—</td>
<td>0–0.123 (0.044)</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>1.47 ± 0.12</td>
<td>1.0</td>
<td>0–0.432 (0.124)</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>4.81 ± 0.32</td>
<td>0.1</td>
<td>0–0.212 (0.081)</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>2.31 ± 0.14</td>
<td>1.0</td>
<td>0–0.678 (0.186)</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>3.79 ± 0.37</td>
<td>—</td>
<td>0.10–3.35 (1.53)</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>3.91 ± 0.21</td>
<td>0.1</td>
<td>0–0.182 (0.056)</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>0.88 ± 0.11</td>
<td>0.1</td>
<td>0–0.06 (0.024)</td>
</tr>
<tr>
<td>Total metals (mg/L)</td>
<td>21.13 ± 0.83</td>
<td>10.0</td>
<td>0.10–7.67 (3.31)</td>
</tr>
</tbody>
</table>

Values in brackets represent average values of parameters during 11 h of column operation.

$^{a}$Data obtained through 11 h of column operation.

sample for various metal ions against Sigma-Aldrich (St. Louis, MO, USA) multi-metal standards in ICP-OES.

Several light and heavy metal ions were identified in ICP-OES wastewater including Na, K, Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Cd and Pb. The effluent discharge standards as proposed by National Environmental Agency, Singapore$^{[14]}$ are presented in Table 1, which indicates the extreme nature of ICP-OES effluent. Most of the heavy metal ions were found to be several folds higher than the effluent discharge limit. For instance, the concentrations of Cd and Cu in the ICP-OES effluent were 39 and 48 times more than the permissible discharge limit, respectively. On the other hand, concentrations of light metal ions, which are less toxic compared to heavy metal ions were well within the discharge standards. The effluent pH value was very low compared to permissible limit of 6 to 9. Additionally, Table 1 also points out that the TDS were 4-fold higher than the permissible discharge standard. Thus, it was clear that several contaminants in the ICP-OES effluent pose serious concern and treatment should be performed before the discharge of effluent.

It is also important to understand the speciation of metal ions in the ICP-OES effluent, which in turn controls their availability to the sorbent. Considering the strong acidic nature of the effluent, all the heavy metal ions were predominately in their divalent form. Control experiments conducted by varying effluent pH until pH 4 revealed no significant changes in metal concentration. Increasing pH beyond 4 resulted in metal precipitation possibly metal hydroxide formation. For instance, while increasing pH of the effluent to 4.5, Fe concentration decreased to 0.21 mg/L from 0.43 mg/L at pH 4. A similar trend was observed for Cr and Pb ions, whose concentrations in the effluent decreased by 27 and 49%, respectively, when the pH increased to 4.5. As far as other metal ions were concerned, % reduction in concentration was less significant (<5%) at pH 4.5. It is worth noting that even though metal hydroxide precipitation is pH sensitive, it also depend on other factors such as concentration of metal and presence of other metals in the mixture.

Optimization of bioremediation process in batch mode

Our past studies have indicated that Sargassum biomass possess good binding capacity towards various heavy metal ions$^{[8,15,16]}$. Thus, in this present study, efforts were made to explore the biosorption potential of Sargassum biomass in multi-metal wastewaters. Initially, the effect of solution pH on metal removal efficiency of Sargassum biomass was studied (Fig. 1). Experiments conducted at unadjusted pH (pH 1.1) indicated that the biosorption performance of Sargassum towards different metal ions in ICP-OES wastewater was poor. The reason for this low performance was due to the nature of binding sites present in the biomass. The carboxylic groups are generally the most abundant group in Sargassum biomass, followed by sulfonic and phosphoryl groups$^{[3]}$.

Through ion-exchange mechanism, these functional groups attract positively charged metal ions$^{[2,3]}$. At strong acidic conditions, these negatively charged sites become...
Fig. 1. Influence of equilibrium pH on metal removal efficiency of Sargassum biomass from ICP effluent.

protonated and thus no longer available to attract metal ions from solution. The situation is likely to be different at high solution pH values. Thus efforts were made to conduct experiments at higher pH values. In general, improved biosorption performance was observed as the pH was increased from 1.1 to 4.0. This means that when the pH is around 4, the carboxyl groups are deprotonated and able to bind positively charged metal ions. It is worth noting that $pK_a$ value of carboxyl groups lies in the range of 3.6 and 4.5.\[8,17\]

Experiments were not conducted beyond pH 4 owing to precipitation of some metal ions. From Figure 1, it can be inferred that Sargassum preferentially removed some metal ions from the ICP-OES effluent. However, it should be noted that initial concentration of each metal ion played a significant role in deciding the biosorption performance of the biomass. For instance, at pH 4, Sargassum exhibited removal efficiency of 87.8% for Co whereas only 47% for Zn even though the biomass removed 4.6 times more Zn (in mg/L) than Co. The treatment of multi-metal effluent is more complex to evaluate because metal ions compete for binding sites and as a consequence displacement of one metal species by another, which has high affinity for biomass binding sites, can occur.\[18\]

Few researchers have established affinity sequence for alginate towards different heavy metal ions which can be correlated with electronegativity atomic mass and ionic radii of metal ions.\[19,20\] However, this correlation can only be feasible in controlled or simulated systems as real conditions tend to have other external factors to influence the order of metal removal. Therefore, no effort was made to study the preference of each metal ion towards Sargassum biomass. Analyzing the pH edge results (Fig. 1), it can be inferred that optimum pH condition to completely utilize the biosorption potential of Sargassum was found to be pH 4 and hence it was maintained in all the subsequent experiments.

The metal removal kinetics of Sargassum biomass was studied with the assumption that this data will be helpful to determine the residence time of solute in column experiments and scale-up processes. Kinetic experiments (Fig. 2) typically showed a rapid uptake of all ions by Sargassum biomass within few minutes of contact, followed by relatively slow attainment of equilibrium. The initial rapid phase occurred within 2 to 10 min for all metal ions, whereas complete equilibrium was achieved within 20 min as evidenced by a plateau.

Batch desorption experiments were conducted to regenerate and reuse Sargassum biomass in multiple cycles. In pH edge experiments (Fig. 1), under strongly acidic conditions, very few metal uptake values were recorded owing to the competition from H$^+$ ions. Thus, it would be logical to assume that the sorbed heavy metal ions can be recovered through reverse direction ion-exchange mechanism by elutants which can supply H$^+$ ions. Therefore, HCl at different strengths (0.01, 0.05 and 0.1 M) were used to regenerate biosorbent for further usage.Irrespective of the strength of HCl used, desorption process resulted in complete elution with efficiencies exceeded 98.1% for all metal ions. The major difference observed among the different strengths of HCl was in the biomass weight loss at the end of desorption process.
Fig. 2. Biosorption kinetics data obtained during treatment of ICP-OES wastewater by *Sargassum* biomass.

The percentage weight loss after HCl desorption was approximately 3.9, 9.2 and 16.5% with 0.01, 0.05 and 0.1 M, respectively. Hence, the least damaging 0.01 M HCl was selected for further experiments. With the aim of evaluating the removal efficiency of *Sargassum* biomass during repeated cycles, regeneration experiments were conducted for three sorption-desorption cycles (Fig. 3). Some reduction of the sorption performance of *Sargassum* biomass was observed as the cycle progressed. This can be explained by leaching of the biomass components by acidic elutants. However, this decline in sorption performance never exceeded 8.1% for any of the metal ions at the end of regeneration experiments. The degree of severity on the biosorbent by 0.01 M HCl was also less, as...

Fig. 3. Regeneration and reuse of *Sargassum* biomass for metal biosorption in three sorption-desorption cycles (sorption pH = 4.0; elutant = 0.01 M HCl).
only 5.6% weight loss was observed at the end of third cycle.

**Performance of Sargassum in continuous flow mode**

With the successful performance of *Sargassum* in batch mode of operation, further efforts were made to examine the potential of biomass in continuous-flow mode. The major advantage of choosing a packed column as a reactor for biosorption is that it efficiently utilizes the sorbent capacity and results in a better quality of the effluent. Preliminary column experiments were performed by loading *Sargassum* biomass in a packed column. However, the biomass showed a tendency of swelling on contact with influent liquid and subsequently blocked the liquid flow inside the column. Hence, high pressure developed which lead to stoppage of column. This problem of swelling is common in seaweeds and is reported by several investigators.[22,23]

The swelling behaviour of *Sargassum* can be directly correlated to the presence of alginate in the biomass cell wall.[24] To tackle this swelling issue, we developed a simple technique by uniformly mixing sand with swelled *Sargassum* biomass. After examining the nature of effluent flow inside the column for 6 h (data not presented), we finalized 40: 60 (*Sargassum*: coarse sand) on volume basis as optimal for efficient liquid flow in packed bed operation without any change in inlet and outlet flow rates. With this finding, the potential of *Sargassum*-sand hybrid sorbent to continuously cleanup ICP-OES wastewater was investigated in a packed column assembly. Important column parameters including the column retention capacity and% removal during entire column operation are presented in Table 2. Since different metal ions of varied concentrations were present in the wastewater, stringent regulatory limit were imposed for column service time, which implies that the column will be stopped for regeneration when any of the outlet metal concentration reaches its corresponding initial concentration.

Figure 4 illustrates the breakthrough curves of each metal ion obtained from hybrid *Sargassum*-sand loaded column during treatment of ICP-OES wastewater. In general, the biosorption performance of hybrid *Sargassum*-sand towards all metal ions was excellent. This high performance by the hybrid sorbent can be attributed to the presence of *Sargassum* biomass as the control experiments conducted in sand-loaded packed column demonstrated the poor adsorption capacity of sand towards all metal ions. Within 5 min of sand-loaded packed column operation, the $C/C_0$ (outlet metal concentration/inlet metal concentration) values of all heavy metal ions were greater than 0.93. For instance, $C/C_0$ value of Mn was approximately 1.0 within 5 min of column operation. In contrary, the hybrid *Sargassum*-sand loaded column was able to retain all heavy metal ions for 11 h before $(C/C_0)_{Mn} = 1$.

This corresponds to 58 bed volumes or 6.6 L of ICP-OES wastewater treated. The performance of *Sargassum*-sand sorbent towards all metal ions in terms of removal efficiency and $C/C_0$ at the end of service time is presented in Table 2. For several metal ions including Cu, Cd and Pb, the hybrid-biosorbent exhibited total removal efficiencies greater than 90%. Although removal efficiency strongly depends on initial metal concentration, it is encouraging to know that hybrid sorbent possesses good biosorption efficiency towards variety of metal ions. As can be seen in batch experiments, column experiments also pointed out the poor affinity of biosorbent towards Cr, Mn and Al (Table 2). Considering the uptake capacity, it can be inferred from Table 2 that hybrid sorbent exhibited mediocre metal biosorption capacity per gram of biosorbent. Apart from expected decrease due to multi-component system, it is important to understand that these values represent only the column operation until 11 h and further capacity of column was not utilized as Mn reached service time concentration.

Concurrently, the concentration profiles of light-metal ions were also monitored (Fig. 5). A rapid increase in their concentrations was observed in initial stages followed by gradual decrease as time progressed. In 10 min of column operation, concentrations of both Ca and Mg ions were 9- and 21-folds increased, respectively, in the outlet-treated water. This confirms the association of ion-exchange mechanism during metal removal by *Sargassum* biomass. Moreover, the effluent pH showed tendency to increase during initial column operation and then decreased as the bed saturation progressed (Fig. 5). The feed pH 4.0 was not reached during the column operation. The increase in outlet pH during the initial stages can be directly correlated with release of light metal ions from the seaweed (Fig. 5);

<table>
<thead>
<tr>
<th>Table 2. Results of <em>Sargassum</em>-sand loaded packed column during the treatment of ICP-OES wastewater.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal</strong></td>
</tr>
<tr>
<td>(C/C_0)_11h</td>
</tr>
<tr>
<td>Uptake based on <em>Sargassum</em> mix (mg/g)</td>
</tr>
<tr>
<td>Uptake based on <em>Sargassum</em></td>
</tr>
<tr>
<td>Removal efficiency (%)</td>
</tr>
<tr>
<td>Elution efficiency (%)</td>
</tr>
</tbody>
</table>

1$C/C_0 =$ outlet metal concentration/inlet metal concentration.

*Assuming that sand possess negligible sorption capacity towards heavy metal ions.
nevertheless, there is usually a large error when converting pH to ion concentration. On the other hand, the hybrid sorbent showed some potential to decrease the conductivity of the treated effluent; however, owing to the mechanism of ion-exchange drastic changes in conductivity was not observed (Table 1).

Column regeneration experiments with 0.01 M HCl indicated that it was possible to clean-up the column within 60 min using only 0.6 L of eluant. As opposed to sorption, desorption process was non-selective. All heavy metal ions exhibited a similar elution curves of “inverted V-shaped,” which implies a sharp increase in concentration followed...
by gradual decrease. The elution efficiencies were greater than 98.4% for all heavy metal ions (Table 2).

**Process evaluation**

Results obtained from the packed column loaded with hybrid sorbent were compared to the standards proposed by the National Environmental Agency, Singapore.[14] During the entire operation period of 660 min, the column was found to be capable of decreasing heavy metal concentrations well below the trade effluent discharge standards (Table 1). However, it is important to understand that the present treatment system unable to majorly influence the physicochemical parameters such as conductivity, TDS and salinity. The treated effluent pH lies in the range of 5.1–5.7, which was slightly below the discharge standard of 6–9. Excess concentrations of Na, K, Ca and Mg ions were observed in treated effluent (Table 1). These ions were leached from the *Sargassum* biomass during biosorption of heavy metal ions through ion-exchange mechanism. It is well known that seaweeds obtain these light metal ions from seawater.[25]

High concentrations of Na, K, Ca and Mg are always related to TDS, water hardness, scale formation and water bitterness.[26,27] However, these light metal ions were well below the discharge standards (Table 1). From these results, it is clear that a biosorbent column is capable of removing major pollutants from the ICP-OES wastewater; however, additional treatment is necessary to comply with discharge standards prior to disposal.

*Sargassum* biomass is considered as a nuisance in Singapore beaches and thus can be obtained free of cost with the approval from concerned authorities. It was also identified that minimal quantity of *Sargassum* is needed for continuous treatment. As an example, if one considers a monthly effluent generation of 1000 L, about 1.32 kg of *Sargassum* and 14.3 kg of sand would be needed for treating the examined wastewater. Once completely utilized in an adsorption column, the exhausted biosorbent can be disposed or further utilized depending on the availability. It should also be noted that the present study already proved the feasibility of reusing *Sargassum* in multiple sorption-desorption cycles. The other sorbent, sand, can be reused any number of times by simple washing with DI water as the material was found to possess negligible sorption capacity towards all the heavy metal ions.

**Conclusions**

The proposed treatment technique is an efficient and inexpensive alternative for complex metal-bearing wastewaters. With the usage of *Sargassum*, it was possible to remove multiple heavy metal ions (Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Cd, and Pb) from highly complicated solutions. Preliminary batch experiments indicated the importance of pH, which influenced the metal speciation as well as sorption performance of *Sargassum*. At optimum pH of 4, *Sargassum* biomass exhibited maximum uptake towards all heavy metal ions. Also, the metal-loaded *Sargassum* was regenerated and subsequently reused for three sorption-desorption cycles with 0.01 M HCl as eluant. The problem of seaweed swelling during column operation was tackled by mixing *Sargassum* with sand at a ratio of 40:60 on volume basis.

As a result, it was possible to operate the column that performed exceedingly well for 660 min before one of the contaminant (manganese) exceeds the service time concentration. During the entire column operation, concentrations of all heavy metal ions were well under the discharge standards. The results did not show a significant decrease in conductivity, TDS and salinity. Consequently, in the design of the process for wastewater treatment, it would appear necessary to introduce a final step to tackle these physicochemical parameters. Thus, it is apparent that the suggested process scheme could find promising applications for the treatment of complex metal-bearing wastewaters.

**Acknowledgements**

The authors gratefully acknowledge the support and contributions of this project to the Singapore-Delft Water Alliance (SDWA).

**References**

Sargassum-sand sorbent to treat metal-bearing wastewaters


