Differences in adsorption mechanisms of heavy metal by two different plant biomasses: reed and brown seaweed

B. Southichak, K. Nakano, M. Nomura, N. Chiba and O. Nishimura

ABSTRACT

The adsorption of Pb(II) by two different biomaterials, reed (Phragmites australis) and brown seaweed (Sargassum horneri) biomass pretreated with CaCl₂, were compared in an attempt to explain the differences in adsorption performance between the two biosorbents. A very interesting characteristic was found in their individual adsorption performances; the Pb(II) adsorption capacity of brown seaweed ($Q_{\text{max}} = 0.45 \text{ mmol/g}$) was much higher than that of reed ($Q_{\text{max}} = 0.05 \text{ mmol/g}$), but its adsorption affinity ($b = 112 \text{ L/mmol}$) was much lower compared with that of reed ($b = 471 \text{ L/mmol}$). To elucidate the mechanism, the elemental components, ion exchange phenomenon and roles of functional groups of these two biosorbents were compared. The higher Pb(II) adsorption by brown seaweed could be due to its richness in total functional groups and calcium contents on its surface. In contrast, the functional complexity, higher zeta potential and $pK_a$ value (deprotonation state) of reed are believed to lead to its high adsorption affinity.

Key words | affinity, biosorption, brown seaweed (Sargassum horneri), mechanism, metal ion, reed (Phragmites australis)

INTRODUCTION

Nowadays, there is a growing interest in utilizing renewable resources and exploiting biological reactions for environmentally friendly products for the treatment of water pollution worldwide (Wase & Forster 1997). Recently, methods of removing heavy metal from aqueous solution using inactive and dead biomass from certain types of seaweed and plants have gained popularity and are being considered for application due to their ability to bind and concentrate heavy metals from very dilute aqueous solutions.

Many kinds of seaweed have been reported to have high uptake capacities for heavy metals, and some species of brown seaweed exhibit much higher uptake values than other types of biomass, higher than activated carbon and comparable to those of synthetic ion exchange resins (Herrero et al. 2006). On the contrary, many plant biomasses, such as common reed, showed lower uptake capacities when exposed to high concentration of heavy metals, although their the adsorption performance was equal or even higher than seaweed in the case of low heavy metal concentration (Southichak et al. 2006).

Although there have been many studies on heavy metal removal from aqueous solutions using different types of natural or synthetic materials as biosorbent, attention has been given mostly to the maximum adsorption capacity ($q_{\text{max}}$) and most research has been dealing only with a particular type of biomass and/or different species belonging to a single type of biomass. The mechanism underlying why the adsorption capacity and/or affinity of one biomaterial is higher than the other is poorly understood. It has been suggested that specific functional groups such as carboxyl, amine, hydroxyl, phosphate and sulhydryl groups are mainly involved in the heavy metal binding by biomass (Sarret et al. 1998). However, very few attempts have been made to investigate parameters that influence the
adsorption affinity of different plant biomass. Therefore, understanding the differences of heavy metal adsorptive characterization by different biomaterials would be a powerful tool for finding novel biomaterials to be used as effective heavy metal biosorbents.

The objective of this study was to elucidate the individual removal mechanism of toxic heavy metal, Pb(II), from aqueous solutions by using reed and brown seaweed biosorbent. First, the adsorption capacity and affinity under favourable conditions of heavy metal solutions were compared. Then the physical and chemical characteristics such as elemental components, ion exchange phenomena, surface charges and roles of functional groups on both biomasses were compared. Finally, the relationship between these parameters and heavy metal adsorption were examined.

METHODS

Reed (Phragmites australis) biomass harvested from a wetland constructed for water purification in Iwate Prefecture, Japan and broken brown seaweed (Sargassum horneri) floating along the Matsushima Bay in Miyagi Prefecture were used as biomaterial for Pb(II) removal. The biomaterials were washed several times with deionised water to remove impurities and salts present in the raw materials. All the samples were dried at 60°C before being turned into a powder with particle sizes between 0.5 and 1 mm, referred to here as virgin reed (VR) and virgin brown seaweed (SW), respectively. Each biomass was then soaked in 0.25 M CaCl₂ solution. The biomass pretreated with CaCl₂ was washed many times with tap water before being dried in an oven and kept until use. The final pretreated biomass is referred to here as R-Ca for reed and SW-Ca for brown seaweed biosorbent, respectively.

The ash contents of the biomass were determined according to American Society for Testing and Material (ASTM) standards. The inorganic components (C, H, N, S) were analyzed using a CHNS analyzer (Vario ELIII Elemental, Japan). The amount of acidic and basic surface oxygen functionalities was determined using a simplified Boehm titration method where the determination of carbonyl groups using sodium ethoxide was not conducted (El-Sayed & Bandosz 2004). The surface charges (zeta potential) of biomass were measured using the Particle Electrophoresis Apparatus (MK.II; Taitec, Japan), equilibrating biosorbent in 0.01M KCl electrolyte solution before measurement. The functional groups present on biomass were analyzed by Fourier transform infrared spectroscopy FTIR (FTIR-84000 S; Shimadzu, Japan). In addition, potentiometric titrations were conducted by suspending a known weight of biomass in 0.1 M NaCl with N₂ gas bubbled through the solution before titration in order to prevent the dissolution of CO₂ gas.

The amount of heavy metal adsorbed to biosorbent at equilibrium conditions, \( q_e \) (mmol/L) can be calculated by using the following equation:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations (mmol/L), \( V \) and \( W \) are the liquid volume (L) and the weight of biomass used (g), respectively.

For the adsorption of Pb(II) on reed and brown seaweed biomass, the isotherm form of Langmuir is used as follows:

\[
q_e = \frac{q_{\text{max}}bC_e}{(1 + bC_e)}
\]

where \( q_e \) is the adsorbed amount (mmol/g), \( C_e \) the equilibrium concentration (mmol/L) and \( q_{\text{max}} \) the adsorption capacity (mmol/g); \( b \) is the Langmuir equilibrium constant (L/mmol) of adsorption which is related to the affinity of binding sites.

RESULTS AND DISCUSSION

The maximum adsorption, \( q_{\text{max}} \), and the adsorption affinity, \( b \), of Pb(II) at pH 3, 4 and 6 are plotted in Figure 1(a), (b) for reed, and Figure 1(c), (d) for brown seaweed biosorbent, respectively. Overall, the amount of Pb(II) adsorbed on both biosorbents increased with increased pH from 3 to 6. The \( q_{\text{max}} \) values of reed and brown seaweed biosorbents obtained from the plot between \( C_e \) and \( C_e/Q_e \) at the equilibrium pH 6 were 0.05 and 0.45 mmol/g, respectively, with in Pb(II) adsorption by brown seaweed 9 times
higher compared to reed biosorbent. The adsorption affinities of reed and brown seaweed biosorbents obtained from the Langmuir adsorption isotherm plotted at different pH solutions were also presented in Figure 1(b) and (d), respectively. As pH was increased from 3 to 6, the adsorption affinity of Pb(II) by reed biosorbent gradually increased from 178 to 471 L/mmol (about 2.6 times increase). In contrast, the adsorption affinity of brown seaweed biosorbent was relatively unchanged around 300 L/mmol at pH 3 and 4, but sharply decreased to 112 L/mmol when solution pH was increased from 4 to 6. This is a 2.6 times decrease in adsorption affinity compared with Pb(II) solution at pH 3. The differences in Pb(II) adsorption suggest that different properties in each biomaterial might be involved in Pb(II) binding. Further chemical characterization of each biomaterial was carried out.

Table 1 shows the elemental contents of C, H, N, and S which accounted for more than 50% by weight of the two biomasses. The higher H/C ratio of reed biomass suggests that it contains higher amounts of plant organic residual (cellulose) than brown seaweed. The content of crude protein was calculated using the formula %N × 6.25, revealing high crude protein content for SW, followed by VR, SW-Ca and R-Ca, respectively. In addition, the presence of sulphur in both biomasses may indicate the presence of sulfate groups on their cell wall that are believed to be able to bind heavy metals (Schewer & Wong 2000).

<table>
<thead>
<tr>
<th>Elements (% by weight)</th>
<th>VR</th>
<th>R-Ca</th>
<th>SW</th>
<th>SW-Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>46.24 ± 0.47</td>
<td>46.38 ± 0.03</td>
<td>34.80 ± 0.43</td>
<td>41.23 ± 3.83</td>
</tr>
<tr>
<td>H</td>
<td>2.11 ± 0.28</td>
<td>2.69 ± 1.84</td>
<td>1.04 ± 0.02</td>
<td>1.20 ± 0.32</td>
</tr>
<tr>
<td>N</td>
<td>11.11 ± 5.71</td>
<td>6.92 ± 2.35</td>
<td>11.35 ± 1.60</td>
<td>10.16 ± 1.32</td>
</tr>
<tr>
<td>S</td>
<td>1.22 ± 0.15</td>
<td>0.92 ± 0.08</td>
<td>2.34 ± 0.13</td>
<td>1.15 ± 0.01</td>
</tr>
<tr>
<td>H/C</td>
<td>0.04</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Total (%)</td>
<td>61</td>
<td>57</td>
<td>50</td>
<td>54</td>
</tr>
</tbody>
</table>

Figure 1 | Adsorption performance of Pb(II) by reed and brown seaweed biosorbent at different pH solutions. (a) and (b) represent the maximum adsorption and adsorption affinity of R-Ca, and (c) and (d) represent the maximum adsorption and adsorption affinity of SW-Ca. (adsorbent dosage: 2 g/L, equilibrium time: 6 h, initial Pb(II) concentration was from 0.48 to 150 μmol/L).
To quantitatively determine the total amount of oxygenated functional groups present on both biosorbents, the simplified Boehm titration method was used. As for the results, the total amount of functional groups on brown seaweed presented higher contents of acidic and basic functional groups compared with reed biomass (Table 2). An increase in functional groups of about 3 times was observed for SW-Ca. The ratio between the amount of Pb(II) adsorbed to the total amount of functional groups on R-Ca and SW-Ca revealed values of 0.92 and 0.65, respectively (Table 3). This suggested that the role of functional groups contributed more than 92% and 65% to Pb(II) adsorption by R-Ca and SW-Ca, respectively.

Figure 2(a) presents the zeta potential (negative charge) on the surface of R-Ca and SW-Ca as a function of pH. The fact that the zeta potential of both biosorbents did not intersect the horizontal axis suggests that the Pb(II) is first adsorbed on the external surface of both biosorbents, (An & Dultz 2007). The zeta potential of SW-Ca gradually increased when pH was increased from 2 to 4 and started to decrease again when pH was further increased from 4 to 8. On the contrary, the zeta potential of R-Ca started to increase from pH 3–6 and remained almost constant at around −64 mV for pH > 6. Overall, R-Ca exhibited higher zeta potential value compared to SW-Ca for every tested pH. At pH 6, R-Ca exhibited a twofold higher zeta potential compared with SW-Ca.

The concentration of Pb(II) solutions influenced the negative charge on the surface of the biomass. As shown in Figure 2(b), the zeta potential of R-Ca and SW-Ca showed the same trend of negative charge reduction when the concentrations of Pb(II) increased to 3 mmol/L. A remarkable decrease in zeta potential was observed for R-Ca at lower Pb(II) concentrations. This implied that Pb(II) covered most of the surface of R-Ca, which led to the increase of positive charge of Pb(II) and the decrease of negative charge of ions on the surface of R-Ca.

Figure 3 shows the change of pH as a function of time using SW-Ca and R-Ca as biosorbent in Pb(II) solution. Two different initial pH levels of 3.0 and 4.5 were set up and the changes in pH were recorded. As shown by Figure 3, after adding SW-Ca to metal solution (initial pH of 3), a rapid increase of pH in the range of 3.0 to 5.1 was observed in the first 6 h, and pH value gradually reached equilibrium after 6 h. A similar trend was obtained when the initial pH was set at 4.5 and the equilibrium pH of the biomass solution was around 6.5. A difference of about 2 points in pH was observed between each adsorption experiment. This may be due to the fact that some ion-exchange phenomenon may occur due to the release of alkaline earth ions into the solution. Conversely, a decrease of about 0.2 points of pH was observed after adding R-Ca to Pb(II) solutions. The tendency of increased solution pH by SW-Ca indicated the release of alkaline ions and OH⁻ into the solution and the decrease in solution pH of R-Ca suggested the release of protons from R-Ca into Pb(II) solution.

Among the alkaline ions released after increasing the pH of metal solutions, the amounts of calcium, magnesium and sodium from the SW-Ca into the solutions were the highest (data not shown), suggesting an ion exchange mechanism being involved. In case of R-Ca, low amount of these alkaline ions were observed.

Stumm & Morgan (1986) reported that sodium is a typical hard ion that is not bound covalently and therefore does not compete directly with the covalent binding of

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### Table 2 | Amount of functional groups on virgin and CaCl₂ pretreated reed and brown seaweed biomass using a simplified Boehm titration method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carboxylic (mmol/g)</th>
<th>Lactonic (mmol/g)</th>
<th>Phenolic (mmol/g)</th>
<th>Base (mmol/g)</th>
<th>Total (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VR</td>
<td>0.04</td>
<td>0.003</td>
<td>0.005</td>
<td>(−)</td>
<td>0.048</td>
</tr>
<tr>
<td>RCa</td>
<td>0.04</td>
<td>(−)</td>
<td>0.006</td>
<td>(−)</td>
<td>0.046</td>
</tr>
<tr>
<td>SW</td>
<td>0.04</td>
<td>0.005</td>
<td>0.008</td>
<td>0.175</td>
<td>0.228</td>
</tr>
<tr>
<td>SW-Ca</td>
<td>0.042</td>
<td>0.015</td>
<td>(−)</td>
<td>0.640</td>
<td>0.697</td>
</tr>
</tbody>
</table>

### Table 3 | Summarized physical/chemical properties of reed and brown seaweed biosorbent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>R-Ca</th>
<th>BSW-Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{\text{max}} ) at pH 6 (mmol/g)</td>
<td>0.05</td>
<td>0.45</td>
</tr>
<tr>
<td>( b ) at pH 6 (L/mmol)</td>
<td>471.00</td>
<td>112.00</td>
</tr>
<tr>
<td>Amount of functional groups (Boehm) (mmol/g)</td>
<td>0.04</td>
<td>0.69</td>
</tr>
<tr>
<td>Total functional groups/( Q_{\text{max}} ) ratio (%)</td>
<td>92.00</td>
<td>65.00</td>
</tr>
<tr>
<td>Zeta potential at pH 6 (mV)</td>
<td>−62.80</td>
<td>−28.42</td>
</tr>
<tr>
<td>Ash content (wt %)</td>
<td>3.60</td>
<td>11.93</td>
</tr>
<tr>
<td>Crude protein content (%)</td>
<td>43.25</td>
<td>63.30</td>
</tr>
</tbody>
</table>
heavy metals by a biosorbent. In case of calcium and magnesium, the equilibrium of alkaline ions released from biosorbent can be summarized as follows:

\[
\text{SW–alkaline ions} + [\text{Pb}]_{\text{solution}} \\
\xrightarrow{k} \text{SW–Pb} + \text{[alkaline ions]}_{\text{solution}}
\]

\[k_{\text{Pb/Ca}} = \frac{[\text{SW–Pb}][\text{Ca}]}{[\text{SW–Ca}][\text{Pb}]} \quad (4)\]

and

\[k_{\text{Pb/Mg}} = \frac{[\text{SW–Pb}][\text{Mg}]}{[\text{SW–Mg}][\text{Pb}]} \quad (5)\]

where

\([\text{SW-Pb}]\) is the amount of Pb adsorbed onto biosorbent (mmol/g)

\([\text{SW-Ca}]\) and \([\text{SW-Mg}]\) are the amounts of Ca and Mg present on biosorbent (mmol/g)

\([\text{Pb}]\) is the Pb concentration remained in the aqueous solution (mmol/L)

\([\text{Ca}]\) and \([\text{Mg}]\) are the concentrations of Ca and Mg released into the solution (mmol/L)

\(k\) is an equilibrium constant of the systems.

Figure 4 shows the \(k_{\text{Pb/Ca}}\) values were higher than \(k_{\text{Pb/Mg}}\) at all tested pH, meaning that the cation of calcium is easier to release from biosorbent than that of magnesium, or that the [Pb] is better adsorbed by a biosorbent which has high calcium content.

A potentiometric acid-base titration method was used to investigate the surface properties of reed and brown seaweed biosorbent in aqueous solution as well as to identify the acid ionisable functional groups or binding sites which can play a role in heavy metal adsorption.
Figures 5 (a) and (b) illustrate the S-shape of acid-base titration curves of VR, R-Ca, SW and SW-Ca. The curves revealed distinct pK\textsubscript{a} values of the functional groups existing on their surface. The pK\textsubscript{a} values less than 4 are attributed to strong acidic functional groups such as phosphoric or sulfonate groups as well as carboxylic groups that are linked to aromatic functions. The pK\textsubscript{a} values at 4 < pH < 7 are attributed to the ionization of carboxylic and some proteic groups and the pK\textsubscript{a} value at pH > 7 is attributable to very weak acidities such as phenolic and amine groups (Ghinwa et al. 2005). Comparing the potentiometric acid-base titration curve of VR with the R-Ca, a smaller volume of NaOH titrant was required and the reaction reached equilibrium faster. The pK\textsubscript{a} value (acidic) of R-Ca decreased from 2.77 to 2.85. This decrease of acidic pK\textsubscript{a} value suggested that it would be easier to ionize protons (H\textsuperscript{+}) from the surface of the reed biosorbent. This indicated a deprotonation state where the biosorbent becomes more negatively charged. In the case of brown seaweed biomass (Figure 5b), a higher volume of NaOH titrant was needed to reach equilibrium. The acidic pK\textsubscript{a} value of this biosorbent also increased from 3.46 to 2.43 which made it difficult for H\textsuperscript{+} to be ionized, thus lowering the negative charge on its surface. The data correlated well with data obtained from the zeta potential experiment, where the negative charge on R-Ca was higher than that on SW-Ca. In all cases, the pK\textsubscript{a} value obtained from the automatic titration showed a pK\textsubscript{a} value lower than 10, therefore, the phenol groups which are characterized by pK\textsubscript{a} > 10 are believed not to be involved in the ionization mechanism of these two biosorbents.

The IR spectra of VR, R-Ca, SW and SW-Ca revealed the presence of ionisable functional groups able to react with metal ion in aqueous solution. As shown in Figure 6, the molecular chemistry of functional groups on the surface of both biosorbent present peaks at 3350 (NH and OH stretching), 2929 (CH\textsubscript{2} stretching vibrations), 1736 (carbonyl C=O), 1510 (aromatic character of lignin), 1650 (amide I C=N), 1550 (amide II N=H and C–N), 1246 (cellulosic), 1160, 1150, and 1080 cm\textsuperscript{-1} (CHO) (Wetzel et al. 2003).

More complex functional groups are present on reed than on brown seaweed as evidenced by many small peaks on the spectra (Figure 6a, b). Comparing VR with R-Ca,
significant decrease of absorption band intensity was observed. This may be explained in terms of the decreasing number of H-bonds caused by the dissociation of the OH groups on biosorbents.

In light of the fact that many functional groups are involved in the heavy metal binding by biomass, the characterization of functional composition of reed and brown seaweed biosorbent using the intensities of selected peaks was conducted. This kind of semiquantitative analysis was proposed by Niemeyer et al. (1992) using soil organic matter across the range of concentration and using the peak ratio technique obtained from FTIR.

The ratio of reactive (O-containing) and recalcitrant (C, H and/or N) functional group heights (O/R) were measured, compared and are shown in Table 4. In short, the ratios comparing all the possible O-containing functional peaks that may associate with heavy metal binding divided by individual recalcitrant peaks were demonstrated in Table 4 (ratio N. 1–3). As for the results, the rank of total O/R ratios was SW > VR > R-Ca > SW-Ca. However, when comparing the individual O-containing functional groups, especially at the peaks of 1736 (Carbonyl C=O) and 1650 (amide I C=O) with the recalcitrant 2929 (CH₂ stretching vibrations), the O/R ratio of R-Ca was conversely higher than VR. This suggested that the pre-treatment of VR with CaCl₂ enhanced the oxygenated functional group due to the conversion of carboxylic to more active carboxylate group. On the contrary, the improvement of oxygenated functional groups on SW-Ca could not be observed at the same peak location. The data obtained from peak ratios can attest to the relative enrichment and/or depletion of specific functional groups within these complex organic spectra.

### CONCLUSION

An understanding of the differences between the adsorptive characteristics of different plant biomasses is necessary to improve and clarify different processes involving biosorption technology. High Pb(II) adsorption was proved to be associated with the abundance of total acidic and basic functional groups present on the cell wall of brown seaweed biomass. These amounts of functional groups presented 65% of the total Pb(II) adsorption. In addition, high content of calcium ion exchanged with Pb(II) was proved to correlate well with the high Pb(II) adsorption by brown seaweed biosorbent. In case of reed biosorbent, high adsorption affinity could be attributed to its higher zeta potential, its ease of deprotonation and the lower amount of Pb(II) adsorbed onto its surface. The amount of functional groups on reed accounted for about 92% of Pb(II) adsorption. Reed biosorbent characterized by more complexity of spectra peaks and many types of pKa value as elucidated by FTIR spectra and potentiometric titration. The complexity in functional group would be associated with the weak acidic functional groups which may constitute a secondary function for metal binding. The high adsorption capacity of brown seaweed and the high adsorption affinity of reed to Pb(II) is of fundamental importance for the removal of high and very dilute Pb(II) ion from waste waters.

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REFERENCES


