Pb(II) biosorption on reed biosorbent derived from wetland: effect of pretreatment on functional groups

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Abstract Reed biomass harvested from wetland constructed for water purification was modified into a biosorbent for Pb(II) removal from aqueous solution. The enhancement of Pb(II) adsorption by reed biosorbent depended not only on the types of reagent used for pretreatment, but also on the pH during the pretreatment process. The mechanisms, as elucidated using relational data obtained from Boehm titration, Fisher esterification and FTIR, involved the conversion of carboxylic groups into carboxylate groups, and proved the role of the carboxylate group, which occupied more than 80% in binding Pb(II). The Langmuir sorption isotherm of Pb(II) by R-NaOH-12 showed $Q_{\text{max}}$ and $b$ values of 0.082 mmol/g and 312.5 g/mmol, suggesting enough adsorption performance to reduce the concentration of Pb(II) to meet the range of WHO guidelines. The salinity of aqueous solution containing NaH$_2$PO$_4$ and NaNO$_3$ promoted the adsorption of Pb(II), while NaCl and Na$_2$SO$_4$ suppressed the adsorption capacity of Pb(II). The adsorption mechanism of reed biosorbent provides valuable insight on the pretreatment effects and the advantages of utilizing this plant as biosorbent for Pb(II) and other heavy metals.

Keywords Biosorption mechanism; functional group; lead(II); pre-treatment; reed

Introduction
Common Reed (Phragmites australis) is one of the cosmopolitan species that form an important component in the freshwater ecosystem (Asaeda et al., 2003). The application of reed to natural and artificial wetlands for wastewater treatment has gained much acceptance worldwide (Karunaratne et al., 2004). However, reed was reported to absorb nutrients and pollutants during its growth period but regenerate them when its decay starts (Weis et al., 2002). Harvesting and disposal of aboveground biomass, which has extracted target nutrients and pollutants from wastewater, is the clearest mechanism for permanently managing water contamination using vegetation. As the strategy to manage and utilize this plant for pollution control, the use of reed biomass harvested from wetland as a new biosorbent material for the removal of heavy metal (HM) from aqueous solution was investigated.

Lead, Pb(II), is considered to be one of the HMs most harmful to the ecological system and human life. Lead is being used as industrial raw material for storage battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing (Jalali et al., 2002). The presence of lead in drinking water even at low concentrations may cause diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome (Lo et al., 1999). Therefore, it is of paramount importance to remove lead from effluent before being discharged into the sewage or into the aquatic environment.

Biosorption has been recommended as a cheaper and more effective technique in removing HM from aqueous solution (Yan and Viraraghavan, 2003). Numerous studies on metal biosorption using different biomass have been reported recently, some indicating that a pretreatment process needs to be done to improve the adsorption capacity by many biosorbent materials (Natalia et al., 2004a, b). The unique capabilities of certain
types of biomass to concentrate and immobilize particularly HM can be more or less selective depending on the type of biomass, the mixture in the solution, the method for biomass preparation, and the chemical–physical process environment (Volesky, 2001). Therefore, it is necessary to look into the mechanisms related to the biosorption process, which up to now have not been well elucidated.

The objectives of this study were: (1) to utilize reed biomass for the removal of Pb(II) from aqueous solution; (2) to study the optimum chemical pretreatment conditions to make reed biosorbent; (3) to study the mechanism involved in the adsorption of Pb(II) by reed biosorbent; and (4) to determine the adsorption performance and influence of solution salinity on the adsorption of Pb(II) onto reed biosorbent.

The aboveground reed biomass harvested from wetland was tested for its ability in removing Pb(II) from aqueous solution. Chemical characteristics of reed biosorbent produced under different pretreatment pH than that associated with the adsorption mechanism were examined using Boehm titration, Fisher esterification and FTIR. Finally, the influences of different salts on the sorption capacity of reed biosorbent on Pb(II) were also investigated.

Materials and methods

Reed biomass and heavy metal solution
Live reed was harvested in August near the mouth of the Nanakita river in Sendai, Japan. The aboveground biomass of reed was cut, washed and then dried in an oven at 65°C for one week. The dried reed was ground using a grinder (T-351, Rong Tsong Iron Co., Taiwan) to a homogeneous powder and passed through a 90 μm sieve (JIS Z 8801, Nonaka Rikaki Co., Japan). The biomass was pretreated with different salts, washed with tap water until neutral pH was reached, and dried in an oven. The reed biosorbent was kept in a desiccator before use. Metal standard stock solutions were obtained from Kanto Chemical Co. Inc., Japan.

Effect of pretreatment of reed biomass with different chemical reagents on adsorption capacity
Pretreatment of reed biomass with different neutral (CaCl₂, NaCl, KCl, MgCl₂) and basic [Ca(OH)₂, NaOH, KOH, Mg(OH)₂, Ba(OH)₂] salts was conducted to determine its effects on Pb(II) adsorption onto reed biosorbent. Their adsorption performance was tested in both low and high Pb(II) concentrations, that is, 0.85 ppm and 7.80 ppm, respectively.

Effect of pretreatment pH on the acid-base properties of reed biosorbent
The pH of NaOH solution used for pretreatment of reed biomass was adjusted to 12, 7 and 4 using HCl solution. Reed biomass was allowed to come into contact with these solutions for one day, washed with water until neutral pH was reached, dried in an oven, and stored in a desiccator until use.

Batch isotherm study
0.1 g of reed biosorbent was allowed to come into contact with Pb(II) solution with concentrations ranging from 0.1 to 40 ppm, and the biosorption capacity (mmol Pb(II)/g biomass) was determined. The optimum conditions for biosorption determined in our preliminary studies were: 0.1 g of biosorbent, 50 mL of Pb(II) solution at pH 4.5, and 6 hours of contact time. These conditions were employed into all biosorption experiments. To obtain basic knowledge of reed biomass as a biosorbent, the equilibrium behavior of metal uptake was fitted into the well known Langmuir sorption isotherm model. The Langmuir isotherm has a theoretical basis, which relies on the chemical or physical interaction (or both) postulated to occur between solute and vacant sites on the adsorbent
surface (Sag and Kutsal, 1995) which can be described as follows:

\[ Q_e = \frac{Q_{\text{max}} b C_e}{1 + b C_e} \]

where \( Q_{\text{max}} \) (mmol/g) is the maximum amount of metal ions adsorbed per unit weight of adsorbent, \( Q_e \) (mmol/g) and \( C_e \) (mmol/L) are the equilibrium metal concentrations in solid and liquid phase, respectively, and \( b \) (L/mmol) is a coefficient related to the affinity between the metal ion and the adsorbent.

**Characterization of reed biosorbent**

This experiment was carried out using Fourier Transform Infrared Spectroscopy (FTIR) (Bio-RAD Win-IR, FIS 165, Japan). The sample was coated with KBr before detection. The IR spectra were collected in the mid-IR range 4,000–800 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) with 64 scans co-added. The surface functional groups containing oxygen were measured using the Boehm titration method (Boehm, 1994). Fisher esterification was conducted to evaluate the role of carboxylic group as described previously (Natalia et al., 2004a, b).

**Effect of solution chemistry on the adsorption of Pb(II) onto reed biosorbent**

The effect of salinity on the adsorption of Pb(II) was determined using different salts (NaCl, NaNO\(_3\), Na\(_2\)SO\(_4\), NaH\(_2\)PO\(_4\)). The concentrations of each salt used were 0.1, 0.5 and 1.0 M. An initial concentration of 1 ppm Pb(II) and pH 4.5 was used for all the experiments.

**Results and discussion**

The results of our batch experiments on the effect of pretreatment with neutral and basic salts on capacity of reed biosorbent to adsorb both low and high concentration of Pb(II) are presented in Figure 1a and 1b, respectively. The amount of Pb(II) adsorbed onto reed pretreated with basic salts was higher compared with that adsorbed onto reed pretreated with neutral salts, especially those pretreated with NaOH, KOH and Mg(OH)\(_2\) in both low and high concentrations of Pb(II). In this study, we selected reed biomass pretreated with NaOH (R-NaOH) to further examine for its sorption mechanism. R-NaOH at different pH conditions was investigated for its capacity to adsorb Pb(II), as well as the change in its functional properties. In Figure 2, the adsorption of reed pretreated with NaOH at pH 12 (R-NaOH-12) showed higher Pb(II) adsorption capacity as compared to those at other pH levels.

![Figure 1 Pb(II) adsorption by pretreated reed biomass with different salts: (a) adsorption of Pb(II) at low initial concentration of 0.85 ppm and (b) adsorption of Pb(II) at high initial concentration of 7.80 ppm (biomass dose = 0.1 g; pH = 4.5; contact time = 6 hours)](https://iwaponline.com/wst/article-pdf/54/10/133/431037/133.pdf)

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This suggests that adsorption performance is affected not only by the reagent used for pretreatment, but also the pH condition during the pretreatment process. Many papers reported different results of the pretreatment to the adsorption of HM. Similar results were observed by Ashkenazy (Ashkenazy et al., 1997) about the enhancement of Pb(II) adsorption by *Saccharomyces uvarum* being boiled in NaOH before use as adsorbent. The discrepancies in the pretreatment with NaOH were also observed. Yan reported the lower amount of Pb(II) removal of pretreated-fungus *Mucor rouxii* biomass extracted from YPG and YM growth media with 0.2 M NaOH compared with live biomass (Yan and Viraraghaven, 2003). A 25% reduction in Cr uptake due to the pretreatment of *Rhizopus nigricans* biomass with 0.1 M NaOH was attributed to the hydrolysis of the protein constituents and deacetylation of chitin (Sudha Bai and Emilia Abraham, 2002). On the other hand, pretreatment of cork biomass with 0.5 M NaCl solution also led to a 30% increase in Cu(II) adsorption reported by Natalia (Natalia et al., 2004a, b). Since it is still not clear about the mechanism involved in the pretreatment process, R-NaOH pretreatment at different pH was examined using FTIR and Boehm titration to gain knowledge about the changes in functional groups.

**Figure 2** Effect of pH pretreatment on the adsorption capacity of Pb(II). (Note: Biomass dose = 0.1 g; contact time = 6 hours; initial Pb(II) concentration = 3.2 ppm)

![Figure 2](https://iwaponline.com/wst/article-pdf/54/10/133/431037/133.pdf)

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**Figure 3** shows the FTIR broad adsorption bands of reed biosorbent from 3,800–800 cm\(^{-1}\), which consists of a strong absorption band of the −OH groups between 3,400–3,290 cm\(^{-1}\), the absorption band of the triple bonds of C=C and C=N between 2,500–2,000 cm\(^{-1}\), the adsorption of double bonds such as C=O and C=C between 2,000–1,500 cm\(^{-1}\) and between 1,500–800 cm\(^{-1}\), the peaks owing to other bond deformation which cannot easily be used to identify the unknown compound (FTIR, 2005).

![Figure 3](https://iwaponline.com/wst/article-pdf/54/10/133/431037/133.pdf)

**Figure 3** FTIR of reed biosorbent under different pH pre-treatment

![Figure 3](https://iwaponline.com/wst/article-pdf/54/10/133/431037/133.pdf)
Since the –OH group only become negatively charged at pH > 10 and played a secondary role in adsorption (Tomas et al., 2003), and the triple bond peaks on reed biosorbent were not clearly identified, we turned our attention to the peak of double bonds, which can be attributed to carboxylic groups reported to have a role in HM binding (Tomas et al., 2003). The peaks obtained from FTIR spectra generally could not provide a quantitative measurement of the functional groups. However, the ratio of the peak height can give an insight on the unit of functional changes occurring on the reed biomass.

To quantitatively determine the change in absorbance peak height, the ratio of the conjugated carboxylic (1,732 cm⁻¹) was compared to its non-conjugated form (1,660 cm⁻¹). As shown in Table 1, their ratios seemed to increase from pH 4–7 and then 7–12. To confirm this data, the amount of oxygenated groups on reed biosorbent was measured using Boehm titration method. Among the acidic functionalities, as shown in Table 2, only carboxylic group was found in reed biosorbent, with concentration gradually decreasing with increase in pretreatment pH up to 12. These results were in accordance with the reduction in peak height of carboxylic obtained from FTIR.

The effect of Fisher esterification reaction was also investigated to determine the roles of carboxylic group in binding Pb(II) from aqueous solution. More than 71% decrease in adsorption for Pb(II) was observed after blocking carboxylic group on reed biosorbent (Table 3). The ratios of the amounts of carboxylic groups calculated from the Boehm titration and the amount of the reduction of Pb(II) adsorption after esterification showed that the role of the carboxylic group accounted for more than 80% of the adsorption of Pb(II) by reed biosorbent.

The roles of carboxylic groups in adsorption were further investigated and characterized using FTIR spectra. Figure 4 shows the spectrum of R-NaOH-12, virgin reed biomass (VR) and esterified reed (ER). If we compare the spectra of R-NaOH-12 with that of VR, we can see that the peak band of the carboxylic group (1,732 cm⁻¹) disappeared.

### Table 1 Peak height ratios of carboxylate/carboxylic of reed biosorbent obtained from FTIR

<table>
<thead>
<tr>
<th>pH</th>
<th>Carboxylic form (1,732 cm⁻¹)</th>
<th>Carboxylate form (1,660 cm⁻¹)</th>
<th>Ratio B/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.092</td>
<td>0.200</td>
<td>2.173</td>
</tr>
<tr>
<td>7</td>
<td>0.055</td>
<td>0.064</td>
<td>1.163</td>
</tr>
<tr>
<td>4</td>
<td>0.074</td>
<td>0.080</td>
<td>1.081</td>
</tr>
</tbody>
</table>

### Table 2 Amount of carboxylic group using Boehm titration

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount of carboxylic group (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>2.18</td>
</tr>
<tr>
<td>7</td>
<td>2.30</td>
</tr>
<tr>
<td>4</td>
<td>2.32</td>
</tr>
</tbody>
</table>

### Table 3 Relationship between the amount of carboxylic group determined by Boehm titration to the amount of Pb(II) determined after esterification (biomass dose = 0.1 g; HM solution = 50 mL)

<table>
<thead>
<tr>
<th>pH of pre-treatment</th>
<th>Qₓ before ER (ppm)</th>
<th>Qₓ after ER (ppm)</th>
<th>Qᵧ eduction (meq/g) = A</th>
<th>% reduction</th>
<th>Carboxylic group (Boehm) (meq/g) = B</th>
<th>Ratio B/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1.555</td>
<td>0.439</td>
<td>2.69</td>
<td>71.10</td>
<td>2.18</td>
<td>0.81</td>
</tr>
<tr>
<td>7</td>
<td>1.535</td>
<td>0.439</td>
<td>2.64</td>
<td>71.40</td>
<td>2.30</td>
<td>0.87</td>
</tr>
<tr>
<td>4</td>
<td>1.536</td>
<td>0.439</td>
<td>2.64</td>
<td>71.40</td>
<td>2.32</td>
<td>0.87</td>
</tr>
</tbody>
</table>
due to its transformation to carboxylate (1,660 cm\(^{-1}\)) at higher absorbance. Thus, the carboxylic group may act as a substrate for the transformation to carboxylate form, the form responsible for adsorbing Pb(II) from aqueous solution. After blocking the carboxylic group, the ER band was significantly decreased as compared to the R-NaOH-12. In addition, the R-NaOH-12 showed a sharp reduction in absorption band loading with 10 or 100 ppm Pb(II), as shown in Figure 5. Moreover, the wave number shifted from 1,660 cm\(^{-1}\) to 1,670 cm\(^{-1}\) after loading with 10 or 100 ppm Pb(II). This suggests that the carboxylate group has a principal involvement in the mechanism for Pb(II) biosorption.

In our investigation, the Langmuir sorption isotherm of Pb(II) by R-NaOH-12 revealed \(Q_{\text{max}}\) and \(b\) values of 0.082 mmol/g and 312.5 g/mmol, respectively. The high initial slope of the sorption isotherm, as shown in Figure 6, indicates a high affinity between Pb(II) and R-NaOH-12. This high adsorption affinity of Pb(II) at low concentration represented about 92% of Pb(II) adsorption capacity that can be removed from aqueous solution to meet the requirements of the World Health Organization (WHO) guideline for drinking water, where the minimum Pb(II) is less than 0.01 mg/L or 0.048 mmol/L (Sawyer et al., 2003). A correlation between the experimental data and the Langmuir adsorption model showed high correlation coefficient for Pb(II) with \(r^2 > 0.99\). From Figure 4, it can be concluded that the adsorption isotherm of Pb(II) on reed biosorbent exhibited Langmuir behaviour, which indicates a monolayer adsorption.

The influence of salinity on Pb(II) adsorption capacity of reed biosorbent exhibited two opposite effects, that of supporting and suppressing the adsorption depending on the type of salt added. As shown in Figure 7, when the concentration of NaCl and Na\(_2\)SO\(_4\)
was increased from 0.1 M to 1.0 M, Pb(II) adsorption decreased by 22 and 28%, respectively. On the contrary, NaNO₃ and NaH₂PO₄ caused no effect and slight enhancement in Pb(II) adsorption capacity, respectively.

This result presents the advantage of using reed biosorbent to adsorb Pb(II) in wastewater, especially the wastewater from plating factories where NaNO₃ and NaH₂PO₄ are the common component in the production process; however, this technology may have
disadvantages in treating wastewater containing high amounts of NaCl or Na₂SO₄, such as those from brine industries.

**Conclusions**

The results of this work present the possibility of using reed biomass as a new biosorbent material for the removal of Pb(II) from aqueous solution. The sorption capacity of reed biomass was influenced not only by the type of pretreatment but also by pretreatment pH. The pretreatment of the biomass with basic salts resulted in higher adsorption capacity and pretreatment pH of 12 greatly enhanced the functional groups on reed biomass. The adsorption mechanism, elucidated using FTIR, Boehm titration and Fisher esterification, showed that the role of carboxylic group is to serve as substrate for the production of more active carboxylate group which accounts for more than 80% of Pb(II) adsorption by reed biomass. The effect of salts present in solution varied depending on the salt used: NaNO₃ and NaH₂PO₄ promoted adsorption ability while NaCl and Na₂SO₄ suppressed adsorption. Since reed biomass is a by-product from constructed wetland, abundant in nature, and with high performance for the removal of Pb(II), the utilization of this plant would gain a lot of merits for reed management as well as provide more information in searching for other biomaterials to be used as biosorbent.

**References**


