# N-5 Development of New Biosorbent for Heavy Metal Removal Using Reed Biomass ヨシバイオマスを利用した新しい重金属吸着剤の開発

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### 1. Introduction

Heavy metal (HM) pollution in water environment is extremely a serious problem that limits the beneficial use of water for living. At present, a number of technologies can be used to remove HM from contaminated water such as filtration, adsorption, chemical precipitation and ion-exchange <sup>1)</sup>. However, these methods are not always efficient especially in removing low HM concentrations, can be relatively expensive and may fail to achieve legal limits. Therefore, there is an urgent need for the development of innovative processes which can remove low concentrations of HM economically.

In this study, we report the development of new biosorbent for heavy metal removal using reed biomass from constructed wetland. Comparing with commercial activated carbon (AC), the adsorption performance of reed biosorbent was discussed based on HM removal efficiency under low HM concentration. The endurance of reed biosorbent was also evaluated by a 3-cycle adsorption-desorption test.

#### 2. Materials and Methods

### 2.1 Production of reed biosorbent

Live reed was collected during August near tidal flat, East of Sendai, Japan. The shoot of the reed was cut, washed and then dried in an oven at 65°C for one week. The dried reed was ground using a grinder to homogenous powder and passed through a 90-µm sieve (JIS Z 8801, Nonaka Rikaki Co., Japan). Reed was then pre-treated with NaOH and was washed thoroughly with tap water until a pH became neutral and then dried in an oven (90°C) over night. All dried pre-treated reed biosorbent with NaOH (RTN) were kept in a dessicator until use. Metal standard stock solutions were obtained from KANTO CHEMICAL CO., INC Japan.

## 2.2 Heavy metal adsorption and desorption experiment

The pH profile of reed biomass was investigated at HM concentrations below 1.0 ppm in batch experiments. About 0.1g of reed biomass was added to 50ml HM solution in the pH range 2-10 under shaken condition for 3 h. The most favorable pH condition for reed biomass to adsorb HM was then applied in the adsorption capacity study, wherein varying the concentrations of HM up to 50 ppm were used. The adsorption capacity and adsorption affinity obtained for RTN were compared to commercial AC. For the endurance test, RTN loaded with HM ion was transferred to a flask containing 50ml of 0.1M HCl desorbing agent. The mixture was shaken for 1h to elute HM from reed biosorbent. After elution, the reed biosorbent was rinsed 3 times with deionized water, then suspended again in HM solution for the next adsorption cycle. The concentrations of HM before and after adsorption on reed biomass were measured by Inductively Coupled Plasma-Mass Spectrometry (Hewlett Packard 4500 Series, Yokogawa Analytical Systems Co., Japan).

### 3. Results and Discussion

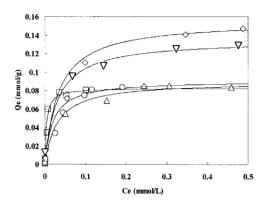


Fig 1. Adsorption isotherm of Pb(II) ( $\Box$ ), Zn(II) ( $\Delta$ ), Cd(II) ( $\circ$ ), Cu(II) ( $\diamond$ ) and Ni(II) ( $\diamond$ ) onto RTN by Langmuir fitting model.

**Table 1.** Langmuir constants and correlation coefficient obtained for reed biosorbent (RTN).

НМ	Langmuir Constants		2
	Qmax (mmol/g)	b(L/mmol)	r <sup>2</sup>
Cu(II)	0.156	75.98	0.97
Cd(II)	0.091	188.67	0.94
Ni(II)	0.135	76.92	0.99
Pb(II)	0.038	370.37	0.99
Zn(II)	0.088	135.1	0.98

**Table 2.** Comparison of the adsorption performance of Reed biosorbent (RTN) and activated carbon (AC)

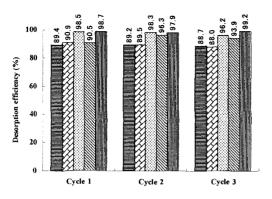
НМ	Ci (mg/L)	m (g)	% HM removal	
			RTN	AC
Zn(II)	5.6	0.1	92.8	88.7
		0.25	98.0	92.8
		0.5	99.0	98.7
Pb(II)	5.1	0.1	99.9	99.3
		0.25	99.9	99.9
		0.5	99.9	99.9
Cd(II)	7.7	0.1	97.7	95.8
		0.25	99.3	98.9
		0.5	99.8	99.8
Ni(II)	8.4	0.1	78.5	91.1
		0.25	97.7	95.4
		0.5	99.3	99.0
Cu(II)	9.3	0.1	70.0	96.9
		0.25	92.7	99.8
		0.5	99.7	99.9

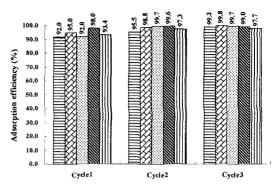
The high sorption of HM by reed biosorbent was observed near neutral pH for Cu(II), Cd(II), Ni(II) and Zn(II), while that for Pb(II) was from the acidic range of pH 4.0 or higher (data not shown).

The single sorption isotherm of the five metals on RTN are presented in Fig 1. At HM concentration lower than 50 ppm, it was found that the order of the metal sorption capacity on a molar basis was Cu(II) > Ni(II) > Cd(II) > Zn(II) > Pb(II), respectively. As shown in Table 1, the adsorption affinity expresses as Langumuir constant b of HM on reed biosorbent revealed a very high value, suggesting that it is more preferable to use as biomaterial for the removal of low HM concentration from aqueous solution. The adsorption by reed biosorbent also fitted very well to Langmuir isotherms with correlation coefficient  $(r^2) > 0.94$  for all HM, suggesting a mono-molecular adsorption process (Fig.1).

To evaluate the efficiency of HM removal by reed biosorbent, the adsorption ability of RTN was compared with that of AC. As shown in Table 2, with the same HM concentration and the amount of adsorbent usage, the adsorption performance by RTN was obviously higher than that of AC for Zn(II), Pb(II) and Cd(II). The adsorption performance for Ni(II) and Cu(II) were comparable to the adsorption performance by AC when the amount of reed adsorbent increased to 0.25g. These results demonstrated superior ability of reed biosorbent compared with AC which commonly used in practical HM treatment.

In endurance test, the adsorption-desorption cycles were repeated 3 times using the same reed biomass. To evaluate the removal efficiency of HM under low concentration, the adsorption-desorption experiment was conducted for Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II) whose initial concentration was lower than 1 mg/L.





- (a) Desorption efficiency of HM from reed biomass by 0.1 M HCl acid elution.
- (b) Adsorption efficiency in adsorption-desorption cycle.

Fig 2. Adsorption and desorption efficiency of heavy metal by reed biomass in adsorption-desorption cycle. Initial concentration for sorption experiment for  $Pb^{2^+}(\boxtimes)$ ,  $Zn^{2^+}(\boxtimes)$ ,  $Cd^{2^+}(\boxtimes)$ ,  $Cu^{2^+}(\boxtimes)$  and  $Ni^{2^+}(\boxtimes)$  was 0.71, 0.64, 0.48, 0.55 and 0.90 mg/L, respectively.

For the first cycle, as shown in Fig 2 (a), more than 90% desorption efficiency was achieved for almost all HM. Figure 2 (b) shows that the removal efficiency of HM by reed biosorbent was more than 92% for all HM, revealing a high regeneration potential of reed biosorbent. In addition, the reed biomass gained more adsorption ability in the 2<sup>nd</sup> and 3<sup>rd</sup> cycle. The biomass lost during three cycles was only about 5%.

### 4. Conclusions

This research highlights new way of utilize reed biomass from constructed wetland as new source of biosorbent for HM removal from aqueous solution. The production of reed biosorbent is energy saving, environmental friendly and help reducing by-product of reed that need to be harvested from constructed wetland, thus promoting the fully utilization of this novel plant in a sustainable way. In this study, reed biomass pre-treated with NaOH showed high adsorption affinity to many kinds of HM even they present in low concentration. Reed biosorbent also performed relatively or even higher in HM removal than that of commercial AC. Moreover, the desorption was simply and the regeneration was highly succeeded. Since reed biomass is a by-product from constructed wetland, abundance in nature, and highly performance for the removal of HM and high endurance for regeneration, therefore, the utilization of this plant would gain a lot of merits to the environmental technology in the future.

### Reference

1) Horsfall Jr, M.; Abia, A.A., 2003. Sorption of cadmium(II) and zinc(II) ions from aqueous solutions by cassava waste biomass (*Manihot sculenta* Cranz), Water Res. 37, 4913-4923.