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Biosorption of Rare Earth Elements, Thorium and Uranium Using *Buccinum Tenuissimum* Shell Biomass

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*In order to evaluate the efficiency of shell biomass as sorbent for rare earth elements (REEs), thorium (Th) and uranium (U), sorption experiment from multi-element solutions containing known amount of REEs, Th and U using *Buccinum tenuissimum* shell was explored. Furthermore, to confirm the characteristics of the shell biomass, the surface morphology, the crystal structure, and the specific surface area of the shell (both original sample and the heat-treatment (480 °C, 6 h) sample) was determined.*

Consequently, the following matters have been mainly clarified. (1) By heat-treatment (480 °C, 6 h), the crystal structure of the shell biomass was transformed from aragonite (CaCO₃) into calcite (CaCO₃) phase, and the specific surface area of the biomass have decreased remarkably (i.e., by a factor of less than one eighth). (2) The shell biomass (both original sample and the heat-treated sample) showed excellent sorption capacity for REEs, although the sorption capacity decreases slightly after heat-treatment. (3) Adsorption isotherms using the shell biomass can be described by Langmuir and Freundlich isotherms satisfactorily for REEs, but not for Th and U in this work. (4) Shell biomass (usually treated as waste material) could be an efficient sorbent for REEs in future.

Key Words : biosorption, rare earth element, thorium, uranium, *Buccinum tenuissimum*, shell biomass

1. Introduction

The demand of rare earth elements (REEs) in modern technology has increased remarkably over the past years^{1),2)}. However, the shortage of trace metals including REEs and the problem of stable supply for these metals has been concerned in recent years. Therefore, the establishment of the removal or recovery method for the trace metals is important from the viewpoint of resources recovery as well as environmental protection.

On the other hand, uranium (U) is known as the sources of nuclear power, and widely dis-

tributed in nature³⁾. Uranium is possible harmful pollutants in the environment. Particularly, it is pointed out that the mining and milling of U minerals result in large quantities of waste materials (tailings), which cause environmental health concerns^{4),5)}. Hence, the proper management of the U tailings by phytoremediation, which is one of the environmentally friendly technologies that use plants to clean up soil from trace element contamination⁶⁾, has been performed recently^{4),5)}.

Among environmentally friendly technologies, biosorption is also currently gaining considerable importance as an alternative technol-

ogy for the treatment of heavy metal waste⁷⁾. Thus biosorption studies using various biomasses have been widely performed in large parts of the world recently^{7)–13)}.

In our research, the objective elements are mainly REEs, Th and U. So far, model experiments for biosorption of REEs and U using seaweed have been carried out in our previous paper¹⁴⁾. In this study, the shell biomass was used as adsorbents of REEs, Th and U.

The shell has an internal structure comprised of three distinct layers. The innermost layer (i. e., hypostracum) consists of aragonite; the middle layer (i. e., ostracum), which is the thickest of the three, consists of various orientations interbedded with protein molecules (conchiolin); and the outermost layer (i. e., periostracum) consists of chitin, which is represented as $(C_8H_{13}NO_5)_n$ ¹⁵⁾. Particularly, it is considered that conchiolin including amino acid group play an important role for collecting trace metal in shell¹⁶⁾.

Considering the above-mentioned, laboratory model experiments for confirming the efficiency of shell biomass as sorbent for REEs, Th and U was designed in present work. Furthermore, to evaluate the characteristics of the shell biomass used in this work, the surface morphology, the crystal structure, and the specific surface area of the biomass (both original sample and the heat-treatment sample) was determined by SEM (Scanning Electron Microscope), by XRD (X-ray powder diffraction), and BET (Brunauer, Emmett and Teller) and Langmuir method, respectively.

2. Experimental

2.1 Samples

Buccinum tenuissimum shellfish used for shell biomass were collected at fishermen's coop-

erative association on the coast of Niigata Prefecture, Japan in June, 2008. After being separated from the meat by boiling, organism shells were washed thoroughly with ultra-pure water after washed with tap water repeatedly. After drying, the shells were ground and sieved through a sieve (SANPO Test Sieves) to remove particles having size more than 600 μm . Sieved material was used for adsorption experiments.

2.2 Apparatus and Reagents

An ICP-MS instrument (Agilent HP4500) was employed to determine the concentration of REEs, Th and U. The specific surface area of biomass sample was measured using Micromeritics TriStar3000. The BET method¹⁷⁾ and Langmuir method¹⁸⁾ were applied to determine the surface area. Nitrogen (N_2) gas was used to determine the adsorption isotherms. The crystal structure and the surface morphology of biomass was determined by X-ray powder diffraction (RIGAKU RINT2500HR) and by SEM (JEOL, JSM-5800), respectively. The measurement of pH in solution was carried out using a pH meter (HORIBA, F-21).

REEs, Th, and U standard solutions used for making the calibration curve were prepared by diluting the standard solutions (XSTC-1 for REEs and XSTC-13 for Th, U; both $10\text{ mg} \cdot \text{dm}^{-3}$ 5% HNO_3 solution) purchased from SPEX CertiPrep, Inc. (USA). All other chemical reagents were purchased from Kanto Chemical Co., Inc. (Japan). All reagents used were of analytical grade, and water ($>18.2\text{ M}\Omega$) which was treated by a ultrapure water system (Advantec aquarius: RFU 424TA) was employed throughout the work.

2.3 Biosorption of REEs, Th and U using shell biomass

For investigating the effects of pH, contact time, sorbent dose and initial concentration on the adsorption of REEs, Th and U, the following sorption experiments were performed using shell biomass. Shell biomass was thoroughly mixed with 100 cm³ of multi-element standard solution including REEs, Th, U in a 200 mL conical flask, and the suspensions were shaken in a water bath at room temperature (25 °C) for an appropriate time. Sorption experiments were conducted in the pH range of 3–7, biosorbent dosage 0.2–3.0 g · dm⁻³, contact time from 10 min to 7 h, and initial concentration from 10 to 500 μg · dm⁻³. The pH of each solution was adjusted by using 0.1 mol · dm⁻³ NH₃ aq/0.1 mol · dm⁻³ HNO₃.

Following each sorption experiment, the suspension containing biomass and the above standard solution was filtered through a 0.10 μm membrane filter (Advantec Mixed Cellulose Ester, 47 mm) to remove REEs, Th and U that have been adsorbed into the shell, and the concentration of these metals in the filtrate was determined with an ICP-MS.

The uptake (q) of REEs, Th and U by each sample was estimated by subtracting the final (after sorption at equilibrium) concentration (C_e) from initial concentration (C_o) in the solution expressed as the following equation :

$$q = (C_o - C_e) V / W \quad [\text{mg} \cdot \text{g}^{-1}] \quad (1)$$

where V is the volume of the solution (in cm³) and W is the dry weight of each adsorbent.

Moreover, to investigate the effect of heat-treatment on metal uptake (i. e., to compare the adsorption capacity of heat-treatment sample with that of raw original material), the shell biomass sample was heated at 480 °C for 6 h in

an electric furnace (ISUZU Muffle Furnace STR-14K), and this heat-treatment sample was also used for the above-mentioned sorption experiments.

Kinetic isotherms of sorption data were studied at varying concentration from 10 to 500 μg · dm⁻³ of initial concentration under optimized condition of pH, contact time and bio-sorbent dosage. The adsorption data obtained for REEs, Th and U were analyzed using Freundlich and Langmuir equations mentioned in next section (2.4).

2.4 Langmuir and Freundlich isotherm model

Two common adsorption model, Langmuir and Freundlich isotherm model was applied based on Dahiya et al.^{(12), (13)} to evaluate the adsorption data obtained in this study.

Langmuir model assumes monolayer sorption onto a surface and is given by

$$C_e / q_e = (C_e / a) + (1 / ab) \quad (2)$$

where C_e (mg · dm⁻³) is the concentration of metal ion at equilibrium in the aqueous solution, q_e (mg · g⁻¹) is the amount of adsorption at equilibrium, a (mg · g⁻¹) is the maximum adsorption capacity and b (dm³ · mg⁻¹) is the equilibrium adsorption constant (Langmuir constant)^{(19), (20)}. A plot of C_e / q_e versus C_e gives a straight line with slope of $1/a$, and intercept is $1/ab$; and b can be related to the adsorption free energy ΔG_{ads} (J · mol⁻¹), by the following equation :

$$\Delta G_{\text{ads}} = -RT \ln b \quad (3)$$

where R is the gas constant (8.314 J · K⁻¹ mol⁻¹), T is the absolute temperature (K) at equilibrium.

The Langmuir constant (b) can be used to

determine the suitability of the adsorbent to adsorbate by using dimensionless parameter, Hall separation factor²¹⁾ (R_L), which is defined as

$$R_L = [1/(1 + bC_0)] \quad (4)$$

where C_0 ($\text{mg} \cdot \text{dm}^{-3}$) is the initial concentration. The slope of the linearized Langmuir isotherm can be used to interpret the type of sorption using the value of R_L as follows :

$R_L < 0$	Unfavorable ;
$R_L > 1$	Unfavorable ;
$R_L = 1$	Favorable ;
$0 < R_L < 1$	Favorable ;
$R_L = 0$	Irreversible

On the other hand, Freundlich isotherm can also be used to explain adsorption phenomenon as given below.

$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_F and $1/n$ indicate the adsorption capacity and the adsorption intensity of the system, respectively. It is shown that $1/n$ values between 0.1 and 1.0 correspond to beneficial adsorption. The linearized Freundlich model isotherm is represented by the following equation :

$$\log_{10} q_e = \log_{10} K_F + (1/n) \log_{10} C_e \quad (6)$$

A plot of $\log_{10} q_e$ versus $\log_{10} C_e$ gives a straight line with slope of $1/n$ and intercept is $\log_{10} K_F$.

3. Results and discussion

3.1 Characteristics of shell biomass

SEM pictures of the shell biomass (both original sample and the heat-treatment sample) are shown in Fig. 1. It is found that the morphology of the biomass surface changed from a rough

Fig.1 SEM pictures of *Buccinum tenuissimum* shell biomass.

(a) : original sample, (b) : heat-treatment (480 °C, 6 h) sample.

and porous state with fine particle to a smooth and relative densification state with big particle by heat-treatment (480 °C, 6 h). The change of surface morphology after heat-treatment corresponds to the fact that the specific surface area of the biomass have decreased by a factor of less than one eighth (i. e., from $3.3166 \text{ m}^2 \cdot \text{g}^{-1}$ to $0.3904 \text{ m}^2 \cdot \text{g}^{-1}$ for BET, and from $5.35 \text{ m}^2 \cdot \text{g}^{-1}$ to $0.612 \text{ m}^2 \cdot \text{g}^{-1}$ for Langmuir) after heat-treatment in this study.

Furthermore, X-ray powder diffraction (XRD) patterns of the shell biomass (both original sample and the heat-treatment sample) are shown in Fig. 2. The crystal structure of the shell biomass was transformed from aragonite (CaCO_3) into calcite (CaCO_3) phase

Fig. 2 X-ray diffraction (XRD) patterns of *Buccinum tenuissimum* shell biomass.

(a) : original sample, (b) : heat-treatment (480 °C, 6 h) sample.

Downward-pointing arrows represent diffraction line of (a) aragonite and (b) calcite, respectively.

by heat-treatment. It is suggested that this transformation of crystal structure can be related to the change of the morphology, leading to the remarkable decrease of specific surface area of the biomass.

3·2 Biosorption of REEs, Th and U using shell biomass

3·2·1 Effect of pH

The effect of pH on sorption potential of shell biomass for REEs, Th and U was investigated at the range of pH 3–7 (in 100 $\mu\text{g} \cdot \text{dm}^{-3}$ of so-

lution using 3.0 $\text{g} \cdot \text{dm}^{-3}$ biomass dosage for contact time of 7 h). Under experimental condition in this work, the biomass showed excellent sorption capacity (more than 98% removal) at pH 3–7 for these elements.

Gupta et al.²²⁾ and Pandey et al.²³⁾ pointed out that the sorption capacities decrease at low pH due to the competition of protons with metal ions for active binding. On the other hand, at higher pH, the subject metals precipitated from the solution as its hydroxides such as at pH 7.3–8.4 for La, at pH 6.8 for Sm, and at pH 6.0 for Lu²⁴⁾.

Hence, pH 5 was taken for further experimental work.

3·2·2 Effect of contact time

The effect of contact time for 100 $\mu\text{g} \cdot \text{dm}^{-3}$ of solution using 3.0 $\text{g} \cdot \text{dm}^{-3}$ biosorbent dosage is investigated at pH 5.

The removal of REEs, Th and U more than 95% was observed within first 10 min, and there was a gradual increase in the uptake of these elements up to the contact time of 30 min. Approximately 99% of REEs, Th and U removal from the solution was observed in 30 min contact time, and after that there is no appreciable change.

Hence, the optimized contact time was taken as 30 min for rest of the experimental work.

3·2·3 Effect of shell biosorbent dose rate

Under optimized condition of pH (i. e., pH 5) and contact time (i. e., 30 min), sorption behavior of shell biomass at different dosages from 0.2 to 3.0 $\text{g} \cdot \text{dm}^{-3}$ has been studied in 100 $\mu\text{g} \cdot \text{dm}^{-3}$ of solution.

The removal of REEs, Th and U more than

90% was observed for $0.2 \text{ g} \cdot \text{dm}^{-3}$ dosage, and the removal increases with the increase of dosage rate from 0.2 to $2.0 \text{ g} \cdot \text{dm}^{-3}$. However, at a dosage more than $3.0 \text{ g} \cdot \text{dm}^{-3}$, slightly decrease of removal was observed.

For rest of the study, $2.0 \text{ g} \cdot \text{dm}^{-3}$ dosage is considered as optimum dosage.

3·2·4 Effect of initial concentration

Study was carried out by varying initial concentrations from 10 to $500 \mu\text{g} \cdot \text{dm}^{-3}$ for contact time of 30 min with a dosage of $2.0 \text{ g} \cdot \text{dm}^{-3}$ at pH 5. There was a continuous increase in the uptake of REEs, Th and U per gram of biosorbent up to the concentration of $100 \mu\text{g} \cdot \text{dm}^{-3}$, but the uptake is almost constant and even decreases at further higher concentration.

Data obtained from the variation of initial concentrations was fitted for the Langmuir and Freundlich isotherms to estimate the relevant parameters mentioned in section 2·4.

3·2·5 Effect of heat-treatment on shell biomass

To investigate the effect of heat-treatment on the adsorption capacity, the heat-treatment (480°C , 6 h) sample was also used for the sorption experiment. In this experiment, the initial concentration was taken as $100 \mu\text{g} \cdot \text{dm}^{-3}$ based on the result of above experiment (3·2·4).

The comparison for sorption capacity of shell biomass before and after heat-treatment is shown in Fig. 3. From this figure, it is found that the heat-treated biomass also showed excellent sorption capacity under this experimental condition, although the sorption capacity decreases relative to that of original material (without heat-treatment sample).

It is suggested that the decrease of sorption

Fig. 3 Comparison of sorption capacity of REEs, Th and U using shell biomasses before and after heat-treatment (480°C , 6 h).

capacity after heat-treatment may be attributable to the remarkable decrease (i. e., by a factor of less than one eighth) of specific surface area of the biomass.

It is known that Th begin to precipitate as its hydroxides at pH 3.5 and precipitate completely at about 6.0²⁴⁾. On the other hand, U (VI) is known to precipitate as its hydroxides at $\text{pH} \geq 4$ ²⁴⁾, although U exists in different forms depending on pH. Uranyl ion (UO_2^{+}) is the major ion form, and at higher pH (i. e., $\text{pH} \geq 5$), the uranyl ion may form complexes with carbonate ions^{4), 25), 26)}. Therefore, it is difficult to rule out the possibility that Th and U were removed to some extent due to precipitation occurred in the solution rather than adsorption to the biomass in our experiment. Hereafter, further investigation to confirm the effect of precipitation is needed in the case of removal of Th and U.

SEM pictures of the shell biomass after adsorption of metals are shown in Fig. 4((a) : original sample, (b) : heat-treatment sample). By comparing SEM pictures in Fig. 1 with that in Fig. 4, it is found that the morphology of each biomass surface has hardly changed even after exposing metals. From this observation,

Fig. 4 SEM pictures of *Buccinum tenuissimum* shell biomass after adsorption of metals.
(a) : original sample, (b) : heat-treatment (480 °C, 6 h) sample.

the biomass should be predicted to withstand the repeated use ; and hence it can be a good adsorbent.

3.3 Kinetics isotherm

The adsorption data obtained for REEs, Th, and U using *Buccinum tenuissimum* shell biomass were analyzed using Langmuir and Freundlich equations.

The correlation coefficient (R^2) of Langmuir and Freundlich isotherm for REEs, Th and U using original shell biomass is shown in Table 1 along with other parameters. From this table, it is found that R^2 value for REEs is comparatively high, particularly for Freundlich isotherm (0.638 – 0.886 for Langmuir isotherm and

0.844 – 0.932 for Freundlich one). However, as for Th and U, R^2 value is remarkably small (0.365 and 0.012 for Langmuir isotherm, 0.165 and 0.129 for Freundlich one), and then other parameters can not be estimated. It indicates that the applicability of these adsorption isotherms is satisfactory for REEs, but not for Th and U in this sample.

The dimensionless parameter Hall separation factor (R_L) for REEs is in the range of $0 < R_L < 1$, which means that the sorption for REEs by this shell biomass is favorable. Furthermore, the negative value of ΔG indicates that the sorption is spontaneous. The higher R^2 value for Freundlich model than for Langmuir isotherm in Table 1 suggests that the adsorption on this sample is due to multilayer coverage of the adsorbate rather than monolayer coverage on the surface. It is noted that the value of $1/n$ less than unity indicates better adsorption and formation of relatively stronger bonds between adsorbent and adsorbate^[2]. That is to say, favorable absorption for REEs by this shell biomass is presented.

On the other hand, R^2 and other parameters of Langmuir and Freundlich isotherm for REEs, Th, U using heat-treatment sample is shown in Table 2. It is noteworthy that R^2 value for REEs in this sample is fairly large (0.947 – 0.982 for Langmuir isotherm and 0.948 – 0.975 for Freundlich one), compared with the original shell biomass (Table 1). Furthermore, this result indicates the stronger the monolayer adsorption (the surface adsorption) on the heat-treatment sample relative to on the original sample (before heat-treatment).

Judging from the value of R_L or $1/n$ in Table 2, the heat-treatment sample also exhibits the favorable conditions for REEs absorption.

From this work, it was quantitatively clari-

Table 1 Coefficient of Langmuir and Freundlich isotherms for REEs, Th and U using original *Buccinum tenuissimum* shell biomass

	Langmuir isotherm					Freundlich isotherm		
	a	b	R^2	$\Delta G_{\text{ads}} / \text{kJmol}^{-1}$	R_L	K_F	$1/n$	R^2
La	4.00E+02	4.90E-01	0.638	-1.53E+01	2.00E-02	115	0.654	0.844
Ce	3.70E+02	1.17E+00	0.886	-1.75E+01	8.45E-03	163	0.583	0.864
Pr	4.00E+02	7.14E-01	0.750	-1.63E+01	1.38E-02	145	0.658	0.853
Nd	4.00E+02	6.10E-01	0.681	-1.59E+01	1.61E-02	133	0.662	0.846
Sm	4.17E+02	6.32E-01	0.740	-1.60E+01	1.56E-02	145	0.709	0.863
Eu	4.17E+02	5.71E-01	0.794	-1.57E+01	1.72E-02	136	0.723	0.883
Gd	4.35E+02	4.18E-01	0.788	-1.50E+01	2.34E-02	114	0.765	0.904
Tb	4.76E+02	3.28E-01	0.800	-1.44E+01	2.96E-02	105	0.778	0.912
Dy	4.76E+02	2.39E-01	0.849	-1.38E+01	4.02E-02	81.8	0.804	0.932
Ho	4.76E+02	1.83E-01	0.870	-1.29E+01	5.19E-02	65.2	0.799	0.924
Er	4.76E+02	1.48E-01	0.878	-1.24E+01	6.33E-02	55.6	0.787	0.920
Tm	4.76E+02	1.35E-01	0.842	-1.22E+01	6.87E-02	52.6	0.785	0.910
Yb	4.76E+02	1.36E-01	0.818	-1.22E+01	6.83E-02	53.3	0.762	0.887
Lu	5.00E+02	1.19E-01	0.786	-1.18E+01	7.75E-02	51.3	0.759	0.877
Th	-	-	0.365	-	-	-	-	0.165
U	-	-	0.012	-	-	-	-	0.129

Table 2 Coefficient of Langmuir and Freundlich isotherms for REEs, Th and U using *Buccinum tenuissimum* shell biomass after heat-treatment (480 °C, 6 h)

	Langmuir isotherm					Freundlich isotherm		
	a	b	R^2	$\Delta G_{\text{ads}} / \text{kJmol}^{-1}$	R_L	K_F	$1/n$	R^2
La	1.92E+02	2.43E-01	0.982	-1.36E+01	3.95E-02	57.2	0.258	0.948
Ce	2.78E+02	2.34E+00	0.972	-1.35E+01	4.10E-03	70.4	0.292	0.956
Pr	3.03E+02	2.29E-01	0.962	-1.35E+01	4.18E-02	71.5	0.321	0.955
Nd	3.13E+02	2.25E-01	0.956	-1.34E+01	4.25E-02	72.5	0.328	0.954
Sm	3.45E+02	2.66E-01	0.948	-1.38E+01	3.62E-02	78.4	0.359	0.962
Eu	3.45E+02	2.48E-01	0.947	-1.37E+01	3.88E-02	76.0	0.364	0.963
Gd	3.03E+02	2.31E-01	0.955	-1.35E+01	4.15E-02	75.0	0.299	0.954
Tb	3.23E+02	2.21E-01	0.961	-1.34E+01	4.32E-02	69.8	0.354	0.968
Dy	3.23E+02	1.95E-01	0.957	-1.31E+01	4.88E-02	66.3	0.358	0.964
Ho	2.94E+02	1.78E-01	0.961	-1.28E+01	5.32E-02	61.0	0.346	0.960
Er	2.94E+02	1.71E-01	0.963	-1.27E+01	5.53E-02	59.1	0.355	0.964
Tm	3.03E+02	1.76E-01	0.964	-1.28E+01	5.39E-02	59.0	0.372	0.968
Yb	3.23E+02	1.81E-01	0.960	-1.29E+01	5.23E-02	60.8	0.395	0.974
Lu	3.33E+02	1.76E-01	0.966	-1.28E+01	5.36E-02	62.4	0.389	0.975
Th	4.00E+02	1.39E-01	0.922	-1.22E+01	6.72E-02	148	0.348	0.688
U	-	-	0.024	-	-	-	-	0.093

fied to some extent that shell biomass could be an efficient sorbent for REEs. It is very significant information from the viewpoint of environmental protection that the shell (usually treated as waste material) can be converted into a biosorbent for REEs.

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要 旨

オオエッチュウバイの貝殻バイオマスを用いた希土類元素，トリウム，ウランの生物吸着

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貝殻バイオマスの希土類元素 (REEs)，トリウム (Th)，ウラン (U) に対する吸着剤としての有効性を検証するため，オオエッチュウバイの貝殻を用いて，既知量の REEs, Th, U を含有した多元素溶液中からの吸着実験を行った。更に，本研究で用いた貝殻の特性を把握するため，この貝殻バイオマス（元の試料及び焼成 (480 °C，6 時間) した試料）の表面状態，結晶構造，比表面積の定量も行った。

その結果，主として以下のことが明らかになった。(1) 焼成 (480 °C，6 時間) を行うことにより，この貝殻バイオマスの結晶構造は，アラゴナイト (CaCO_3) からカルサイト (CaCO_3) への変化が確認され，また表面積も顕著に (1/8 倍以下) 低下した。(2) 焼成後，吸着能は若干低下したものの，この貝殻バイオマス（元の試料及び焼成した試料のいずれも）は，REE に関して優れた吸着能を示した。(3) 本研究における貝殻バイオマスによる吸着等温線は，REE については Langmuir 及び Freundlich 吸着等温線に十分に適応するが，Th, U については必ずしも適応しない。(4) 貝殻（通常，廃棄物として扱われる）バイオマスは，今後，REEs の有用な吸着剤となりうる。