

Biosorption of uranium(VI) from aqueous solution by biomass of brown algae *Laminaria japonica*

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ABSTRACT

The uranium(VI) adsorption efficiency of non-living biomass of brown algae was evaluated in various adsorption experimental conditions. Several different sizes of biomass were prepared using pretreatment and surface-modification steps. The kinetics of uranium uptake were mainly dependent on the particle size of the prepared *Laminaria japonica* biosorbent. The optimal particle size, contact time, and injection amount for the stable operation of the wastewater treatment process were determined. Spectroscopic analyses showed that uranium was adsorbed in the porous inside structure of the biosorbent. The ionic diffusivity in the biomass was the dominant rate-limiting factor; therefore, the adsorption rate was significantly increased with decrease of particle size. From the results of comparative experiments using the biosorbents and other chemical adsorbents/precipitants, such as activated carbons, zeolites, and limes, it was demonstrated that the brown algae biosorbent could replace the conventional chemicals for uranium removal. As a post-treatment for the final solid waste reduction, the ignition treatment could significantly reduce the weight of waste biosorbents. In conclusion, the brown algae biosorbent is shown to be a favorable adsorbent for uranium(VI) removal from radioactive wastewater.

Key words | biosorption, brown algae, *Laminaria japonica*, radioactivity, uranium, waste reduction

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INTRODUCTION

Radioactive wastewater containing uranium is mainly generated during the operation of nuclear power plants or related facilities such as nuclear research laboratories and nuclear fuel manufacturing plants. Due to its radioactivity and high toxicity, uranium is one of the most seriously hazardous materials for the environment (Yang & Volesky 1999), and it is a carcinogen that causes cancer in the human body (Khani 2011). Uranium occurs naturally in diverse valence states, but it exists mainly as soluble uranium (VI), uranyl ion (UO_2^{2+}), in acidic conditions in the solution (Kim *et al.* 2009; Khani 2011). Some methods have been developed for the treatment of uranium wastewater, including chemical precipitation, adsorption, ion exchange, solvent extraction, evaporation, and electrochemical treatment (Bayramoglu *et al.* 2006; Fu & Wang 2011). However, several drawbacks such as the high treatment cost, secondary waste, and low efficiency at low uranium concentration remain unresolved; therefore, the development of an efficient technology for the treatment of uranium-containing wastewater is required.

Recently, biosorption technology using microorganisms, plants, and other various biomasses has been considered as an alternative to the metal adsorption process using chemical adsorbents (Volesky & Holan 1995). Studies on uranium biosorption by several species of brown algae such as *Sargassum fluitans*, *Cystoseira indica*, *Padina* sp., *Sargassum hemiphyllum*, and *Undaria pinnatifida* have been carried out over the last two decades (Yang & Volesky 1999; Sakamoto *et al.* 2008; Khani *et al.* 2008; Khani 2011). Alginic acid occurring in all brown algae has been considered as a material capable of forming complexes with uranium (Gok & Aytas 2009) when the non-living biomass of brown algae is used without any pretreatment. The biosorption of uranium by protonated brown algae was studied as an ion exchange process between protons in biomass and soluble uranium ions (Yang & Volesky 1999). Kinetic, thermodynamic, and equilibrium studies have also been carried out, some of which have shown that the Langmuir isotherm model is suitable for describing the biosorption equilibrium

of uranium by brown algae (Khani *et al.* 2008; Khani 2011). In order to apply the brown algae biosorbent in the actual uranium removal process, such theoretical studies and comparative evaluations with other materials should be combined. Also, further enhancement schemes are still required to improve the performance of uranium removal from radioactive wastewater and to overcome the drawbacks of former treatment processes.

In this study, a feasibility test of biosorption for uranium removal was performed by comparing with former adsorbents and precipitants, for the first time. Also, the adsorption properties of uranium by pretreated brown algae were evaluated in different operating conditions.

MATERIALS AND METHODS

Uranium wastewater

The simulated radioactive wastewater was prepared by dissolving uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in deionized (DI) water as 10 and 100 mg/l of initial uranium concentrations. In order to evaluate the removal efficiency of uranium at different conditions, the ionic strength of the simulated wastewater was changed by sodium nitrate (NaNO_3), and its pH was adjusted to 0 or to 12 by adding nitric acid (HNO_3) or sodium hydroxide (NaOH) to the solution.

Preparation of adsorbents and precipitants

The non-living biomass of brown algae was obtained from the Korean southern coast. Three types of brown algae, *Sargassum fulvellum*, *Undaria pinnatifida*, and *Laminaria japonica*, were selected for the preparation of the surface-modified biosorbents. The brown algae were dried in an oven at 60 °C overnight, and ground in a mortar. They were classified by sieving into four different sizes (>2, 2–0.2, 0.2–0.05, and <0.05 mm). Surface modification of each classified biomass was carried out by mixing 0.1 M hydrochloric acid (HCl) as 10 g biomass per litre and stirring for 12 h at room temperature. After the acidification, the biomass was rinsed several times with deionized water. The surface-modified biomass was then dried in an oven at 60 °C overnight.

The uranium adsorption efficiency of several chemical adsorbents and precipitants was compared with that of the prepared biosorbents. The selected adsorbents, activated carbon (AC), acidified-activated carbon (AAC), zeolite types 4A, X and Y, and mordenite (MOR) were tested in

the same conditions as those for testing of the biosorbents. AC is a common adsorbent for the removal of various toxic materials, and AAC is known to be more efficient for uranium adsorption because of the increase of surface functional groups (Abbasi & Streat 1994). In the case of zeolites, the sorption of uranium ions from the liquid phase has been studied using zeolite X, zeolite Y, MOR, and clinoptilolite etc. (Olguin *et al.* 1999). It is known that uranyl ions (UO_2^{2+}) are mainly exchanged with the cations from the large cavities of these zeolites. The same procedure was used for the acidification of activated carbon. Calcium oxide (CaO), calcium hydroxide ($\text{Ca}(\text{OH})_2$), and sodium hydroxide (NaOH) as precipitants were also used for the comparative uranium removal experiments. Except for the AAC, all the other adsorbents and precipitants were commercially available chemicals at a reagent grade.

Adsorption experiments

The uranium biosorption was evaluated in various experimental conditions using several types of biosorbents prepared with different particle sizes. All the batch experiments were conducted using a rotary shaker at a room temperature of 25 ± 1 °C. The uranium concentrations of the liquid samples obtained from the adsorption experiments were analyzed using a colorimetric method with Arsenazo III (StreLOW *et al.* 1976) to calculate uranium adsorption capacity (q_u , mg/g), distribution coefficient (K_d), and removal efficiency (R , %), which are based on the following equations:

$$q_u = (C_i - C_f)V/m \quad (1)$$

$$K_d = (C_i - C_f)V/C_f m \quad (2)$$

$$R = (C_i - C_f)100/C_i \quad (3)$$

where C_i is the initial uranium concentration (mg/l), C_f is the final uranium concentration (mg/l) from the supernatant solution, V is the solution volume (ml), and m is the mass of adsorbents (g). The analytical data were assessed using a quality control system, including duplicates, blanks, and standard reference samples, during all procedures for accuracy and precision, which demonstrated percentage error (%) of less than 6.2% and relative standard deviations (%) of less than 4.3%.

After the biosorption experiments, the finally obtained biomass samples contaminated with uranium were analyzed using scanning electron microscopy (SEM) (SNE 4500M,

SEC, Korea) and electron dispersive spectroscopy (EDS) (QUANTAX, Bruker, Germany) for the morphologic and elemental analyses, respectively. In order to measure the weight reduction rate of the biosorbents by ignition treatment, a thermal analyzer (TA) (DSC2920-TGA2950, TA Instruments, USA) was used. The temperature in the TA instrument was increased from 25 °C to around 1,100 °C at a heating rate of 8 °C/min. The weight reduction of MOR was also measured as the control sample.

RESULTS AND DISCUSSION

Comparison of adsorbents

The uranium removal efficiencies of several chemical adsorbents and prepared biosorbents were evaluated at 100 mg/l initial uranium concentration and pH 4. One gram per litre of each adsorbent was used in the 6-h batch experiment. Although the chemical adsorbents are commonly considered as useful materials for uranium removal processes, the brown algae biosorbents prepared in this study showed much higher uranium adsorption capacities than the chemical adsorbents compared under the same experimental

condition (Table 1). Also, the result that the distribution coefficients of the brown algae biosorbents were more than 10^4 strongly demonstrated their high performance for the uranium removal from the solution. Although the data of uranium adsorption capacities were not the maximum values because they are strongly dependent on the initial uranium concentration, the overall removal efficiencies based on the distribution coefficients were similar to or higher than the corresponding literature data (Yang & Volesky 1999; Khani 2011). The highest uranium adsorption capacity and distribution coefficient among the biosorbents in this study were obtained with *L. japonica* biosorbent; further specific evaluations of biosorption were therefore carried out using *L. japonica* biosorbent.

Adsorption properties of biosorbents

Figure 1 shows that the kinetics of uranium uptake were mainly dependent on the particle size of the prepared *L. japonica* biosorbent, which gave us the optimal particle size for stable operation of the wastewater treatment process. Although the maximum uranium adsorption capacities did not differ for the particle sizes, the adsorption rate significantly increased with decrease of particle size

Table 1 | Uranium adsorption capacity (q_u , mg/g) and distribution coefficient (K_d) in DI water containing 100 mg/l uranium (pH 4) after shaking for 6 h with 1 g adsorbents per litre

	Activated carbon		Zeolite				Brown algae		
	AC	AAC	4A	X	Y	MOR	<i>S. fulvellum</i>	<i>U. pinnatifida</i>	<i>L. japonica</i>
q_u	3.5	37.3	26.9	37.6	70.7	71.6	93.2	94.1	96.4
K_d	3.6×10	6.0×10^2	3.7×10^2	6.0×10^2	2.4×10^3	2.5×10^3	1.4×10^4	1.6×10^4	2.7×10^4

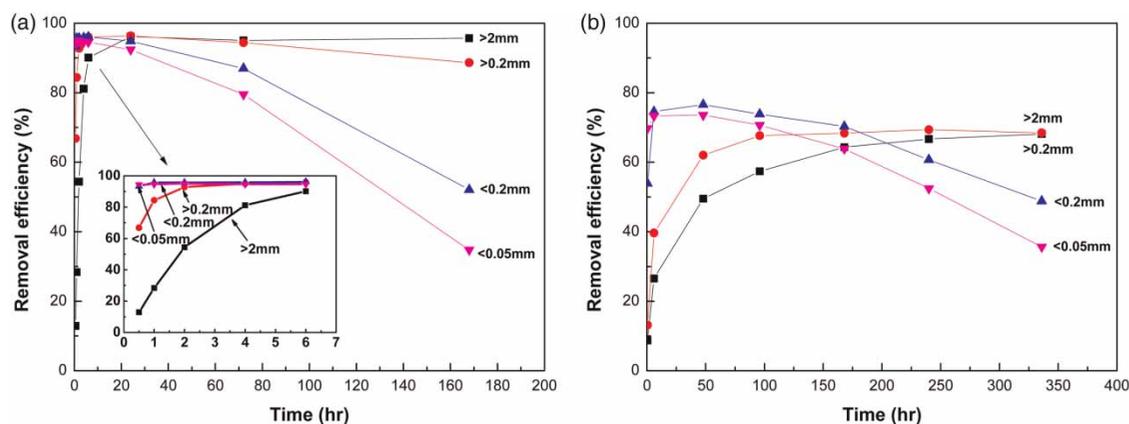


Figure 1 | Uranium removal efficiencies (%) of *L. japonica* biosorbents (1 g/l) with time in (a) DI water and (b) 1 M NaNO₃ containing 100 mg/l uranium at pH 4. (Inset box: enlarged figure of uranium removal efficiencies (%) within 6 h.)

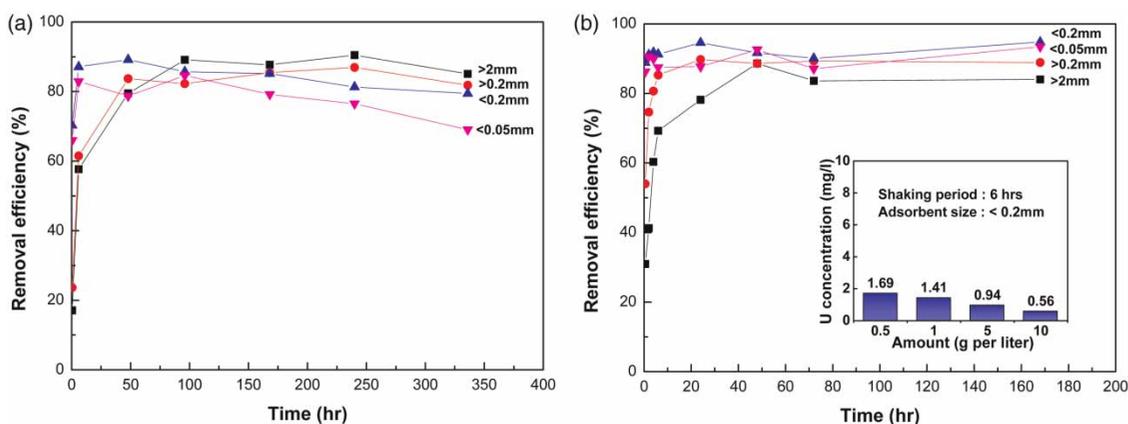


Figure 2 | Uranium removal efficiencies (%) of *L. japonica* biosorbents at concentration of (a) 1 g/l and (b) 5 g/l with time in 1 M NaNO₃ containing 10 mg/l uranium at pH 4. (Inset box: uranium concentrations (mg/l) in the solution treated with different amounts of biosorbent.)

(inset box of Figure 1(a)). The adsorption rate constants of sizes >2, 2–0.2, 0.2–0.05, and <0.05 mm calculated by using the pseudo second order reaction model were 7.5×10^{-5} , 1.5×10^{-3} , 2.5×10^{-2} and 2.8×10^{-1} within 6 h, respectively. Moreover, the desorption rate after a long contact time was significantly increased for the small particles. Such a desorption reaction indicates that the uranium ions' unstable binding is more dominant than the strong chemical complexation onto the biosorbent, although they are exchanged with protons introduced to the binding sites by the acid pretreatment. Particle sizes larger than 0.2 mm showed relatively slow adsorption reaction, and particle sizes smaller than 0.05 mm showed excessive desorption rate, which gave us the optimal range of particle size, 0.2–0.05 mm. The uranium adsorption capacity decreased with the increase of the ionic strength of the solution (Figure 1(b)), which indicates the competitive adsorption with sodium ions. Because the biosorbent does not have selectivity for a specific single ion, it should be considered that treating the actual wastewater containing complex and various ions might have more limitations than the simple matrix solution used in the laboratory.

Similar trends for the adsorption kinetics for different particle sizes were observed at the condition of lower initial uranium concentration (10 mg/l) with 1 M sodium nitrate (Figure 2(a)). Because of the high ionic strength in the solution, the residual uranium concentration of the treated solution could not meet the criterion (IAEA recommended criterion of 1×10^{-2} Bq/ml as radioactivity, which is about 1 mg/l of uranium as chemical concentration). The inset box of Figure 2(b) shows that 5 g *L. japonica* biomass injection in one litre was sufficient for uranium removal to less than 1 mg/l. Also, 2 h of reaction time was enough for the *L. japonica* biosorbents of these particle sizes (Figure 2(b)).

Although there have been many studies supporting the feasibility of biosorption, we have shown here the most appropriate operating conditions with respect to the biosorbent particle size and sorption kinetics, for the first time.

The effect of pH on the uranium adsorption efficiency of *L. japonica* biosorbent showed that the highest uptake occurred at pH 4 in a solution with 1 M sodium nitrate (Table 2), which is consistent with previous uranium biosorption studies (Khani *et al.* 2008; Gok & Aytas 2009). While uranium exists mainly as soluble uranyl ion (UO₂²⁺) in strongly acidic conditions, other hydrolyzed complex ions ((UO₂)₃(OH)₅⁺, (UO₂)₂(OH)₂²⁺, and UO₂OH⁺) coexist at pH 4, which is a more favorable condition for adsorption onto the binding sites (Yang & Volesky 1999; Kim *et al.* 2009). On the other hand, anionic complex ions are predominant in neutral and alkaline conditions with low uranium contents (Kim *et al.* 2009), which causes a decrease of uranium removal efficiency with a pH increase to more than 4.

Figure 3 shows SEM images of *L. japonica* biosorbents. It was clearly observed that the inside of *L. japonica* biosorbent was a porous structure, whereas the outer skin was not. Such a porous inside structure might enable the uranyl and other hydrolyzed ions to easily infiltrate and be adsorbed. Figure 4 presents a SEM image of the cross-section of

Table 2 | Uranium removal efficiency (%) of *L. japonica* biosorbents (0.2–0.05 mm, 5 g biosorbents per litre) in 1 M NaNO₃ containing 100 and 10 mg/l uranium after shaking for 6 h at different pHs

pH	0	2	3	4	6	8	12
U 100 mg/l	13.1	71.8	85.7	87.9	n.a. ^a	n.a.	n.a.
U 10 mg/l	36.3	85.6	89.2	94.7	92.0	90.0	87.1

^aNot analyzed. (Hydroxide precipitation occurred at 100 mg/l initial uranium concentration.)

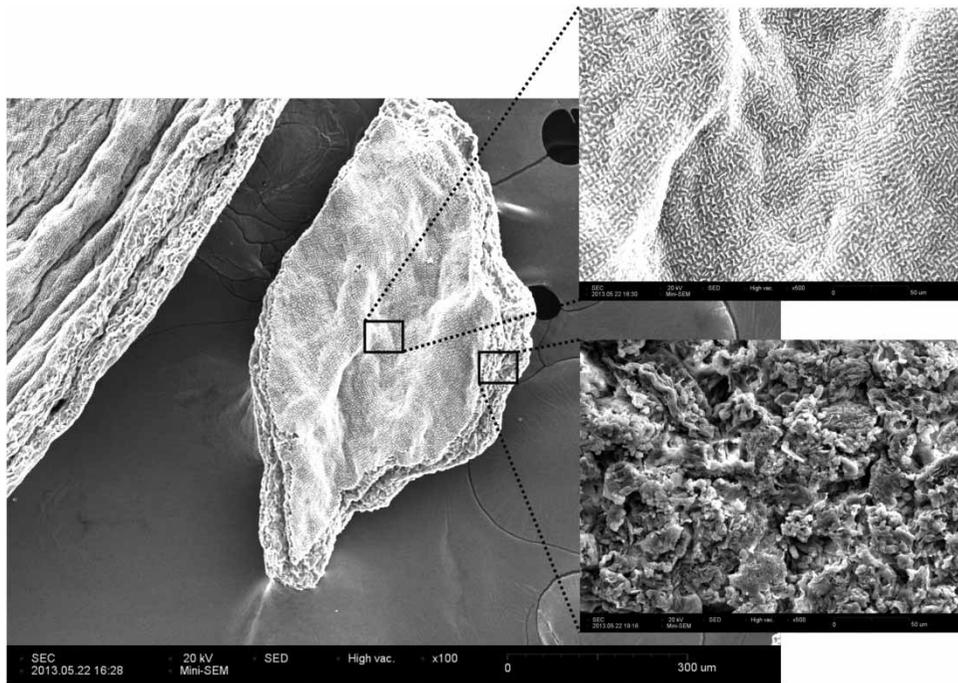


Figure 3 | SEM images of *L. japonica* biosorbents.

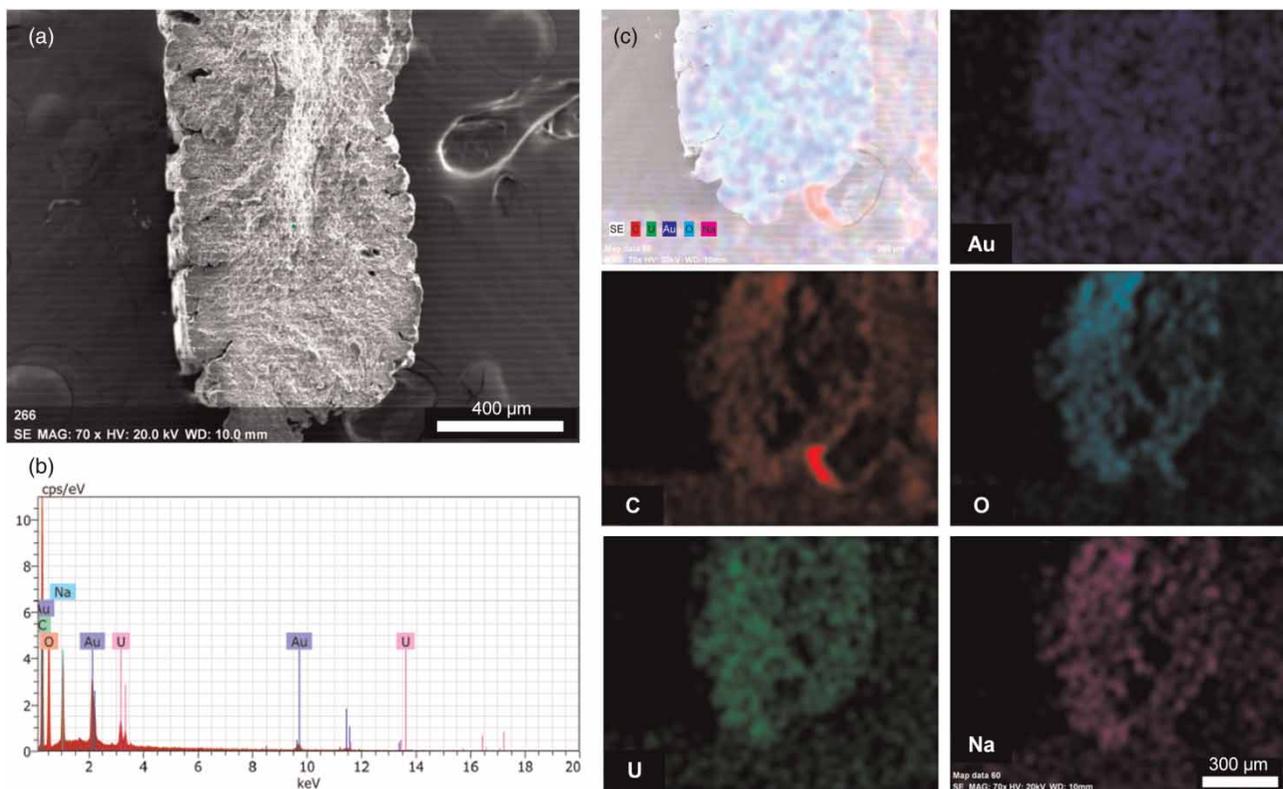


Figure 4 | (a) SEM image, (b) quantitative analysis, and (c) elemental mapping by EDS of cross-sectional *L. japonica* biosorbent after uranium adsorption in 1 M NaNO_3 .

L. japonica biosorbent with semi-quantitative analysis and elemental mapping by EDS after uranium adsorption in 1 M sodium nitrate condition. Uranium was well distributed in the biosorbent, which could explain the different uranium adsorption properties for the different particle sizes. As mentioned above, the maximum uranium adsorption capacities did not differ for the particle sizes because the total binding sites were the same. However, the ionic diffusivity in the biomass was the dominant rate-limiting factor; therefore, the adsorption rate was significantly increased with a decrease of particle size. A considerable amount of sodium was confirmed from both semi-quantitative analysis and elemental mapping, whereas the result of uranium adsorption in DI water was not confirmed (data not shown). The competitive adsorption of uranium and sodium ions was visibly confirmed from these results.

Performance evaluation of biosorbents

Up to the present, the chemical precipitation of heavy metals from wastewater has been considered as the most traditional and applicable process due to its simplicity and inexpensive cost (Fu & Wang 2011). Also, for the uranium wastewater treatment in nuclear industries, such as nuclear fuel manufacturing plants, chemical precipitation using limes (CaO and/or Ca(OH)₂) has been one of the major processes. Figure 5 shows the uranium removal efficiencies of *L. japonica* biosorbents and other precipitants (5 g/l) in 1 M sodium nitrate containing different uranium concentrations. For the removal of a relatively high concentration of uranium, the limes precipitated the uranium with a long operation time (more than 1 week) in both shaking and static conditions. The adsorption reaction of *L. japonica* biosorbents was extremely fast, so

that the maximum removal of uranium was achieved within 2 h. In general, chemical precipitation is adapted to treat wastewater containing high concentrations of metal ions and it is ineffective when the metal ion concentration is low, because the chemical precipitation is theoretically impossible when the concentration is lower than the solubility of the precipitates. For example, uranium is precipitated as uranium peroxide (UO₄) by adding excess hydrogen peroxide (H₂O₂) to an acidic solution of uranyl ions (Kim et al. 2011). Although this technique has been considered an effective method for uranium recovery, the solution after the uranium peroxide precipitation still contains several mg/l of residual uranium, which should be removed for the wastewater release. In the case of the lower initial uranium concentration (1 mg/l) simulating the above cases, the precipitants did not remove the uranium; however, the biosorbents reduced the uranium concentration to a non-detectable level in less than 30 min (Figure 5(b)). These comparative experiments strongly demonstrated the satisfactory performance of the prepared biosorbents compared with others.

Post-treatment for solid waste reduction

The management of radioactive solid waste is very important due to the extremely high cost of disposal. Therefore, the reduction of radioactive solid waste has been one of the technologies urgently required in the nuclear industry. This section finally suggests the possibility of volume reduction of waste biosorbents after the uranium removal from wastewater. Because the major component of brown algae is organic carbon, it should be decomposed at a high temperature. Figure 6(a) shows the weight reduction of *L. japonica* biosorbent and MOR (as a control) by ignition treatment. Although

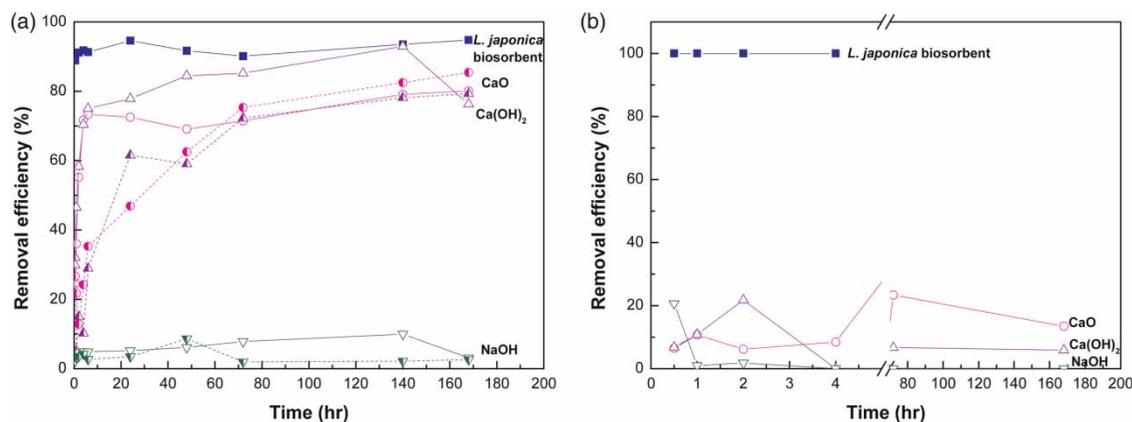


Figure 5 | Uranium removal efficiencies (%) of *L. japonica* biosorbents and other precipitants (CaO, Ca(OH)₂, and NaOH) at 5 g/l in 1 M NaNO₃ containing (a) 10 mg/l and (b) 1 mg/l uranium at pH 4. (Solid lines: shaking condition, dotted lines: static condition.)

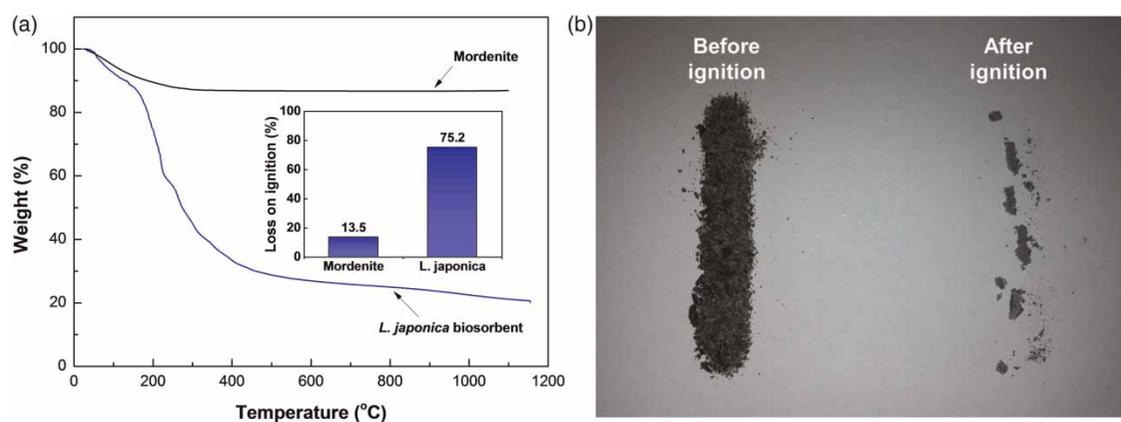


Figure 6 | (a) Weight (%) reduction of MOR and *L. japonica* biosorbent by ignition treatment (heating rate: 8 °C/min, inset box: loss on ignition (%) after heating for 6 h at 550 °C). (b) Picture of *L. japonica* biosorbent before and after ignition treatment.

the reduction of MOR, an aluminosilicate mineral, was negligible, that of the biosorbent was significant. The inset box of Figure 6(a) shows that the loss on the ignition of biosorbent was 75.2% after heating for 6 h at 550 °C. Also, the significant volume reduction could be visibly confirmed by comparison of before and after ignition treatment (Figure 6(b)). Therefore, the brown algae biosorbents have a strong advantage when reduced by ignition treatment.

CONCLUSIONS

From the results of comparative experiments using biosorbents and other chemical adsorbents/precipitants, it was demonstrated that the brown algae biosorbent could replace the conventional chemicals for uranium removal. We have shown here that the kinetics of uranium uptake was mainly dependent on the particle size of the biosorbents. The optimal particle size, contact time, and injection amount for the most appropriate operation of the wastewater treatment process were determined, for the first time. As a post-treatment for the final solid waste reduction, the ignition treatment could significantly reduce the weight of waste biosorbents. In conclusion, the surface-modified biosorbent from brown algae has been shown to be a favorable adsorbent for uranium removal from radioactive wastewater.

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