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Biomass Potential of Virgin and Calcined Tapioca (Cassava Starch) for the Removal of Sr(II) and Cs(I) from Aqueous Solutions

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In this study, we prepared novel adsorbents containing virgin and calcined tapioca products for removing strontium (Sr(II)) and cesium (Cs(I)) from aqueous solutions. The characteristics of tapioca, along with its capacity to adsorb Sr(II) and Cs(I), were evaluated. Multiple tapioca products were prepared and tested. The adsorbent prepared by boiling the tapioca followed by calcination at 300°C (BTP300) was the most effective. In addition, adsorption was affected by the adsorbent's surface properties. The Sr(II) and Cs(I) adsorbed onto BTP300 could be recovered through desorption by hydrochloric acid at different concentrations, which indicates that BTP300 can be used several times for adsorption/desorption. The results of this study suggest that BTP300, which was produced from tapioca biomass, can remove Sr(II) and Cs(I) from aqueous solutions.

Key words tapioca; calcination treatment; boiled treatment; strontium; cesium

The Great East Japan earthquake occurred on March 11 2011, and distributed radioactive substances throughout the area surrounding the Fukushima Daiichi power plant. The dominant radioactive elements were ⁹⁰Sr and ¹³⁷Cs, posing a serious threat to the environment and human health. As they have long half-lives (29 years for ⁹⁰Sr and 30 years for ¹³⁷Cs) and high water solubility, hazardous ⁹⁰Sr and ¹³⁷Cs will persist in the environment for centuries. Additionally, the tissues of living organisms adsorb ⁹⁰Sr and ¹³⁷Cs, mistaking them for essential cations.^{1,2}) It is, therefore, very important to remove these radioactive substances from wastewater. Several methods of removing ⁹⁰Sr and ¹³⁷Cs from aqueous solutions have been studied, including bioremediation, liquid-liquid solvent extraction, chitosan adsorption, and modified graphene oxide adsorption.^{1,3–5}) Of these, adsorption is the most effective and economical method of removing radioactive substances from aqueous solutions, and several adsorbents have already been studied.⁶) In addition, adsorbents produced from waste biomass have received special attention, because they are cheap, readily available, simple to modify, and environmentally friendly.

Starch consists of amylose, amylopectin, and a naturally-abundant renewable polymer.⁷) Several commercial starch-based products have been developed, and more are currently being investigated.^{7,8}) Tapioca (native cassava starch) currently has one purpose, with low additional value. However, several approaches have been investigated to expand its usage (such as physical, chemical, or biological methods).⁷) Over seven million tons of tapioca starch were produced in Thailand in 2004, the majority of which were exported to Japan.⁹) Tapioca biomass waste is disposed of in Thailand. Tapioca (cassava starch) is also produced in other parts of the world (Nigeria, Indonesia, Brazil, and Ghana). Therefore, its waste is readily available and cheaper than artificial adsorbents. The usage of natural or modified tapioca is increasing in a variety of fields because due to some of its inherent properties (such as its high resistance to acidity and fiber shape).¹⁰) Previous studies have

reported that waste biomass and its byproducts can adsorb heavy metals and radionuclide contamination.^{11–15}) However, the capacity of tapioca to adsorb radioactive substances (⁹⁰Sr and ¹³⁷Cs) has not yet been analyzed. If the adsorption of radioactive substances by tapioca could be explored, the value and applicability of tapioca waste would drastically increase.

The aim of this study was to explore the capability of tapioca products to remove radioactive substances (⁹⁰Sr and ¹³⁷Cs). Virgin and modified tapioca products were prepared, and their characteristics were investigated. In addition, we evaluated the adsorption kinetics and isotherms, and the effects of pH and temperature on the adsorption process, as well as the ability of strontium (Sr(II)) and cesium (Cs(I)) to desorb from the tapioca.

Experimental

Materials Virgin tapioca (TP) was obtained from Tawan Produce Co., Ltd. (Bangkok, Thailand). Calcined tapioca was prepared by heating the TP in a muffle furnace at 500 or 1000°C for 2 h (denoted as TP500 and TP1000, respectively). Boiled tapioca (BTP) was prepared by boiling virgin TP in water for 20 min (1 g TP per 20 mL water). Calcined BTP was prepared by heating BTP in a muffle furnace at 250, 300, 400, 500, and 1000°C for 2 h (denoted as BTP250, BTP300, BTP400, BTP500, and BTP1000, respectively). Standard solutions of strontium in 0.1 mol/L nitric acid (1000 mg/L Sr), cesium (CsCl in water; 1000 mg/L), sodium hydroxide, and hydrochloric acid were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Yield percentages were calculated by the mass difference before and after calcination (Table 1).

The morphologies and crystallinities of the samples were evaluated by scanning electron microscopy (SEM, SU1510, Hitachi High-Technologies Co., Tokyo, Japan). The specific surface area was measured using a NOVA4200e specific surface analyzer N42-25E (Quantachrome Instruments Japan G.K., Kanagawa, Japan). X-ray diffraction (XRD) analysis

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Table 1. Sample Preparation at Different Conditions

Sample	Calcination in the air	Boiled	Calcination in the nitrogen	Yield (%)
TP	×	×	×	—
TP500	○	×	×	10
TP1000	○	×	×	10
BTP	×	○	×	95
BTP250	×	○	○	77
BTP300	×	○	○	38
BTP400	×	○	○	17
BTP500	×	○	○	15
BTP1000	×	○	○	3

was conducted using a Mini Flex II (Rigaku Co., Tokyo, Japan). Elemental analysis was conducted using an electron probe microanalyzer (EPMA, JXA-8530F, JEOL Ltd., Tokyo, Japan). The measurement conditions were as follows: accelerating voltage, 15.0 keV; probe current, 20 nA; and beam diameter, slot.

Amounts of Sr(II) and Cs(I) Adsorbed by the Tapioca Products The prepared adsorbents (0.05 g) were added to either Sr(II) or Cs(I) solutions at 1000 µg/L (50 mL) and shaken at 100 rpm for 24 h at 25°C. Each sample was then filtered through a 0.45 µm membrane, and the filtrate was analyzed through inductively coupled plasma-atomic emission spectrometry (ICP-OES, iCAP 7600 Duo, Thermo Fisher Scientific Inc., Kanagawa, Japan) or inductively coupled plasma-mass spectrometry (ICP-MS, ICPM-8500, Shimadzu Co., Kyoto, Japan) for Sr(II) or Cs(I), respectively. The amounts of Sr(II) and Cs(I) adsorbed onto the adsorbent were calculated using Eq. 1.

$$q = (C_0 - C_e)V/W \quad (1)$$

where q is the amount of the element adsorbed (µg/g), C_0 is the initial concentration (µg/L), C_e is the equilibrium concentration (µg/L), V is the solvent volume (L), and W is the weight of the adsorbent sample (g). The data are expressed as the mean ± standard error (S.E.); $n=3$.

Adsorption Isotherms of Sr(II) and Cs(I) by the Tapioca Products Solutions were prepared using 0.05 g of the adsorbent and 50 mL of aqueous strontium or cesium at 0.1–10 mg/L, and were shaken at 100 rpm for 24 h at 5, 25, or 50°C. The amount adsorbed was calculated using Eq. 1. The data are expressed as the mean ± S.E.; $n=3$.

Effects of Contact Time and pH on the Adsorption of Sr(II) and Cs(I) by the Tapioca Products To test contact time, solutions were prepared with 0.05 g of the adsorbent and 50 mL of aqueous strontium or cesium at 10 mg/L and shaken at 100 rpm for 0.5, 1, 3, 6, 20, and 24 h at 25°C.

To test the effects of pH, solutions were prepared with 0.05 g of the adsorbent and 50 mL of aqueous strontium or cesium at 10 mg/L. The initial pH values of the solutions (ranging from 2 to 10) were maintained with hydrochloric acid or sodium hydroxide. The solutions were shaken at 100 rpm for 24 h at 25°C. The amount of Sr(II) or Cs(I) adsorbed was calculated by Eq. 1. The data are expressed as the mean ± S.E.; $n=3$.

Amount of Sr(II) and Cs(I) Adsorbed and Desorbed by BTP300 Solutions were prepared with 0.6 g of the adsorbent and 100 mL of aqueous strontium or cesium at 100 mg/L, and shaken at 100 rpm for 24 h at 25°C. The samples were then

filtered through a 0.45-µm membrane, and the filtrate was analyzed using ICP-OES or ICP-MS for Sr(II) or Cs(I), respectively. The amount adsorbed was calculated using Eq. 1.

After adsorption, the adsorbent was collected, dried, and then used in the desorption experiment. The dried adsorbent was added to 50-mL solutions of 1, 10, 100, and 1000 mmol/L hydrochloric acid. The suspensions were shaken at 100 rpm for 24 h at 25°C, and then filtered through 0.45 µm membranes. The concentrations of Sr(II) and Cs(I) were measured by ICP-OES and ICP-MS, respectively. The amount of strontium or cesium desorbed was calculated using Eq. 2.

$$d = C_e V/W \quad (2)$$

where d is the amount desorbed (mg/g), C_e is the concentration after desorption (mg/L), V is the solvent volume (L), and W is the weight of the adsorbent sample (g).

The adsorption/desorption cycle of BTP300 using 10 mmol/L hydrochloric acid was repeated three times.

Results and Discussion

Effect of Boiling and Calcination Treatment on Morphology Figure 1 contains the SEM images of the adsorbents. The TP particles were spherical, and broke after calcination, indicating that the TP structure was affected by calcination in air. In contrast, the BTP's surface was very smooth and even. The BTP's surface was broken by calcination in nitrogen. The yields of TP500 and TP1000 were both approximately 10%, suggesting that calcination cannot efficiently produce tapioca adsorbents for wastewater purification. However, the yield of BTP was 95%, indicating that little mass was lost during boiling. In addition, the yields of BTP250 and BTP300 (38–77%) were greater than those of BTP500 and TP1000 (10%) (Table 1). Moreover, we previously confirmed that the capability of TP500 and TP1000 produced under air or nitrogen to adsorb Sr(II) and Cs(I) were very similar. Therefore, considering costs, we selected calcination under air. The yield of BTP250–BTP1000 produced under air was significantly lower than that produced under nitrogen, which indicates that calcination under nitrogen after boiling is an efficient method of preparing tapioca waste for use as an adsorbent.

The amounts of Sr(II) and Cs(I) adsorbed by TP were very low (Fig. 2). The TP500 (941.8 µg/g), BTP300 (833.5 µg/g), and BTP1000 (857.1 µg/g) adsorbed the largest amounts of Sr(II), while BTP300 (863.0 µg/g), BTP400 (949.3 µg/g), and BTP500 (891.8 µg/g) adsorbed the largest amounts of Cs(I). In addition, the yield of BTP300 was 38%, indicating that this tapioca waste biomass treatment achieved high efficiency. Therefore, we selected TP, TP500, and BTP300 as adsorbents in the following experiments.

Effect of Boiled and Calcination Treatment on Crystalline Structure The XRD patterns of TP, TP500, and BTP300 are shown in Fig. 3. The peaks of TP were confirmed by XRD analysis, and show that TP exhibits an A-type crystalline pattern, with major reflections at $2\theta=15.3$ and 23.4° , and an unresolved double at 17 and 18° .^{7,16} These peaks were not detected for TP500 and BTP300, indicating that the tapioca structure was broken and became amorphous by calcination alone or calcination after boiling. Similar results were reported by Pari *et al.*,¹⁷ who studied the hydrothermal carbonization and KOH activation of raw cassava and

Fig. 1. SEM Images of Adsorbents

Fig. 2. Amount of Sr(II) and Cs(I) Adsorbed

Initial concentration: 1000 μg/L, Sample volume: 50 mL, Adsorbent: 0.05 g, Temperature: 25°C, Contact time: 24 h, 100 rpm, ■: Sr(II), □: Cs(I).

tapioca flour materials. The yields of cassava and tapioca flour from a high treatment temperature and KOH activation were 25.51–44.62%.¹⁷⁾ However, the yield percentage of BTP300 was approximately 38%. The treatment cost of this study was much lower than that of the previous study. Therefore, the treatment method for preparing tapioca adsorbents in this study is economical and efficient.

The specific surface areas of TP, TP500, and BTP300 were 72.4, 276.7, and 531.3 m²/g, respectively (mean particle sizes of

2 mm, 45, and 90 μm, respectively). The specific surface areas of TP500 and BTP300 were greater than those previously reported for other biomass-based adsorbents (0.377 m²/g and 0.296 m²/g for crosslinked persimmon and tea leaves, respectively),¹¹⁾ indicating that the adsorbents obtained in this study could effectively remove adsorbates.

Adsorption Isotherms of Sr(II) and Cs(I) The adsorption isotherms of Sr(II) and Cs(I) at different temperatures are shown in Fig. 4 (vertical and horizontal axes indicate the

amount adsorbed and the residual concentration after adsorption, respectively). TP adsorbed the lowest amount, followed by TP500, and BTP300 adsorbed the highest amount. The adsorption of all samples increased with higher initial concentrations. To determine the best-fit adsorption model, the experimental data were analyzed using the Langmuir and Freundlich isotherm models.¹⁵⁾ Their linear formation can be described by Eqs. 3 and 4.

$$C_e/q_e = C_e/W_s + 1/(K_L W_s) \quad (3)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

where C_e ($\mu\text{g/L}$) and q_e ($\mu\text{g/g}$) are the equilibrium concen-

tration and amount adsorbed, respectively; K_L (L/mol) and K_F are the Langmuir and Freundlich adsorption coefficients, respectively; W_s is the maximum adsorption capacity; and $1/n$ is the heterogeneity of the adsorption sites and an indicator of isotherm nonlinearity.^{18–20)} Table 2 shows the parameters obtained from the Langmuir and Freundlich models of Sr(II) and Cs(I) adsorption at 25°C. The correlation coefficients of the Langmuir models (0.940–1.000, excluding the adsorption of Sr(II) onto TP) showed a better fit than those of the Freundlich models (0.889–1.000, excluding BTP300). The fitted results indicate that Sr(II) and Cs(I) exhibited monolayer adsorption. In addition, TP presented the lowest W_s value, followed by TP500, BTP300 presented the highest value. Sr(II) and Cs(I) readily adsorbed to the surface of the samples when $1/n$ was within 0.1–0.5, but was not readily adsorbed when $1/n > 2$. This finding is also consistent with previous reports, in which Sr(II) and Cs(I) were easily adsorbed onto sample surfaces when $1/n < 2$ (0.12–1.73).²¹⁾

These findings indicate that the adsorption of Sr(II) and Cs(I) onto samples is affected by the adsorbent's surface. Therefore, we examined the adsorbents' surfaces before and after adsorption (Fig. 5). At an initial concentration of 10 mg/L (Fig. 5, (a)), we could not identify strontium or cesium on the adsorbent's surface, but at an initial concentration of 1000 mg/L, we could identify them (cold and warm in colors Fig. 5 indicate low and high concentrations, respectively). These results suggest that the adsorbent's surface is a very important factor for the removal of Sr(II) and Cs(I) from an aqueous solution. In addition, the amount of Sr(II) and Cs(I) increased in the following order: TP < TP500 < BTP300 (the specific surface areas of TP, TP500, and BTP300 are 72.4, 276.7, and 531.3 m²/g, respectively), indicating that the adsorption capability depends upon the physical

Fig. 3. XRDs of TP, TP500, and BTP300

Fig. 4. Adsorption Isotherms of Sr(II) and Cs(I) at Different Temperatures

Initial concentration: 0.1–10 mg/L, Sample volume: 50 mL, Adsorbent: 0.05 g, Temperature: 5–50°C, Contact time: 24 h, 100 rpm, ●: BTP300, ○: TP500, ◆: TP.

Fig. 5. Qualitative Analysis of Adsorbents Surface before and after Adsorption

Initial concentration of (a) and (b) is 10 and 1000 mg/L, respectively.

Table 2. Parameters for Langmuir and Freundlich Models of Sr(II) and Cs(I) Adsorption (25°C)

Samples	Element	Freundlich model			Langmuir model		
		K_F	$1/n$	r	K_L (L/mol)	W_s ($\mu\text{g/g}$)	r
TP	Sr(II)	0.17	0.63	0.971	3.3×10^5	270	0.004
	Cs(I)	0.51	0.64	1.000	1.6×10^5	833	1.000
TP500	Sr(II)	2.67	0.12	0.889	7.0×10^4	1250	0.989
	Cs(I)	1.25	0.71	0.976	1.3×10^4	11111	0.999
BTP300	Sr(II)	2.37	0.22	0.643	5.3×10^4	1667	0.940
	Cs(I)	-1.81	1.73	0.572	1.3×10^4	12500	0.993

properties of the tapioca adsorbent. No previous studies present comparable data.

Thermodynamic Parameters of Adsorption The adsorption thermodynamics were considered because they can indicate whether the process is spontaneous or not, and provide insight into adsorption behaviors.³⁾ Thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy changes (ΔS), were calculated by Eqs. 5–7, respectively.^{3,22)}

$$\Delta G = -RT \ln K_{\text{eq}} \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$\ln K_{\text{eq}} = \Delta S/R - \Delta H/RT \quad (7)$$

where R is the gas constant (8.314 J/mol/K), and T is the absolute temperature (K). ΔH and ΔS are obtained from the slope and intercept, respectively, of a line plotting $\ln(q_e/C_e)$ against

Table 3. Thermodynamic Parameters of Sr(II) and Cs(I) Adsorption onto BTP300

Samples	Temperature (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
Sr(II)	5	-2.2	2.9	17.3
	25	-1.7		
	50	-3.0		
Cs(I)	5	-0.5	20.9	76.9
	25	-1.8		
	50	-4.0		

$1/T$. The K_{eq} values determined from the adsorption isotherms can be used to determine the corresponding values of ΔG of adsorption at different temperatures. The thermodynamic parameters of Sr(II) and Cs(I) adsorption onto BTP300 are given in Table 3. The negative ΔG values indicate that the adsorption of Sr(II) and Cs(I) onto BTP300 are spontaneous

Fig. 6. Effect of Contact Time on the Adsorption of Sr(II) and Cs(I)

Initial concentration: 10 mg/L, Sample volume: 50 mL, Adsorbent: 0.05 g, Temperature: 25°C, Contact time: 0.5–24 h, 100 rpm, ●: BTP300, ○: TP500, ◆: TP.

Table 4. Kinetic Parameters of Sr(II) and Cs(I) Adsorption onto BTP300

Samples	$q_{e, \text{exp}}$ ($\mu\text{g/g}$)	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e, \text{cal}}$ ($\mu\text{g/g}$)	k_1 (1/h)	r	$q_{e, \text{cal}}$ ($\mu\text{g/g}$)	k_2 ($\text{g}/\mu\text{g h}$)	r
Sr(II)	1487	941	−0.08	0.901	1454	5.5×10^{-3}	0.991
Cs(I)	6815	2154	−0.11	0.788	6788	3.7×10^{-4}	0.999

processes. In addition, the ΔG values further decreased with increasing temperature (−2.2 to −3.0 kJ/mol for Sr(II) and −0.5 to −4.0 kJ/mol for Cs(I), when temperature increased from 278 to 323 K), which suggests better Sr(II) and Cs(I) adsorption at higher reaction temperatures.^{5,23} The positive ΔH values (2.9 and 20.9 kJ/mol for Sr(II) and Cs(I), respectively) indicated that the processes were endothermic. The positive ΔS values (17.3 and 76.9 J/mol/K for Sr(II) and Cs(I), respectively) indicate that there was an increase in randomness at the solid-solution interface during Sr(II) and Cs(I) adsorption onto BTP300.³

Effects of Contact Time on the Adsorption of Sr(II) and Cs(I) The adsorption kinetics of Sr(II) and Cs(I) onto the adsorbent samples were investigated through batch experiments. Adsorption was rapid during the first 30–60 min and saturation was reached within 3–6 h, with the exception of BTP300 for Sr(II) (Fig. 6). A previous study reported that Cs(I) adsorption achieved equilibrium faster than Sr(II).²⁴ Similar trends were observed in this study. The adsorption equilibrium can be achieved within 24 h under the experimental conditions used here. Therefore, 24 h was selected as the time required to achieve the adsorption equilibrium.^{5,18}

The pseudo-first- and -second-order kinetic models are expressed by the non-linear Eqs. 8 and 9, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (9)$$

where q_e and q_t are the amounts of Sr(II) and Cs(I) adsorbed ($\mu\text{g/g}$) at a given equilibrium and time, respectively, and k_1 (1/h) and k_2 ($\text{g}/\mu\text{g h}$) are the pseudo-first- and -second-order

rate constants.¹¹ The kinetic parameters of Sr(II) and Cs(I) adsorption onto BTP300 are shown in Table 4. The adsorption kinetics of Sr(II) and Cs(I) onto BTP300 were well-fitted by pseudo-second-order models, with higher correlation coefficients ($r=0.991$ – 0.999) than those of the pseudo-first-order model ($r=0.788$ – 0.901). In addition, the $q_{e, \text{exp}}$ values (1487 $\mu\text{g/g}$ for Sr(II) and 6815 $\mu\text{g/g}$ for Cs(I)) were closer to the $q_{e, \text{cal}}$ values in the pseudo-second-order model (1454 $\mu\text{g/g}$ for Sr(II) and 6788 $\mu\text{g/g}$ for Cs(I)). These results suggest that the chemical process was the rate-limiting step in Sr(II) and Cs(I) adsorption.^{3,18}

Effects of pH on the Adsorption of Sr(II) and Cs(I) pH is an important factor that controls biosorption processes. Previous studies have reported that pH affects the surface charge of the adsorbent, degree of ionization, and speciation of adsorbates in solution.^{1,25,26} The effects of solution pH on the adsorption of Sr(II) and Cs(I) are shown in Fig. 7. The amounts of Sr(II) and Cs(I) adsorbed increased with increasing pH, indicating that pH plays an important role in these adsorption processes. Similar trends have been reported in previous studies.^{3,5,15,18} Solution pH before and after adsorption using TP changed slightly (data not shown). However, changes in solution pH with BTP300 (2.17–6.61 for Sr(II) and 2.09–6.01 for Cs(I)) were greater than those with TP500 (2.23–4.82 for Sr(II) and 2.08–5.07 for Cs(I)).

At low pH values, the overall surface charge of tapioca becomes positive as the protonation reaction is facilitated, and, at high pH values, the surface charge becomes negative due to a decrease in the protonation reaction. Therefore, high pH results in increased Sr(II) and Cs(I) adsorption.^{5,11,27,28} These results show that adsorption is related to the chemical properties of tapioca adsorbents (based on the electrostatic interactions

Fig. 7. Effect of pH in Solution on the Adsorption of Sr(II) and Cs(I)

Initial concentration: 10mg/L, Sample volume: 50mL, Adsorbent: 0.05g, Temperature: 25°C, Contact time: 24h, pH in solution: 2–10, 100rpm, ●: BTP300, ○: TP500, ◆: TP.

Fig. 8. Amount of Sr(II) and Cs(I) Adsorbed or Desorbed Using BTP300

Adsorption condition; Initial concentration: 100mg/L, Sample volume: 100mL, Adsorbent: 0.6g, Temperature: 25°C, Contact time: 24h, 100rpm. Desorption condition; Sample volume: 50mL, Adsorbent: 0.1g, Temperature: 25°C, Contact time: 24h, 100rpm, ■: Adsorption, □: Desorption.

between Sr(II) or Cs(I) and the tapioca adsorbent's surface).

In addition, we also compared the adsorption capabilities of other biomass adsorbents to those of TP500 and BTP300. The amount of Sr(II) or Cs(I) adsorbed onto TP500 and BTP300 was greater than that adsorbed onto dolomite powder (1.14mg/g for Sr(II)) or acra shell biomass (3.99mg/g for Cs(I)), as reported in previous studies.^{29,30} These results suggest that TP500 and BTP300 can remove Sr(II) and Cs(I) from aqueous solutions more efficiently than other adsorbents.

Sr(II) and Cs(I) Adsorption and Desorption with BTP300 The amounts of Sr(II) and Cs(I) adsorbed onto BTP300 and desorbed using different concentrations of HCl are shown in Fig. 8. Sr(II) and Cs(I) could both be recovered from BTP300 with the application of a HCl solution. The amount desorbed increased with increasing HCl concentration. The recovery percentages of Sr(II) were 14, 25, 28, and 31% for 1, 10, 100, and 1000mmol/L HCl, respectively, and those of Cs(I) were 60, 90, 92, and 92% for 1, 10, 100, and 1000mmol/L HCl, respectively. As mentioned above (Fig. 6),

solution pH is an important factor in the removal of Sr(II) and Cs(I) from aqueous solutions. In addition, the adsorption capacity was greater under basic pH conditions than that under acidic pH conditions. At high HCl concentrations, the pH of the solution decreases and the adsorption capability decreases, so low HCl concentrations should be used for desorption process. In addition, the recovery percentage does not change drastically for lower concentrations, and they are more environmentally friendly than a 1000mmol/L HCl solution. Therefore, we selected the 10mmol/L HCl solution for use in desorption processes in this study.

The experiment demonstrates that BTP300 can be recovered with a 10mmol/L HCl solution, and that the recovered BTP300 can be recycled (Fig. 9). BTP300 could be used a minimum of three times, in the same conditions. The total adsorbed and desorbed amounts and the recovery percentages for Sr(II) were 4.26, 1.17mg/g, and 27.4%, respectively, and for Cs(I) they were 21.9, 20.6mg/g, and 94.1%, respectively. The adsorption capacity slightly decreased in subsequent ad-

Fig. 9. The Repetition of Adsorption/Desorption of Sr(II) and Cs(I)

Adsorption condition; Initial concentration: 100 mg/L, Sample volume: 100 mL, Adsorbent: 0.6 g, Temperature: 25°C, Contact time: 24 h, 100 rpm. Desorption condition; Sample volume: 50 mL, Temperature: 25°C, Contact time: 24 h, 100 rpm, ■: Adsorption, □: Desorption.

sorption/desorption cycles, which could have been caused by a loss of mass and functional adsorption sites on the BTP300 surface during desorption.³¹⁾ These results indicate that BTP300 has good potential for removing Sr(II) and Cs(I) in industrial applications.

Conclusion

BTP300 was prepared from tapioca, and its adsorption of Sr(II) and Cs(I) was evaluated. BTP300 has a higher adsorption capacity than TP and TP500. The Sr(II) and Cs(I) adsorbed onto BTP300 was readily desorbed using hydrochloric acid. The adsorption/desorption cycle can be repeated at least three times under the studied conditions. The results of this study indicate that an efficient and effective adsorbent for the removal of Sr(II) and Cs(I) from aqueous solutions can be produced from tapioca. This paper provides a basis for further exploration into tapioca biomass reuse and a strategy for remediating environmental water pollution.

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Conflict of Interest The authors declare no conflict of interest.

References

- Ghorbanzadeh Mashkani S., Tajer Mohammad Ghazvini P., *Biore-sour. Technol.*, **100**, 1915–1921 (2009).
- Jalali-Rad R., Ghafourian H., Asef Y., Dalir S. T., Sahafipour M. H., Gharanjik B. M., *J. Hazard. Mater.*, **116**, 125–134 (2004).
- Liu F., Liu Y., Xu Y., Ni L., Meng X., Hu Z., Zhong G., Meng M., Wang Y., Han J., *J. Environ. Chem. Eng.*, **3**, 1061–1071 (2015).
- Riddle C. L., Baker J. D., Law J. D., McGrath C. A., Meikrantz D. H., Mincher M. B. J., Peterman D. R., Todd T. A., *Solvent Extr. Ion Exch.*, **23**, 449–461 (2005).
- Wang X., Yu J. T., *J. Radioanal. Nucl. Chem.*, **303**, 807–813 (2015).
- Wu Y., Zhang X. X., Kim S. Y., Wei Y., *J. Nucl. Sci. Technol.*, **53**, 1968–1977 (2016).
- Li H., Liu Y., Gao X., Li X., *J. Chem. Technol. Biotechnol.*, **91**, 977–984 (2016).
- Malafaya P. B., Elvira C., Gallardo A., San Román J., Reis R. L., *J. Biomater. Sci. Polym. Ed.*, **12**, 1227–1241 (2001).
- Chavalparit O., Ongwandee M., *J. Clean. Prod.*, **17**, 105–110 (2009).
- Flores S., Famá L., Rojas A. M., Goyanes S., Gerschenson L., *Food Res. Int.*, **40**, 257–265 (2007).
- Gurung M., Adhikari B. B., Alam S., Kawakita H., Ohto K., Inoue K., Harada J., *Chem. Eng. J.*, **231**, 113–120 (2013).
- Kawasaki N., Tominaga H., Ogata F., Kakehi K., *Chem. Eng. J.*, **157**, 249–253 (2010).
- Ogata F., Tominaga H., Yabutani H., Kawasaki N., *J. Oleo Sic.*, **60**, 363–368 (2011).
- Ogata F., Kangawa M., Iwata Y., Ueda A., Tanaka Y., Kawasaki N., *Chem. Pharm. Bull.*, **62**, 247–253 (2014).
- Pangeni B., Paudyal H., Inoue K., Kawakita H., Ohto K., Gurung M., Alam S., *Waste Biomass Valorization*, **5**, 1019–1028 (2014).
- Whittam M. A., Noel T. R., Ring S. G., *Int. J. Biol. Macromol.*, **12**, 359–362 (1990).
- Pari G., Darmawan S., Prihandoko B., *Proc. Environ. Sci.*, **20**, 342–351 (2014).
- Li D., Zhang B., Xuan F., *J. Mol. Liq.*, **209**, 508–514 (2015).
- Langmuir I., *J. Am. Chem. Soc.*, **40**, 1361–1403 (1918).
- Freundlich H. M. F., *J. Phys. Chem.*, **57**, 385–470 (1906).
- Abe I., Hayashi K., Kitagawa M., *J. Jpn. Oil. Chem. Soc.*, **25**, 145–150 (1976).
- Liu Y., Liu Y. J., *Separ. Purif. Tech.*, **61**, 229–242 (2008).
- Tahir S. S., Rauf N., *J. Chem. Thermodyn.*, **35**, 2003–2009 (2003).
- Yavari R., Huang Y. D., Ahmadi S. J., Bagheri G., *J. Radioanal. Nucl. Chem.*, **286**, 223–229 (2010).
- Aksu Z., Isoglu I. A., *Process Biochem.*, **40**, 3031–3044 (2005).
- Dahiya S., Tripathi R. M., Hegde A. G., *Bioresour. Technol.*, **99**, 179–187 (2008).
- Ghorbanzadeh Mashkani S., Tajer Mohammad Ghazvini P., Agha Aligol D., *Bioresour. Technol.*, **100**, 603–608 (2009).
- Malekzadeh F., Ghorbanzadeh Mashkani S., Ghafourian H., Soudi M. R., *World J. Microbiol. Biotechnol.*, **23**, 905–910 (2007).
- Dahiya S., Tripathi R. M., Hegde A. G., *J. Hazard. Mater.*, **150**, 376–386 (2008).
- Ghaemi A., Torab-Mostaedi M., Ghannadi-Maragheh M., *J. Haz-ard. Mater.*, **190**, 916–921 (2011).
- Ogata F., Imai D., Toda M., Otani M., Kawasaki N., *J. Ind. Eng. Chem.*, **34**, 172–179 (2016).