



# Bioleaching and removal of radiocesium in anaerobic digestion of biomass crops: Effect of crop type on partitioning of cesium

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## ARTICLE INFO

### Article history:

Received 30 March 2020

Received in revised form 22 July 2020

Accepted 17 November 2020

### Keywords:

Anaerobic digestion

Radioactive cesium

Biomass crops

Partition behavior

## ABSTRACT

Cultivation of biomass crops for energy production is a promising land-use for farmland abandoned owing to radionuclide fallout. However, radionuclides in soil are easily taken up in the crop. To understand phase partitioning of radiocesium Cs (RCs) during anaerobic digestion (AD) of crops, semi-continuous AD experiments were carried out using two types of RCs-contaminated crops. Analysis of fractionated digestate effluent revealed that AD of the crops released RCs into the water phase (up to 82 %), and the efficiency of RCs solubilization depended on crop biodegradability. Adsorption treatment for removal of RCs from the water phase of the digestate indicated a water–zeolite partition coefficient of 0.287 L/g. The efficiency of removal from the water phase was 90 % at an adsorbent dose of 30 g/L.

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## 1. Introduction

The 2011 nuclear accident at the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) released radioactive nuclides, including Xe, I, Cs, and Sr, to the atmosphere [1]. These substances were widely spread by wind and deposited over the land in the Tohoku region of northeastern Japan. <sup>137</sup>Cs is of particular interest because of its relatively long half-life. It has been estimated that the soils have been contaminated with depositions of more than 100,000 MBq/km<sup>2</sup> (around FDNPP) and 10,000 MBq/km<sup>2</sup> (neighboring prefectures) of radiocesium (RCs) [2]. According to an RCs deposition map [3], areas with RCs activity concentrations of >600 kBq/m<sup>2</sup> on 14 June 2012 were concentrated within a 50-km radius of the FDNPP. To minimize the harm to human health and the living environment, Special Decontamination Areas covering 11 municipalities around the FDNPP were designated [4], in which RCs activity concentrations in inhabited areas have been greatly reduced by decontamination work of the national government. However, residents' motivation to resume agriculture within a 5-km radius of the FDNPP is still very low.

The cultivation of biomass crops for energy production is a promising land use for such areas. The RCs is still present in the surface soil and is easily taken up by plant roots [5], contaminating crops. Compared with incineration, anaerobic digestion (AD) of

RCs-contaminated crops has the advantage of no requirement for air pollution control equipment to collect ash particles with a high concentration of RCs from flue gas [6]. Instead, RCs is retained in solid and liquid phases in the form of Cs<sup>+</sup> ions in AD. Although farms can use the digestion residue as a liquid fertilizer, this could lead to the release of RCs into groundwater. Meanwhile, RCs retained in farmland carries a potential risk of exposing farm workers to radiation. It has been reported that most RCs remains in the soil surface of rice fields (the plow layer) even when the soil is disturbed by farming processes such as spring tillage, flooding and puddling [7]. For these reasons, RCs should be removed from the biomass energy system, which comprises the crop cultivation and the biogas plant used to process contaminated crops. RCs released from FDNPP has been incorporated in various clay minerals in the soil and is tightly adsorbed to the high-affinity interlayer region of lamellar silicate minerals [8]. Since it is not readily desorbed from these adsorption sites, direct removal of RCs from soil is not practical [9]. The removal of RCs from digested liquid is, however, a valid and feasible way if RCs in soil entrained to an AD reactor is leached out and then adsorbed with an adsorbent with a high selectivity to RCs. Most commonly, RCs is removed from soil or water by physicochemical adsorption methods using adsorbents. Co-existing cations such as NH<sub>4</sub><sup>+</sup>, however, can desorb RCs [10]. Therefore, understanding the chemical state and dynamics of RCs in anaerobic digestate is important for adsorption treatment. In the removal of RCs by adsorption, its dissolution from solids such as soil particles is of great concern [10]. It has observed that RCs accumulated by plants is released into the water column during plant decomposition in aquatic ecosystems [11]. Similarly, AD is

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likely to release RCs into the bulk solution of digestate through microbial degradation. Radionuclide solubilization by microorganisms has been investigated by several researchers [12]. Biodegradation of metal-organic complexes and subsequent release of metals and/or radionuclides are referred to as heterotrophic leaching [12,13]. The roles of microorganisms in heterotrophic leaching are to provide organic acids as effective chelating agents and to accelerate the movement of metals in soil [12]. On the other hand, it has been reported that a portion of the released RCs is taken up by microorganisms and concentrated inside microbial cells [13]. Anaerobic degradability varies widely among crops [14], so the amount of RCs released might also depend on crop type. Researchers have measured RCs distribution coefficients (particulate/dissolved forms) in river, soil, and sediment samples [15,16], but that of plants decomposed in a bioreactor is not yet understood. Therefore, phase partitioning of RCs between bulk solution and suspended solids in AD needs to be examined in detail.

There have hitherto been no reports focusing on this subject, so this is the first study to investigate the influence of RCs concentration on methanogenic microbial activity. The roles of radiation have been discussed in the past few decades in the fields of environmental microbial ecology and biotechnology. Both positive and negative impacts of radiation on microbial growth have been observed at different radiation intensities [17–19], and thus it has a potential impact on AD performance. The phase partitioning of RCs during anaerobic digestion of biomass crops was then investigated. Sorghum and *Miscanthus × giganteus* were grown in hydroponic culture including RCs and used in AD experiments to examine the effects of crop type on RCs partitioning. After long-term semi-continuous operation of two continuously mixed reactors using sorghum or *M. × giganteus* as the sole substrate, the partitioning behavior of RCs in the two types of digestate samples was investigated. Characteristics of RCs removal from bulk solution of digestate were also determined using adsorption treatment.

## 2. Materials and methods

### 2.1. Digestion feedstock

Plants were grown in a temperature-controlled room at 25 °C. Sweet sorghum (*Sorghum bicolor* (L.) Moench) and *M. × giganteus*, which are highly productive grass crops, were grown in polystyrene boxes with at least 16 holes bored in each lid to support them. The boxes were filled with 9 L of culture medium containing RCs and illuminated with white grow lights at 10 000 lx for 12 h every day. The culture medium for the sorghum was prepared using 1.6 g/L of Hoagland's No. 2 Basal Salt Mixture powder (Sigma-Aldrich) and eluate from biomass incineration fly-ash added to the medium to give 20 Bq/L of RCs activity. The culture medium for *M. × giganteus* contained 303.3 mg/L KNO<sub>3</sub>, 472.3 mg/L Ca (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 136.1 mg/L KH<sub>2</sub>PO<sub>4</sub>, 246.5 mg/L MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.773 mg/L H<sub>3</sub>BO<sub>3</sub>, 2.893 mg/L MnSO<sub>4</sub>·5H<sub>2</sub>O, 0.575 mg/L ZnSO<sub>4</sub>·7H<sub>2</sub>O, 0.062 mg/L CuSO<sub>4</sub>·5H<sub>2</sub>O, 0.072 mg/L MoO<sub>3</sub>, 14.7 mg/L Fe(III)-EDTA, 26.8 mg/L NH<sub>4</sub>Cl, 154.3 mg/L Na<sub>2</sub>SiO<sub>3</sub>, and 20 Bq/L fly-ash eluate. The whole stem of crop biomass except the roots was manually harvested with scissors after 2–3 months' culture. It was then air-dried for 4–5 days at 40 °C in a drying chamber and milled in an electric kitchen blender. The particle size of the treated crop ranged from 0.5 to 2 mm, with most of it passing through a 2-mm stainless steel sieve.

### 2.2. Batch and semi-continuous AD experiments

Batch testing was performed in a glass serum vial (60 mL working volume) covered with a layer of aluminum foil tape to

prevent radiation release. The seed sludge consisted of digestion effluent from the sorghum-fed reactor used for the semi-continuous AD experiment mentioned below. The substrate used for the batch test was dried sorghum powder not contaminated by RCs (Volatile solids (VS) 0.918 g/g, COD 1.214 g/g VS). The substrate and seed sludge were mixed to give a feed-to-inoculum ratio of 0.3 (VS/VS) and RCs eluate solution was added to suit different RCs conditions (0, 30, or 100 Bq/L). Finally, approx. 10 mL of deoxygenated water was added to make a 70-mL mixture in a glass vial. The spout of the glass vial was closed using a rubber cap and it was then sealed with an aluminum cap after replacing the headspace with N<sub>2</sub> gas. All the vials were incubated at a rotation speed of 120 rpm in a temperature-controlled shaker (35 °C). The volume of daily gas production was determined using a glass gas-tight syringe. Specific methanogenic activity (SMA) was determined using the Gompertz equation for cumulative methane gas production [14]:

$$G(t) = G_0 \times \exp \left\{ -\exp \left[ \frac{R_{\max} \times e}{G_0} (\lambda - t) + 1 \right] \right\} \quad (1)$$

where  $t$  is the time incubated,  $R_{\max}$  is the SMA (mL/g VS<sub>added</sub>/d) and  $\lambda$  is the duration of lag phase (d). Each experiment was conducted in triplicate.

Seed sludge for semi-continuous AD experiments was taken from a full-scale mesophilic anaerobic digester (37 °C) treating cow manure in the Tohoku region of northeastern Japan. The chemical properties of the seed sludge were as follows. Total solids (TS) 19.3 g/L, VS 12.3 g/L, pH 7.94, Alkalinity 7513 mg/L as equivalent of CaCO<sub>3</sub>, volatile fatty acids (VFAs) < 10 mg/L as equivalent of acetate. In two 400-mL (working volume) insulated glass cylinder reactors, the digestate was continuously mixed by a magnetic impeller at 300 rpm. Mixing is an important factor in anaerobic mono-digestion of fibrous biomass, as it creates an accumulated floating layer of undigested mass that can be problematic for mechanical mixing systems inside a digester [20]. Because of the low wettability of fibrous biomass such as sorghum stem and *M. × giganteus*, they tend to float, interfering with mixing during AD. In this study, stirring at 300 rpm was the minimum intensity to ensure complete mixing. The reactor temperature was maintained at 35 °C with a heating stirrer. Hydraulic retention time (HRT) was 60 days during the first 25 days (start-up), and then 30 days for the next 100 days. As substrate, 1.08 g milled biomass, 3.35 mL supplementary nutrient solution, and 8.9 mL water was added, and around 12 mL of digestate was withdrawn, to maintain 400 mL working volume, every day at a given time during the latter period. The supplementary nutrient solution provided 30 mg/L Fe, 3 mg/L Co, 3 mg/L Ni, and 30 mg/L S. The influent TS concentration was ~80 g/L. The biogas produced was stored in a 1-L gas bag and the volume produced was measured daily by withdrawing the gas through a calibrated syringe. A small portion of the gas taken from headspace of the reactor was used for gas chromatography to determine the composition.

### 2.3. RCs measurements

To investigate RCs partitioning, daily digestion effluent was stored starting at day 60 in a 30-day HRT until about 300 mL had been collected. First, ~100 g digestion effluent was centrifuged at 10 000×  $g$ . The supernatant was put aside for filtration, and the residual sediment was resuspended in 80 g of reverse-osmosis-purified water and centrifuged at 10 000×  $g$  again. This procedure was performed three times. Suspended particles in the bulked supernatant (~300 g) were collected on a glass fiber filter (GA-100, nominal pore size 1.0 μm, Advantec) and then the filtrate was sequentially passed through membrane filters with pore sizes of 5.0, 3.0, 1.0, 0.8, 0.65, and 0.45 μm (mixed cellulose ester

membrane filter, Advantec). The filtrate was evaporated in a PTFE beaker until about 60–70 mL remained. RCs activity in the residual solution was measured in a U8-type polypropylene container with a germanium semiconductor detector (GMX40, Seiko EG&G). The cation-exchangeable fraction in the centrifuged sediment and on all filter papers was extracted with 200 mL ammonium acetate solution (1 M, pH 7) for 2 h at 25 °C and 200 rpm. After centrifugation at 10 000× g, the supernatant was filtered through membrane filters with pore sizes of 5.0, 1.0, 0.65, and 0.45 μm, and the filtrate was collected as the cation-exchangeable fraction. It was evaporated in a PTFE beaker to 60–70 mL. The RCs activities of the cation-exchangeable fraction and the residue (the centrifuged sediment and membrane filters from the previous extraction step) were measured with the germanium detector.

For batch RCs sorption tests, RCs-contaminated model digestate samples were prepared by mixing fly-ash eluent and digestate effluent taken from a pilot biogas plant treating sorghum to give ~30 Bq/L of RCs activity. After 6 h mixing at 200 rpm, the model samples were centrifuged at 10 000× g and filtered through glass fiber filters (GA-100, 1.0 μm; GS-25, 0.6 μm; Advantec). 150 mL of filtrate was then mixed with 0.15, 1.5, 4.5, or 15 g of synthetic zeolite A-3 (14–30 mesh, Fujifilm Wako) or 0.075, 0.15, 0.45, or 1.5 g of Prussian blue beads (PB-MC beads, Kanto Kagaku) in a 250-mL polypropylene bottle. The bottle was shaken on a horizontal multi-shaker at 200 rpm for 6 h. Supernatant was obtained by sequential filtrations through a glass fiber filter (GA-100) and membrane filters with pore sizes of 3, 1, and 0.45 μm. Initial and final RCs activities of supernatants were determined with the germanium detector, and the amount of RCs adsorbed was calculated as the difference. An additional experiment was carried out focusing on the effect of ammonium concentration on sorption characteristics: A 30-Bq/L RCs solution was prepared in reverse-osmosis-purified water using fly-ash eluent and NH<sub>4</sub>Cl (0, 500, 1500, 3000, 5000 mg-NH<sub>4</sub><sup>+</sup>/L) at pH 7. The solution was mixed with 1 g zeolite or 1 g Prussian blue beads in a 2-L polypropylene bottle on the horizontal multi-shaker at 200 rpm for 2 h. The RCs activity of the supernatant was determined with the germanium detector.

#### 2.4. Analytical methods

The biogas composition was determined by gas chromatograph (GC: GC-8A, Shimadzu) equipped with a thermal conductivity detector and a Porapak Q stainless steel column (GL Science). Samples for measurement of contents of VFAs (acetic, propionic, butyric, and valeric), NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, and soluble chemical oxygen demand (S-COD) were prepared by centrifuging digestate samples

at 10 000 ×g for 5 min and filtering through 0.45-μm-pore filters. The concentrations of VFAs were determined by GC (GC-2014, Shimadzu) equipped with a flame ionization detector and a DB-WAXetr capillary column (Agilent J&W). The total COD and S-COD concentrations of digestate were determined by using COD Digest Vials (Hach, Loveland, CO, USA) in accordance with the manufacturer's instructions. The COD concentrations of crop biomass were determined in line with the method for high-strength samples [21]. NH<sub>4</sub><sup>+</sup> concentration was measured by indophenol blue absorptiometry, and K<sup>+</sup> concentration was measured with an ion meter (K-11; Horiba). Electrical conductivity was determined with an electrical conductivity meter (Horiba). TS, Total Suspended Solids (TSS), and VS were determined according to the US EPA Standard Method. The pH was determined on sampling with a pH meter (TOA-DKK) equipped with a GST-5821C probe. Cation exchange capacity (CEC) was measured by the method for anaerobic sludge [22].

Cation selectivity coefficients for the adsorbents used in this study were determined using the following procedure. The zeolite and Prussian blue beads were saturated with NH<sub>4</sub><sup>+</sup> by triple washing with 10 mM ammonium acetate. Excess salt was removed through repeated washing (once with reverse-osmosis-purified water and three times with 80 % methanol). The adsorbents were then air-dried in a draft chamber for one day. 50 mL of blended solution of CsCl and NH<sub>4</sub>Cl was mixed with 0.75, 1.5, or 3 g of the dried zeolite or Prussian blue beads in a 100-mL polypropylene bottle. The total concentration of cations in the blended solution was 20 mM and the equivalent ratios of Cs<sup>+</sup>/NH<sub>4</sub><sup>+</sup> in the solution series were 4:1, 1:1 and 1:4. The bottle was shaken on a horizontal multi-shaker at 200 rpm for 4 h. After centrifugation and filtration via a 0.2-μm pore-size membrane filter, the supernatant (Extract A) was removed and the adsorbents were washed with water and 80 % methanol. They were then air-dried again. Exchangeable Cs<sup>+</sup> and NH<sub>4</sub><sup>+</sup> (adsorbed to zeolite or Prussian blue beads) was extracted in 50 mL of 1 M potassium acetate (pH 7) for 6 h. After centrifugation, supernatant (Extract B) was collected. The cation content in Extracts A and B was measured using an ion chromatograph (IC-2010, TOSOH).

### 3. Results and discussion

#### 3.1. Effect of RCs concentration on methanogenic activity

Average values of cumulative methane production in the batch AD experiment at different concentrations of RCs (0, 30, 100 Bq/L) are summarized in Fig. 1. Methane production reached around

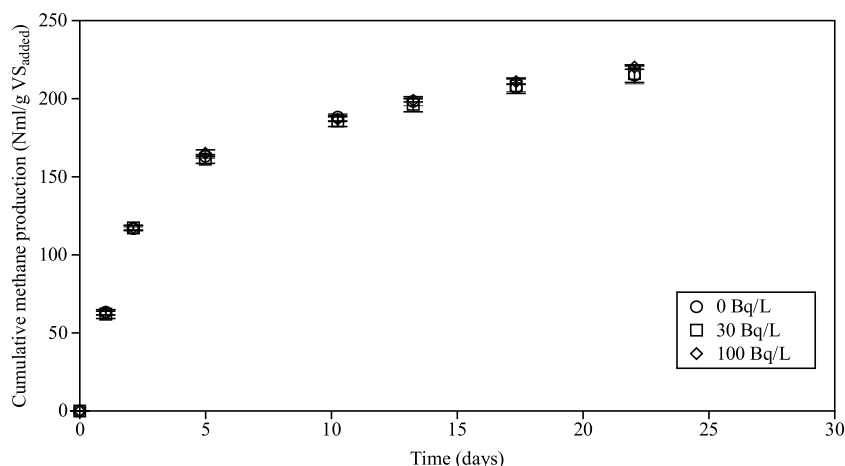
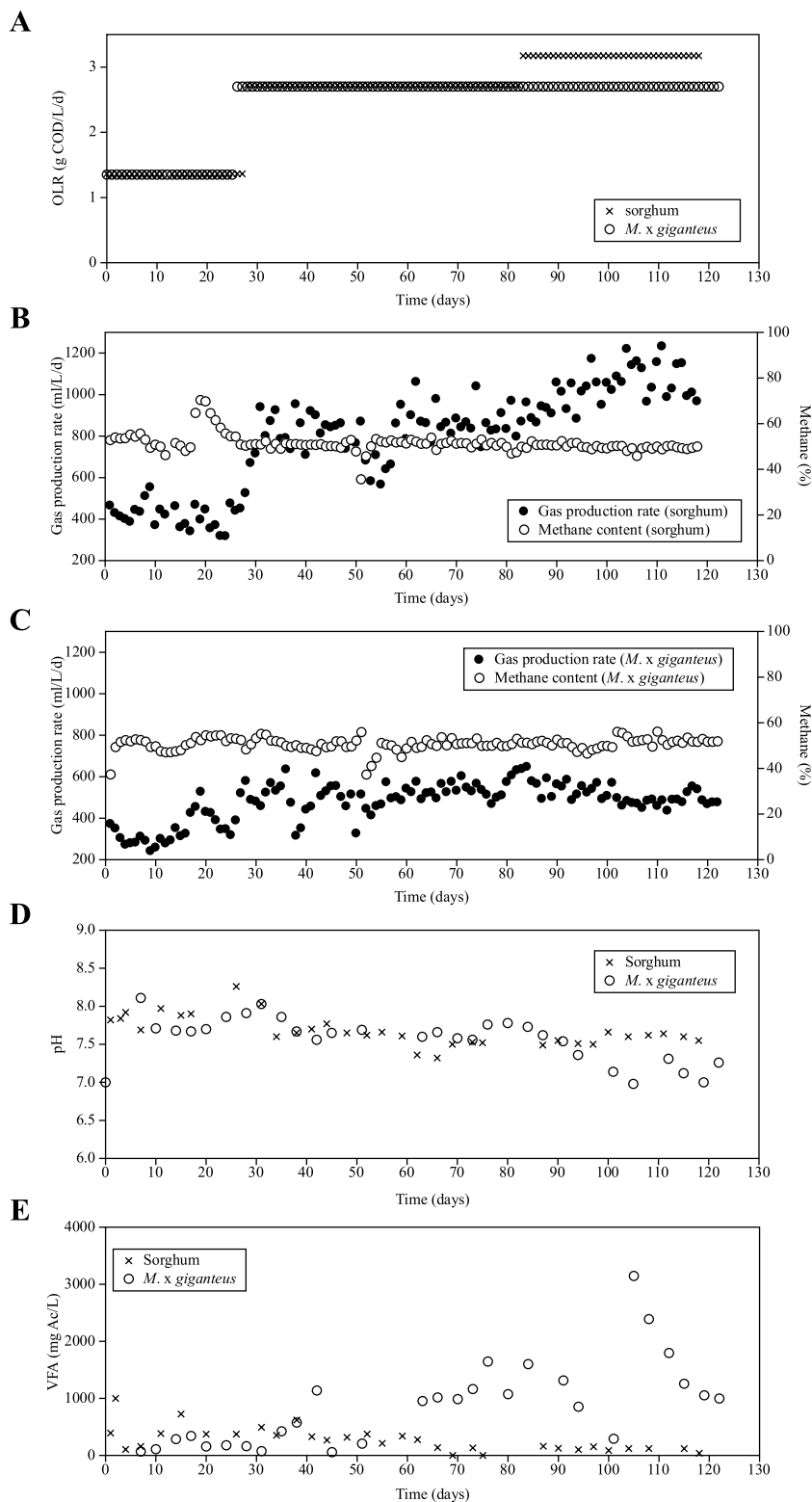


Fig. 1. Cumulative methane production in the batch test of AD at different RCs concentrations (n = 3).

220 Nml/g VS<sub>added</sub> in the first 22 days. The theoretical maximum methane potential, based on the COD concentration of the substrate, was 433 Nml/g VS<sub>added</sub>. The values obtained at day 22 were about half the theoretical maximum value, which put them within an appropriate range. The SMAs based on the methane production curves were  $48.7 \pm 0.9$  (0 Bq/L),  $48.2 \pm 1.7$

(30 Bq/L),  $48.7 \pm 1.7$  (100 Bq/L) Nml/g VS<sub>added</sub>/d, respectively. The duration of the lag phase ( $\lambda$ ) was zero under these conditions, suggesting no inhibition of methanogenesis. Analysis of variance of these three average values revealed there to be no significant difference ( $p$  value=0.9) in SMA values among these three conditions. An obvious negative impact of long-term radiation



**Fig. 2.** Reactor performance: (A) organic loading rate (OLR); (B, C) biogas production rate and methane content in (B) sorghum-fed and (C) *M. x giganteus*-fed reactors; (D) pH in effluent; (E) VFA concentration in effluent.

exposure (more than 3 days) on microbial activity has been observed at much higher radio tritium activities (~MBq/L) in some earlier studies [18,19]. One study reported the positive effects of lower levels of radon radiation (1.4 Bq/L) on microbial growth, although the duration of radiation exposure was only 1–5 h [17]. As Selivanova reported [18], exposure to radiation can temporarily stimulate microbial activity but has a negative effect in the long run. RCs also has a lower ionization density of radiation than radon, an alpha particle-emitting element, tested above. The extremely low level of RCs activity (30, 100 Bq/L) tested in this study is unlikely to have had a significant negative effect on digestion performance.

### 3.2. Reactor performance during the semi-continuous experiments

#### 3.2.1. Time course of reactor performance

After the 25-day start-up period, the organic loading rates (OLRs) of the reactors were steady at 2.7 g COD/L/d (Fig. 2A). On day 83, feedstock sorghum was replaced with newly harvested material, increasing OLR slightly to 3.1 g COD/L/d in the sorghum-fed reactor.

Based on influent VS, the OLRs ranged from 2.1–2.6 g VS/L/d at an HRT of 30 days. In studies of semi-continuous AD of sorghum [23–25] and *M. × giganteus* [25], operation was successful at OLRs of 1.5–4.0 g VS/L/d, but failed at higher OLRs because of pH drop [24]. The OLRs here were within the appropriate range. There was a big difference in methane yield between the sorghum-fed and *M. × giganteus*-fed reactors (Fig. 2B, C). Although the methane contents in the biogas from both reactors were around 50 %, the rate of biogas production of the sorghum-fed reactor was nearly twice that of the *M. × giganteus*-fed reactor. The calculated average methane yields between days 85 and 122 were 195.9 N mL/g-VS<sub>added</sub> (sorghum-fed) and 125.7 N mL/g-VS<sub>added</sub> (*M. × giganteus*-fed). In a 45-day batch AD of *M. × giganteus* silage [26], the methane production potential was 172–186 N mL CH<sub>4</sub>/g-VS<sub>added</sub>, only half that of maize silage (381 N mL/g-VS<sub>added</sub>). This low methane potential from *M. × giganteus* was attributed to the higher cellulose and lignin contents [26]. As other researchers have pointed out, of the components of energy crops, fiber fractions such as lignin, cellulose and hemi-cellulose have the greatest impact on the rate of methane production [14]. One study has revealed a wide variation in removal efficiencies of organic components, including VS, lignin, cellulose and hemi-cellulose among crops [25]. *M. × giganteus* showed not only low VS removal efficiency of around 45 % but also low removal efficiency of the fiber fraction [25]. A possible explanation of this trend was differences in the chemical composition of lignin, as monomers produced from the biodegradation of lignin can be converted into different intermediates that have different biodegradation rates. In another study, the methane potential from sorghum in 60 days was around 340 N mL CH<sub>4</sub>/g-VS<sub>added</sub> [23]. The methane yields here were 60 % (sorghum-fed) and 70 % (*M. × giganteus*-fed) of those potential values. Both reactors maintained the appropriate pH range above 7.0 during the experiments (Fig. 2D). The VFA level in the *M. × giganteus*-fed reactor increased to up to 3100 mg/L as acetate equivalent during the 30-day HRT (Fig. 2E), resulting in the slight decline of pH. However, there was no significant problem in operation throughout the experiment.

#### 3.2.2. Characteristics of digestion effluents

The higher residual COD concentration in the *M. × giganteus*-fed reactor (Table 1) reflects the lower methane yield discussed above. This result is consistent with very low VS removal (< 45 %) in AD of *M. × giganteus* among the 10 crops tested [25]. Since there was no big difference in S-COD between the two reactors, the results mean the *M. × giganteus*-fed reactor was richer in particulate COD. Cation

**Table 1**

Average values of characteristics of digestion effluent at HRT of 30 days.

Substrate	Sorghum	<i>M. × giganteus</i>
COD (g/L)	43.5 ± 7.9	57.5 ± 7.0
S-COD (g/L)	5.2 ± 0.1	5.8 ± 0.8
NH <sub>4</sub> <sup>+</sup> (mM)	30.4 ± 13.8	45.7 ± 3.9
K <sup>+</sup> (mM)	62.0 ± 5.3	40.6 ± 3.1
EC (mS/cm)	7.9 ± 1.8	7.4 ± 0.7
CEC (meq/100 g-TSS)	59.1 ± 5.1	53.2 ± 2.2
CEC (meq/L-digestate)	19.0 ± 1.8	32.8 ± 1.3

exchange is likely to greatly affect the behavior of RCs in the digestate. In particular, NH<sub>4</sub><sup>+</sup> and K<sup>+</sup>, as major cations in crop digestate [27], should be taken into consideration, because Cs<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and K<sup>+</sup> have similar ionic radii and exchange selectivities for adsorbents [28]. There is no clear difference in the sum of NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> between the two reactors (Table 1). In addition, similar EC levels between the reactors suggest comparable total cation concentrations in the digestate. By contrast, CEC per unit volume of digestate diverges between the reactors, probably owing to the large difference in particulate COD contents. That is, the *M. × giganteus*-fed reactor has more undecomposed crop residues in digestate, which provide functional groups that contribute to the increase in CEC.

### 3.3. RCs partition and adsorption treatment

#### 3.3.1. Partitioning of RCs in digestate

The digestate effluent samples were fractionated into 3 parts (water-soluble, ion-exchangeable, residual). Notably, whereas 82.3 % of RCs in the sorghum digestate was water-soluble, only 33.7 % of that in the *M. × giganteus* digestate was (Table 2). The *M. × giganteus* digestate was also characterized by a high percentage of ion-exchangeable RCs. The difference in the water-soluble fraction between the two reactors can be explained by the poorer biodegradability of *M. × giganteus* (Fig. 2; Table 1). One reason for the low percentage of water-soluble RCs in the *M. × giganteus*-fed reactor could be that the residual crop biomass held RCs in its tissues. Another reason could be that it held more cationic RCs on its surface, owing to the high CEC of the *M. × giganteus* digestate. The decrease in radioisotopes during biological wastewater treatment was thought to be due to adsorption onto particulate sludge and its settlement [29]. This should also be due to cation exchange on the sludge surface. Our results suggest that degradation of feedstock biomass in AD releases RCs into the water phase, and the RCs solubilization efficiency depends on the biodegradability of the feedstock.

#### 3.3.2. Partitioning of RCs between water phase of digestate and adsorbent

A possible way to remove leached RCs before digestate is applied as a liquid fertilizer is adsorption of dissolved RCs onto adsorbents. Because the partitioning of RCs between bulk solution and adsorbent is useful for determining the optimum dose of

**Table 2**

Average RCs activities (<sup>134</sup>Cs + <sup>137</sup>Cs) in each fraction of digestate at HRT of 30 days.

Substrate	Fraction	RCs (Bq/L digestate)	Percentage (%)
Sorghum	Water-soluble	32.4 ± 11.1	82.3
	Ion-exchangeable	3.8 ± 1.3	9.6
	Residual	3.2 ± 1.6	8.1
<i>M. × giganteus</i>	Water-soluble	19.1 ± 3.2	33.7
	Ion-exchangeable	20.2 ± 3.4	35.8
	Residual	17.3 ± 1.9	30.6

n = 3.

adsorbent, it was examined using zeolite and Prussian blue beads at different doses. The coefficient of partitioning ( $K_d$ ) between dissolved and adsorbed RCs and removal efficiency of RCs from the water phase were evaluated using the obtained results.

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} \quad (2)$$

$$\text{Removal efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium activities of RCs (Bq/L) in the digestate,  $V$  is the volume of the digestate tested (0.15 L), and  $m$  is the mass of the adsorbent (g). The relationship between dissolved and particulate (adsorbed) RCs activities suggests a constant partitioning between the two phases within the range of zeolite dose from 1 to 100 g/L (Fig. 3A). Similarly, a constant partitioning between the two phases was obtained in the range of Prussian blue bead dose from 0.5 to 3 g/L (Fig. 3B). The slope of the regression line gives the coefficient of partitioning ( $K_d$ ) between dissolved and adsorbed RCs. The  $K_d$  value for Prussian blue beads (5.25 L/g) was 18 times greater than that for zeolite (0.289 L/g). The efficiency of removal of RCs increased exponentially with the increase in zeolite dosage (Fig. 3C), reaching 90 % at 30 g zeolite/L. The removal efficiency of RCs using Prussian blue beads increased more sharply with doses from 0.5 to 3 g Prussian blue beads/L, reaching 99 % at 3 g/L. These results suggest that Prussian blue beads can remove the leached RCs more efficiently from digestate. The  $K_d$  value for zeolite is lower than those obtained from other samples; for example,  $K_d = 1.9$  L/g in synthetic groundwater and raw

bentonite [30] and  $K_d = 1.72\text{--}5.06$  L/g with different types of zeolites in RCs standard solution [31]. The  $K_d$  value for Prussian blue here is also low compared to those obtained from seawater (300–800 L/g) [32]. Since the adsorption of RCs is based on cation exchange, a specific cation concentration determines partitioning. The low value of  $K_d$  here is likely to be related to the high concentration of competitive ions in the digestate; previous studies used RCs solutions with lower concentrations of competitive cations [27,28]. Further, using impregnated zeolite as an adsorbent decreased  $K_d$  sharply from 2 to 0.3 L/g with increasing concentrations of  $\text{Na}^+$  from 0 to 3 M [33]. This result supports the above hypothesis that increased competitive cations reduce  $K_d$ . In AD, great variation in  $\text{NH}_4^+$  concentration among reactors fed different crops has been reported [25]. Next, the effect of  $\text{NH}_4^+$  on RCs adsorption to adsorbents was examined. The batch adsorption experiment using fly-ash eluent solution (30 Bq/L) and two adsorbents (zeolite and Prussian blue beads) at different concentrations of  $\text{NH}_4^+$  clearly showed that the  $\text{NH}_4^+$  concentration reduces adsorption of RCs onto adsorbents, particularly the zeolite (Fig. 4). Especially, the zeolite showed a sharp decrease in efficiency with the increase in  $\text{NH}_4^+$  concentration. The  $K_d$  between bulk and adsorbent could vary widely, as properties of digestate vary greatly. The difference in decrease between the two adsorbents may be related to difference in Cs ion selectivity for adsorbents. The Cs ion selectivity coefficients for each adsorbent used in this study were evaluated in the experiments. The basic principle of cation association with  $\text{NH}_4$ -saturated adsorbents in the cation-exchange tests can be described by the following equations.

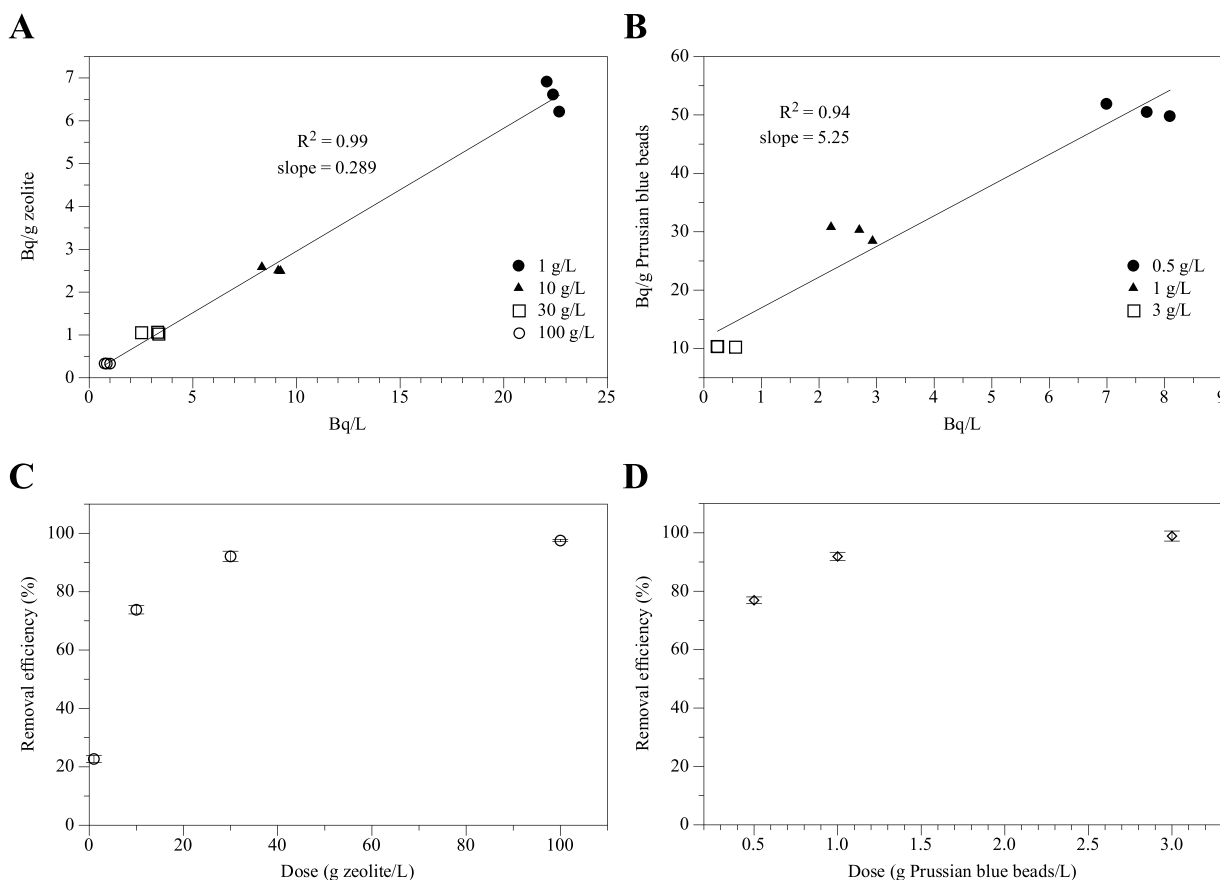


Fig. 3. (A), (B) Relationship between concentration of dissolved RCs in bulk solution of digestate and of particulate RCs adsorbed to zeolite and Prussian blue. (C), (D) Efficiencies of RCs removal from the water phase.

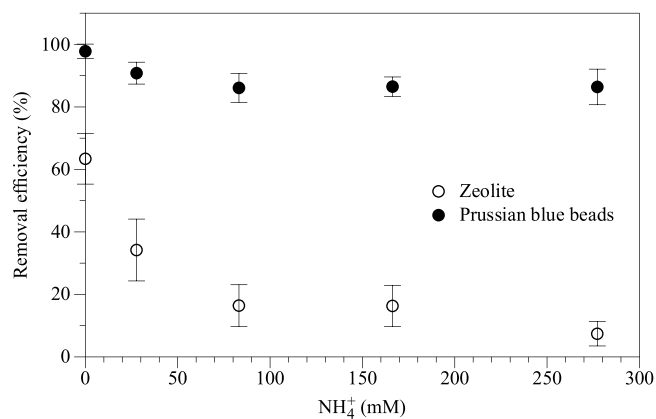


Fig. 4. Efficiencies of RCs removal by two adsorbents at different NH<sub>4</sub><sup>+</sup> concentrations.

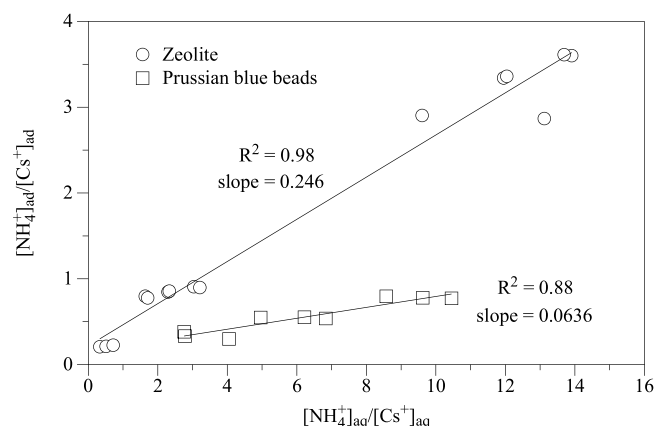


Fig. 5. Selectivity coefficients for Cs<sup>+</sup> to adsorbents (zeolite and Prussian blue beads) related to NH<sub>4</sub><sup>+</sup>.

where X represents adsorbents. When Cs<sup>+</sup> is added into the solution, Cs<sup>+</sup> forms associations with adsorbents, exchanging some portions of the adsorbent-associated NH<sub>4</sub><sup>+</sup> into the bulk solution. The selectivity coefficient ( $K_{Cs}^{NH_4}$ ) of Cs towards adsorbents with respect to NH<sub>4</sub><sup>+</sup> is set out as Eq. (5).

$$K_{Cs}^{NH_4} = \frac{[NH_4^+]_{ad}[Cs^+]_{aq}}{[NH_4^+]_{aq}[Cs^+]_{ad}} \quad (5)$$

where [NH<sub>4</sub><sup>+</sup>]<sub>aq</sub> and [Cs<sup>+</sup>]<sub>aq</sub> are the cation concentrations in the aqueous phase (meq/L), [NH<sub>4</sub><sup>+</sup>]<sub>ad</sub> and [Cs<sup>+</sup>]<sub>ad</sub> are those in the adsorbent phase (meq/g). Fig. 5 shows the relationship between [NH<sub>4</sub><sup>+</sup>]<sub>aq</sub>/[Cs<sup>+</sup>]<sub>aq</sub> and [NH<sub>4</sub><sup>+</sup>]<sub>ad</sub>/[Cs<sup>+</sup>]<sub>ad</sub> in the cation selectivity coefficient experiments using two adsorbents. The slope of the regression line gives the  $K_{Cs}^{NH_4}$  according to Eq. (6).

$$\frac{[NH_4^+]_{ad}}{[Cs^+]_{ad}} = K_{Cs}^{NH_4} \frac{[NH_4^+]_{aq}}{[Cs^+]_{aq}} \quad (6)$$

The  $K_{Cs}^{NH_4}$  values obtained from the results in Fig. 5 were 0.246 for zeolite and 0.0636 for the Prussian blue beads. The two values lower than 1 indicated a greater affinity of Cs<sup>+</sup> for adsorption than NH<sub>4</sub><sup>+</sup>. The much lower value for Prussian blue beads suggests that they provide highly selective adsorption of Cs ions in the presence of NH<sub>4</sub><sup>+</sup>. This result strongly supports the high removal efficiency of RCs in the NH<sub>4</sub><sup>+</sup>-rich digestate when using Prussian blue beads.

A vital practical problem in the application of biomass energy technology to radioactively contaminated soil is the protection of human health and the environment. In this study, it was

demonstrated for the first time that the semi-continuous AD of an RCs-contaminated crop could be successfully operated for long periods of time, and that most RCs was eluted into the aqueous phase during AD. Utilizing digestate as liquid fertilizer is essential for a circular economy. However, the correct treatment is needed to stabilize RCs and minimize any leaching or runoff to the environment. From the above results, an adsorbent with high selectivity for Cs should be selected for efficient and effective removal of RCs from the aqueous phase of digestate when biomass feedstock with a significant N content is used. The efficient removal of RCs at the optimal dose of adsorbent shown in this study suggests the feasibility of enhanced safety in AD of RCs-contaminated crops.

#### 4. Conclusions

This study is the first to demonstrate the potential for long-term successful operation of semi-continuous AD in the presence of low levels of RCs. However, the efficiency of release of RCs from RCs-contaminated crops into the aqueous phase (up to 82 %) depends on the biodegradability of the crop type. To effectively remove RCs from the aqueous phase of digestate before fertilization, an adsorbent with a high exchange selectivity of Cs ions should be used. The efficient removal of RCs at the correct dose of adsorbent suggests the attainability of enhanced safety in AD of RCs-contaminated crops.

#### CRedit authorship contribution statement

**Takuro Kobayashi:** Conceptualization, Investigation, Data curation, Formal analysis, Writing - original draft. **Hidetoshi Kuramochi:** Supervision, Project administration, Writing - review & editing. **Kai-Qin Xu:** Writing - review & editing. **Takao Aizawa:** Resources, Project administration.

#### Declaration of Competing Interest

None.

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