



# Selective encapsulation of cesium ions using the cyclic peptide moiety of surfactin: Highly efficient removal based on an aqueous giant micellar system



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## ABSTRACT

Cyclic peptide of surfactin (SF) is one of the promising environment-friendly biosurfactants abundantly produced by microorganisms such as *Bacillus subtilis*. SF is also known to act as an ionophore, wherein alkali metal ions can be trapped in the cyclic peptide. Especially, SF is expected to show high affinity for Cs<sup>+</sup> because of the distinctive cavity size and coordination number. In this study, we reported the specific interaction between SF and Cs<sup>+</sup> and succeeded in the highly efficient removal of Cs<sup>+</sup> from water using giant SF micelles as a natural sorbent. The specific interaction between SF and Cs<sup>+</sup> to form their inclusion complex was revealed by nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy. We found that SF micelles selectively encapsulate Cs<sup>+</sup>, which was suggested by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS). A highly effective separation of Cs<sup>+</sup> immobilized on the surface of the SF micelles was also achieved through facile centrifugal ultrafiltration in 91% even in coexisting with other alkali metal ions such as Na<sup>+</sup> and K<sup>+</sup>. Thus, the use of the giant micellar system of SF with its high Cs<sup>+</sup> affinity and distinctive assembling properties would be a new approach for the treatment of contaminated soil and water.

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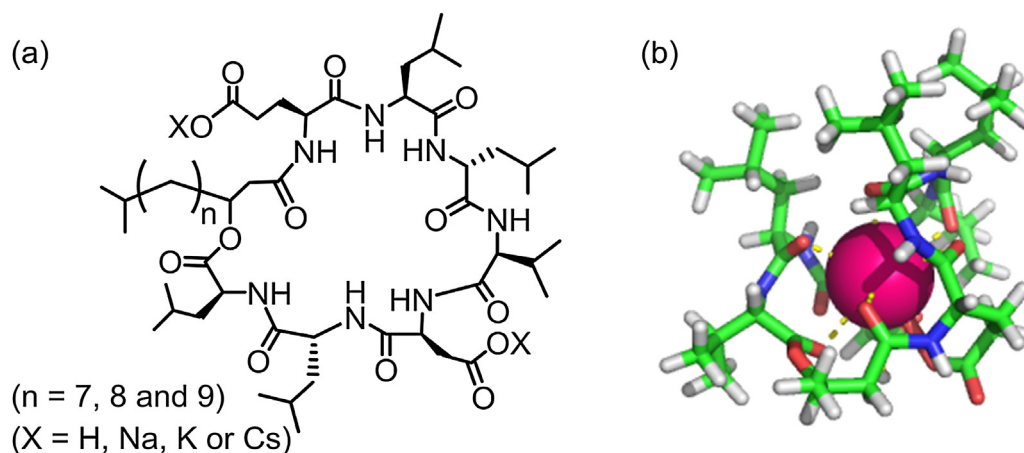
## 1. Introduction

Cyclic peptides have attracted molecules not only because they do not have terminal end groups, but also because their topological features can influence the chemical, physical, and biological properties of the molecules [1]. Recent progress in cyclic peptide libraries encouraged by both genetic and synthetic methods enabled their application as drugs as well as supramolecular structures in material sciences [2]. Cyclic peptides are also known to act as ionophores, wherein alkali metal ions can be trapped *via* M···O=C interactions in the amide groups and transported across cell membranes [3–5]. Among alkali metal ions, Cs<sup>+</sup> has received considerable attention in Japan because of the spread of radioactive <sup>137</sup>Cs from nuclear

reactor accidents into the environment [6]. Cyclic peptides can be potentially used as novel sorbents since Cs<sup>+</sup> follows the same biological pathways and binds at the same ionophore or enzyme sites as K<sup>+</sup> [7–9]. Recently, several cyclic peptides used as sorbents for alkali metals have been reported to form unique self-assembled structures [10,11]. However, its application in the treatment of contaminated soil and water in nuclear accident areas is limited because these molecules are generally difficult to obtain in mass production and an efficient recovery system after Cs<sup>+</sup> binding has not yet been established.

The cyclic heptapeptide surfactin (SF, Fig. 1), having a long alkyl chain of length  $n = 7–9$ , is known to act as an ionophore for mono and divalent metal cations [12–14]. Moreover, it is abundantly produced by microorganisms such as *Bacillus subtilis* and also regarded as a promising environment-friendly surfactant (often called biosurfactant) that exhibits high biodegradability, in addition to high surface activity, unique self-assembling properties, and low

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**Fig. 1.** (a) Structure of surfactin (SF). (b) CAChe-minimized structure of SFCs. An alkyl chain of SF is omitted for clarity.

toxicity [15–19]. It is reported that SF micelles can bind divalent heavy metal ions ( $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ), and can remove the elements from contaminated soils using the membrane filtration technique [20]. SF is expected to be useful as a novel sorbent for large monovalent  $\text{Cs}^+$  because it also has two carboxylate groups ( $\text{R-COO}^-$ ) that bind  $\text{Cs}^+$  to give a neutral salt ( $\text{RCOOCs}$ ) through a similar mechanism as polyether ionophores [21]. It also has a heptapeptide moiety, providing an ideal coordination number for  $\text{Cs}^+$  (between 6 and 8). The cavity diameter (4–7 Å) is larger than that of the ion (3.38 Å), making it suitable for  $\text{Cs}^+$  encapsulation as shown in the estimated model of the SF monocation salt (SFCs) in Fig. 1(b) [11,22]. Moreover, SF forms giant micelles in aqueous solution, with the heptapeptide moieties aligned on the surface (Fig. 2). High binding affinity and effective removal of  $\text{Cs}^+$  can thus be achieved through micellar-enhanced ultrafiltration (MEUF), a low-energy separation process combining entrapment by surfactant micelles and ultrafiltration. Herein, we report for the first time the effective removal of  $\text{Cs}^+$  from water using SF micelles. We found that SF micelles show an excellent binding affinity for  $\text{Cs}^+$ , revealed by nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) and inductively coupled plasma mass spectrometry (ICP-MS) reveal that SF micelles show an excellent selectivity for  $\text{Cs}^+$ . A highly effective separation of  $\text{Cs}^+$  immobilized on the SF micelles was also achieved through facile centrifugal ultrafiltration.

## 2. Materials and methods

### 2.1. Materials

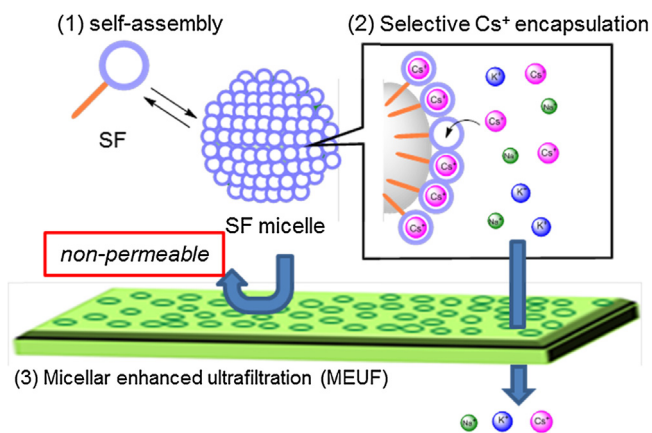
Surfactin sodium salt (SFNa) was kindly supplied by Kaneka. Co. Ltd., Japan. Purity of SFNa were ascertained by analytical RP-HPLC (Inertsil SIL-100A 5 mm C18 column, 0.46 cm  $\times$  25 cm, GL Sciences Inc.) using a mobile phase consisting of acetonitrile/water (80/20) containing 0.1% trifluoroacetic acid (TFA). It is known that natural surfactins produced by microorganisms are constituted by a heptapeptide (L-Glu-L-Leu-D-Leu-L-Val-L-Asp-D-Leu-L-Leu) with a different aliphatic chain length [23]. The RP-HPLC chromatogram revealed that SFNa includes mainly three different kinds of species. Molecular masses of each fraction were then determined by MALDI-TOFMS spectrometry (autoflex speed TOF/TOF, Bruker Daltonics Inc.) using sinapic acid as a matrix. It was found that they are a mixture of SFNa having a fatty acid chain of C13 (17%), C14 (52%) and C15 (31%), respectively. CsCl, NaCl, KCl and  $\text{Cs}_2\text{CO}_3$  were purchased from Wako. Co. Ltd., Japan. Ultra-pure water was obtained from Milipore (Milli Q) apparatus. The deuterated water ( $\text{D}_2\text{O}$ ) and dimethyl sulfoxide ( $\text{DMSO-}d_6$ ) were purchased from Cambridge Isotope Laboratories Inc., U.S.A.

### 2.2. Surface activity

Surface tension measurements were performed by the Wilhelmy plate method at 25 °C using a DY-500 surface tension meter (Kyowa Kaimen Kagaku Co.). Before use, calibration was carried out with ultra-pure water. The Pt plate was cleaned by flaming and glassware was rinsed sequentially with tap-water and ultra-pure water. Aqueous solutions of SFNa with various concentrations were kept at 25 °C overnight in order to reach in equilibrium. The size distributions of the micelles were measured with a DLS-7000 instrument (Otsuka Electronics Co., Japan) using a 488 nm wavelength 75 mW Ar laser as a light source at 25 °C. The time-dependent correlation function of the scattered light intensity was measured at a scattering angle of 30°. In this study, the particle size distributions were determined by using histogram method.

### 2.3. Binding affinity of SF micelles for $\text{Cs}^+$

Binding affinity of SF micelles for  $\text{Cs}^+$  was measured by MALDI-TOFMS spectrometry (autoflex speed TOF/TOF, Bruker Daltonics Inc.), where sinapic acid was used as matrix. The instrument was operated in reflector positive-ion (RP) mode employing a mass



**Fig. 2.** Cartoon representation of  $\text{Cs}^+$  removal from water using the micellar system of surfactin (SF).

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