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Radioactive cesium removal from nuclear wastewater by novel inorganic and conjugate adsorbents

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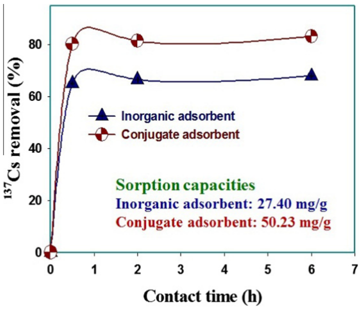
HIGHLIGHTS

- Inorganic and conjugate adsorbent were performed for selective Cs uptake.
- Crown ether immobilized conjugate adsorbent was effective for Cs removal.
- Radioactive ^{137}Cs can be efficiently removed even in the presence of Na and K.
- Both adsorbents are reversible and reusable without significant loss of performances.

GRAPHICAL ABSTRACT



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ABSTRACT

This work was focused on the promising inorganic and ligand immobilized conjugate materials for selective and high capacity of radioactive cesium (Cs) removal from radioactive liquid waste in Fukushima after an accident at Daiichi Nuclear Power Plant hit by the Great East Japan Earthquake and tsunami on 11 March 2011. The conjugate adsorbent was prepared by direct immobilization of dibenzo-18-crown-6 ether onto mesoporous silica monoliths. The Cs sorption behavior was investigated using batch equilibrium technique. The applicability of the inorganic conjugate adsorbent for Cs removal from aqueous test solutions was assessed, and the effective parameters such as solution pH, contacting time, initial Cs concentration and ionic strength of Na and K ion concentrations were evaluated systematically. The effective pH range for high Cs capacity was possible within the pH range 5.5–7.0 and the maximum sorption capacities were 50.23 and 27.40 mg/g for conjugate adsorbent and inorganic adsorbent, respectively. The results clarified that conjugate adsorbent had the higher selectivity towards Cs even in the presence of high concentration of Na and K ions rather than the inorganic adsorbent due to strong Cs–π interaction of benzene ring. The conjugate adsorbent was efficiently decontaminated the radioactive Cs from waste solution with high sorption efficiency. The data also revealed that both adsorbents worked well for removing of dissolved radioactive Cs even in the presence of high concentration competing ions. The adsorbents were reused in several cycles after elution operation with a suitable eluent (0.20 M HCl). Therefore, the prepared adsorbents could be used as low-cost potential adsorbents for the selective radioactive Cs decontamination from Fukushima wastewater samples.

1. Introduction

In the Great East Japan Earthquake on March 11, 2011, the nuclear accident was happened at the Fukushima Daiichi Nuclear Power Plant and consequently, releases of several radionuclides

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such as ^{134}Cs, ^{137}Cs, ^{131}I, and ^{90}Sr into the surrounding environmental areas. However, the direct release of ^{137}Cs into the environment is considered the most abundant radionuclide. Then the control of cesium, particularly ^{137}Cs, in liquid wastes has drawn much attention all over the world because of its destructive effects on the environment [1]. Cesium (Cs) is chemically similar to sodium and potassium; there is high possibility to enter in various environments and easily assimilated by terrestrial and aquatic organisms. In case of ingestion and accumulation, cesium is deposited in the soft tissues all over the body and creating an internal hazard such as thyroid cancer [2–5]. Moreover, ^{137}Cs removal from low-level radioactive liquid waste is not only reducing the radioactivity of the waste but also recover ^{137}Cs as an excellent source for gamma irradiators [6]. Therefore, effective and selective adsorbents are highly demanded to remove Cs from radioactive wastewaters.

Several physical–chemical methods have been investigated for the decontamination of radionuclide Cs from wastewater including solvent extraction, chemical precipitation, membrane process, coagulation, electrochemical and ion-exchange [7–14]. The solvent extraction, ion exchange and adsorption methods are most widely used based on ionic selectivity and efficiency. Solvent extraction using macrocyclic ligand such as crown ethers, calix-crowns, and chlorinated cobalt dicarbollide has shown highly selective to Cs [15–17]. However, high costs of equipment and chemicals, large scale application of solvent extraction is restricted. Therefore, adsorption has been widely used in the removal of radionuclide owing to its simple operation and economical cost. Several clay minerals such as zeolite, bentonite vermiculite, and montmorillonite are used for Cs removal from aqueous solution; however, competitive interactions of Na and K is block Cs adsorption and make the clay minerals as less effective adsorbents [18,19]. The Prussian blue supported materials are also treated as Cs removal from water [20]. However, these are not reusable, produced huge waste and make another problem for the environment.

Recently, highly selective ligand immobilized mesoporous materials have been received great attention due to high surface area, large pore volumes, high adsorption capacity, and fast kinetic performances, and reusability for several cycles use. The mesoporous materials can modify to nano-engineered adsorbents by functionalization of ligands for effective separation and removal of target ions. Crown ethers based macrocyclic ligands have been extensively used in solvent extraction system for Cs separation based on the crystal ionic radius of the Cs ion and the cavity of the crown ether ligand. The strong interactions between cation–π interactions of benzene ring are reported by several researchers [17,21]. However, the high cost and produced huge sludge have been made the solvent extraction as major hurdle in the large-scale use for Cs separation. In this connection, macrocyclic ligand of dibenzo-18-crown-6-ethers (DB18C6) was immobilized onto mesoporous silica for preparation of new class conjugate adsorbent.

There are several types of supported materials are prepared based on surface area, pore volumes and pore sizes. Mesoporous silica using F_{108} possesses large pore sizes and volumes, uniform channel and large surface area exhibit an excellent carrier for constructing powerful solid state adsorbent materials. Moreover, ordered mesoporous materials could be used as supports for immobilization for ligand molecules without changing functional activity to capture the target metals ions [22,23]. Then a new branch of research into the synthesis of mesoporous materials combined with organic ligand containing functional groups has evolved and rectifies as a powerful new class adsorbent material for Cs removal from wastewater [8,24].

In this work, mesoporous inorganic silica was also tested as inorganic adsorbent (IA) to compare with the prepared ligand immobilized adsorbent. The DB18C6 ligand was successfully immobilized onto mesoporous silica monoliths to keep open functionality of the ligand for Cs uptake from radioactive wastewater. Moreover, one-step direct method was used to prepare the DB18C6 immobilized on mesoporous silica monoliths as new class ligand immobilized conjugate adsorbent (CA). Various issues such as mesoporous silica processing, characterization, adsorbents preparations, solution pH, adsorption equilibrium, kinetics, foreign ions effect, reversibility were discussed systematically in detail. In addition, real radioactive samples in Fukushima were performed from the practical stand point of real application.

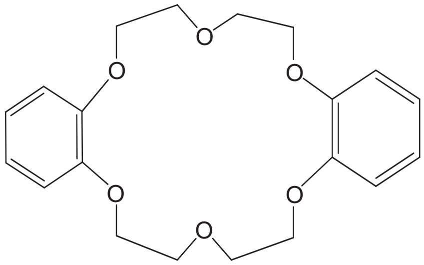
2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethylorthosilicate (TMOS) and the triblock copolymers of poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) designated as F108 ($EO_{141}PO_{44}EO_{141}$) were obtained from Sigma–Aldrich Company Ltd., USA. The crown ether of DB18C6 was purchased from Tokyo Chemical Industry (TCI) Co., Ltd., Japan. The structure of DB18C6 is shown in Scheme 1. Cesium chloride (CsCl) source of Cs ion, sodium chloride and potassium chloride for the source of Na and K ions were purchased from Wako Pure Chemicals, Osaka, Japan. Ultra-pure water prepared with a Millipore Elix Advant 3 was used throughout in this work.

2.2. Preparation of inorganic mesoporous silica and conjugate adsorbent

Mesoporous silica monoliths were synthesized by using direct templating method of lyotropic liquid crystalline phase of F108 ($EO_{141}PO_{44}EO_{141}$, MW: 14,600) as a soft template. The preparation of mesoporous silica monoliths procedure involved adding TMOS and triblock copolymers (F108) to obtain a homogenized sol–gel mixture based on the F108/TMOS mass ratio. An acidified aqueous solution was added to the mixture to quickly achieve the desired liquid crystal phase and then to promote hydrolysis of the TMOS around the liquid crystal phase assembly of the triblock copolymer surfactants. The mesoporous silica monoliths were synthesized following the reported methods [25]. In typical conditions, the composition mass ratio of F108:TMOS:HCl/H_2O was 1.4:2:1 respectively. Mesoporous silica monoliths were synthesized by using direct templating method of lyotropic liquid crystalline phase of F108 as the soft template. Homogeneous sol–gel synthesis was achieved by mixing F108/TMOS in a 200 mL beaker and then shaking at 60 °C until homogeneous. The exothermic hydrolysis and condensation of TMOS occurred rapidly by addition of acidified aqueous HCl acid (at pH = 1.3) solution to this homogeneous solution. Then the methanol produced from the TMOS hydrolysis was removed by using a diaphragm vacuum pump connected to a rotary evaporator at 45 °C. The organic moieties were then removed



Scheme 1. Structure of dibenzo-18-crown-6 ether (DB18C6).