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Selective cesium removal from radioactive liquid waste by crown ether immobilized new class conjugate adsorbent

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HIGHLIGHTS

- DB24C8 crown ether was functionalized for preparation of conjugate adsorbent.
- Radioactive ^{137}Cs can be selectively removed by the conjugate adsorbent.
- Adsorbent can effectively capture Cs even in the presence of a high amount Na & K.
- Adsorbent is reversible and able to be reused without significant deterioration.

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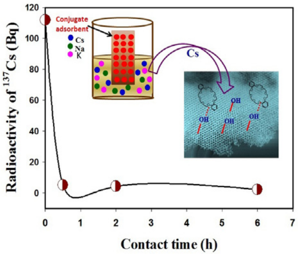
GRAPHICAL ABSTRACT



ABSTRACT

Conjugate materials can provide chemical functionality, enabling an assembly of the ligand complexation ability to metal ions that are important for applications, such as separation and removal devices. In this study, we developed ligand immobilized conjugate adsorbent for selective cesium (Cs) removal from wastewater. The adsorbent was synthesized by direct immobilization of dibenzo-24-crown-8 ether onto inorganic mesoporous silica. The effective parameters such as solution pH, contact time, initial Cs concentration and ionic strength of Na and K ion concentrations were evaluated and optimized systematically. This adsorbent was exhibited the high surface area-to-volume ratios and uniformly shaped pores in case cavities, and its active sites kept open functionality to taking up Cs. The obtained results revealed that adsorbent had higher selectivity toward Cs even in the presence of a high concentration of Na and K and this is probably due to the Cs–π interaction of the benzene ring. The proposed adsorbent was successfully applied for radioactive Cs removal to be used as the potential candidate in Fukushima nuclear wastewater treatment. The adsorbed Cs was eluted with suitable eluent and simultaneously regenerated into the initial form for the next removal operation after rinsing with water. The adsorbent retained functionality despite several cycles during sorption-elution-regeneration operations.

1. Introduction

The Great East Japan Earthquake and accompanying tsunami have damaged the Fukushima Daiichi Nuclear Power Plant and several radioactive nuclides were released into the atmosphere. Of these nuclides, the direct release of radioactive cesium (Cs) into the environment is high and represents the largest accidental release into the ocean in history [1–3]. Radioactive Cs contamination is potentially important and also poses a serious threat to human health and environment. The Cs is of special concern due to its long half-life (30.2 y), mobility (it can be present in food and water) in the environment, and the prevalence of the great risk to the

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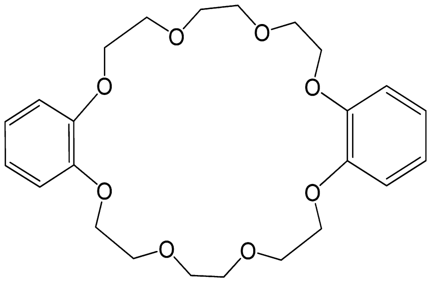
environment from the high-dosage of Cs. Moreover, cesium can easily be incorporated in terrestrial and aquatic organisms because of its chemical similarity to potassium. The radioactive Cs can enter the body and gets more or less uniformly distributed throughout the body, with higher concentration in muscle tissues and lower in bones, thereby creating an internal hazard [4–6]. Therefore, nuclear waste containing Cs needs to be treated prior to expanding to the environment.

The cleanup of radioactive Cs is very difficult due to the lack of knowledge of behavior of ultra-trace ions that compete with the high amount of monovalent cations. Therefore, selective cesium ion separation and removal from nuclear waste is of significant interest and is a challenging task. Solvent extraction methods involving the crown ethers have shown promising Cs separation from waste solutions. A number of crown ethers have been extensively used for Cs extraction, which has a good match between the cavity of the crown ether and the crystal ionic radius of the Cs ion. There are several reports investigated involving the extraction of Cs with the 18/24-membered and crown ethers [7–9]. The crown ethers have yielded promising results for selective separation of Cs from complex water and nuclear waste solutions. However, the prohibitive cost of these compounds has been a major hurdle in their use in the large-scale process for potential applications.

There are various technologies that have been developed over the years to remove radioactive Cs from wastewater, including co-precipitation, solvent extraction, ion-exchange and adsorption processes, and solid phase extraction [10–13]. However, the co-precipitation and solvent extraction have drawbacks such as low selectivity and generation of large amounts of secondary wastes. Adsorption is one of the most popular methods and attractive processes for the treatment of cesium-bearing waste waters. This process is flexible, simple, compact, and efficient enough to achieve decontamination factors of several orders of magnitude, and does not require any toxic organic solvent [14–16]. However, the selection of the wastewater treatment methods is based on the concentration of waste contaminants and the cost of treatment. The widespread industrial use of low-cost adsorbents for wastewater treatment is strongly recommended and investigated due to their technical feasibility, engineering applicability and cost effectiveness. Therefore, many scientists have tried hard to find efficient and low-cost materials for selective decontamination of Cs containing water and low-level waste. The Prussian blue supported carbon nanotubes materials, and zeolite are used for Cs removal from water [6]. However many of these adsorbents are not reusable, and often have concomitant environment hazards.

Nanoscience and nanotechnology have gained considerable importance due to the needs and applications of nanomaterials in almost all areas of human endeavor. Nanomaterials are suitable candidates to fulfill requirements of high sensitivity and selectivity in solid–liquid phase extraction and removal of metal ions [17–19]. Due to the huge specific surface area and absence of internal diffusion resistance, nanoscale adsorbents may have superior performance for removing toxic contaminants (high sorption capacity and fast sorption kinetics) from water and waste effluents. The mesoporous inorganic silica materials have been modified with a wide variety of chemical functionalities using ligands forming a new class of nano-engineered adsorbents. Adsorbents containing different functional ligands for the selective sorption and recovery of heavy metals [20], lanthanides [21], precious metals [22] and toxic metals [23] were reported by our research group. The organic ligand in inorganic silica surfaces by covalent bonds followed co-condensation into the inorganic framework cross-links to accessible target ions capturing with high sensitivity.

In the present study, dibenzo-24-crown-8 ether (DB24C8) immobilized onto mesoporous inorganic silica materials was investigated as a new class of adsorbent for Cs removal from radioactive waste solution in Fukushima. The preparation approach and combination of organic and inorganic materials makes it possible to take advantage of the enhanced Cs retention and ease of separation. The adsorbent has high surface area; large pore volumes implied a promising new class conjugate adsorbent for Cs removal. The functionalized crown ethers immobilized adsorbent for the effective coordination ability with Cs is the important aspect to understand the Cs–π interaction of the benzene ring with a stable complex mechanism. The main objective of this work was to develop suitable adsorbent for efficient Cs removal with high selectivity and cost-efficiency. Therefore, the present work is significant for the development of Cs separation technology. Several parameters were investigated systematically, including mesoporous material processing, characterization, adsorbent preparation, pH of the initial solution, sorption capacity, the competing ions effect, and reuse studies. The conjugate adsorbent also performed to remove the radioactive Cs containing samples to evaluate the potential practical application in Fukushima, Japan.



Scheme 1. The structure of macrocyclic ligand of dibenzo-24-crown-8 ether (DB24C8).

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 DB24C8 was purchased from Tokyo Chemical Industry (TCI) Co., Ltd., Japan. The structure of DB24C8 is shown in Scheme 1. The cesium chloride (CsCl) source of Cs ion, and metal salts for the source of metal ions were purchased from Wako Pure Chemicals, Osaka, Japan. Ultra-pure water prepared with a Millipore Elix Advant 3 was used throughout this work.

2.2. Preparation of mesoporous inorganic silica monoliths and conjugate adsorbent

The F108 ($EO_{141}PO_{44}EO_{141}$, MW: 14,600) surfactant was used as scaffolding in preparation of inorganic silica materials. The procedure for preparation of mesoporous silica monoliths 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 [24]. 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