



Nanostructured potassium copper hexacyanoferrate-cellulose hydrogel for selective and rapid cesium adsorption

Yonghwan Kim^a, Yun Kon Kim^a, Sungjun Kim^a, David Harbottle^b, Jae W. Lee^{a,*}

^aDepartment of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

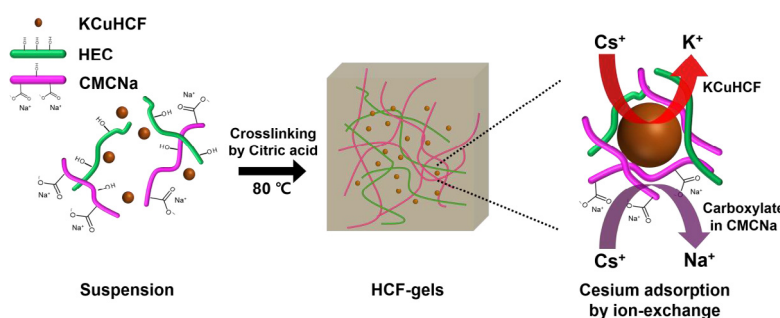
^bSchool of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

HIGHLIGHTS

- Potassium copper hexacyanoferrate immobilized in a cellulose hydrogel (HCF-gels) as a Cs⁺ adsorbent.
- HCF-gels exhibited a superior Cs adsorption capacity (2.06–2.32 mmol g⁻¹).
- Enhanced adsorption kinetics (90% removal in 1 h) and high selectivity ($K_d \approx 10^5$) for Cs⁺ even in seawater conditions.

GRAPHICAL ABSTRACT

Potassium copper hexacyanoferrate (KCuHCF) was immobilized in a cellulose-based hydrogel for the effective adsorption of cesium ions (HCF-gels). Cesium adsorption occurs both in KCuHCF particle and carboxylate of carboxymethyl cellulose (CMCNa) in the HCF-gels.



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ABSTRACT

Potassium copper hexacyanoferrate (KCuHCF) was synthesized and immobilized in a cellulose-based hydrogel made of carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC) for the adsorption of cesium ions in aqueous solutions. The immobilization with the cellulose-based hydrogel facilitated the dispersion of nano-sized KCuHCF particles, showing the unprecedented adsorption capacity of the composite. In Cs⁺ removal experiments, KCuHCF-cellulose hydrogel composites (HCF-gels) exhibited exceptional Cs⁺ adsorption capacities (2.06–2.32 mmol g⁻¹) which was attributed to the presence of ion-exchangeable sites (COO⁻Na⁺) in the cellulose hydrogel. The HCF-gels also exhibited a rapid Cs⁺ removal (90.1% removal for 0.15 mmol L⁻¹ of Cs⁺ in 1 h) with the uptake reaction kinetics expressed by a pseudo-second order kinetics model. Notably, the HCF-gels could adsorb Cs⁺ selectively (>90%) in seawater containing 0.11 mmol L⁻¹ Cs⁺. Such specificity with fast kinetics is due to the high ion accessibility from the inherent nature of hydrogels and the highly dispersed KCuHCF nanoparticles in the composites.

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1. Introduction

Due to the increased demand on world energy and the need to address global warming, nuclear power has been considered a

* Corresponding author.

E-mail address: jaewlee@kaist.ac.kr (J.W. Lee).

sensible alternative to thermal power plants, generating about 10.6% of the world's electricity in 2013 [1]. Despite its efficient and carbon-free energy production, nuclear power is sometimes perceived as a threat because power production generates waste which requires treatment and continuous monitoring due to high levels of radioactivity, and the potential for uncontrolled release of radionuclides. For example, the incident at the Fukushima

Daiichi nuclear power plant in 2011 caused large areas (soils and seawater) in Japan to become environmentally contaminated with radionuclides [2].

Among these radioelements, ^{137}Cs , a strong gamma emitter, is considered particularly problematic due to its long half-life (30.2 years) and transferability in the biosphere caused by its chemical similarity to potassium [3,4]. These radionuclides can be recovered using a range of diverse methods such as coprecipitation, evaporation/concentration, adsorption/ion-exchange, and chromatography [5]. However, in the case of a nuclear incident and a large scale release, those methods except for adsorption with ion-exchange are not suitable for the treatment of contaminated seawater due to the large volume of radioactive waste to be processed, and also the extremely low concentration of ^{137}Cs compared to competitive ions such as Na^+ , K^+ and Ca^{2+} [6,7]. Thus, it is desirable to develop ^{137}Cs selective adsorbents both for site operations and environmental decontamination.

A variety of Cs^+ adsorbents including synthetic inorganic materials such as zeolites [8], silicotitanates [9], and chalcogenides [10] have been considered due to their radiation stability and high thermal stability. However, their low Cs^+ selectivity limits their application in large-scale clean-ups. Recently mesoporous silica supported organic ligand adsorbents have been reported, but they are still in the development phase [11–13]. Alternatively, hexacyanoferrates containing transition metals have been widely studied, because the method of synthesis is relatively simple and cost-effective using a precipitation reaction between transition metals and hexacyanoferrate precursors [14]. Hexacyanoferrates possess a perovskite-like face-centered cubic structure with a channel size of 3.2 Å, so that hydrated ions including Cs^+ , K^+ and NH_4^+ are able to permeate while larger hydrated ions such as Na^+ and Ca^{2+} are unable to exchange [15–17]. It has been reported that potassium copper hexacyanoferrate (KCuHCF) has high Cs^+ sorption capacity and selectivity compared to other metal hexacyanoferrates [18]. Despite the superb adsorption property and low production costs, direct use of KCuHCF as an adsorbent is not effective because its recovery following radionuclide adsorption is difficult due to its submicron size in the filtration process [17]. To overcome this drawback and use the adsorbent efficiently in large-scale processes, numerous studies have reported immobilization of submicron particles of metal hexacyanoferrates combined with various support materials [18,19].

In general, immobilization techniques can be categorized as either i) grafting onto support materials or ii) encapsulation using polymers. Since the former strategy immobilizes ion-exchangers onto the support surface, porous materials such as mesoporous silica [19,20] and carbon allotropes [21–24] are normally used. For the latter, ion-exchangers can be immobilized by encapsulation in polymer matrices such as chitin [3,18], alginate [21,25], and polyacrylic acid [26]. With the encapsulation method, it is feasible to control the shape, such as bead and film formation, as well as to load considerable quantities of active ion-exchangers compared to the grafting method. Previous studies on polymer encapsulation [18,21] have focused on immobilization but not on enhancing the adsorption potential of the immobilizing composite material, because the supporting matrices generally showed low adsorption potentials.

Due to their abundant hydroxyl groups and mechanical strength, chemically modified celluloses have been studied [27]. Hydrogels based on carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC) crosslinked with citric acid (CA) have been reported as a superabsorbent because of its open-porous structure and hydrophilicity [28–30]. Because high water retention and diffusivity are important properties for immobilizing media, cellulose-based hydrogels can be an attractive option for the immobilization of KCuHCF particles.

Thus, this work introduces a facile, low-cost and effective method to immobilize KCuHCF using a cellulose-based hydrogel. Carboxylate anion (COO^-Na^+) sites in the CMC are the ion-exchangeable sites, so that Cs^+ adsorption capacity can be maintained after the KCuHCF particles are dispersed in the cellulose hydrogel network. In other words, a synergy between the hydrophilic, ion-exchangeable sites in the cellulose hydrogel and the high Cs^+ selectivity by the KCuHCF particles is desirable for effective Cs^+ remediation. Thus, the physicochemical characterization of the cellulose hydrogel, bulk KCuHCF, and HCF-gels was done to investigate the effect of their structures and chemical states on the adsorption performance. Moreover, the Cs^+ adsorption performance was investigated in terms of the equilibrium capacity, kinetics, competitive adsorption with co-existing ions and material stability to determine the adsorption mechanism and its potential application in large-scale clean-ups.

2. Materials and methods

2.1. Materials

Potassium hexacyanoferrate ($\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$), sodium carboxymethyl cellulose (CMCNa, average molecular weight: 700,000 Da, degree of substitution (DS): 0.9, viscosity: 2500–6000 cP), hydroxyethyl cellulose (HEC, average molecular weight: 250,000 Da, DS: 1, viscosity: 80–125 cP), citric acid (CA) and untreated seawater were purchased from Sigma Aldrich. Copper sulfate ($\text{CuSO}_4\cdot 5\text{H}_2\text{O}$) was acquired from KANTO Chemical Co. Inc., and cesium chloride (CsCl , 99.9% purity) was obtained from Alfa Aesar. All chemicals were used without further purification.

2.2. Synthesis of cellulose hydrogel and KCuHCF

The cellulose-based hydrogel film was synthesized by adopting a previously published method [28]. HEC and CMCNa at a 1:3 wt ratio were used as the cellulose backbone, and 20 wt% CA (based on the total weight of the two celluloses) was used as a crosslinking agent. It was reported that HEC, which is a nonionic polymer, is necessary to reduce the electrostatic repulsion between CMCNa to promote the formation of an open-porous structure [28,30]. First, 0.25 g HEC powder was dissolved in 100 mL deionized water under magnetic stirring at room temperature for 1 h until a clear solution was observed. Then 0.75 g CMCNa powder was slowly added to the solution while avoiding the formation of particle aggregates. After 24 h, 0.2 g CA was added to this highly viscous and clear solution. The final solution was poured into a petri dish and dried at 30 °C in an oven for 24 h. Then, the sample was heated to 80 °C and kept at this temperature for 24 h to complete the crosslinking reaction. The obtained film was washed several times with deionized water and subsequently dried.

Bulk KCuHCF particles were synthesized in water by precipitation. First, 0.362 g $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and 0.507 g $\text{K}_4\text{Fe}(\text{CN})_6$ were dissolved in two separate beakers with each 50 mL deionized water. Then the $\text{K}_4\text{Fe}(\text{CN})_6$ solution was continuously added to the CuSO_4 solution dropwise under magnetic stirring for 4 h, until reaching a molar ratio of copper and iron equal to 1.2:1. The KCuHCF fine particles were separated via centrifugation and washed several times with deionized water. The final product was allowed to dry at 80 °C in an oven.

2.3. Synthesis of the KCuHCF-cellulose hydrogel composites

The schematic procedure to synthesize KCuHCF-cellulose hydrogel composites is shown in Fig. 1. First, 0.25 g HEC was dissolved in 50 mL deionized water with $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ at different

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