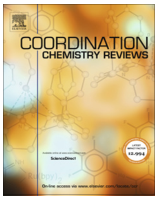
Coordination Chemistry Reviews 374 (2018) 430–438

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Metal hexacyanoferrates-based adsorbents for cesium removal

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ARTICLE INFO

Article history:
Received 6 May 2018
Accepted 21 July 2018

Keywords:
Metal hexacyanoferrates
Cesium
Adsorption
Adsorbent
Separation

ABSTRACT

Metal hexacyanoferrates (MHCFs), as typical coordination polymers, are efficient adsorbents for the monovalent cesium ion, which is a major product of uranium fission and the most commonly existing radionuclide in radioactive wastewater. Due to the comparable sizes between their structure lattices and hydrated cesium ions, MHCFs can selectively adsorb cesium ions with a background of other coexisting ions by ion-exchange. The main drawback is associated with its microcrystalline structure, that leads to weak mechanical strength and high flow resistance. Modification is necessary to make it capable for large scale application. This review is mainly focused on MHCF-based adsorbents for the highly efficient removal of cesium ions. The physicochemical structure together with its pros and cons as adsorbents for cesium removal are discussed along with proposed modification methods, including size control, immobilization and magnetic modification. Among these methods, immobilization by various kinds of organic (e.g., alginate, chitosan, fibers and PAN) and inorganic supporters (e.g., silica and glass) by embedding or in-situ synthetic methods are highlighted. The adsorption mechanisms and regeneration methods are also discussed, and some suggestions are given for future research.

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https://doi.org/10.1016/j.ccr.2018.07.014
0010-8545/

1. Introduction

As a typical coordination polymer, metal hexacyanoferrates (MHCFs) are composed of transition metal ions (e.g., Cu^{2+}, Co^{2+}, Ni^{2+} and Fe^{3+}) together with coordinated CN bridges. MHCFs are also referred to as Prussian blue (ferro hexacyanoferrate, FeHCF) and its analogs, and are widely applied in many fields, including but not limited to, dyeing, information storage [1], energy storage [2], biomedicine [3] and environmental remediation [4]. Among these applications, MHCFs as an adsorbent for cesium removal have aroused great interest for a long time [5]. So far, they have been regarded as the most promising adsorbent over others in terms of adsorption selectivity and capacity for cesium ions.

Radiocesium is a fission product that has a negative effect on ecosystems and human health due to its radioactivity and chemical toxicity [6]. Compared with other short life fission products (e.g., ^{131}I ($t_{1/2}$ = 8 d) and ^{89}Sr ($t_{1/2}$ = 50 d)), ^{137}Cs has a longer half-life of more than 30 years. The separation of long-life radionuclides from aqueous solutions can greatly reduce the time required for safe storage for natural decay. In addition, it is also one of the main radionuclides in polluted seawater, which was used as emergency cooling water in the Fukushima Daiichi nuclear power disaster. Furthermore, with a chemical similarity to K^+, soluble radiocesium is prone to be taken into body by a cell membrane transport mechanism, resulting in element poisoning, as well as internal exposure of radiation. Therefore, it is of great importance to separate cesium ions from aqueous solutions for ecological security and sustainable development [7].

Cesium removal is vital, yet challenging, especially after the Chernobyl disaster and the Fukushima Daiichi nuclear plant accident [7]. Most adsorbents (e.g., activated carbon and chitosan-based adsorbents) show a low cesium adsorption capacity [8,9]. Although some adsorbents (e.g., graphene oxide) present a good adsorption capacity for cesium ions, they show a higher affinity towards most heavy metal ions and other radionuclides [10]. It has been noted that among substantial adsorbents, only MHCFs could reach 99.99% removal efficiency of cesium ions from water and wastewater [7].

This review is mainly focused on MHCF-based adsorbents in terms of their physicochemical structures, modification methods and adsorption mechanism towards cesium ions, as well as their regeneration.

2. Physicochemical structure of MHCFs

As shown in Fig. 1(a), MHCFs have a face-centered cubic lattice structure with an open zeolite-like morphology. This unique structure contains a narrow channel of about 3.2 Å, giving it an ion-sieving capability to larger hydrated cations [4]. Due to the similar size between structure lattices and hydrated cesium ions, cesium ions can be selectively adsorbed into MHCFs [7]. At the same time, the cesium ions in the cages of cyanide-bridged metal frameworks will slowly vibrate and resonate with a low-frequency terahertz light, as shown in Fig. 1(b). Utilizing this feature, terahertz technology can be used for non-contact sensing of cesium ions in dangerous or harmful environments [11]. In addition, MHCFs show good radiation stability (0–300 kGy) with a high Cs adsorption affinity and negligible metal dissolution [12]. These merits justify MHCFs as potential adsorbents for cesium ions.

MHCFs are usually prepared by the reactive precipitation of two kinds of precursors: a soluble transition metal salt (M) and hexacyanoferrates (HCF) [4]. Various kinds of precursors can used to produce single metal hexacyanoferrates or multi-metal hexacyanoferrates [13–15]. Apart from particular cases [16], Prussian blue and its analogs share the same cubic structures and maintain the core characteristic of cesium selectivity. However, they still exhibit some distinct features, including the tolerable pH range and adsorption capacity. For example, Prussian blue exhibits the best adsorption performance under pH 8, whilst its analogs can be stable at higher pH values.

The removal of radiocesium can also be achieved by reactive precipitation involving the simultaneous binding of radionuclides and the formation of the MHCFs. These precipitations are usually very fine particles, resulting from the difficulty of settling and filtering. Additionally, a large quantity of precipitants is necessary for the disposal of large volumes of radioactive wastewater with low concentrations of cesium ions. Therefore, researchers have turned to the preparation of granular solids suitable for column operations, such as MHCF solids, rather than soluble ferrocyanides.

The synthetic conditions influence the properties of the MHCFs (e.g., composition, particle size, crystalline structures and cell parameter). These conditions include the type, concentration and ratio of the precursors, as well as the addition order/velocity, reaction temperature and the maturation (or aging) [4]. Exhaustive reviews on the effect of the synthetic conditions on the structures of MHCFs were published by the research group of Loos-Neskovic [17,18]. In spite of its outstanding adsorption capacity and selectivity for cesium ions, an MHCF prepared by the general method shows irregular properties, too fine particles and insufficient mechanical stability, which is not suitable for column operations or separation. Therefore, modification is necessary.

3. Modified MHCFs for cesium adsorption

For years, MHCFs have been regarded as the most promising adsorbents due to their selectivity for cesium ions in the background of other co-existing ions, as well as their rather higher adsorption capacity, as shown in Table 1. However, the highly

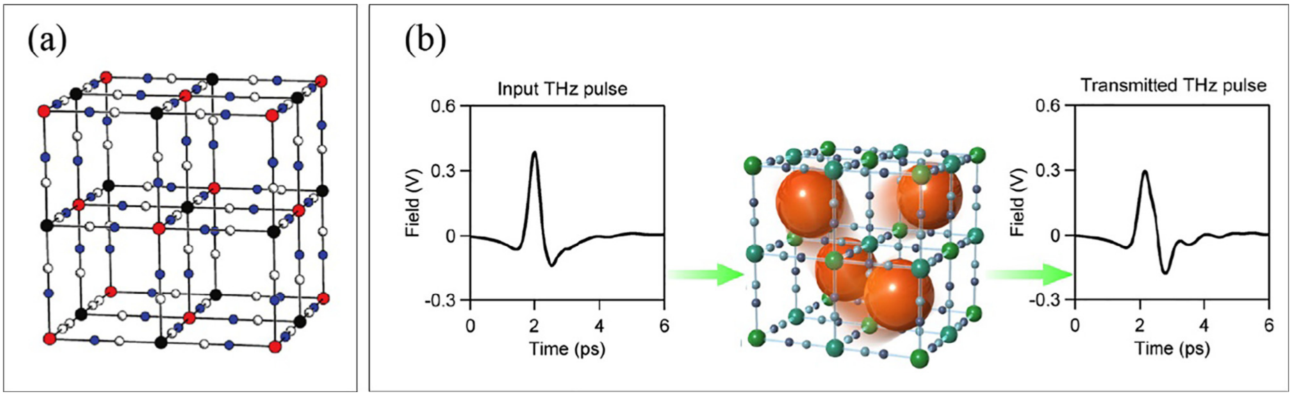

Fig. 1. (a) the structure of MHCFs (Color scheme: C, blue; N, white; Fe^{2+} red; transition metal ions, black); (b) illustration of applying THz-TDS measurement of the Cs vibration in MHCFs.