

# Synthesis and characterization of magnetic hexacyanoferrate (II) polymeric nanocomposite for separation of cesium from radioactive waste solutions

Reda R. Sheha

Nuclear Chem. Dept., Hot Lab Center, Atomic Energy Authority, P.O. 13759, Cairo, Egypt

## ARTICLE INFO

### Article history:

Received 5 April 2012

Accepted 21 August 2012

Available online 30 August 2012

### Keywords:

Nanoparticles  
Hexacyanoferrate  
Iron ferrite  
Cesium  
Sorption

## ABSTRACT

Nanocrystalline potassium zinc hexacyanoferrate loaded on nanoscale magnetite substrate was successfully synthesized for significantly enhanced removal of cesium from low-level radioactive wastes. A description was given for preparation and properties of these precursors. The physicochemical properties of these nanocomposites were determined using different techniques including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Data clarified that supporting potassium zinc hexacyanoferrates on iron ferrite nanoparticles increased their thermal stability. Further, Fourier transform infrared spectra confirmed that the nanocomposites were well coordinated and incorporated in the polymer matrix. The average particle sizes, of these nanoparticles, determined by SEM had a good agreement with XRD results. Based on characterization data, the prepared zinc hexacyanoferrates were proposed to have a zeolitic rhombohedral structure with cavities can host alkali metal ions and water molecules. The magnetic analysis showed a super-paramagnetic behavior. Batch technique was applied to evaluate the influences of initial pH value, contact time, and competing cations on the efficiency of cesium removal. The sorption process was fast initially, and maximum separation was attained within 2 h of contact. Cesium exchange was independent from pH value and deviate from ideal exchange phenomena. In neutral solutions,  $\text{Cs}^+$  was retained through exchange with  $\text{K}^+$ ; however, in acidic solution, phase transformation was proposed. Sorption capacity of these materials attained values amounted  $1965 \text{ mg g}^{-1}$ . The synthesized nanocomposites exhibited different affinities toward Cs(I), Co(II), and Eu(III) elements and showed a good ability to separate them from each other.

© 2012 Elsevier Inc. All rights reserved.

## 1. Introduction

The operations of nuclear power plants as well as nuclear fuel reprocessing and radioisotopes production facilities (RPF) generate large amounts of high level radioactive wastes (HLRW). The major contaminants of these wastes are fission products and actinides. The recovery of valuable elements, lanthanides, and actinides from high level nuclear wastes is an area of worldwide concern [1,2]. Among the main fission products released, cesium radioisotopes stand as the most important fission products because of their high fission yield, long half-life ( $^{137}\text{Cs}$  ( $T_{1/2} \sim 30.17$  year),  $^{135}\text{Cs}$  ( $T_{1/2} \sim 2.3 \times 10^6$  year),  $^{134}\text{Cs}$  ( $T_{1/2} \sim 2.06$  year)) and serious environmental impacts [3]. Radioactive cesium contamination is of serious social and environmental concerns. It presents serious threat to human health and environment because it is a strong gamma emitter has high solubility that enhances its migration through groundwater to the biosphere [4,5]. Besides, cesium can be easily incorporated in terrestrial and aquatic organisms because of its chemical similarity to potassium. The solubility/mobility of cesium was amounted

up to 186, 209, 261, and 400 g/100 g of water at  $\sim 20^\circ\text{C}$  for CsCl,  $\text{CsHCO}_3$ ,  $\text{Cs}_2\text{CO}_3$ , and CsOH, respectively [6]. Besides its high mobility, cesium can travel in airborne dust particles and can be present in food and water. Therefore, the migration of  $^{137}\text{Cs}$  has become a key criterion of performance assessment in radioactive waste repository construction [7]. In addition, cesium radionuclides are considered potentially dangerous to human health, if exposed via ingestion route, cesium is 100% absorbed from the gut to the body and is distributed fairly uniformly throughout the body's soft tissues. Actually,  $^{137}\text{Cs}$  is the major cause of Thyroid Cancer in Belarus, which took 70% of the fallout from the Chernobyl Nuclear Disaster [8].

Selective separation of cesium ions from nuclear wastes is a subject of significant interest and chemically a challenging task. These monovalent ions lack chemical unique characteristics and can be competed for reactive sites by monovalent Group I and divalent Group II cations. The ever increasing pressure to separate cesium radioactive species requires constant upgrading and development of new treatment technologies. These new technologies should be based on highly selective materials, which are hard to decompose over a wide range of pH, remain stable at high temperatures, and

E-mail addresses: rsheha68@yahoo.com, reda.sheha@eaea.org.eg

are resistant to ionizing radiation [9,10]. In this concern, solid phase extraction techniques employing inorganic ion exchangers has attracted a lot of attention due to high selectivity, rapid separation, and high thermal and radiation stabilities [8]. The real challenge for solid phase separation is to select the most promising types of adsorbent, mainly in terms of high capacity and adsorption rate, high selectivity, and low cost. Many studies had presented transition metal hexacyanoferrates as promising candidates for separation of radioactive cesium from nuclear wastes over a wide pH range even in the presence of high salt loadings [11–13]. Recent studies have reported their potentiality for therapy of animals and humans affected by nuclear accidents [14].

Transition metal hexacyanometallates usually have an open channel framework appropriate for small molecules separation, and their crystal structure is closely related to the coordination adopted by the metal centers. In hexacyanometallates, the involved transition metals are usually found with octahedral coordination within the cubic unit cell (Fm-3m). Some zinc hexacyanoferrates have been reported as hexagonal where Zn<sup>2+</sup> atom is found tetrahedrally coordinated to four N atoms from CN ligands. Such coordination provides a relatively high thermal stability to these materials and also an interesting porous framework because both metal centers have saturated their coordination sphere with atoms from the bridge group (-CRN-) [15]. Hexacyanoferrates obtained by chemical precipitation are physically fragile and require a solid support when used in columns. Several types of support materials can significantly improve the hydrodynamic characteristics of these materials [16].

In recent years, there is a growing interest in application of nanoparticles as sorbents for pollutant removal. Compared with traditional milli- or micro-sized materials, nanoscale particles have quite different physicochemical properties. Most of atoms on the surface of nanoparticles are unsaturated and can easily bind with other atoms. Due to the huge specific surface area and absence of internal diffusion resistance, nanoscale sorbents may have superior performance for removing contaminants (e.g., high adsorption capacity and fast adsorption kinetics) [17]. By rendering the nanoparticles magnetic, through the acquisition of magnetism, a powerful new class of sorbent materials could be developed for fast and potential remediation purposes [18]. These magnetic nanoparticles exhibit a finite-size effect resulting in a higher adsorption capacity for metal removal as well as selective adsorption properties and ease of phase separation [19]. Several recent studies have shown that magnetic nanostructured particles can be successfully applied to adsorb different metal ions [20–23]. Thus, deposition of insoluble hexacyanoferrates on magnetic nanostructured particles of Fe<sub>3</sub>O<sub>4</sub> produces an efficient, economic, and scalable nanocomposite that could be highly preferred for potential application in separation of radioactive cesium. Although the expected relevance of such novel materials, no previous studies were recently reported on the structure and cesium uptake properties of Zn hexacyanoferrate nanocomposites.

In this work, the approach is to achieve a further increase in the separation efficiency of radionuclides through combining iron oxide nanoparticles as a support and hexacyanoferrate as an active phase and polyacrylonitrile (PAN) as a binding matrix. This combination makes it possible to take advantage of the enhanced metal retention and ease of separation as well as the improved granular strength. Hence, new composite materials, in which the outer layer is made of Zn hexacyanoferrates deposited on iron ferrite nanoparticles and immobilized with PAN binder, were prepared and used in removal of radioactive cesium from nuclear wastes. Further, the role of experimental conditions and preparation procedures of the nanoparticles on their separation potential is a relevant issue in this study.

## 2. Experimental

### 2.1. Chemicals and reagents

The radioactive tracer <sup>134</sup>Cs was prepared through a neutron irradiation of cesium carbonate at the Egyptian Second Research Reactor, ETRR-2. For this purpose, a suitable weight of target materials was wrapped in a thin aluminum foil and placed in thick aluminum irradiation capsule and irradiated in ETRR-2 core adjusted with thermal neutron flux of 10<sup>14</sup> n cm<sup>-1</sup> s<sup>-1</sup>. After cooling, the sample was dissolved in appropriate solvent, evaporated to dryness, and redissolved in double distilled water. Ferric chloride (FeCl<sub>3</sub>, 162.21 g mol<sup>-1</sup>) was supplied from Redel, Germany. Ferrous chloride (FeCl<sub>2</sub>·4H<sub>2</sub>O, 198.81 g mol<sup>-1</sup>) and Zinc chloride (ZnCl<sub>2</sub>, 136.29 g mol<sup>-1</sup>) were purchased from Aldrich Chemical Laboratories. Potassium hexacyanoferrate (K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O, 422.39 g mol<sup>-1</sup>) was supplied from BDH, UK. All other chemicals and reagents used in this work were of analytical grade purity and used without further purification.

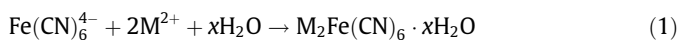
### 2.2. Preparation of composites

#### 2.2.1. Magnetic nanoparticles

Fe<sub>3</sub>O<sub>4</sub> nanoparticles (RF1) were prepared by coprecipitating Fe<sup>2+</sup> and Fe<sup>3+</sup> ions with ammonia solution in an inert atmosphere. Ferric and ferrous chlorides (molar ratio 2:1) were dissolved in bidistilled water at a concentration of 0.3 M iron ions. Chemical precipitation was achieved at 25 °C under vigorous stirring by adding NH<sub>4</sub>OH solution (29.6%), and the pH value was maintained at about 11 during precipitation process. Thereafter, the precipitate was heated at 60 °C for 60 min in presence of N<sub>2</sub> gas to prevent iron oxidation. The obtained nanoparticles were recrystallized in a mixture of isopropyl alcohol and acetone with ratio 3:2 and then washed by bidistilled until constant pH of 6.9 was sequentially attained. Then, they were dried at room temperature and finally sieved to different mesh sizes. Particulates have the range 0.170–0.135 mm were used in the rest of experiments.

#### 2.2.2. Potassium zinc hexacyanoferrate (II)

Metal ferrocyanides are usually prepared in a colloid form from the soluble ferrocyanide, K<sub>4</sub>Fe(CN)<sub>6</sub>, and a divalent transition metal salt such as ZnCl<sub>2</sub> by the following reaction:



where M stands for divalent elements; the product formula M<sub>2</sub>·Fe(CN)<sub>6</sub>·xH<sub>2</sub>O can be alternatively replaced by A<sub>2n</sub>M<sub>2-n</sub>Fe(CN)<sub>6</sub>·xH<sub>2</sub>O, in which A stands for Na<sup>+</sup> or K<sup>+</sup>, and n indicates one of the numbers: 0, 1, or 2. Practically, the produced product may be one of the structures A<sub>2</sub>M<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub> or M<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>. The product, thus obtained, may have the composition of Zn<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub> if an excess amount of ZnCl<sub>2</sub> was used, while using a little amount of ZnCl<sub>2</sub> during preparation may result in the production of K<sub>2</sub>Zn<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>.

Zinc hexacyanoferrate (RZ1), used in this study, was prepared by adding 0.1 M ZnCl<sub>2</sub> solution gradually drop by drop into a 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O solution under agitation. After complete addition of ZnCl<sub>2</sub> solution, agitation was continued for 3 more hours. Then, the mixture was let overnight for settling, and then supernatant was separated by decantation. After that, the precipitate was washed three times with bidistilled water and dried at 70 °C. The appropriate Zn/Fe molar ratio in the preparation was determined by the following experiments. After settling the precipitate, drops of ZnCl<sub>2</sub> solution were added to the supernatant of the mixture followed by several drops of K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O solution, and the occurrence of turbidity was observed. Occurrence of

Download English Version:

<https://daneshyari.com/en/article/607962>

Download Persian Version:

<https://daneshyari.com/article/607962>

[Daneshyari.com](https://daneshyari.com)