



Ion exchange and structural properties of a new cyanoferrate mesoporous silica material for Cs removal from natural saline waters



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ARTICLE INFO

Article history:

Received 20 October 2016

Received in revised form 15 December 2016

Accepted 20 December 2016

Available online 21 December 2016

Keywords:

Cesium decontamination

Ferrocyanide

Inorganic ion exchanger

Modeling

Sorption

Vanselow

ABSTRACT

The demand for effective and inexpensive treatment for decontamination of waters from radionuclides, such as ^{137}Cs , is presently high. In this context a selective adsorbent material for Cs (SORBIMATECH[®] 202) was designed, consisting of potassium/copper ferrocyanide nanoparticles deposited in the mesoporosity of silica grains. Several batch experiments were carried out in order to obtain kinetic and thermodynamic data concerning the ion exchange. Isotherms and measurements of distribution coefficients ($K_{d,\text{Cs}}$) in waters of increasing salinity (pure water, Ca-bicarbonate fresh water and seawater) were conducted in a radioactive environment. This study shows a fast ion-exchange kinetics (<5 min), due to the open silica porosity combined to cyanoferrate nanoparticles, as well as high selectivity with $K_{d,\text{Cs}}$ in fresh and sea waters (10^6 and 2.0×10^5 mL/g, respectively). These experiments also demonstrated the competitive effects of the major cations present in natural waters (K^+ , Na^+ , Mg^{2+} and Ca^{2+}) and led to the determination of the Vanselow's selectivity coefficients. Integrating this dataset into the CHESS geochemical speciation code allowed the correct modeling of $K_{d,\text{Cs}}$ values in these different water types over a wide range of Cs concentrations. The dataset can be extrapolated to the modeling of other K-ferrocyanides and effluent compositions.

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1. Introduction

The ever-increasing pressure to reduce the release of radioactive species into the environment requires constant improvement of technologies for waste treatment and for dose minimization. Recently, the Fukushima disaster required the development of appropriate processes for the removal of radionuclides resulting from accidental discharge. Various treatments may be applied depending on the effluent's composition and radionuclide targeted for extraction (co-precipitation, ion exchange, sorption) [1,2]. Ion exchange in a fixed-bed column is one of the most common and efficient methods to treat radioactive effluents. Moreover, this process produces a minimal amount of final waste.

Among these radionuclides, ^{137}Cs is considered the most abundant and hazardous element due to its presence in many types of waste and its relatively long half-life (30 years). A number

of studies have been carried out on the extraction of cesium using inorganic ion exchangers such as zeolite [2,3], silicotitanate [4] or inorganic phosphate [5]. Nevertheless, cyano-bridged coordination polymers based on hexacyanometallates and transition metal ions $\text{K}_x\text{M}_y[\text{Fe}(\text{CN})_6]_z$ (where M = a bivalent transition metal ion), also called Prussian blue analogous (PBA), present a higher selectivity for the extraction of radioactive cesium ions from contaminated waters over a wide range of pH values [6–14]. These bulk materials are actually used in stirred reactors at industrial scale for the selective extraction of $^{137}\text{Cs}^+$ from contaminated effluents.

However, the main drawback of these materials is related to their small grain size, preventing their use in fixed-bed columns due to pressure loss and clogging. In powder form, their low adsorption kinetics is also a problem for a column process. One way to overcome these drawbacks is to insert a selective hexacyanoferrate compound in a solid porous matrix so that it becomes suitable for a column process: the porosity of the support and the nanosize of the hexacyanoferrate inside the porosity improve the adsorption rate. Since a few years, numerous composite solids (organic or inorganic) loaded with hexacyanoferrate particles have

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been proposed for cesium removal [15–22]. Most of these composites use silica supports and are obtained by successive impregnation of porous silica or polymer modified silica by bivalent transition metal ions and a hexacyanoferrate precursor. These materials are able to reach high capacity and selectivity, but the kinetics of sorption is relatively slow which is an obstacle to their use in a continuous process, and moreover in a column process. However, their final compositions are not well controlled and thus their sorption properties are relatively poorly reproducible. Some of us have recently reported an original approach for preparing porous silica-based nanocomposites containing Prussian blue-type nanoparticles (3–6 nm) covalently grafted inside the pores of silica [15,17]. These nanocomposites were obtained by successive coordination of cobalt ions Co^{2+} and hexacyanoferrate $[\text{Fe}(\text{CN})_6]^{3-}$ (Fe(III)) precursors on amino sites present on the surface of the support.

However, these materials were synthesized with expensive reagents, organic solvents and many steps, hindering the industrialization of this process. Moreover, the hexacyanoferrate particles thus obtained do not contain alkali ions inside the crystal lattice. The sorption capacity is therefore low and the Cs adsorption process leads to the release of the divalent metal that could be an issue for the final decontaminated liquid effluent. Here we use a new simpler synthetic route based on silica supports containing pure potassium copper hexacyanoferrate (with Fe(II)) KCuFC nanoparticles inserted inside the pores. This new material called Sorbmatech 202 (S202) could also be easily synthesized on a large scale. In this paper we report the structural characterization and the ion exchange properties of S202, as well as very fast ion exchange ability and high selectivity. This makes S202 promising for an efficient decontamination of saline effluent by a column process.

From the perspective of industrial development, ion exchange occurring in the case of KCuFC must be perfectly mastered and modeled. In this work, several water compositions were studied, from pure water (deionized water) to a Ca-bicarbonate fresh water and seawater. This study further demonstrates that the competitive effect of ions present in natural waters is only active when cesium is at trace concentrations. In this study, first the exchange reaction coefficients between the cation K^+ from the solid exchanger S202 and the cations from the aqueous solutions (Cs^+ , Na^+ and Mg^{2+}) were experimentally determined through isotherms using ^{133}Cs and a doped ^{137}Cs solution in batch mode. Then, ion exchange data were used to determine the full set of selectivity coefficients. Subsequently, modeling of the isotherms was performed for each water composition to check dataset consistency and the ability to model the cesium uptake by this new material in complex aqueous solutions with competitive cations. These coefficients have been set into the CHESS geochemical speciation code allowed the correct modeling of $K_{d,\text{Cs}}$ values in these different water types over a wide range of Cs concentrations and they can be extrapolated to other K-ferrocyanide and many effluent compositions.

2. Material and method

2.1. Material synthesis

The porous support consisted of a commercial silica-gel (SIGMA ALDRICH 35–60 mesh) with a mean initial pore volume of $0.75 \text{ cm}^3/\text{g}$, a mean pore size diameter of 6 nm, and a specific area of $500 \text{ m}^2/\text{g}$. This support was loaded with nanoparticles of KCuFC distributed over the porosity. For this, the silica-gel was functionalized with a two-step method: first APTES (3-Amino-propyl)-triethoxysilane was grafted on the silica surface by a hydrolysis-condensation reaction with silanol groups on the

surface. This grafting was performed in absolute EtOH (99.9%) solvent at 60°C over 24 h. The amino-grafted silica was then analyzed by TGA to calculate the amount of amino group inserted into the silica support: about 0.150 mmol/g of amino group was grafted onto silica. Details of the synthesis procedure is given in [23].

The growth of KCuFC nanoparticles (NP) was first initiated by contacting the amino silica with a 10^{-2} mol/L $\text{Cu}(\text{NO}_3)_2$ solution at room temperature and with stirring over 24 h. Silica granules turned instantly blue. Then the solid was washed with pure water and filtered. The second step was to add this solid to a solution composed of K^+ and $\text{Fe}(\text{CN})_6^{4-}$ agitated for 24 h. Both these steps, Cu-solution and then K-solution, consisted of an impregnation cycle. Three impregnation cycles were performed to obtain the final material.

2.2. Characterization method

The concentrations of K, Cu and Cs in an aqueous solution from non radioactive batch sorption experiments were analyzed by the following three methods: inductively-coupled plasma mass spectrometry (ICP-MS Thermo Scientific) used for very low Cs concentrations, Atomic Absorption Spectrometry (AAS with a PERKIN ELMER spectrometer) used for higher Cs concentrations and inductively-coupled plasma atomic emission spectroscopy (ICP-AES Thermo Scientific) for other cations. Radiochemical analyses were performed by gamma counting (Eurisys, measured with a germanium detector) to analyze the amount of residual ^{137}Cs in the radioactive solutions.

To determine the chemical composition of the materials, a sample of approximately 50 mg was weighed for mineralization. This aliquot was dissolved in a hot (130°C) HNO_3/HF solution leading to brown precipitates. This mixture was filtered and rinsed with pure water, and a first solution (50 mL) was obtained (Solution 1). The residue remaining in the filter was calcined for 5 h at 900°C . After cooling, the deposit obtained was digested in HNO_3 , resulting in a second solution (Solution 2). These solutions were analyzed by ICP-AES (atomic emission spectrometry coupled with a plasma torch) Thermo ICAP 7400DV for the elements K, Cu, Fe and Si.

X-ray diffraction data were collected using an X'Pert PRO-PANalytical apparatus with a Cu anticathode. The angular range of $2\theta = 10\text{--}70^\circ$ was scanned at $0.08^\circ \text{ min}^{-1}$ using 0.02008 steps. The KCuFC raw phases were analyzed by Rietveld refinement, using TOPAS 4.2 software and Le Bail pattern matching [24]. The profile parameters (cell, dimensions, peak shape . . .) were refined. The peak shape was described by a pseudo-Voigt function with the Caglioti formula [25].

Surface area was obtained using nitrogen adsorption isotherms on an ASAP2020 apparatus from Micrometrics. Samples were degassed under vacuum at 70°C over two days prior to analysis. Surface area was determined using the Brunauer-Emmet-Teller (BET) method. Pore distribution was determined using the Barret-Joyner-Halenda (BJH) method.

SEM image analysis were performed with a high-resolution MERLIN field-emission SEM (Carl Zeiss). TEM image were collect with a MET FEI Titan Themis apparatus.

2.3. Batch sorption experiments

Sorption experiments were performed in batch mode using a rotating agitator at room temperature by contacting the solid with the solution. The solid and liquid phases were separated by filtration through a $2 \mu\text{m}$ syringe filter and the liquid was analyzed

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