



# Immobilization of inorganic ion-exchanger into biopolymer foams – Application to cesium sorption



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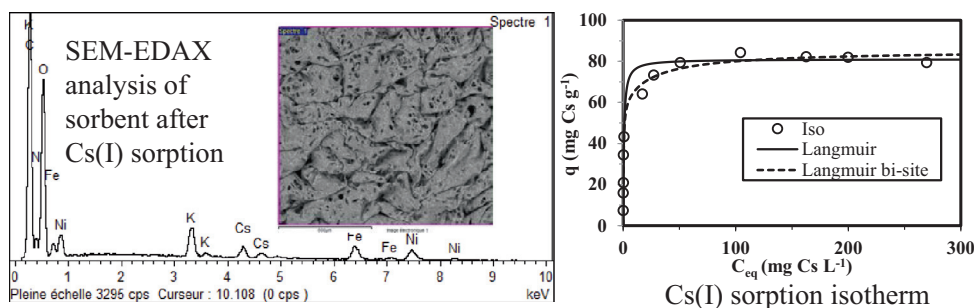
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## HIGHLIGHTS

- Highly porous composites are prepared for immobilizing nickel potassium ferrocyanide.
- The composite material is very efficient for removing Cs(I) in the range pH 2–8.
- The process is selective for Cs(I) even in presence of large excess of Na(I), K(I).
- Kinetics are controlled by the pseudo-second order rate equation.
- The discs can be used for dynamic and reactive filtration of radionuclide solutions.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nickel–potassium ferrocyanide (along with other ferrocyanide sub-products, as shown by mineralization, SEM–EDX and XRD analyses) has been immobilized in highly porous discs of chitin for the sorption of Cs(I) from near neutral solutions. The immobilization process allows synthesizing stable materials that can bind up to 80 mg Cs g<sup>−1</sup> (i.e., 240 mg Cs g<sup>−1</sup> ion-exchanger). Cesium sorption is hardly affected by the pH between pH 2 and 8. The sorbent is selective to Cs(I) even in the presence of high concentrations of Na(I), K(I), Rb(I) or NH<sub>4</sub><sup>+</sup>. The pseudo-second order rate equation fits well kinetic profiles: the rate coefficient increases with the flow rate of recirculation (to force the access to potentially non-interconnected pores), as an evidence of the control of uptake kinetics by diffusion properties. In fixed-bed columns, the breakthrough curve is accurately described by the Clark model and the sorption capacity (at sorbent saturation) is consistent with the values obtained in sorption isotherms. Preliminary tests performed on <sup>137</sup>Cs spiked solutions confirm the efficiency of the material for the treatment of effluents bearing radionuclides.

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## 1. Introduction

Nuclear energy contributes in many countries, including France, as an important power source. The safety control of this industrial sector is a key parameter for its development, not only in its normal operative conditions but also in the case of incident, or

emergency. Recently, the Fukushima accident illustrated the necessity of developing appropriate processes for the recovery of radionuclides from accidental discharge. There are also specific needs for the development of new processes for the recovery and/or separation of radionuclides from highly saline solutions in normal operative conditions; for example in the life cycle (re-treatment) of the nuclear combustible where a number of radioelements are produced during fission reactions.

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At Fukushima, a large amount of radionuclides were released into water, soil and air. Among radionuclides,  $^{137}\text{Cs}$  is considered the most abundant and hazardous due to diverse sources and relatively long half-life. As a result, numerous efforts have been undertaken to find effective and low cost methods to remove cesium from waste solutions.

Cesium recovery is generally operated using inorganic ion-exchangers such as ferrocyanides derivatives (including Prussian Blue) [1–8], zirconium phosphate [9–11], titanium phosphate [10], titanium dioxide [12] and ammonium molybdophosphate [13]. The main disadvantage of these materials is the size and the dispersion of these micro-particles that require appropriate solid/liquid separation techniques for recovering spent sorbents. Their application in fixed-bed columns is almost impossible due to clogging, and head pressure loss. For these reasons these inorganic ion-exchangers are generally functionalized by deposition/grafting on appropriate supports or encapsulation in specific materials, such as mineral oxide [14–17] or zeolite [18] supports, carbon fibrous materials [19,20], biosorbent [21], polymers [22–25] and biopolymers [26]. The challenge is combining the retention/confinement of the inorganic ion-exchanger and the optimization of mass transfer properties. Indeed, the immobilization of the inorganic ion-exchanger in a matrix may contribute to strongly increase the resistance to mass transfer (especially intraparticle diffusion). Biopolymers have recently retained great attention for the immobilization and encapsulation of a number of mineral sorbents [27], ion-exchangers [26,28–31], liquid extractants [33,33] or ionic liquids [35]. Their encapsulating properties are used for the synthesis of spherical resins or hybrid sorbents. Alginate and chitosan are two polysaccharides (renewable resources) that were extensively tested for the last decade for the elaboration of new supports based on their physical versatility: indeed, these biopolymers can be readily conditioned under different forms such as beads, membranes, fibers, tubes and scaffolds (foams and sponges).

Different systems based on chitosan or alginate have been investigated for elaborating hybrid foams (combining biopolymers and ionic liquids or inorganic ion-exchangers) to (a) bind metal anions [36], (b) prepare supported catalysts under the form of spherical resins [37], discs [38] and cylindrical foams [37,38]. The same procedure was used for the immobilization of nickel potassium hexacyanoferrate ion-exchanger in a chitin-based matrix (conditioned under the form of highly porous discs) for the binding of Cs(I) from acidic or neutral solutions (See [Additional Material Section, Fig. AM1](#)). Due to the partial solubility of chitosan in acidic solutions the reacetylation of the biopolymer was operated on the discs (containing the inorganic ion-exchanger) to improve the chemical stability of the hybrid material. The hybrid discs were immobilized in a filtration membrane holder and they were tested in a static mode with recirculation of the solution through the membrane (See [Additional Material Section, Fig. AM2](#) for the description of operating system). The sorption properties of the material were tested in a first step on synthetic inactive solutions of Cs(I) through the study of pH effect, the impact of competitor ions, the investigation of uptake kinetics (considering the impact of recirculation flow rate, in order to evaluate the contribution of mass transfer properties), and sorption isotherms. The sorption of Cs(I) is also tested in fixed-bed columns (dynamic mode) and the stability of the sorbent is evaluated through (a) the quantification of nickel and iron release in the sorption mode, and (b) a first attempt to desorb Cs(I). Finally, the decontamination factor was evaluated on saline solutions spiked with  $^{137}\text{Cs}$ . SEM and SEM-EDX analyses have also been carried out in order to characterize the materials (morphology and structure of the hybrid foams, distribution of elements before and after Cs(I) sorption).

## 2. Materials and methods

### 2.1. Materials

Potassium ferrocyanide ( $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ , Riedel-de Haën), nickel sulfate ( $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ , Chem-Lab), acetic anhydride ( $\text{C}_4\text{H}_6\text{O}_3$ , Sigma-Aldrich) were supplied as reagent grade products. Acetic acid (80% w/w, Carlo Erba), ethanol (96% w/w, Sodipro) were technical products. Chitosan (molecular weight  $125,000\text{ g mol}^{-1}$ , deacetylation degree: 87%) was supplied by Aber-Technologies (France). Cesium nitrate was purchased from Merck AG (Germany).

### 2.2. Synthesis of sorbent

The synthesis of the potassium-nickel ferrocyanide ( $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ ) was prepared by reaction of two precursors, potassium ferrocyanide (9.0672 g, 0.0215 mole) and nickel sulfate (7.25 g, 0.0276 mole), in 500 mL of demineralized water under strong agitation for 30 min. The precipitate was recovered by centrifugation (for 5 min at 9000 rpm). The solid was re-suspended in 500 mL of demineralized water together with 15 g of chitosan. The suspension was maintained in strong agitation for 15 min before adding dropwise 15 mL of acetic acid. The suspension was maintained in strong agitation for 90 min; this agitation time is sufficient for achieving the complete dissolution of the biopolymer.

The second step in the process consisted in conditioning the material as highly porous foams. The mixture was poured in Petri dishes (using 18 g of the homogeneous suspension in 15 cm-diameter Petri dishes) before being frozen at  $-80\text{ }^\circ\text{C}$  for 90 min. The water being frozen formed a porous network in the frozen discs. By freeze-drying water was sublimated and the porous network was maintained in the discs.

The third step consisted in the reacetylation of amine groups using acetic anhydride. The reacetylation may contribute to increase the chemical stability of the biopolymer, especially in terms of pH range. Chitosan being soluble in acidic solutions, the reacetylation of glucosamine moieties to acetylglucosamine (to form chitin) will offer the possibility to use the material also in acidic solution. For the reacetylation of chitosan, 5 g (dry) of the material was maintained in a mixture of ethanol (800 mL) and acetic anhydride (200 mL) under reflux.

The last step consisted in the careful rinsing of the materials (to remove traces of acetic anhydride that did not react, and other possible impurities), followed by a final freeze-drying.

### 2.3. Characterization of sorbent

#### 2.3.1. SEM and SEM-EDX analysis

The morphology and the distribution of inorganic ion-exchanger and Cs element in the materials were determined with a Scanning Electron Microscope coupled with Energy Dispersive X-ray analysis (SEM-EDX). SEM observations were performed using an Environmental Scanning Electron Microscope (ESEM) Quanta FEG 200, equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system. The use of environmental SEM allowed the direct observations of materials, without previous metallization of the samples. The topography of the samples was observed using secondary electron flux while the backscattered electrons were used for the identification and localization of heavy metals at the surface of the materials (by phase contrast). SEM-EDX facilities were used for the detection of elements and their semi-quantitative analysis (Cs and principal elements representative of the inorganic ion-exchanger; i.e., Fe, K and Ni elements).

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