Journal of Hazardous Materials 287 (2015) 171–179

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Chitin-Prussian blue sponges for Cs(I) recovery: From synthesis to application in the treatment of accidental dumping of metal-bearing solutions

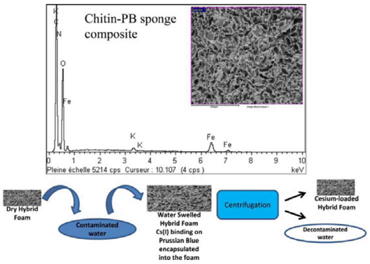
C. Vincent[a,b], Y. Barré[b], T. Vincent[a,1], J.-M. Taulemesse[c], M. Robitzer[d], E. Guibal[a,*,1]

[a] Ecole des mines d'Alès, Centre des Matériaux des Mines d'Alès, C2MA/MPA/BCI, 6 avenue de Clavières, F-30319 Alès Cedex, France
[b] Commissariat à l'Energie Atomique, CEA Marcoule, DEN/DTCD/SPDE/LPSD,BP 17171, F-30207 Bagnols sur Cèze, France
[c] Ecole des mines d'Alès, Center des Matériaux des Mines d'Alès, 6 avenue de Clavières, F-30319 Alès Cedex, France
[d] Institut Charles Gerhardt – UMR5253, CNRS-UM2-ENSCM-UM1, ICGM-MACS-R2M2, 8 rue de l'Ecole Normale, F-34296 Montpellier Cedex 05, France

HIGHLIGHTS

- Prussian blue microparticles incorporated in chitin sponges.
- Efficient Cs(I) sorption after water absorption by dry hybrid sponge.
- Water draining after sorption for metal confinement and water decontamination.
- High decontamination factors and distribution coefficients for Cs(I) and ^{137}Cs(I).
- Effect of freezing conditions on porous structure and textural characterization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 October 2014
Received in revised form
30 December 2014
Accepted 14 January 2015
Available online 17 January 2015

Keywords:
Prussian blue
Chitin
Sponge
Cesium
Sorption
Water absorption
Structure-synthesis correlation

ABSTRACT

Prussian blue (i.e., iron[III] hexacyanoferrate[II], PB) has been synthesized by reaction of iron(III) chloride with potassium hexacyanoferrate and further immobilized in chitosan sponge (cellulose fibers were added in some samples to evaluate their impact on mechanical resistance). The composite was finally re-acetylated to produce a chitin-PB sponge. Experimental conditions such as the freezing temperature, the content of PB, the concentration of the biopolymer and the presence of cellulose fibers have been varied in order to evaluate their effect on the porous structure of the sponge, its water absorption properties and finally its use for cesium(I) recovery. The concept developed with this system consists in the absorption of contaminated water by the composite sponge, the *in situ* binding of target metal on Prussian blue load and the centrifugation of the material to remove treated water from soaked sponge. This material is supposed to be useful for the fast treatment of accidental dumping of Cs-contaminated water.

1. Introduction

Radioelements (including ^{137}Cs, which is a strong gamma emitter with high solubility and easy migration properties through groundwater to the biosphere, based on its chemical similarity

---

* Corresponding author. Tel.: +33 466782734; fax: +33 466782701.
E-mail address: Eric.Guibal@mines-ales.fr (E. Guibal).

[1] T.V. & E.G. are associated members of ICGM-MACS-R2M2.

http://dx.doi.org/10.1016/j.jhazmat.2015.01.041
0304-3894/

to potassium) are generated along the conventional operation of nuclear power plants and the treatment of the effluents generated in the processing of spent nuclear fuels is a critical step in the management of nuclear facilities. Apart these conventional and well-controlled effluents, accidents such as the Fukushima disaster in 2011 are generating hazardous sources of radioelement-bearing solutions. The development of treatment processes for the fast and efficient recovery of radioelements, even in complex media (such as sea water), is thus a priority for reinforcing the safety of the entire nuclear industry. In the case of conventional controlled effluents several processes exist using ion-exchangers (such as Prussian blue, PB), titanate-based materials or clays and mineral oxides. In the case of accidental dumping of small amounts of contaminated effluents there is a need for developing alternative processes capable of simultaneously recovering and treating the contaminated water. This is the objective of the present work: associating (a) a sponge, which is targeted to absorb water, and (b) an ion-changer tailored for binding the radioelement. The elimination of water by centrifugation in the next step, allows releasing decontaminated water while the radioelement is concentrated on the hybrid solid phase.

Prussian blue (PB) is an ion-exchanger (IE) that is well known for its affinity for some light earth metal ions such as cesium(I) or rubidium(I) but also for thallium(I) [1]. This is part of the conventional treatment of acute poisoning with radioactive Cs (Radiogardase®) [2]. For medical applications, Prussian blue is conditioned under the form of tablets/capsules to be ingested; cesium binding to insoluble PB occurs in the gastro-intestinal tract before being excreted from natural ways. Prussian blue is generally synthesized by reaction of potassium (or sodium) hexacyanoferrate with iron(III) chloride giving different compounds with different solubility properties. In the presence of an excess of iron(III) chloride, PB turns from a soluble/colloidal form ($KFe[Fe(CN)_6]$) to an insoluble form generally described as $Fe_4[Fe(CN)_6]_3$. Cesium(I) is then exchanged with K or Fe present on the lattice of the IE (cubic lattice structure) [1]. Actually, the composition and properties of these PB-based compounds are strongly influenced by the experimental conditions used for PB synthesis, such as molar ratio between the precursors, the order of addition and mode of agitation: the proportion of K and Fe exchangeable moieties may strongly change and the solubility of the final product as well. Several studies on PB analog (other metal–potassium hexacyanoferrate compounds) have clearly shown the importance of these operating parameters on the properties of final products [3–5]. The presence of colloidal species makes difficult the recovery of the IE at the end of the synthesis procedure and in some cases the addition of a coagulant/flocculant (such as chitosan) was reported to contribute to (a) charge neutralization, and (b) agglomeration for ready recovery and further inclusion in biopolymer matrix [6].

In any cases the small size of these IE particles makes their use complex at large scale due to difficulty in recovery (coagulation/flocculation, settling etc.); and it is generally helpful immobilizing the IE in a suitable matrix (biopolymer, polymer) or at the surface of a specific mineral support (silica, activated carbon, zeolite etc.) [7–13]. These methods lead to materials that can be used in tank reactor, fixed-bed columns for the treatment of controlled contaminated water streams. Biopolymers such as alginate and chitosan have been recently reported as potential encapsulating materials for the immobilizations of IEs, including double metal hexacyanoferrate [8,14–17]. The physical versatility of the biopolymers allows developing different shaping and conditioning of these materials such as beads [11,15], membranes, fibers [18], or tubes [19], but also very highly porous foams [20–22]. The present study combines the incorporation properties of chitosan for PB with a specific conditioning of the biopolymer under the form of highly porous sponges. In order to improve the chemical resistance of the material with changing operational conditions (pH changes, especially), the composites are finally reacetylated for producing chitin-PB sponges [23,24]. Cellulose fibers are introduced in the composite to reinforce the mechanical stability of the material [25,26]. The objective is to design a sponge that could be used for the treatment of contaminated water in the case of accidental dumping. After the absorption of metal-containing water on the composite sponge, the IE (i.e., PB) rapidly binds Cs(I) ions though ion-exchange mechanism (more generally adsorption). After water wringing (or centrifugation) from wetted sponge, decontaminated water can be environmentally friendly rejected to water discharge network while the metal is confined in the composite sponge. In order to reach this objective the present study (a) synthesizes a series of composite materials (containing chitosan (further reacetylated to chitin), Prussian blue (BP) particles and cellulose fibers (which may contribute to improve the mechanical resistance of the foams) and (b) compares their structural and textural properties; their ability to absorb water and finally to bind Cs(I) (both in natural and nuclide forms; i.e., ^{133}Cs and ^{137}Cs, respectively).

2. Material and methods

2.1. Materials

Potassium hexacyanoferrate ($K_4[Fe(CN)_6],3H_2O$, Riedel-de Haën), iron(III) chloride ($FeCl_3,3H_2O$, Chem-Lab), acetic anhydride ($C_4H_6O_3$, 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 g mol^{-1}, deacetylation degree: 87%) was supplied by Aber-Technologies (France). Cesium nitrate was purchased from Merck AG (Germany). Cellulose fibers were prepared from an Ahlstrom raw paper substrate (Pont-Evêque, France) by dilacerations and rehydration. This is a Roburflash-type paste prepared from resinous wood (long fibers) and with poor refinery level (flash).

2.2. Synthesis of composite sponge

The elaboration of composite materials followed basically five main phases: (a) the synthesis of PB, (b) the stabilization of the complex with chitosan, (c) the shaping (and freeze-drying) of chitosan-PB sponges, (d) the freeze-drying of the sponge, and (e) the reacetylation of chitosan to prepare chitin-PB sponge.

The synthesis of PB complex consisted in the mixing of two precursors for 30 min under strong agitation: (i) potassium hexacyanoferrate (100 mL, 3.62 g), and (ii) iron(III) chloride was used (100 mL, 2.23 g). The molar ratio between iron(III) and potassium hexacyanoferrate was set at 1.2:1. The hexacyanoferrate solution was injected in the metal precursor solution drop-by-drop. At the end of this first step, 1 L of demineralized water was added to the suspension. This suspension was then added to 2 L of chitosan solution (at 0.05%, w/w) to stabilize the complex (charge neutralization, partial or complete) and improve the settling of the material that can be readily recovered by filtration on paper membrane. This wet material (chitosan-stabilized complex, CSC) was thus mixed with 100 mL of water and 100 mL of a 4% w/w chitosan solution in two steps: softly, and then under UltraTurax (24,000 rotations min^{-1}, for 5 min). This last step was also performed changing the concentration of chitosan solution to 6% w/w to prepare two different compounds with final chitosan concentrations of 2% and 3% w/w, respectively. In order to verify the impact of PB load in the material the amount of IE was divided by 2 or by 3 to prepare the corresponding lots. The last parameter that was varied was the presence of cellulose fibers added at the level of 1% w/w in the final suspension.