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Biopolymers as Encapsulating Agents for the Immobilization of Prussian Blue and Analogues for the Sorption of Cesium

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Abstract. Prussian Blue (PB, iron hexacyanoferrate) is an efficient micron-sized sorbent that can be encapsulated in a biopolymer matrix (chitin) for the treatment of Cs(I)-bearing solutions. Different conditionings have been designed for the treatment of Cs-contaminated effluents (with natural Cs(I) solutions, and with ¹³⁷Cs spiked solutions). The sorbents conditioned under the form of beads or discs can be used in columns while sponges can be used for the treatment of accidental discharge of effluents (contaminated water absorption by the sponge, metal ions sorption on the ion-exchanger, treated water removal by centrifugation, metal concentration in the composite material).

Introduction

Prussian Blue and analogues (metal hexacyanoferrates) are very efficient ion-exchangers for the sorption of cesium cations [1-3]. Their micro- or nano-size requires complex filtration or centrifugation systems. To improve the practical application of these sub-micronic size ion-exchangers it may be helpful immobilizing the particles in or at the surface of a support [4, 5]. The challenge is thus the simultaneous retention of micro/nano particles and the efficient mass transport of target metal ions through the encapsulating matrix. Chitosan have been used for the encapsulation of the ion-exchanger particles. Different conditionings of the hybrid materials have been designed including spherical beads and highly macroporous foams. This work gives an overview of these different techniques with a focus on their sorption properties for cesium and analogues. The ion-exchanger is synthesized by reaction of its specific precursors before being incorporated in the biopolymer solution and conditioned (shaping). The last step consists in the reacylation of the biopolymer to improve its resistance in acidic solutions (pH range). These materials have been tested for the sorption of Cs(I) on both natural and ¹³⁷Cs(I) effluents.

Materials and methods

Sorbents The metal hexacyanoferrate complexes are prepared by mixing the two precursors for 30 min under strong agitation: (i) potassium hexacyanoferrate (100 mL, 3.62 g), and (ii) metal sulfate (except for iron complex, where iron(III) chloride was used) (100 mL). The molar ratio between the metal precursor and the potassium hexacyanoferrate was systematically set at 1.2:1 (Fe: 2.23 g; Ni: 2.70 g; Zn: 2.96 g; Co: 2.89 g; Cu: 2.57 g). This suspension (in 1 L of water) was then added to 2 L of chitosan solution (at 0.05 %, w/w) to stabilize the complexes (by charge neutralization), CSC. CSC (centrifugate) was mixed with 100 mL of water and 100 mL of a 4 % w/w chitosan using UltraTurax (for 5 min). For gel beads, the shaping of the material was performed by pumping the viscous chitosan/stabilized complex suspension through a thin nozzle into a liquid N₂ bath. Frozen beads were finally freeze-dried. For the foams, the shaping was performed by dropping the viscous chitosan/stabilized complex suspension into plane rectangular

molds that were frozen at $-80\text{ }^{\circ}\text{C}$. After the freezing step, the materials were rapidly recovered from the molds and freeze-dried overnight. The final step consisted of the re-acetylation of chitosan. One gram of metal-HexaCNFe/chitosan composite was mixed with 40 mL of ethanol and 10 mL of acetic anhydride under reflux for 1 h. The products were then rinsed once with ethanol to remove non-reacted reagent and finally with demineralized water before being freeze-dried [6-8].

Adsorption tests. All cesium solutions were prepared from a stock solution (1 g Cs L^{-1}) by dilution with 0.1 M sodium nitrate solution (background salt). All freeze-dried sorbent particles were moistened before being used (24 h in water). Experiments were performed at $20.0 \pm 1.5\text{ }^{\circ}\text{C}$. Uptake kinetics were obtained by contact (under stirring) of 1 L of cesium solution (C_0 : 10 mg Cs L^{-1}) with 0.1 g (m, dry weight) of metal-potassium hexacyanoferrate/chitin composite for 48 hours. Samples were collected, filtrated and analyzed by atomic absorption spectrometry (AAS, Varian AA20 spectrometer). Sorption isotherms were obtained by contact, on a reciprocal shaker, of 0.1 g of metal-potassium hexacyanoferrate/chitin composite, with 50 mL of cesium solution (V, L) varying C_0 between 5 and 400 mg Cs L^{-1} . Residual concentration at equilibrium (C_{eq} , mg Cs L^{-1}) was analyzed by AAS after filtration. The sorption capacity (q , mg Cs g^{-1}) was calculated by the mass balance equation. The discs experiments were performed by pumping the solution in a recirculation mode (at high flow rate) through the discs immobilized in a membrane support; other experimental conditions were identical. For experiments on foams, a given amount of dry sponge was added to a given volume of solution. The amount of solution (V, L) in contact with the sponge was set a little higher than the corresponding water absorption values. The sponge was simply used in a static mode. After fixed contact time the soaked sponge was centrifuged and Cs(I) residual concentration was measured by AAS. The tests on $^{137}\text{Cs(I)}$ sorption have been operated using the same procedure. Typically, 1 mL of $^{137}\text{Cs(I)}$ spiked solution was put in contact with a piece of sponge (about 75 mg) for 1 min or for 3 min. The wet sponge was transferred to a centrifugation tube filled with glass beads. After centrifugation the sponge was removed and the tube was rinsed with water. Fifty mL were dropped in the analytical flask for gamma counting (using a Eurisy Mesures counter equipped with a Ge detector). The initial activity of the solution (A_0 , Bq L^{-1}) was 37000 Bq L^{-1} . The residual activity (A_f , Bq L^{-1}) was measured for calculating the decontamination factor (DF: A_0/A_f) and the distribution coefficient (K_{d137} , L g^{-1} : $C_{\text{sorbent}}/C_{\text{solution}} = (A_0 - A_f)V/(mA_f)$).

Results and discussion

Fig. 1 shows the structure of composite sorbents (scanning electron microscope photographs) for beads (Fig. 1a), discs (Fig. 1b) and foams (Fig. 1c). The porous structure is clearly identified by large pores and alveoli. The presence of the ion-exchanger is also confirmed by SEM-EDX analysis (SEM coupled with electron dispersive X-ray analysis, Fig. 1c) on composite sponge; similar observations were obtained with the other conditionings. XRD analysis (not shown) confirmed that K element was exchanged with Cs element while TEM analysis showed that ion exchanger particles were a few tens of nanometer in size.

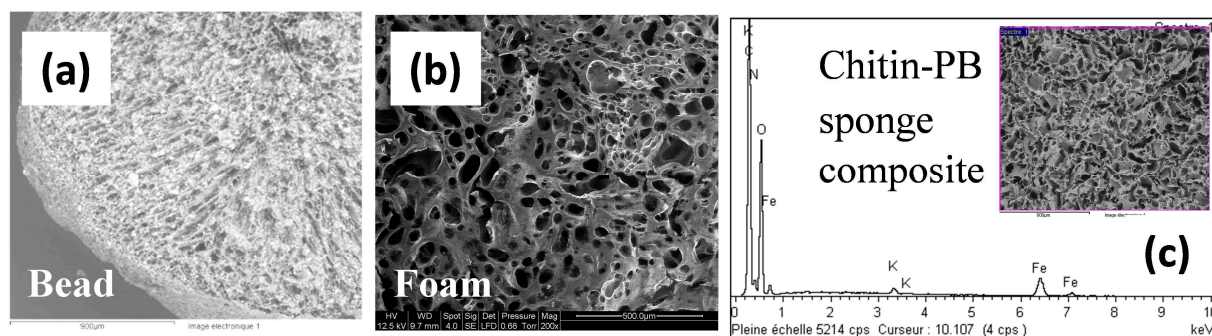


Figure 1. Prussian Blue (or analogues)/chitin composites (beads (a), foams (b) and sponges (with SEM-EDX analysis (c)).

Cesium (I) sorption isotherms (Fig. 2a) and uptake kinetics (Fig. 2b) were obtained with PB (and analogues) immobilized in chitin beads. The sorbents can be ranked according the sequence: $\text{Cu} > \text{Co} \approx \text{Ni} > \text{Zn} > \text{Fe}$ in terms of maximum sorption capacity and $\text{Zn} > \text{Cu} \approx \text{Ni} > \text{Co} > \text{Fe}$ for kinetics. Since some of the counter metal ions can be exchanged and released in the solution during Cs(I) sorption and due to the relative costs of these counter metals, PB was selected for further studies (despite lower sorption performance). Sorption capacities as high as $200\text{--}600 \text{ mg Cs g}^{-1}$ composite were obtained; in most cases the equilibrium was achieved within 24–36 hours (under selected sorbent dosage and metal concentration). The sorption isotherms were modeled with the Langmuir equation (solid lines on Fig. 2a). Uptake kinetics is controlled by the resistance to intraparticle diffusion (Crank equation [4] was used for modeling kinetics profiles; solid lines on Fig. 2b) with intraparticle diffusion coefficients ranging between $2 \times 10^{-10} \text{ m}^2 \text{ min}^{-1}$ and $49 \times 10^{-10} \text{ m}^2 \text{ min}^{-1}$.

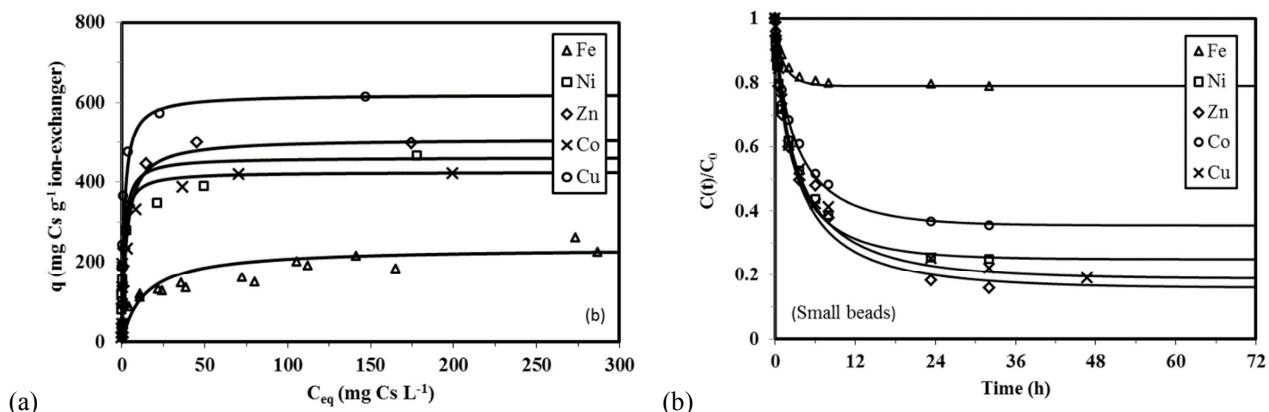


Figure 2. Cs(I) sorption isotherms (a) and uptake kinetics (b) for different metal hexacyanoferrate complexes immobilized in chitin beads (pH 5–6; kinetics: C_0 : 10 mg Cs L^{-1} ; SD: $1 \text{ g sorbent L}^{-1}$).

The effluents contaminated with Cs(I) are frequently complex, containing high concentrations of other salts including monovalent cations that can interfere with Cs(I) for ion-exchanged with nickel potassium hexacyanoferrate (Ni-KHCFe); this is, for example, the case of effluents issued from Fukushima site. Ni-KHCFe-immobilized in chitin macroporous discs was used for Cs(I) sorption in the presence of increasing concentrations of Na(I) (the solution was pumped through the support in a recirculation mode). Fig. 3a shows that even with concentrations as high as $1 \text{ mol Na(I) L}^{-1}$ the sorption capacity was not drastically reduced. Similar trends were obtained with K(I) and NH_4^+ .

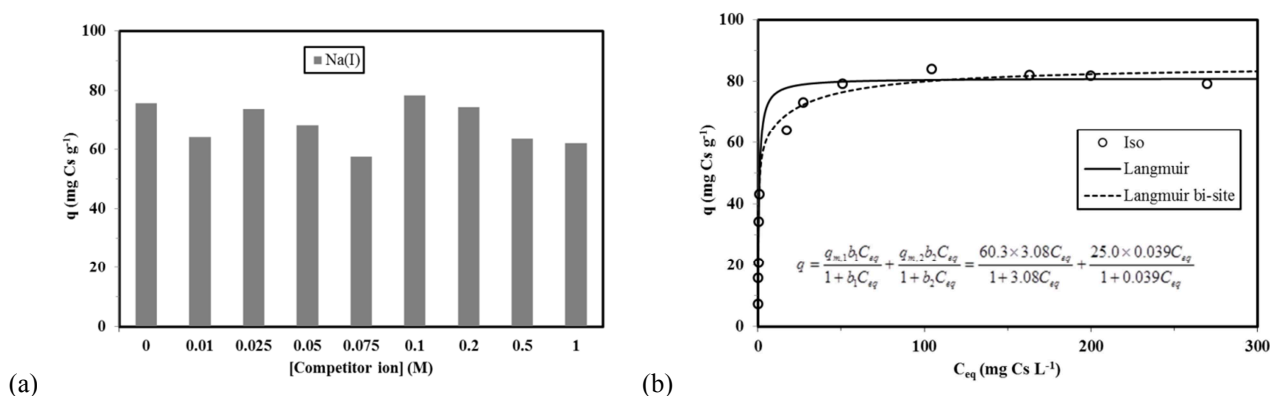


Figure 3. Effect of salt concentration on Cs(I) sorption (a) and Cs(I) sorption isotherm on Ni-K hexacyanoferrate immobilized in chitin discs (b) (pH 7–7.4; C_0 : 135 mg Cs L^{-1} ; SD: 2 g L^{-1}).

The sorption isotherm showed a maximum sorption capacity close to 80 mg Cs g^{-1} (Fig. 3b). The initial slope of the isotherm is quite steep: this shows the strong affinity of the sorbent for Cs(I). The isotherm can be modeled using the Langmuir bi-site equation [5]. This may indicate that Cs(I) is sorbed on two different reactive groups (coexistence of different hexacyanoferrate complexes with different affinities for cesium).

Table 1 reports the treatment of cesium-containing solutions (^{137}Cs spiked solutions) using beads and macroporous discs (pumping with recirculation mode). Similar experiments were performed with composite sponges. In this case the sponge is used for absorbing contaminated water; after 3-minutes contact (and cesium binding on PB microparticles) water was removed by centrifugation. Both the decontamination factor (DF) and the distribution coefficient (K_d) were quite high: these results confirm that the composite materials are efficient for the treatment of effluents containing radioelements; they allow concentrating ^{137}Cs in the immobilized PB (or analogue).

Table 1. Cs(I) sorption performance for ^{137}Cs -spiked solutions using PB- chitin composites.

	Beads	Discs	Foams
A_0 (Bq L ⁻¹)	41000	37000	37000
A_f (Bq L ⁻¹)	55	21	< 6
C_0 (mmol Cs L ⁻¹)	2×10^{-2}	-	0.98×10^{-5}
C_{eq} (mmol Cs L ⁻¹)	2.7×10^{-5}	-	1.5×10^{-7}
Decontamination factor (A_0/A_f)	745	1762	> 6200
K_d (L g ⁻¹)	433	1869	> 88000

Conclusions

Biopolymers can be used for the immobilization of micro or nano-size ion-exchangers such as iron potassium hexacyanoferrate (Prussian Blue or analogues). These composite materials can be designed under different forms: beads and macroporous discs can be used in conventional sorption process (batch or fixed-bed systems for beads; fixed bed for sponges) or for the treatment of incidental discharge of contaminated water (foams: absorption/ adsorption/centrifugation sequence). The macroporous structure improves accessibility of micro-particles to the solution and allows using these materials as filtrating reactive supports. The composite sorbents are efficient for removing both stable Cs and ^{137}Cs . Composite foams are particularly promising as sponges for the absorption of accidental discharge of contaminated effluent: metal solution is absorbed and after short contact time (and metal sorption on ion-exchanger) the centrifugation of the sponge removes the treated solutions (the radioelement being concentrated in the sorbent).

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