



Breakthrough studies of the adsorption of Cs from freshwater using a mesoporous silica material containing ferrocyanide

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HIGHLIGHTS

- In flow adsorption of Cs using mesoporous silica containing ferrocyanide nanoparticles.
- Diffusion in the material is fast enough to allow high flow rate.
- Role of the operating parameters: Darcy velocity and column geometry.
- A reactive transport model coupling ion diffusion and exchange inside the porous adsorbent.

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ABSTRACT

The selectivity and fast exchange kinetics of porous silica adsorbents containing Cu or K ferrocyanide make them ideal candidates for the column decontamination of ^{137}Cs effluents. The exchange thermodynamics of the K^+ ions in Sorbmatech® (S202, one such adsorbent) with the major cations present in natural (fresh or sea) water have recently been studied in competition with Cs^+ sorption to properly model batch data. This article reports an evaluation of this material for continuous, column processes of freshwater decontamination. Experimental data show that its performance is excellent under these conditions, with a steep breakthrough curve of Cs at column exit. The sorption capacity of S202 is completely retained at high flow rates (up to $10\text{ m}\cdot\text{h}^{-1}$ Darcy velocity) and its column behavior remains ideal down to a height/diameter ratio of 2. A reactive transport model accounting for dispersive flow through the bed coupled to ion diffusion and exchange inside the porous adsorbent grains accurately reproduces the experimental data.

1. Introduction

The nuclear fuel cycle produces radioactive effluents, from different sources, that need to be treated specifically before they are released into the environment. An additional potential source of radioactive pollution are effluents from nuclear accidents such as contaminated (fresh and sea) water from the Fukushima disaster. There is therefore a substantial demand for effective yet inexpensive methods to decontaminate the radionuclide-contaminated water, and transfer the contamination into a sorbent easier to manage. ^{137}Cs is one of the most abundant and hazardous radionuclide because it is found in many types of waste and has a relatively long half-life (30 years). Its selective extraction from the effluent is therefore necessary, but the presence of naturally occurring alkali and alkaline earth ions makes this difficult in contaminated

water. This is the context in which Sorbmatech® 202 (S202), a selective adsorbent for Cs, was developed. This material consists of potassium/copper ferrocyanide nanoparticles inserted inside mesoporous silica grains. Although pure ferrocyanide adsorbents can extract cesium selectively, their small grain size means that they cannot be used in fixed-bed columns because of pressure loss and clogging. Their low adsorption kinetics in powder form is also problematic for column processes. One way to overcome these drawbacks is to insert selective ferrocyanide (hexacyanoferrate) nanoparticles in a solid porous matrix to make it amenable to column processes: the porosity of the support and the high surface/volume ratio of the hexacyanoferrate particles inside the pores improves the adsorption rate. Numerous composite solids (organic or inorganic) loaded with hexacyanoferrate particles have thus been proposed for cesium removal in the past few years [1–14].

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The fast Cs^+ sorption kinetics measured for S202 [11] suggest that this material should remain effective in column processes at high flow rates. Studies in batch processes with freshwater have shown that competitive effects involving naturally present cations should be taken into account however [11]. A model was also developed in this study that reproduced the experimental data points precisely, especially at low Cs^+ concentrations. Freshwater was therefore chosen as the Cs-containing effluent in the present study of column processes. The conditions investigated here are thereby similar to those in which S202 would be used in practice.

The fixed-bed column behavior of this material was characterized at flow rates much lower than would be used in industrial applications. Therefore, to make our results transposable to higher scales, we investigated the effects of two important parameters—the Darcy (or linear flow) velocity and the geometric ratio of the height (H) of the bed over the diameter (D) of the column (H/D)—whose careful adjustment ensures optimal performance. The flow rate needs to be high to allow large volumes of effluent to be treated rapidly. However, the faster the Darcy velocity is, the more convective flow dominates over diffusion, meaning that the cations are adsorbed deeper in the bed or not at all. The maximum capacity of the material is not reached and leakage occurs prematurely from the column. This can be avoided by increasing the depth of the bed to ensure sufficient contact and guarantee that the column flow-through is balanced. Using low H/D ratios may reduce the decontamination efficacy of the column. However, if the H/D ratio is too high, this can lead to load loss at the top of the column, which could increase the cost of the process.

This article presents the experimental procedures and tests performed to optimize the operating parameters for column decontamination using S202. The hydrodynamic flow in the column and measurements of load loss and the distribution of dwell times are then used to model the set of breakthrough curves obtained. Finally, four of the breakthrough curves corresponding to different velocities and geometries are modeled using the reactive transport software Optipur [15].

2. Material and methods

2.1. Characteristics of the adsorbent and solution used

The synthesis and Cs adsorption properties of S202 in aqueous solutions have been described previously [11]. This material consists of a mesoporous silica matrix with pores around 8 nm in diameter, and grain size of 250–500 μm containing $\text{K}_2\text{Cu}(\text{Fe}(\text{CN})_6)$ nanoparticles that selectively extract Cs. The grains have an irregular, roughly octahedral, shape. As reported previously [11], the material's specific surface area ($S_{\text{BET}} = 280 \text{ m}^2\text{g}^{-1}$) was obtained by measuring nitrogen adsorption–desorption isotherms and applying the BET model [16]. The mean pore diameter ($d_p = 7.9 \text{ nm}$) was calculated using the BJH model [17]. The total pore volume ($V_p = 0.58 \text{ cm}^3\text{g}^{-1}$) of the material was obtained from the point on the isotherm at which the relative pressure was equal to 1. The volumetric mass density of the material ($\rho = 3.4 \text{ g}\cdot\text{cm}^{-3}$) was measured by helium pycnometry. The porosity of the material (equal to 0.17, dimensionless) was then quantified by dividing the pore volume by the density of the material (V_p/ρ).

To account for competition effects and in view of using the process to decontaminate natural water, the Cs adsorption experiments were performed at room temperature in freshwater at pH 7.9 containing $5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ Cs nitrate purchased by Sigma Aldrich (purity 99%). The full composition of the solution used is given in Table 1; the main cations are Ca^{2+} and Mg^{2+} whereas the concentration in solution of K^+ (i.e. the exchangeable cation present in the solid S202) is low. Under these conditions, the adsorption capacity and distribution coefficient ($K_{d,\text{Cs}}$) of S202 for Cs were found to be $0.180 \text{ meq}\cdot\text{g}^{-1}$ and $330 \text{ mL}\cdot\text{g}^{-1}$, respectively. The concentration of ions in solution was measured by Atomic Absorption Spectroscopy for Cs and other ions were analyzed by ICP-AES.

Table 1

Average composition of the freshwater used for Cs adsorption tests.

	Concentration ($\text{mol}\cdot\text{L}^{-1}$)
Na^+	2.8×10^{-4}
K^+	4.4×10^{-5}
Mg^{2+}	1.1×10^{-3}
Ca^{2+}	2.0×10^{-3}
Cl^-	1.9×10^{-4}
SO_4^{2-}	1.3×10^{-4}
HCO_3^-	5.9×10^{-3}
NO_3^-	6.0×10^{-5}
SiO_2	2.5×10^{-4}
pH	8

2.2. Set-up used for measuring breakthrough curves

The setup used for the breakthrough curve experiments is shown in Fig. 1. The Cs-containing solution was placed in a 5 L Pyrex flask and pumped into the column using a peristaltic pump (Ismatec IP ISM942) for low flow rates or an HPLC pump (RHOS Prep Pump) for high flow rates. A manometer was placed at the column head to measure load loss. The column flow-through was gathered in an automatic fraction collector (Labomatic Vario-4000) with a three-way valve. The pumps and fraction collector were connected to the column via screw connectors.

The operating parameters recorded for each breakthrough experiment were: i) the mass of adsorbent in the column (m_{ads} in g), ii) the column geometry and iii) the Darcy or linear velocity U ($\text{m}\cdot\text{h}^{-1}$). The geometry of the column was characterized by the height and volume of the bed H (cm) and V (mL or L), the diameter and corresponding effective cross-sectional area of the column D (cm) and Ω (m^2), as well as the dimensionless ratio H/D . The Darcy velocity was obtained by dividing the volumetric flow Q_v (mL or L) by the effective cross-sectional area of the column, $U = Q_v/\Omega$.

Two laboratory columns, 1 or 2.5 cm in diameter were used, with corresponding effective cross-sectional areas of 7.9×10^{-5} and $4.9 \times 10^{-4} \text{ m}^2$, respectively. The column diameters are more than 10 times the grain size so edge effects can be ignored [18], provided the H/D ratio is above a certain threshold value. Below this, preferred paths appear and premature leakage occurs. The values chosen for the operating parameters for each breakthrough experiment are listed in Table 2.

2.3. Breakthrough curves

The breakthrough experiments involved measuring the Cs concentration C ($\text{mol}\cdot\text{L}^{-1}$) at the exit of the column as a function of time as the simulated effluent flowed through. A series of 5 mL samples of the flow-through were extracted at various times and analyzed. The breakthrough curves represent the evolution of this Cs concentration as a function of time or the flow-through volume V (L). The half-breakthrough time $t_{1/2}$ (s) or volume $V_{1/2}$ is the time (volume) at which the Cs concentration at column exit is half the initial concentration of the effluent. The amount of Cs extracted per gram of adsorbent Q ($\text{mol}\cdot\text{g}^{-1}$) when a volume V_1 passed through the column was calculated using

$$Q(V_1) = \frac{C_0 V_1 - \int_0^{V_1} C dV}{m_{\text{ads}}} \quad (1)$$

where m_{ads} is the total mass of adsorbent (g), and C_0 is the Cs concentration at the entry of the column.

Since, as shown on RTDs curve (section 4.4), there is little axial dispersion in the column (due to hydrodynamic effects or the sorption kinetics), the plug flow reactor model can be used to calculate $V_{1/2}$ from the adsorbent's $K_{d,\text{Cs}}$.

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