



Cs⁺ removal and optical detection by microporous lanthanide silicate Eu-AV-20 in a fixed-bed column



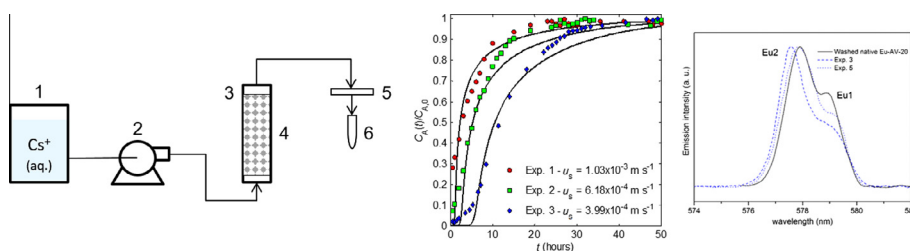
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HIGHLIGHTS

- Microporous silicate Eu-AV-20 synthesised for Cs⁺ removal from aqueous solutions.
- Fixed-bed ion exchange experiments performed under distinct operating conditions.
- Modelling based on Nernst–Planck, Thomas, Bohart–Adams, Yoon–Nelson and Clark equations.
- Reliable correlation and prediction of breakthrough curves with Nernst–Planck based model.
- Photoluminescence spectroscopy disclosed the potential of Eu-AV-20 for Cs⁺ sensing.

GRAPHICAL ABSTRACT



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ABSTRACT

Microporous silicate Eu-AV-20 has recently proved to be a promising ion exchange material for cesium removal from aqueous solutions, and its potential for Cs⁺ photoluminescence sensing was additionally demonstrated. In this work, Cs⁺ removal was performed in a fixed-bed column, and the influence of linear velocity and mass of ion exchanger on the breakthrough curves was analysed. The experimental data were modelled on the basis of Nernst–Planck (NP) equations and with four well-known analytic models. The analytic expressions provided low errors (root mean square deviation, RMSD, between 3.20% and 6.47%); the 2-parameter NP-based model fitted the data quite well (RMSD = 6.66% for correlation and 6.54% for prediction), yielding crucial information on both the transport mechanism within the Eu-AV-20 particles, and the intrinsic dynamic behaviour of the fixed-bed ion exchange column. Taking into account that Eu-AV-20 samples loaded with different amounts of Cs⁺ exhibited distinct photoluminescence spectra, our results reinforce the potential of AV-20 materials for Cs⁺ sensing, which raises the possibility of online monitoring the ion exchange in a fixed-bed column using an optical fibre and a spectrometer.

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1. Introduction

Nuclear wastes are complex systems containing fission products including two long-lived cesium isotopes (¹³⁵Cs and ¹³⁷Cs with a half-life of 2.3 million years and 30.17 years, respectively). The negative effects of cesium are well known and encompass

Nomenclature

A or A^{z_A}	counter ion initially in solution	r	radial position in the particle (m)
A_C	Clark model parameter	R^2	coefficient of determination
B or B^{z_B}	counter ion initially in the exchanger	R_p	particle radius (m)
C_b	solute concentration at breakthrough time in Clark model (mol m^{-3})	RMSD	root mean square deviation (%)
C_A	concentration of counter ion A in solution (mol m^{-3})	SEM	scanning electron microscopy
$C_{A,0}$	initial concentration of counter ion A in solution (mol m^{-3})	t_{50}	Yoon–Nelson parameter: time for $C_A/C_{A,0} = 0.5$, (h)
D_i	self-diffusion coefficient of counter ion i ($\text{m}^2 \text{s}^{-1}$)	t	time (h or s)
D_L	axial dispersion coefficient ($\text{m}^2 \text{s}^{-1}$)	t_{st}	stoichiometric time (h)
D_{AB}	interdiffusion coefficient of NP model ($\text{m}^2 \text{s}^{-1}$)	t_b	breakthrough time (h)
D_m	diffusion coefficient of Cs^+ in water ($\text{m}^2 \text{s}^{-1}$)	T	absolute temperature (K)
Exp. j	experiment number j	u	superficial velocity (m s^{-1})
i and j	generic counter ions	v	flow rate ($\text{m}^3 \text{s}^{-1}$)
k_{BA}	Bohart–Adams mass transfer coefficient ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)	Z	dimensionless longitudinal coordinate in the column
k_f	convective mass transfer coefficient (m s^{-1})	z_i	electrochemical valence of counter ion i
k_{Th}	Thomas rate constant ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)	<i>Greek letters</i>	
k_{YN}	Yoon–Nelson rate constant (h^{-1})	ε	bed void fraction
l	column longitudinal coordinate (m)	ρ_s	density of ion exchanger
L	length of the fixed-bed (m)	θ	dimensionless time
Ln-silicate	lanthanide silicate	τ	space time (s)
m	mass of ion exchanger (Eu-AV-20) (g)	ω	Clark model rate parameter (h^{-1})
n	Freundlich isotherm constant	<i>Subscripts</i>	
NDP	number of data points	0	initial conditions
NP	Nernst–Planck	A	counter ion initially present in the bulk solution (Cs^+)
PXRD	powder X-ray diffraction	B	counter ions initially present in the ion exchange (K^+ and Na^+)
$q_{A,max}$	maximum solute concentration in the particle in Bohart–Adams model (mol m^{-3})	BA	Bohart–Adams model
$q_{A,0}$	solid loading in equilibrium with feed concentration, $C_{A,0}$	calc	calculated value
q_i	molar concentration of counter ion i in the particle (mol m^{-3})	eq	equilibrium value
\bar{q}_i	average concentration of counter ion i in the particle (mol m^{-3})	exp	experimental value
Q_{Th}	Thomas model parameter; maximum solute concentration in the solid (mol kg^{-1})	Th	Thomas
		s	solid
		YN	Yoon–Nelson model

medullary dystrophy, disorders of the reproductive function, and adverse effects on the liver and renal functions of mammals [1]. In soil and water environments cesium exists predominantly as a free monovalent ion (Cs^+) since the formation of organic and inorganic cesium complexes is insignificant [2]. Several approaches may be deployed to eliminate cesium from radioactive aqueous wastes, such as chemical precipitation, evaporation, reverse osmosis, filtration, solvent extraction, ion exchange and adsorption [3]. However, ion exchange is usually preferred for water and wastewater remediation, particularly when high-purity water is required [3–5], since they allow concentrating metal ions to a level where disposal, destruction, or subsequent use are affordable.

Ion exchange can be implemented as a batch process in a stirred tank or in a continuous fixed-bed (column) operation. The last alternative is preferred from an industrial point-of-view because: (i) it is the most effective configuration for cyclic sorption–desorption stages; (ii) a nearly solute-free effluent may be obtained until the exchanger agent in the bed approaches equilibrium; (iii) the removal efficiency is usually better due to higher sorbate concentration gradients between solution and solid. Some examples of ion exchange studies in fixed-beds include the uptake of zinc by NaY zeolite [6], the removal of mercury and lead by titanosilicates ETS-4 and ETS-10, respectively [7,8], and the sorption of cesium by titanosilicate granules [9]. Most recently, the elimination of Hg(II)

and Pt(IV) from aqueous solutions have been studied using fixed-beds composed of chelating resins [10–12].

Inorganic ion exchangers are well-known for their chemical, thermal, mechanical and radiation stabilities, and typically exhibit high capacity and selectivity towards a wide variety of monovalent and divalent metal cations [3,4,10–20]. Concerning the specific use of inorganic solids for Cs^+ removal, three main families have been studied, zeolites [18,19], hexacyanoferrates [20,21] and titanosilicates [9,22,23]. Nevertheless, their use in fixed-bed experiments is limited [9,24,25].

In the early years of this century, the synthesis of zeolite-type rare-earth or lanthanide-silicate (Ln-silicates) materials was an emerging field due to their interesting optical properties associated to transitions between 4f orbitals, which generate atomic-like emission spectra displaying characteristic sharp lines [26,27]. The existence of other species in the vicinity of the emitter lanthanide may affect the photoluminescence spectra, which raises the possibility of exploring such optical properties for sensing the presence of molecules/ions [27].

The microporous Ln-silicate Eu-AV-20 and the mineral tobermorite 11 Å [28] have a similar crystal structure, encompassing $5.8 \text{ \AA} \times 6.8 \text{ \AA}$ channels and cavities containing exchangeable Na^+ and K^+ ions coordinated with framework oxygen atoms and water molecules [29]. Furthermore, the presence of stoichiometric amounts of europium affords photoluminescence properties to

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