Examining samarium sorption in biochars and carbon-rich materials for water remediation: batch vs. continuous-flow methods

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HIGHLIGHTS

• Batch and continuous-flow methods were valid to determine Sm sorption capacities.
• Cation exchange was a relevant mechanism for Sm sorption in biochars.
• Biochars and coal fines are green alternatives to activated charcoals for Sm sorption.

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ABSTRACT

Samarium (Sm) sorption from aqueous solutions was evaluated in biochars (derived from castor meal (CM), eucalyptus forest residues (CE), sugarcane bagasse (SB) and green pericarp of coconut (PC)) and in other carbon-rich materials (coal fines (CF); two commercial activated charcoals (GAC, NGAC)) by applying batch and continuous-flow sorption experiments. Batch experiments revealed great $K_d$ values, in the range of $10^4$–$10^5$ L kg$^{-1}$, and high Sm sorption percentages (>97%, except for SB) in the range of environmental representative concentrations, using as-received materials, with no further treatments. Maximum sorption capacities were derived from sorption isotherms using the Langmuir model (from 1.2 to 37 mg g$^{-1}$). Continuous-flow sorption experiments permitted to obtain maximum sorption capacities by mass balance and by fitting the experimental breakthrough curves to Thomas and Yan models. CF exhibited the greatest maximum sorption capacity (40 mg g$^{-1}$) besting the commercial activated charcoals, while CM was established as the best biochar (7.2 mg g$^{-1}$), with similar results to NGAC (12 mg g$^{-1}$) but worse than GAC (36 mg g$^{-1}$). The contribution of cation exchange in Sm sorption was confirmed to be significant for most materials based on the analyses of cations leached during continuous-flow sorption experiments. Maximum sorption capacities derived from Langmuir fitting correlated well with maximum sorption capacities obtained from continuous-flow experiments. Both methods were confirmed to be suitable to determine the maximum Sm sorption capacity of the materials and then to propose the most suitable materials that can act as alternative to commercial activated charcoals.

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1. Introduction

Lanthanides (LN) are considered contaminants of emerging concern. They are present in fertilisers (Otero et al., 2005) and in industrial activities producing lightning devices and magnets, among others (Goonan, 2011). Recently, rising demand and difficulties associated with recycling (Jowitt et al., 2018) have led to an increase in LN environmental levels at worldwide scale. Amongst LN, La, Ce, Sm and Gd are the most relevant elements due to their large impact in soils, sediments, and water compartments. Currently, areas in central and south Africa and America are facing higher concentrations of LN in soils near industrial and mining areas than historical background records (Adeel et al., 2019). Clear signs of anthropogenic LN in water and soils have also been reported around Europe (Kulaksiz and Bau, 2013; Rogan et al., 2013; Ding et al., 2014; Tan et al., 2015). Whereas sorption parameters of the tested materials. Finally, a proposal is made of the most suitable materials for the treatment of LN contaminated waters.

2. Materials and methods

2.1. Materials

Four biochars produced by slow pyrolysis at a temperature of 350 °C, heating rate of 5 °C min⁻¹, and residence time of 70 min (Deoumer et al., 2015) were used in this work. Their feedstocks were: castor meal (CM), eucalyptus forest residues (CE), sugarcane bagasse (SB), and green pericarp of coconut (PC). Biochars were sieved to a particle size <2 mm before analyses. More information about the materials is given in Section 1 of Supplementary Material.

Additionally, three carbon-rich materials were used to compare their Sm sorption capacity with that of biochars: coal fines (CF), and two commercial activated charcoals supplied by Merck: an untreated activated charcoal (GAC) and the steam-activated charcoal Norit® for potable water processing (NGAC). CF was sieved to <2 mm before analyses, whereas GAC and NGAC were analysed as received (GAC <2 mm; NGAC <1 mm).

The material’s characterisation consisted in the analysis of total carbon, hydrogen, and oxygen (%C, %H, %O); total organic carbon (TOC), cation exchange capacity (CEC), pH at the point of zero charge (pH psyche), specific surface area (SSA) at a particle size <2 mm and functional groups identification by Fourier-transform infrared spectroscopy (FT-IR) of materials before and after batch sorption experiments. More details about the physicochemical characterisation of materials is given in Section 2 of Supplementary Material.

2.2. Batch sorption experiments

2.2.1. Sorption isotherms

Stock Sm solutions were prepared by dissolving weighed amounts of Sm(NO₃)₃·6H₂O (Merck). Batch sorption experiments were performed in 80 mL polypropylene tubes. Two-gram samples of the materials were end-over-end shaken for 24 h (a suitable contact time to reach equilibrium (Fristak et al., 2017), as 6–8 h have been reported as enough to complete the sorption process (Kitäyahali et al., 2010; Kolodynska et al., 2013)) with 50 mL of Sm stock solutions, at initial concentrations within 0.06–10 mg L⁻¹ range for biochars and 0.06–50 mg L⁻¹ range for the rest of carbon-rich materials. Suspensions were centrifuged at 10,000 rpm for 15 min with a Beckman J2-HS Centrifuge. The resulting supernatants were decanted off and filtered through 0.45 μm nylon filters. Filtered supernatants were acidified to 1% HNO₃ and stored at 4 °C until analysis of Sm and major cations (Ca, Mg, K, Na).

Blank experiments were also performed equilibrating materials with double deionised water. Resulting supernatants were characterised in terms of dissolved organic carbon (DOC), pH, and water-soluble Sm, Ca, Mg, K, and Na.

The Sm sorbed concentration (C_{sorb}, mg kg⁻¹) was calculated from the initial (C₀, mg L⁻¹) and equilibrium (C_{eq}, mg L⁻¹) solution.
concentrations using Eq. (1):

\[ C_{\text{res}} = (C_i - C_{eq}) \cdot V/m \]  

(1)

where \( m \) is the mass of material (kg) and \( V \) is the volume of solution added (L).

The solid-liquid distribution coefficient, \( K_d \) (L kg\(^{-1}\)), was calculated as the ratio between \( C_{\text{res}} \) and \( C_{eq} \) (Eq. (2)):

\[ K_d = \frac{C_{\text{res}}}{C_{eq}} \]  

(2)

In addition, sorption percentages (S, %) were calculated as follows:

\[ S = \frac{(C_i - C_{eq})}{C_i} \cdot 100 \]  

(3)

2.2.2. Fitting of sorption isotherms

The experimental values of \( C_{eq} \) and \( C_{\text{res}} \) obtained at increasing initial Sm concentrations were used to construct the sorption isotherms, which were subsequently fitted to the Langmuir model (Eq. (4)):

\[ C_{\text{res}} = b \cdot K_d \cdot C_{eq} / (1 + K_d \cdot C_{eq}) \]  

(4)

where \( b \) (mg kg\(^{-1}\)) estimates the maximum sorption capacity, which is related to the amount of available sorption sites of a given material, and \( K_d \) (L mg\(^{-1}\)), the Langmuir constant, represents the bonding energy of the available sites and it is related to the slope of the initial linear part of a Langmuir sorption isotherm. More information about the data treatment is given in Section 3 Supplementary Material.

2.2.3. Desorption test to evaluate sorption reversibility

The desorption tests were performed under the same conditions as sorption experiments, at three concentration levels (0.06, 1, and 6 meq L\(^{-1}\)). The remaining mass of material after the sorption experiments was dried at 40°C until a constant weight was achieved experimentally (Yan et al., 2001; Xu et al., 2013). The Yan model has recently been used to describe the sorption of cations in continuous flow sorption columns (Araneda et al., 2011) and it assumes negligible axial dispersion in the column and considers an extremely small external and internal diffusion resistances during the sorption process (Thomas, 1948). The model is described by the following non-linear equation (Eq. (7)):

\[ q_{exp} = q_{exp,max} / m = \left( \frac{m_{i}}{m_{i} - \sum_{i=1}^{n} m_{i}} \right) / \left( \frac{C_{eq} \cdot F \cdot t}{\sum_{i=1}^{n} (C_{eq} \cdot F \cdot t)} \right) \]  

(7)

where \( m_{i} \) (mg) is the mass of Sm sorbed at time \( t \) obtained from the calculation of the Sm mass input \( m_{i} \) and output \( m_{i} \cdot F \) (L min\(^{-1}\)) is the flow rate; and \( f \) (min) is the elapsed time with which the fraction was collected. If the time corresponds to the total operation time, the maximum sorption capacity \( q_{exp,max} \) is obtained.

2.3. Continuous-flow sorption experiments

2.3.1. Obtention of breakthrough curves

The set-up consisted in a column (1.6 cm internal diameter, 10 cm length) packed with 3–3.5 g of material, with silica filters on column top and bottom. The solutions were dispensed by a peristaltic pump (GLISON Minipuls 3) connected to the column. The packed material was first preconditioned with double deionized water for 20 min. Then, Sm solutions were pumped and effluent fractions were automatically collected with a fraction collector (GLISON FC 204) at specified time intervals, every 10 min from the start of the experiment up to 180 min and every 40 min from 180 min until the end of the experiment. A detailed scheme is presented in Fig. S1 in Supplementary Material. The total operation time (1200–2000 min) was adapted according to the sorption capacity that materials exhibited in previous batch assays. Collected fractions were acidified with a 1% HNO\(_3\) concentration and stored at 4°C until analysis.

To check whether initial conditions of flow rate and Sm concentration affect the assessment of the maximum sorption capacities of the materials, previous experiments with selected materials (PC and CF) were carried out. When testing flow rate, the experimental conditions were 0.25, 0.5, and 1 mL min\(^{-1}\), at a Sm initial concentration of 5 meq L\(^{-1}\). When testing the effect of initial Sm concentration, experimental conditions were 1, 2 and 5 meq L\(^{-1}\) for PC, and 5, 7.5 and 10 meq L\(^{-1}\) for CF, at a flow rate of 0.5 mL min\(^{-1}\) for the two materials.

To obtain the maximum sorption capacities of the materials within a reasonable operational time, the following conditions were used according to the sorption capacities obtained from the above-mentioned batch experiments: SB was assayed at 2 meq L\(^{-1}\) and 0.25 mL min\(^{-1}\); CM, CE, PC at 5 meq L\(^{-1}\) and 0.25 mL min\(^{-1}\); and CF, GAC, NGAC at 10 meq L\(^{-1}\) and 0.5 mL min\(^{-1}\).

The breakthrough curves were obtained by plotting the ratio between Sm concentration at time \( t \) and the initial Sm concentration \( C_{eq} \) versus time. More information about the possible different profiles of the breakthrough curves is given in Fig. S2 in Supplementary Material.

The sorbed Sm concentration \( q_{exp} \) at time \( t \) was obtained by mass balance, following Eq. (6):

\[ q_{exp} = m_{i} / m = \left( \frac{m_{i}}{m_{i} - \sum_{i=1}^{n} m_{i}} \right) \]  

(6)

where \( m_{i} \) (mg) is the mass of Sm sorbed at time \( t \) obtained from the calculation of the Sm mass input \( m_{i} \) and output \( m_{i} \cdot F \) (L min\(^{-1}\)) is the flow rate; and \( f \) (min) is the elapsed time with which the fraction was collected. If the time corresponds to the total operation time, the maximum sorption capacity \( q_{exp,max} \) is obtained.

2.3.2. Elucidating the contribution of the cation exchange to Sm sorption

To assess the contribution of the cation exchange mechanism to Sm sorption, blank experiments with the materials were conducted to quantify the washed-off fraction of major cations (Ca, Mg, K, Na) in the absence of Sm. The blank assays were performed with the same experimental conditions of material mass, flow rate and operational time as those with Sm.

2.3.3. Fitting of breakthrough curves

The breakthrough curves were fitted to Thomas and Yan models to derive sorption parameters that do not depend on the operational time, unlike the previous \( q_{exp} \) quantified by mass balance.

The Thomas model integrates a pseudo-second order reversible kinetics and the sorption Langmuir equation. It assumes negligible axial and radial dispersion in the column and considers an extremely small external and internal diffusion resistances during the sorption process (Thomas, 1948). The model is described by the following non-linear equation (Eq. (7)):

\[ C_t / C_e = 1 / (1 + \exp(K_{th} \cdot (q_{th} \cdot m - C_t \cdot F \cdot t) / F)) \]  

(7)

where \( C_0 \) (mg L\(^{-1}\)) is the initial concentration, \( C_t \) (mg L\(^{-1}\)) the concentration at time \( t \) (min), \( K_{th} \) (L min\(^{-1}\) mg\(^{-1}\)) the Thomas rate constant, and \( q_{th} \) (mg g\(^{-1}\)) the maximum sorption capacity predicted by the model. A limitation of this model is that when the experimental time is zero, the modelled \( C_t / C_0 \) differs from zero, which is not consistent and can lead to predicted maximum sorption capacities deviated from those achieved experimentally (Yan et al., 2001; Xu et al., 2013).

The Yan model has recently been used to describe the sorption of cationic species in continuous-flow experiments (Araneda et al., 2011). It is an empirical model aiming at correcting the Thomas model deviations at short and long times of the breakthrough curve (Yan et al., 2001) due to a \( C_t / C_e \) value which is zero at zero time and an exponential factor adjusting the slope of the curve. It is represented by Eq. (8):

\[ C_t / C_e = 1 - 1 / (1 + (C_0 \cdot F \cdot t / (q_{yan} \cdot m))^a) \]  

(8)

where \( q_{yan} \) (mg g\(^{-1}\)) is the maximum sorption capacity predicted by the model and \( a \) is the dimensionless model parameter.

2.4. Analytical measurements

Sm and major cations (Ca, Mg, K, Na) present in the solutions originated from batch and continuous-flow sorption experiments were determined by inductively coupled plasma optical emission
spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). More details are given in Section 4 of the Supplementary Material.

3. Results and discussion

3.1. Physicochemical characterisation of materials

Main physicochemical properties of the samples were analysed to better discuss Sm sorption mechanisms. Table 1 summarises the main physicochemical properties of the tested materials. The C content increased from CF to biochars and activated charcoal, and derived C/H and C/O ratios were also much higher for activated charcoal due to their low O content. The C/O ratios are related to aromaticity (Suliman et al., 2016) and could affect the sorption capacity. Similar C and TOC values indicated no presence of carbonate phases. Activated charcoal presented the highest SSA, while CF and biochars exhibited much lower values denoting that it might not be the main factor affecting sorption. CEC values were high for all materials, with remarkably high values for CF and GAC, whereas SB and NGAC showed the lowest CEC values among the tested materials. The sum of the exchangeable cations and $\Sigma_{\text{exch}}$/CEC ratios indicated a varying relative CEC occupancy among materials, with PC and GAC exhibiting the highest ratios. pH values ranged from slightly acid (SB) to basic (GAC). For biochars and CF, pH was higher than $pH_{\text{pzc}}$, thus indicating that surfaces were negatively charged due to the ionisation of oxygen-containing functional groups (i.e., carbonyl, carboxylic). Then, materials could establish electrostatic interactions with cations (Qiu et al., 2008). Biochars, especially CM and CE, exhibited the highest DOC values, whereas the lowest were observed for CF and activated charcoal. For all materials, the DOC concentrations were high enough to be able to chelate LN in solution (Xu et al., 2007; Armstrong and Wood, 2012). Finally, water-soluble concentrations of major cations were significant for all materials, with PC and CM showing the highest concentrations, and NGAC having the lowest concentration.

Considering the speciation of Sm at the sorption pH of the different materials, it can be anticipated that precipitation of Sm(OH)$_3$ was not a significant sorption mechanism. Thus, the Sm species that are expected to interact with the materials must be Sm$^{3+}$ and SmOH$^{2-}$.

3.2. Examination of Sm sorption with batch tests

A similar Sm sorption pattern was observed for all materials. A $C_{\text{eq}}$ vs. $C_{\text{conc}}$ Langmuir-shaped sorption isotherm was obtained, which consisted in an increase of $C_{\text{eq}}$ with $C_{\text{conc}}$ until reaching a plateau at high concentrations, indicating the saturation of the sites involved in the Sm sorption and the absence of an on-going precipitation process. Fig. 1 plots the $C_{\text{eq}}$ vs. $C_{\text{eq}}$ and $Q_k$ vs. $C_{\text{eq}}$ sorption isotherms obtained for CM, CF and the activated charcoal GAC. The sorption isotherms of the rest of the materials can be found in Fig. S3 in Supplementary Material.

High initial Sm concentrations were needed to saturate the CF and activated charcoal to evidence the Langmuir sorption pattern. The $Q_k$ vs. $C_{\text{eq,conc}}$ representation showed that $Q_k$ values at the lowest $C_i$ range were lower than expected, which can be attributed to competitive effects for Sm sorption due to the solution components. At this range, $C_{\text{eq}}$ were around $10^{-3}$ meq L$^{-1}$ for biochars, and $10^{-4}$-$10^{-5}$ meq L$^{-1}$ for CF and activated charcoal, then enabling the formation of soluble chelates with DOC. Furthermore, competitive effects could also appear due to a much higher concentration of cations than Sm in solution, especially for CM and PC materials. Then, $Q_k$ increased with the increase in $C_i$, overcoming competitive effects and, subsequently, it decreased with a further $C_i$ increase as sorption sites were saturated. In agreement with the conclusion from speciation studies, precipitation was discarded as sorption isotherms did not show the characteristic pattern for a precipitation phenomenon: a sharp increase in $C_{\text{eq}}$ at a reasonably constant value of $C_{\text{eq}}$.

Table 2 summarizes the sorption parameters derived from experimental data and Langmuir fitting. Maximum $Q_k$ values ($Q_{k,max}$) higher than $10^5$ L kg$^{-1}$ were obtained for the activated charcoal, which are commercial materials prepared for having high sorption characteristics. Values of $Q_{k,max}$ for biochars and CF were higher than $10^4$ L kg$^{-1}$ (except for the SB biochar, probably due to its lowest CEC among biochars and slightly acidic pH). With such high $Q_{k,max}$ values, S$_{max}$ were higher than 99.5% in all cases. Values of $Q_k$ at the lowest initial concentration ($Q_k$ at the lowest concentration) followed a similar sequence among materials to that of $Q_{k,max}$. The lower values of $Q_{k,conc}$ than $Q_{k,max}$ as mentioned before, were attributed to competition effects. Despite the presence of competitive effects at low $C_i$ (more representative of the environmental concentrations range), most biochars (except for SB) could remove more than 97% of Sm from the aqueous solution.

The maximum sorption capacity, derived from the b parameter of the Langmuir model, followed the CEC sequence, except for the NGAC material, for which can be anticipated that cation exchange would not be a relevant mechanism for Sm sorption. The rest of materials presented a good correlation between b and CEC (log-transformed data; R$^2 = 0.87$, p-value < 0.05), with a slope that did not statistically differ from one, suggesting that cationic exchange could be a relevant mechanism for Sm sorption, especially in biochars.

The lack of sorption data in the literature, in addition to the scarce characterisation of materials, hampers the comparison of our results with other studies, which often present treated materials with enhanced sorption capacities (Hadjittofi et al., 2016; Liatsou et al., 2017). The only possible comparison is with Fristák et al. (2017), who reported an europium (Eu) sorption capacity of 0.89 mg g$^{-1}$, much lower than the ones obtained in this work, in an untreated biochar with similar particle size to those of our materials.

Regarding desorption data, the low desorption percentages obtained (from 0.1 to 5.5% in biochars and coal fines, being completely negligible for the activated charcoal) revealed the high irreversibility of the Sm sorption process in the materials. Detailed information is given in Table S1 in Supplementary Material.

| Parameter | CM | CE | PC | SB | CF | GAC | NGAC |
|-----------|----|----|----|----|----|-----|-------|
| C (%)     | 55 | 70 | 65 | 65 | 50 | 75  | 79    |
| H (%)     | 6  | 4  | 4  | 4  | 2  | 0.5 | 0.5   |
| O (%)     | 22 | 26 | 24 | 22 | 21 | 9   | 2     |
| C/H ratio | 0.77 | 1.5 | 1.4 | 1.4 | 2.1 | 13  | 13    |
| C/O ratio | 3.3 | 3.6 | 3.6 | 3.9 | 3.2 | 11  | 53    |
| TOC (%)   | 55 | 65 | 63 | 60 | 43 | 73  | 79    |
| DOC (mg L$^{-1}$) | 1140 | 208 | 94 | 95 | 6.9 | 3.5 | 3.1   |
| pH        | 7.3 | 7.2 | 7.2 | 6.0 | 8.0 | 10.1 | 8.7   |
| $pH_{\text{pzc}}$ | 6.4 | 6.3 | 5.7 | 5.2 | 7.5 | 10.4 | 10.9  |
| SSA (m$^2$ g$^{-1}$) | <1 | <1 | <1 | 1.3 | 7.3 | 580 | 964   |
| CEC (meq kg$^{-1}$) | 101 | 96 | 100 | 52 | 633 | 167 | 45    |
| $\Sigma_{\text{exch}}$ (meq kg$^{-1}$) | 59 | 53 | 67 | 19 | 307 | 102 | 3.5   |
| $\Sigma_{\text{exch}}$/CEC ratio | 0.58 | 0.55 | 0.67 | 0.36 | 0.48 | 0.61 | 0.08  |
| $\text{C}_{\text{exch}}$ (meq kg$^{-1}$) | 31 | 27 | 6.1 | 10 | 218 | 71  | 2.3   |
| $M_{\text{exch}}$ (meq kg$^{-1}$) | 17 | 13 | 9.3 | 2.9 | 59 | 26  | 0.38  |
| $K_{\text{exch}}$ (meq kg$^{-1}$) | 10 | 9.7 | 37 | 5.6 | 29 | 3.4 | 0.15  |
| $N_{\text{exch}}$ (meq kg$^{-1}$) | 0.85 | 2.9 | 15 | 0.74 | 0.96 | 1.8 | 0.67  |
| $\Sigma_{\text{M}_{\text{exch}}}$ (meq L$^{-1}$) | 8.1 | 3.5 | 16 | 1.5 | 2.8 | 3.5 | 0.26  |
| $C_{\text{exch}}$ (meq L$^{-1}$) | 1.4 | 0.63 | 0.042 | 0.45 | 0.33 | 0.40 | 0.13  |
| $M_{\text{exch}}$ (meq L$^{-1}$) | 2.0 | 1.1 | 0.24 | 0.32 | 0.28 | 1.1 | 0.025 |
| $K_{\text{exch}}$ (meq L$^{-1}$) | 4.7 | 1.3 | 10 | 0.70 | 2.1 | 1.5 | 0.003 |
| $N_{\text{exch}}$ (meq L$^{-1}$) | 0.043 | 0.46 | 5.3 | 0.058 | 0.068 | 0.54 | 0.037 |

$\Sigma_{\text{M}_{\text{exch}}} = C_{\text{exch}} + M_{\text{exch}} + K_{\text{exch}} + N_{\text{exch}}$; WS: water soluble;
$\Sigma_{\text{M}_{\text{exch}}} = C_{\text{exch}} + M_{\text{exch}} + K_{\text{exch}} + N_{\text{exch}}$.
3.3. Examination of Sm sorption by continuous-flow experiments

3.3.1. Description and fitting of breakthrough curves

In a first step, PC and CF materials were used to check whether the flow rate and initial Sm concentration affected the final value of $q_{\text{exp}}$. Fig. S4 in the Supplementary Material plots the breakthrough curves and summarises the $q_{\text{exp,max}}$ obtained when varying these conditions. The first plateau was always observed for CF, whereas it was not for PC. The resulting $q_{\text{exp,max}}$ values depended much more on the material than on the experimental conditions. An increase in $F$, keeping $C_o$ constant, did not lead to systematically higher $q_{\text{exp,max}}$ values, which kept relative constant for a given material. Regarding the effect of $C_o$, significant changes on the $q_{\text{exp,max}}$ were not either observed. Then, it was concluded that the maximum sorption capacity of PC and CF was not affected by $F$ or $C_o$ in the range of values tested. These conclusions were extrapolated to all the materials to be tested in this work.

Fig. 2 plots the breakthrough curves obtained for all the materials examined, along with their fittings to Thomas and Yan models. Biochars and activated charcoals revealed similar sorption profiles that were distant from the ideal breakthrough curves assumed by the fitting models, as the first plateau was not generally observed and significant site saturation was noted at short times. A progressive saturation from $C_t/C_o=0.5$ onwards took place, although a complete saturation ($C_t/C_o=1$) was not noticed. Unlike the rest of materials, CF nearly exhibited the ideal profile of a continuous-flow breakthrough curve, with a clear sigmoidal-shaped curve.

Table 3 summarises the values of $q_{\text{exp,max}}$ as well as of the sorption parameters derived from the fitting of the breakthrough curves to Thomas and Yan models. The highest $q_{\text{exp,max}}$ was exhibited by CF, even higher than that of activated charcoals, whereas CM presented the highest among biochars, in agreement with previous results from batch experiments.

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Table 2

| Material | $K_{d,\text{conc min}}$ (L kg$^{-1}$) | $S_{\text{conc min}}$ (%) | $K_{d,\text{max}}$ (L kg$^{-1}$) | $S_{\text{max}}$ (%) | $b$ (meq kg$^{-1}$) |
|----------|-----------------------------------|--------------------------|---------------------------------|---------------------|-------------------|
| CM       | 1750                              | 98.6                     | 48800                           | 99.9                | 169               |
| CE       | 1350                              | 98.2                     | 14900                           | 99.8                | 89                |
| PC       | 859                               | 97.2                     | 75300                           | >99.9               | 127               |
| SB       | 134                               | 84.3                     | 5110                            | 99.5                | 23                |
| CF       | 1570                              | 98.4                     | 87900                           | >99.9               | 746               |
| GAC      | 23500                             | 99.9                     | >10$^7$                         | >99.9               | 647               |
| NGAC     | 12600                             | 99.8                     | >10$^7$                         | >99.9               | 283               |

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Fig. 1. $C_{\text{sorb}}$ vs. $C_{\text{eq}}$ sorption isotherms of CM, CF and GAC (left) fitted to Langmuir model (blue line) and $K_d$ vs. $C_{\text{sorb}}$ sorption isotherms of CM, CF and GAC (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Assuming the non-ideal pattern of the breakthrough curves for most materials in this work, it is expected that both models might show limitations in the fitting of the experimental data and subsequent prediction of sorption parameters. Yan model adjusted the data slightly better than Thomas model, with correlation coefficients generally higher than 0.95, probably due to the above-mentioned Thomas model limitations. Yan model adapts better to a wide range of sorption patterns due to the “a” parameter. Despite the limitations of the Thomas model fitting, the derived $K_{TH}$ parameter was useful to quantitatively estimate the sorption rate towards a final state of saturation of the material. Higher $K_{TH}$ indicated materials which were quickly saturated, such as CE and SB, whereas the opposite (slow saturation rate) was observed for other materials, such as GAC.

Differences between $q_{exp,max}$ and sorption capacities predicted by Thomas and Yan models were observed for a few materials, although the sequence of values among materials agreed. The models generally underestimated the maximum sorption capacity, probably caused by the general absence of ideal sigmoidal-shaped curves. In fact, the models best predicted the maximum sorption capacity for CF, which better adapted to an ideal breakthrough curve.
## 3.4. Assessment of cationic exchange contribution to Sm sorption

The overall concentration of Ca$^{+}$Mg$^{+}$K$^{+}$Na cations was quantified in the solutions originated from the continuous-flow experiments with Sm to assess the contribution of the cationic exchange mechanism to the sorption process. The overall concentration of Ca$^{+}$Mg$^{+}$K$^{+}$Na had two contributions: cations solubilised (washed-off) by water (which are quantified with blank experiments) and cations exchanged with Sm. Therefore, the amount of sorbed Sm (expressed as meq L$^{-1}$) along the experiment can be compared with the Ca$^{+}$Mg$^{+}$K$^{+}$Na concentrations attributed to an exchange process, obtained from the overall concentration minus the washed-off contribution. Details on the comparison between the Sm sorbed and Ca$^{+}$Mg$^{+}$K$^{+}$Na exchanged profiles for all materials are given in Fig. S5 in Supplementary Material.

### Table 3
Sorption parameters derived from the continuous-flow experiments for the tested materials.

| Material | $q_{exp,\max}$ (mg g$^{-1}$) | $k_{th}$ (L min$^{-1}$ g$^{-1}$) | $q_{th}$ (mg g$^{-1}$) | $R^2$ | $a$ | $q_{Yan}$ (mg g$^{-1}$) | $R^2_{Yan}$ |
|----------|----------------|-----------------|----------------|--------|--------|----------------|--------|
| CM       | 7.2            | 0.032           | 5.2            | 0.90     | 1.6 | 4.6 | 0.98         |
| CE       | 4.1            | 0.14            | 1.3            | 0.77     | 1.4 | 1.2 | 0.86         |
| PC       | 3.8            | 0.051           | 1.6            | 0.71     | 0.96 | 1.2 | 0.95         |
| SB       | 0.95           | 0.26            | 0.37           | 0.86     | 1.2 | 0.27 | 0.98         |
| CF       | 40             | 0.032           | 36             | 0.97     | 5.7 | 36  | 0.97         |
| GAC      | 36             | 0.0070          | 25             | 0.89     | 1.2 | 17  | 0.99         |
| NGAC     | 12             | 0.051           | 4.3            | 0.85     | 1.3 | 3.4 | 0.95         |

Fig. 3. A) Changes over time of Ca$^{+}$Mg$^{+}$K$^{+}$Na concentrations in collected fractions in experiments with Sm and without Sm (blank experiments) and B) Mean values of the cationic exchange contribution (%) to Sm sorption.
Fig. 3A plots the changes over time of the overall Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na and washed-off concentrations, whereas Fig. 3B shows the ratio between the exchanged Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na with respect to the sorbed Sm, as a way to estimate the cationic exchange contribution to Sm sorption. As these ratios slightly fluctuated along the operational time, mean ratio values calculated at different operational times are given in Fig. 3B. The contribution of washed-off cations to the overall Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na concentration was generally very large for all biochars. Once Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na concentrations were corrected, a significant relative contribution of cationic exchange to Sm sorption was observed for all tested biochars. CM and PC presented the highest cationic exchange contribution among biochars (78 and 87%, respectively), whereas the contribution was lower for SB and CE materials (25–40%). These values followed the sequence of relative CEC occupancy (see ΣM\textsubscript{exch}/CEC ratios in Table 1), thus confirming the relevant role of the cationic exchange mechanism in biochars. These results were also in agreement with the good correlation between b and CEC parameters, as previously observed in batch sorption experiments. In addition, other relevant mechanisms may play a significant role in Sm sorption by biochars, such as electrostatic interactions, in agreement with the fact that biochar surfaces were negatively charged (Section 3.1), or inner-sphere surface complexation with oxygen-containing groups, which agrees with lanthanide sorption in biochars reported in literature (Kołodnyńska et al., 2018). These functional groups (e.g., carboxylic and carbonyl groups) were confirmed to be present in all biochars, as shown in their FT-IR spectra (Fig. S6 in Supplementary Material), in which C-O and C=O stretching bands, and O-H bending band were observed. These regions of the spectra may be attributed to residual lignin contents in biochars (Horikawa et al., 2019). FT-IR spectra of materials after Sm sorption did not present significant bands’ shifts attributable to sorption mechanisms, hence they are not presented here.

Unlike biochars, CF and GAC exhibited a much lower contribution of the washed-off cations to the overall Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na concentrations, which led to significant contributions of the cationic exchange process (72 and 43%, respectively). However, the systematic differences between Sm and Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na exchanged concentrations observed for GAC material indicated an additional, relevant sorption mechanism. Thus, cation exchange played an important role in the sorption process in CF, especially, but also in GAC material, which agreed with their high CEC values and high relative CEC occupancies. Finally, NGAC presented extremely low Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na exchanged concentrations during all the experiment and the Sm concentration profile differed to that of the Ca\textsuperscript{2+}+Mg\textsuperscript{2+}+K\textsuperscript{+}+Na exchanged concentrations, thus indicating the cationic exchange did not play a role in Sm sorption in this material (1% of contribution, see Fig. 3B). This pattern agreed with its low CEC occupancy (around 8%). No characteristic bands of oxygen-containing functional groups were observed in the FT-IR spectra of GAC and NGAC (Fig. S7A), hence discarding surface complexation sorption mechanism. Therefore, the great sorption exhibited by NGAC must have been caused by an alternative mechanism, such as cation–π interactions attributable to its C/O and then high aromaticity, as previously reported (Sandara et al., 2020), which could also be present in GAC. Apart from the scarcity of bands observed, the spectra of Sm-loaded activated chars did not register significant bands’ shifts attributable to sorption mechanisms.

3.5. Critical comparison of sorption parameters derived from batch and continuous-flow experiments

Maximum sorption capacities derived from continuous-flow experiments (q\textsubscript{exp,max}) and batch sorption tests (b parameter from the Langmuir fitting) were critically compared to finally assess whether the results derived from the two experimental approaches were comparable. Sorption capacities from both sorption methods, expressed in the same units, and the derived correlation can be found in Fig. S7 in Supplementary Material. The correlation equation between the maximum sorption capacities calculated from batch and continuous-flow experiments had a high regression coefficient (R\textsuperscript{2} = 0.98), along with a slope and an intercept that did not statistically differ from one and zero, respectively. Thus, batch experiments exhibited sorption capacities matching with the ones obtained experimentally in continuous-flow for the seven materials tested, hence validating both methods as viable ways to quantify at laboratory level the maximum Sm sorption capacity of target sorbent materials. This correlation confirms that differences between the values obtained by the two methods were much lower than differences among materials, confirming the ability of both methods to screen the sorption capacities of candidate materials. Therefore, the choice between the two methods should be based on other criteria rather than on the quantification of the sorption capacities. If information about the sorption process dynamics and sorption progression in time is to be obtained, continuous-flow sorption experiments will be a suitable choice, whereas batch sorption experiments could be more appropriate when testing a high number of materials in a short period of time to obtain information about not only the quantity of sorption sites but also on their quality regarding target contaminant concentration, based on the quantification of the K\textsubscript{d} parameter.

4. Conclusions

Batch and continuous-flow sorption experiments permitted to satisfactorily evaluate Sm sorption capacities of tested untreated biochars and carbon-rich materials. The two complementary experimental approaches could be used to determine maximum sorption capacities and screen the viability of candidate materials to be used as sorbents. Batch tests also permitted to identify the materials with highest Sm sorption affinity sites (K\textsubscript{d}), whereas sorption percentages exhibited by biochars and coal fines revealed that they could be entirely viable choices to remove Sm from contaminated waters, even without applying any activation treatment to enhance their sorption capacities. Regarding continuous-flow experiments, the non-ideal breakthrough curves obtained made it difficult that Thomas and Yan models could perfectly fit the experimental results, although dynamics of the mechanisms governing sorption could be observed. Cationic exchange was observed to be a relevant mechanism in Sm sorption for all biochars and some carbon-rich materials (CF and GAC), along with other secondary sorption mechanisms proposed, such as surface complexation (for biochars) or cation-π interactions (GAC and NGAC). In this context, results confirm that untreated biochars and coal fines could be satisfactorily applied as a more sustainable and lower cost alternative to commercial activatedchars to remove Sm, and probably other LN, from contaminated waters at concentrations of environmental concern.

CRediT author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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