Ammonium recovery from municipal wastewater by ion exchange: development and application of a procedure for sorbent selection

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SUPPLEMENTARY MATERIAL

Table S1

Physico-chemical characteristics of the tested sorbents. Values were taken from the resin/zeolite datasheet, unless otherwise specified.

Adsorbent	Chabazite / Phillipsite	Zeolite ZSM-5	Amberlyst 15WET	Relite MAC-1	Relite MAC-5
Type	Natural zeolite	Synthetic zeolite	SAC[a]	WAC[a]	WAC[a]
Polymeric structure	-	-	PS-DVB[b]	PS-DVB[b]	Acrylate-DVB[b]
Functional group	-	-	Sulfonic acid	Carboxylic	Iminodiacetate
Ionic form as shipped	-	NH_4^+	H^+	Na^+	Na^+
SiO_2/Al_2O_3 molar ratio	2.8	50	-	-	-
Cation exchange capacity (*meq $g_{dry\ resin}^{-1}$*)[c]	2.4[d]	[e]	4.6[d]	5.3	1.4
Dry/wet weight ratio	0.72[d]	0.65[c]	0.55[d]	0.51[d]	0.44[d]
Particle diameter (μm)	355 – 710	1000-1500	650 – 800	425 – 1180	300 – 1180

[a] SAC: Strong Acid Cation resin; WAC: Weak Acid Cation resin.

[b] PS: polystyrene; DVB: divinylbenzene.

[c] Maximum amount of cations that can be taken up by 1 g of dry sorbent. It corresponds to the total concentration of accessible active sites in the cation exchange sorbent.

[d] Experimentally determined.

[e] Data not available.

Table S2

Adsorbent media pre-treatment procedures and characterization

All sorbent materials were pre-treated according to the following procedure: i) washing 5 times with deionized (DI) water to remove fine particles (100 g L^{-1} of sorbent media, stirring at 250 rpm for 30 minutes); ii) chemical treatment to convert the sorbent to the selected ionic form (Na$^+$, K$^+$ or H$^+$) before the batch or continuous tests; Na$^+$ conversion was performed with two pre-treatments with a 100 g L^{-1} NaCl solution, 250 rpm of stirring for 1 hour; similarly, the K$^+$ form was achieved using a 100 g L^{-1} KCl solution and H$^+$ using a HCl 50 g L^{-1} solution; only for ZSM-5, conversion to H$^+$ was attained by calcination at 450°C for 4 h; iii) double rinse with DI water. All sorbents were eventually filtered with 25 μm cellulose filters with a Whatman's system (GE Healthcare, Chicago, Illinois, USA) connected to a vacuum pump, before being weighed for the experimental tests.

The properties of the most promising sorbent (Chabazite/Phillipsite) were investigated according to the following methods: (a) true density of granules was obtained by helium pycnometer (Multivolume pycnometer 1305, Micrometrics); (b) specific surface area, measured using a Thermo Scientific™ Surfer (Thermo Fisher Scientific, Waltham, MA, USA) by means of nitrogen adsorption at 77 K, was then calculated by the Brunauer–Emmett–Teller (BET) method; (c) crystalline phases were identified by X-ray diffraction (XRD) on the powdered sample, using a Powder Diffractometer Bruker D8 Advance with CuKα radiation (Bruker, Karlsruhe, Germany); the dominant crystalline phases were identified comparing the peaks with the database of the diffractometer; (d) pore size distribution in the 0.007–100 μm range was analysed by mercury intrusion porosimetry using a Thermo Finnigan Pascal 140 and a Thermo Finnigan Pascal 240 (Thermo Fisher Scientific, Waltham, MA, USA).

Table S3

Composition of the Bologna WWTP effluent and Falconara AnMBR effluent, used for the isotherm and continuous flow tests.

Compound	Symbol	Unit	Bologna WWTP effluent	Falconara AnMBR effluent
Ammonium nitrogen	NH_4-N	$mg\ N\ L^{-1}$	3.9 ± 0.3[a]	17 ± 2[a]
Sodium	Na^+	$mg\ L^{-1}$	101 ± 8	214 ± 7
Potassium	K^+	$mg\ L^{-1}$	13 ± 2	24 ± 3
Magnesium	Mg^{2+}	$mg\ L^{-1}$	14 ± 1	32 ± 1
Calcium	Ca^{2+}	$mg\ L^{-1}$	83 ± 6	97 ± 9
Phosphate	PO_4-P	$mg_P\ L^{-1}$	1.0 ± 0.2	2.3 ± 0.2
Chloride	Cl^-	$mg\ L^{-1}$	150 ± 12	311 ± 3
Nitrate	NO_3^-	$mg_N\ L^{-1}$	6.7 ± 0.5	2.5 ± 1
Sulphate	SO_4^{2-}	$mg\ L^{-1}$	104 ± 9	45 ± 1
Biological oxygen demand	BOD_5	$mg_{O2}\ L^{-1}$	15 ± 2	42 ± 1
Chemical oxygen demand	COD	$mg_{O2}\ L^{-1}$	29 ± 2	38 ± 5
Total suspended solids	TSS	$mg\ L^{-1}$	5.3 ± 0.6	0.010 ± 0.001
Density		$mg\ L^{-1}$	1.00 ± 0.002	1.00 ± 0.002
pH	pH	-	7.9 ± 0.2	7.9 ± 0.2

[a] Before conducting the lab scale tests, this effluent was spiked with NH_4Cl to achieve 40 $mg_N\ L^{-1}$.

Table S4

Adsorption kinetic tests

Preliminary kinetic tests were performed to evaluate the time needed to reach equilibrium between the NH_4^+ concentration in the liquid and solid phases for each adsorbent material tested in this study. These tests were conducted in 250-mL glass bottles with the synthetic NH_4-N solution and the Bologna WWTP effluent (Table S3), at 20-22°C, pH = 7-8, stirring at 200 rpm. The resin concentration was set to 1.1 g dry resin/L both in the kinetic tests and in the single-point isotherm tests, as a compromise between the opposite needs to ensure a satisfactory solid-liquid mixing in the orbital shaker and to attain a sufficiently high decrease in liquid phase concentration between the initial and the equilibrium values, and therefore a sufficiently low experimental error. Each test was set up in triplicate. Samples were taken every 5 minutes for the first 15 minutes, every 15 minutes until the first hour, every 30 minutes up to the 2nd hour and every 60 minutes up to the 7th hour. A final point was taken after 24 h. The results indicated that the time to reach a concentration equal to 99% of the asymptotic value measured at 24 h varied between 1 h (Amberlyst 15WET, Na^+ form, synthetic solution) and 5 h (Chabazite/Phillipsite, Na^+ form, Bologna WWTP effluent). The equilibrium time for the subsequent isotherm tests was thus cautiously set at 7 h.

Table S5

Operating conditions of the isotherms performed with Amberlyst 15WET in Na^+ form and Chabazite/Phillipsite in Na^+ and K^+ forms.

Sorbent	Amberlyst 15WET		Chabazite / Phillipsite			Chabazite / Phillipsite	
Ionic form	Na^+		Na^+			K^+	
Solution or WWTP effluent used	NH_4Cl solution	Bologna WWTP effluent	NH_4Cl solution	Bologna WWTP effluent	Falconara AnMBR effluent	NH_4Cl	Falconara AnMBR effluent
N equilibrium concentration (mg_N L^{-1})	2.8 - 800	2.8 - 740	2.8 - 740	2.8 - 740	1.5 - 400	4.2 - 430	2.8 - 460
Sorbent conc. ($g_{dry\ resin}$ L^{-1})	1.3	1.3	1.8	2	2	2	2

Table S6

Modeling of the adsorption isotherm tests

Experimental isotherms were interpolated by means of the Langmuir and Freundlich models:

$$\textbf{\textit{Langmuir}} \qquad C_{S,eq} = \frac{C_S^\infty \cdot C_{L,eq}}{\frac{1}{K_{eq}} + C_{L,eq}}$$

$$\textbf{\textit{Freundlich}} \qquad C_{S,eq} = K_F \cdot C_{L,eq}^{1/n}$$

where: $C_{S,eq}$ (g_N $g_{dry\ resin}^{-1}$) and $C_{L,eq}$ (g_N L^{-1}) indicate respectively the amount of sorbed N-NH4$^+$ per unit mass of adsorbent and the N-NH4$^+$ concentration in the liquid phase at equilibrium; C_S^∞ (g_N $g_{dry\ resin}^{-1}$) the maximum amount sorbed per unit mass of adsorbent, corresponding to a complete monolayer on the adsorbent surface; $K_{eq,}$ ($L_{pore\ volume}$ mg_N^{-1}) the constant related to the affinity between the binding sites and N-NH4$^+$; K_F ($mg_N^{1-1/n}$ $L^{1/n}$ $g_{dryresin}^{-1}$) the sorption capacity in the Freundlich model; $1/n$ (-) the sorption intensity in the Freundlich model.

The equilibrium N concentration in the solid phase, $C_{S,eq}$ (mg_N $g_{dry\ resin}^{-1}$), was determined as:

$$C_{S,eq} = \frac{(C_{L,0} - C_{L,eq}) \cdot V_L}{m_S}$$

where m_S is the mass of dry adsorbent ($g_{dry\ resin}$ L^{-1}), $C_{L,0}$ and $C_{L,eq}$ the initial and final NH$_4$-N concentration in the liquid phase (mg_N L^{-1}) and V_L the liquid volume (L).

The model parameters were estimated by non-linear least squares regression of the calculated solid phase concentrations ($C_{S,eq,calc,i}$) to the corresponding experimental values ($C_{S,eq,i}$). The best-fitting model was selected on the basis of the correlation coefficient R^2, defined so as to take into account the number of model parameters:

$$R^2 = 1 - \left(\frac{\sum_{i=1}^{N}\left(C_{S,eq,i} - C_{S,eq,calc,i}\right)^2}{N - P - 1} \right) \Bigg/ \left(\frac{\sum_{i=1}^{N}\left(C_{S,eq,i} - C_{S,eq,m}\right)^2}{N - 1} \right)$$

where N indicates the number of experimental tests in the studied isotherm, and P the number of model parameters.

Table S7

Adsorption breakthrough curves operational conditions and simulation with the Thomas model

The adsorption operational conditions were selected on the basis of the following elements: i) the pH was maintained equal to the natural one of the tested effluents (7.9); this value represents a suitable compromise between the contrasting needs to maintain the pH higher than the point of zero charge of the tested sorbents, to ensure a very low H^+ concentration and to shift completely the NH_4^+/NH_3 equilibrium towards NH_4^+; ii) temperature was maintained constant at 22°C through a jacket connected to a temperature-controlled bath, in order to favor the exothermic NH_4^+ sorption; iii) the EBCT was varied in the 4-10 minutes range, in order to find a compromise between the reduction in column size attainable in real applications by reducing the EBCT and the risk to reduce ion exchange performances if an excessively low EBCT leads to a marked increase of the non-equilibrium mass transfer zone in the column.

The NH_4^+ adsorption breakthrough curves were simulated by means of the Thomas model:

$$C_L(x,t) = \frac{C_{L,0}}{1 + e^{\left[C_{S,eq} \cdot m \cdot \frac{x}{L} - C_{L,0} \cdot Q \cdot t + C_{L,0} \cdot BV \cdot \varepsilon \cdot \frac{x}{L} \cdot \frac{K_{Th}}{Q} \right]}}$$

where $C_L(x,t)$ and $C_{L,0}$ (mg_N L^{-1}) are respectively the N-NH_4^+ liquid-phase concentrations at height x (m) in the column at time t (h) and the average concentration fed to the column during the test, m (g_{dry}) the mass of dry resin packed in the column, x (m) the zeolite bed height in a generic point of the column, L (m) the maximum zeolite bed height (0.60 m), Q (L h^{-1}) the flowrate fed to the column, BV (L) the resin bed volume, ε (-) the effective porosity of the packed bed, $C_{S,eq}$ (mg_N $g_{dry\ resin}^{-1}$) the resin capacity at saturation (i.e. in equilibrium with $C_{L,0}$) and K_{Th} (L h^{-1} mg^{-1}) the Thomas rate constant. The best-fitting values of $C_{S,eq}$ and K_{Th} were estimated using the Solver add-in in Microsoft Excel, using for the other parameters input values derived from experimental measurements or from elaboration of the fluid-dynamic tests.

Table S8

Best estimates of the parameters relative to the fitting with the Thomas model (Table S7) of the breakthrough tests conducted with Chabazite/Phillipsite and with Falconara AnMBR effluent, at EBCTs varying in the 4-10 min range. The operational conditions and performance parameters relative to each test are reported in Table 2.

Test ID	$C_{S,eq}$	K_{Th}	R^2
	$mg_N\ g_{dry\ resin}^{-1}$	$L\ h^{-1}\ mg^{-1}$	
BO-Na$^+$-10min	8.1±0.2	0.0068±0.0009	0.991
FA-K$^+$-10min-a	5.7±0.1	0.0068±0.0008	0.993
FA-K$^+$-10min-b	5.4±0.1	0.0091±0.0006	0.985
FA-K$^+$-10min-c	6.2±0.1	0.0083±0.0006	0.992
FA-K$^+$-8min	5.9±0.1	0.0092±0.0007	0.983
FA-K$^+$-6min	6.1±0.1	0.0105±0.0008	0.994
FA-K$^+$-4min	7.3±0.2	0.0107±0.0013	0.988
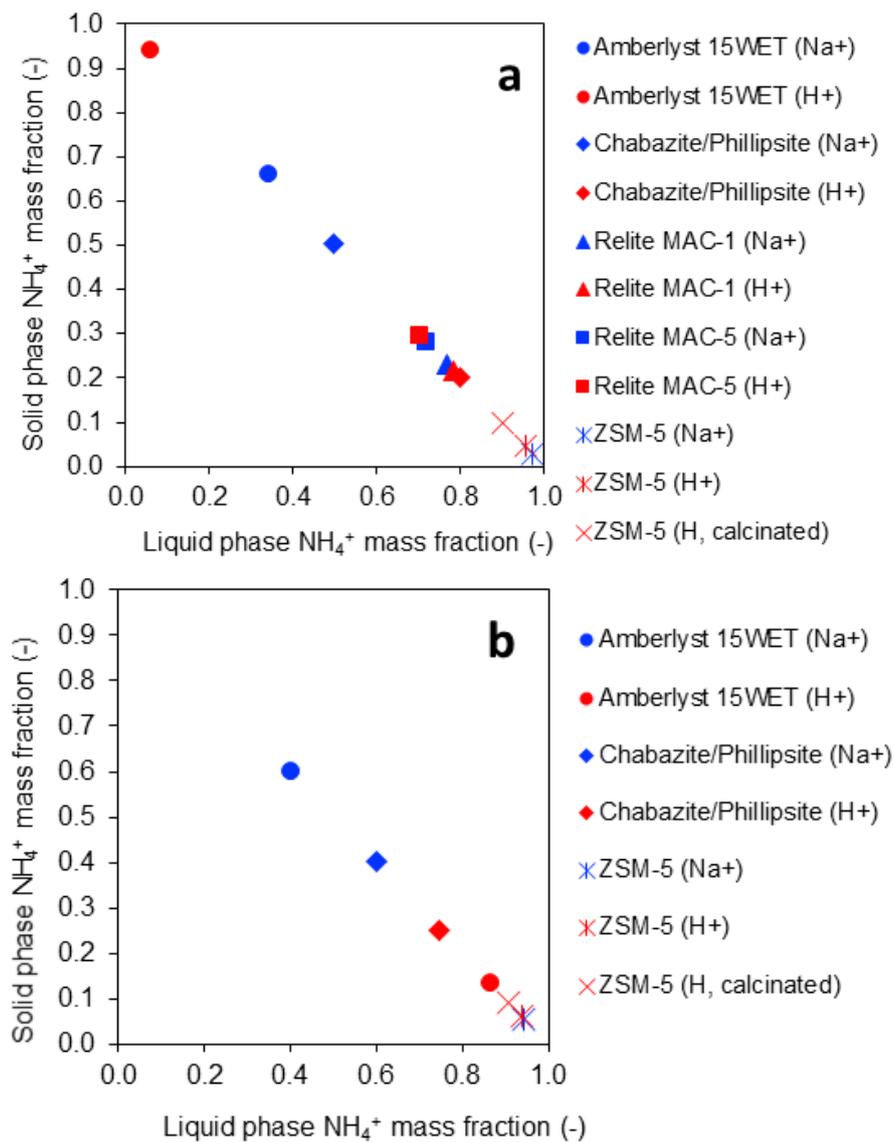
Fig. S1. Single point batch tests performed with Amberlyst 15WET, Chabazite/Phillipsite and ZSM-5, using (a) a synthetic solution containing NH4+ as the only cation and (b) the Bologna WWTP effluent.
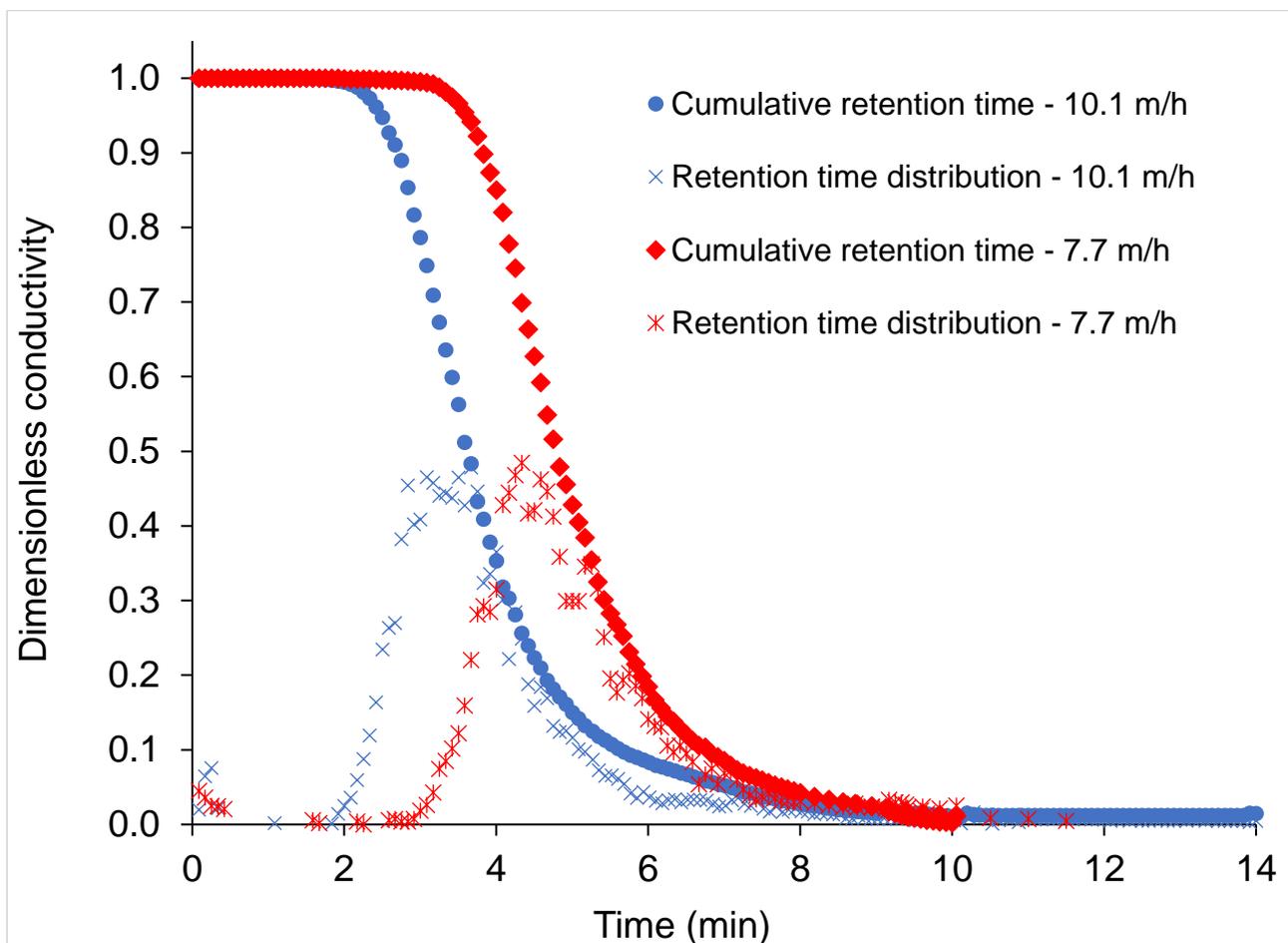
Figure S2. Cumulative retention time and retention time distribution curves obtained in the frontal analysis tests performed in the 60-cm column packed with Chabazite/Phillipsite. Tests performed at superficial velocities of 7.7 and 10.1 m h^{-1}.
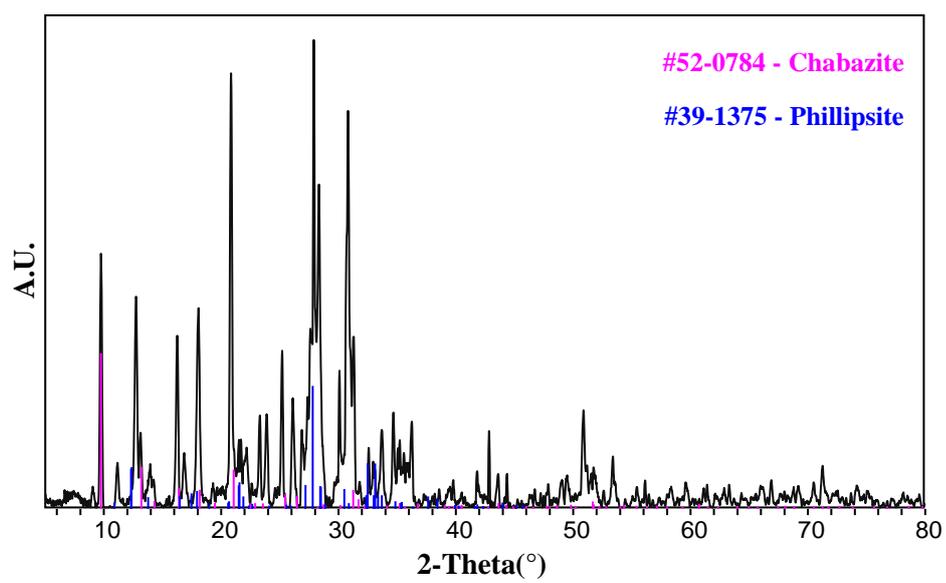
Figure S3. Powder XRD diffraction pattern of Chabazite/Phillipsite.
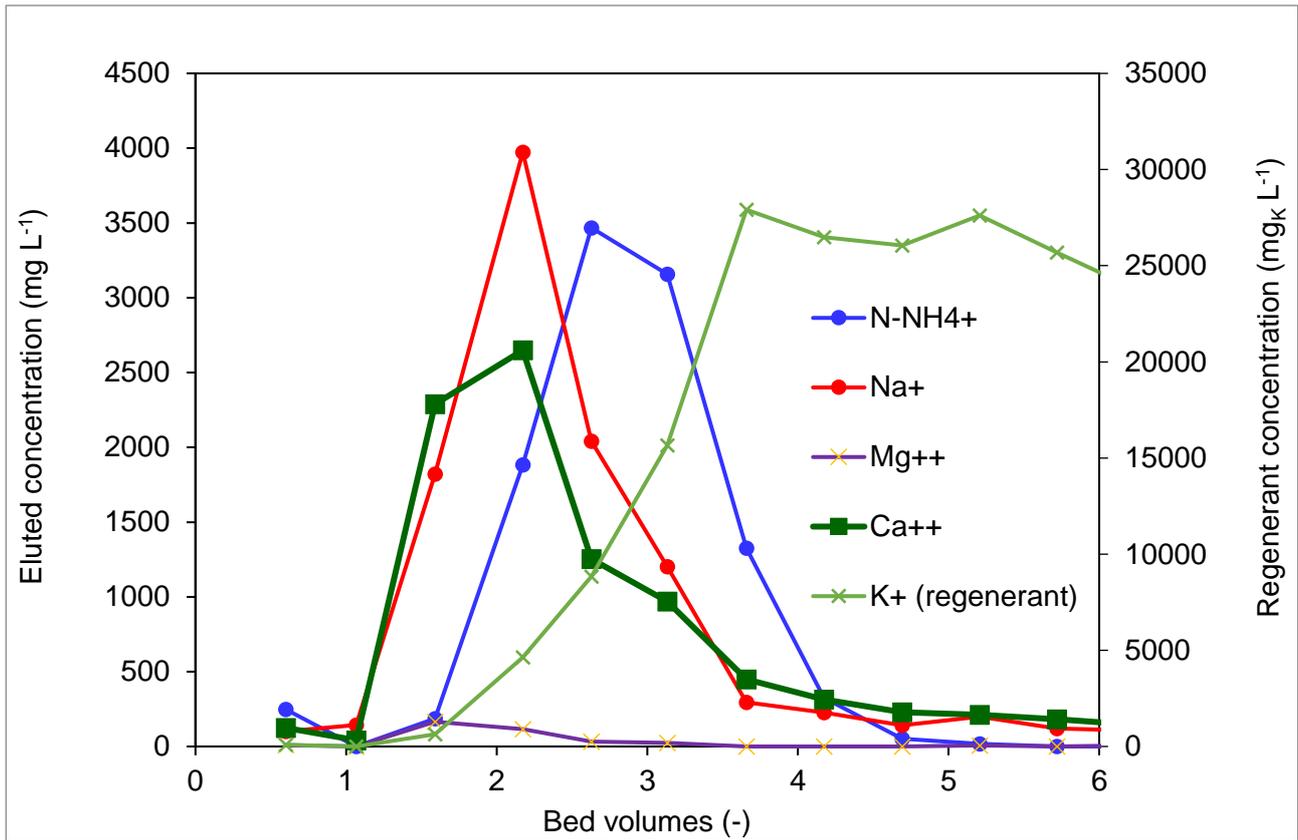
Figure S4. Breakthrough curves relative to the different cations, during the desorption of Chabazite/Phillipsite conducted with KCl 50 g/L, at an EBCT of 60 minutes (test FA-K$^+$-10min-c, Table 2).