



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

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ABSTRACT

Ion exchange represents one of the most promising processes for ammonium recovery from municipal wastewater (MWW). However, most previous studies on ammonium ion exchange did not optimize the process or evaluate its robustness under real operational conditions. This experimental study aimed at (i) developing a procedure for the selection of a sorbent for selective ammonium removal/recovery from MWW, (ii) validating the procedure by applying it to several sorbents, (iii) performing a preliminary optimization and robustness assessment of ammonium removal/recovery with the selected sorbent. The application of the procedure to natural and synthetic zeolites and a cation exchange resin confirmed that batch isotherm tests need to be integrated by continuous-flow tests. The selected sorbent, a natural mixture of Chabazite and Phillipsite, resulted in high performances in terms of cation exchange capacity ($33 \text{ mg}_N \text{ g}_{\text{dry}}^{-1} \text{ resin}$), ammonium operating capacity ($5.2 \text{ mg}_N \text{ g}_{\text{dry}}^{-1} \text{ resin}$), ammonium recovery yield (78–91%) and selectivity towards ammonium. The process performances resulted stable during 7 adsorption/desorption cycles conducted with MWW treatment plant effluents in a 60-cm column. The switch to a highly saline effluent produced in a hotspot of seawater intrusion did not determine significant changes in performances. Contact time was reduced to 6 min without any decrease in performances. Potassium – well tolerated by crops – was selected as the regenerating agent, in the perspective to produce a desorbed product to be re-used as fertilizer. The study shows that Chabazite/Phillipsite has a high capacity to recover ammonium from MWW in a circular economy approach.

1. Introduction

Wastewater (WW) is increasingly considered as a source of water, energy and fertilizing nutrients such as nitrogen and phosphorous [1–3]. Nitrogen (N) is a key element for the growth of crops and plants [2]. The global demand for chemical fertilizers production is increasing with an 1.8% annual rate [4]. In addition, most of the N used in agriculture is fixed by the energy-intensive Haber Bosch process, which consumes 1–2% of annual global energy supply [4]. Moreover, only 17% of the ammonium produced by the Haber Bosch process is consumed for crop fertilization [5], the remaining is lost to atmosphere and freshwaters,

causing eutrophication [6].

N in wastewater exists in many forms: ammonium (NH_4^+), ammonia (NH_3), nitrogen gas (N_2), nitrite (NO_2^-), nitrate (NO_3^-) and organic N. Ammonium represents the main form in municipal WW (MWW) and the most polluting in the hydrosphere [7]. Ammonium is typically removed from MWW through the nitrification/denitrification process that converts it into gaseous N_2 [5]. However, this biological process is characterized by a relevant energy consumption and does not allow any N recovery.

On the other hand, several technologies allow the removal and recovery of NH_4^+ from WW in a circular economy perspective. Suitable

Abbreviations: AnMBR, anaerobic membrane bioreactor; BT, breakthrough; BP, breakpoint; BV, bed volume; CEC, cation exchange capacity; d_p , average resin particle diameter; EBCT, empty bed contact time; HETP, height equivalent to a theoretical plate; MWW, municipal wastewater; SAC, strong acid cationic resin; WAC, weak acid cationic resin; WW, wastewater; WWTP, wastewater treatment plant.

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technologies when ammonium is present at high concentrations are stripping, membrane processes and chemical precipitation as struvite [8].

Stripping, consisting in the removal of ammonium from MWW by its conversion in gaseous NH_3 , requires a uniform temperature greater than 15°C , a continuous high aeration and chemicals for maintaining $\text{pH} > 9.5$. Therefore, it is generally not applied in large-scale wastewater treatment plants. Membrane separation requires a pressure gradient as driving force for ammonium flow. The need to frequently replace membranes determines a high operational and maintenance cost. Ammonium can also be recovered simultaneously with phosphate at alkaline condition via struvite precipitation. However, the large-scale application of precipitation is affected by the presence of other ions and by the difficult market placement of struvite experienced in several countries [8].

When NH_4^+ is at medium/low concentration, as in the case of municipal wastewater (MWW), adsorption and ion-exchange (IE) are very promising technologies for N recovery [7]. The exchanger cation of the adsorbent material is replaced with ammonium. A temporary binding is established, that can be dissolved when the regeneration step leads to the exchange of ammonium with a regenerating cation. Compared to other techniques, IE and adsorption present favorable characteristics: high affinity towards ammonium, high removal efficiency, low-cost, simplicity of application and operation. Despite the operational cost associated to the periodic replacement of the adsorbent material and to the chemicals required for regeneration, IE and adsorption have a very high potential for full scale application in wastewater treatment plants to recover ammonium [8].

Many materials have been proposed for this purpose: natural minerals such as zeolites [9,10], and commercial ion exchange polymeric resins [11–14].

Zeolites are tectosilicates consisting of 3-dimensional frameworks of $\text{SiO}_4^{4-}\text{-AlO}_4^{5-}$ tetrahedra. In zeolite structures some quadrivalent Si is replaced by trivalent Al, giving rise to a deficiency of positive charge which is counterbalanced by mono- and divalent exchangeable cations. Thanks to their low cost, large availability, high cation exchange capacity (CEC), selectivity towards ammonium and ease of regeneration, several zeolites were proposed for NH_4^+ removal, in particular Clinoptilolite [10,15], Mordenite [16,17] and Chabazite [18,19]. The NH_4^+ adsorption efficiency of zeolites is affected by mineral lattice structure [9], temperature, pH , NH_4^+ concentration [18,20], pre-treatments [21–23].

Recently, several attempts were made to synthesize or engineer zeolites to increase their capacity towards NH_4^+ . Zeolite-N and ZSM-5 are among the most promising synthetic or engineered zeolites for ammonium recovery from MWW. Zeolite-N has a high ammonium exchange capacity, up to $55 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ [24], however it's no more commercially available [23]. Although chemical synthesis obtains more uniform and pure materials than natural zeolites in terms of reticular structures, pore size and channels, natural zeolites have greater mechanical strength. Langwaldt [19] studied the behavior of Chabazite and 7 different Clinoptilolites by means of adsorption isotherms and continuous tests conducted with synthetic ammonium solutions, reporting a $36 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ CEC for a Chabazite, and $12\text{--}19 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ for 7 Clinoptilolites; Leyva-Ramos [18] obtained CECs in the $34\text{--}41 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ range for a Chabazite tested in different cationic forms, in batch conditions and synthetic ammonium solution; Guida [23] estimated $52 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ for a natural Clinoptilolite and $60 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ for an engineered Zeolite-N. Zhao reported in batch conditions a CEC of $16 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ for a synthetic zeolite obtained from coal fly ash [25]; Liu obtained a CEC of $25 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ for a zeolite P1 synthesized from fly ash [26]; Lv reported $17 \text{ mg}_\text{N} \text{ g}_\text{dry}^{-1} \text{ resin}$ for a Sodalite-type N-A-S-H synthesized from fly ash [27]. However, most of the previous works were conducted by batch tests and using synthetic ammonium solutions. Furthermore, very few works focused on the desorption and recovery of ammonium from the adsorbent material.

The main novelties of this work are: (i) the assessment of the NH_4^+ adsorption/recovery performances from actual MWW using a natural zeolite consisting in a mixture of Chabazite and Phillipsite, whereas the previous works conducted with natural zeolites were conducted mainly with synthetic solutions and never with natural mixtures of different types of zeolites (e.g., [18,19]); (ii) the assessment of the robustness of a continuous-flow NH_4^+ adsorption/recovery process, by comparing the performances obtained with different WW types, including a highly saline one coming from a hotspot of seawater intrusion (Falconara, Italy), whereas the previous studies were conducted mainly with synthetic solutions and never with two different wastewater types; and (iii) the assessment of the stability of the NH_4^+ adsorption / recovery process with a natural zeolite during repeated cycles conducted with actual MWW, whereas only one previous study evaluated the process long-term stability using an engineered synthetic zeolite [23].

This experimental study aimed at (i) developing a procedure for the selection of a suitable sorbent for the selective removal and recovery of NH_4^+ from MWW, articulated in a combination of batch and continuous-flow tests, (ii) validating the procedure by applying it to a range of sorbents including natural and synthetic zeolites and a cation exchange polymeric resin, and (iii) performing a preliminary optimization and a robustness assessment of the NH_4^+ removal/recovery process conducted with the selected sorbent.

2. Materials and methods

2.1. Adsorbent media characteristics and pre-treatment procedures

Different sorbents were tested in this work: a natural Italian zeolite composed of a natural mixture of Chabazite and Phillipsite (Apostolico & Tanagro s.n.c., Naples, Italy), the synthetic ZSM-5 zeolite (ThermoFisher Scientific, Waltham, Massachusetts, USA), the strong acid cationic (SAC) resin Amberlyst 15WET (Dow Chemicals, Midland, Michigan, USA) and the weak acid cationic (WAC) resins Relite MAC-1 and Relite MAC-5 (Resindion, Mitsubishi Chemical, Tokyo, Japan). The main characteristics of these materials are reported in Table S1, Supplementary Material. The size distributions of the commercial resins were in the $0.3\text{--}1.2 \text{ mm}$ range. Chabazite/Phillipsite was sieved at $0.355\text{--}0.710 \text{ mm}$. This range was chosen as a compromise between the opposite needs to curb packed column clogging and pressure drop on one side, and to minimize preferential pathways and wall effects on the other side. The pre-treatment procedures applied to the sorbent materials and the methods applied to investigate their properties are described in Table S2, Supplementary Material.

2.2. Wastewater and synthetic solution composition

Isotherms and continuous flow tests were conducted with 3 types of solutions and WWs: i) a synthetic solution of different concentrations of NH_4Cl in de-ionized water, used to perform isotherms in the absence of cationic competitors; ii) the effluent of the Bologna (Italy) full scale municipal wastewater treatment plant (WWTP), sampled after secondary treatment and disinfection; iii) the effluent of a pilot-scale anaerobic membrane bioreactor (AnMBR) that treats the saline MWW of Falconara Marittima (Italy, [28]), sampled after the membrane module. Both effluents were spiked with NH_4Cl to obtain $40 \text{ mg}_\text{N} \text{ L}^{-1}$ (2.9 mM) so as to mimic the average ammonium content of the effluent of a hypothetical WWTP that does not include a nitrogen removal step. The composition of both effluents is reported in Table S3, Supplementary Material. Moreover, as Falconara is a hotspot of seawater intrusion, the Falconara AnMBR effluent is characterized by double concentrations of Na^+ , K^+ , Mg^{2+} , PO_4^{2-} and Cl^- compared to the Bologna effluent.

2.3. Adsorption isotherm tests

To assess the best performing sorbents to be further tested by means

of isotherms and continuous flow tests, and the more suitable ionic form of each sorbent, a single-point isotherm screening was performed in 250-mL bottles, at an initial N concentration of $40 \text{ mg}_N \text{ L}^{-1}$, at $1.1 \text{ g}_{\text{dry resin}} \text{ L}^{-1}$. Glass bottles were placed in a rotatory shaker (200 rpm, $20\text{--}22^\circ \text{C}$) for 7 h, to reach equilibrium between the NH_4 concentration in the liquid and solid phases. The duration of the experiment was defined based on the results of preliminary kinetic tests (Supplementary Material, Table S4). These single-point tests were performed both with the NH_4Cl solution (pH 7.4) - to assess the sorbed NH_4^+ concentrations in the absence of competition by other cations - and with the Bologna WWTP effluent (pH 7.9; Table S3).

Based on the single-point isotherm results, complete isotherm tests were subsequently performed with the two best performing materials, both with the synthetic NH_4Cl solution and with the two effluents. The isotherm operating conditions are reported in Table S5, Supplementary Material. Glass bottles were placed in a rotatory shaker (200 rpm, $20\text{--}22^\circ \text{C}$) for 7 h. For each isotherm point conducted with WWTP effluent, the desired N initial concentration was reached by mixing 100 mL of effluent with 0.005–1 mL aliquots of different NH_4Cl solutions, so as to maintain the effect of dilution of competing anions at negligible levels ($< 1\%$).

Each test was performed in triplicate and the 95% confidence intervals were calculated from the standard deviation of the mean values. The experimental data were interpolated by means of the Langmuir and Freundlich models. Model equations and best-fit procedures are reported in Table S6, Supplementary Material. Model parameters were estimated by non-linear least squares regression of the calculated N solid phase concentrations to the corresponding experimental values [29].

2.4. Breakthrough tests

2.4.1. Column packing and fluid dynamic characterization

The lab-scale breakthrough (BT) tests were carried out in a PVC column with a total volume of 0.167 L, a total height of 1.26 m and an inner diameter of 13 mm. The column was packed with the sorbent dispersed in a de-ionized water slurry (100 g L^{-1}) following the Rohm and Hass procedure [30]. The resin slurry was added up to a final bed height of 60 cm, the minimum value commonly used in industrial applications. Then, the sorbent was activated in either Na^+ or K^+ form through the elution of 10 bed volumes (BVs) of either NaCl or KCl 100 g L^{-1} with an empty bed contact time (EBCT) of 10 min [9].

The fluid dynamic behavior of each adsorption bed was studied before the adsorption experiments by means of a conventional frontal analysis test conducted with KCl 10% w/v after conditioning the column with a KCl 5% w/v solution. The tests were conducted in the EBCT range applied in the continuous adsorption tests (4–10 min). Electrical conductivity (EC) was measured at the column outlet with a CO11 conductivity probe (VWR, Radnor, Pennsylvania, USA). The packing quality of the resin bed was evaluated in terms of three indicators: i) height equivalent of a theoretical plate (HETP), ii) reduced plate height (HETP/ d_p where d_p is the average diameter of the particles) and iii) asymmetry factor, defined as the ratio between the leading and tailing semi-width of the peak at 10% of the peak height. These indicators were evaluated as described by Frascari et al. [31].

2.4.2. Continuous flow adsorption/desorption breakthrough tests

Several adsorption / desorption tests were conducted with Amberlyst 15WET and Chabazite/Phillipsite in different forms, as illustrated in detail in Sections 3.3 and 3.4. NH_4 -spiked Bologna or Falconara effluent was fed downstream in the column with a Masterflex L/S 0.1 HP 1–100 rpm peristaltic pump (Avantor, Radnor, PA, US). Cation outlet concentrations were normalized by the average inlet concentration.

Adsorption performances were quantified by means of the following indicators, referred to a breakpoint (BP) corresponding to an average concentration of $4 \text{ mg}_N \text{ L}^{-1}$ in the effluent and evaluated as described previously [31–33]: i) number of treated bed volumes (BVs), defined as

(WW volume treated)/(resin BV); ii) NH_4^+ adsorption yield (Y_{ads}), defined as (N mass sorbed at BP)/(N mass fed at BP); iii) resin utilization efficiency (η_{resin}), defined as (N mass sorbed at BP)/(N mass sorbed at saturation); iv) operating capacity, defined as (N mass sorbed)/(resin dry mass). The operating capacity quantifies the amount of N sorbed in correspondence with a given breakpoint, in tests conducted with actual WW and therefore characterized by competition from other cations. Conversely, CEC (Section 2.5) is the maximum capacity of each resin, quantified by means of tests conducted with synthetic solutions of only NH_4^+ or only K^+ , i.e., in the absence of cation competition. The experimental N outlet concentrations were interpolated by means of the Thomas Model (Table S7, Supplementary Materials).

Eventually, the desorption/regeneration procedure was performed by counter-current elution of 2 BVs of de-ionized water, then 10 BVs of NaCl or KCl ($10\text{--}100 \text{ g L}^{-1}$ range) to regenerate the resin and recover the N-rich product [9]. Desorption performances were quantified by means of the NH_4^+ recovery yield, defined as (N mass desorbed)/(N fed during the adsorption step).

2.5. Analytical methods

Cation analysis were performed with an HPIC method using an Integriion ion chromatograph (ThermoFisher Scientific, Waltham, Massachusetts, USA) equipped with an IonPac™ CS12A-8 μm 4×250 mm column, a CG12A-8 μm 4×50 mm guard column and an Electrolytically Regenerated Suppressor CDRS600 4 mm. The eluent was 20 mM methanesulfonic acid at 1 mL min^{-1} and 30°C . pH was measured by employing a pH glass electrode with built-in temperature sensor connected to a MU 6100 L multi meter (VWR, Radnor, Pennsylvania, USA). The total CEC of each sorbent was assessed in a 10-cm high column in which the sorbent - previously packed and conditioned in the desired form - was saturated initially with a 2 N solution of NH_4Cl ($28 \text{ g}_N \text{ L}^{-1}$, a concentration 700 higher than the typical NH_4^+ concentration in municipal wastewater), and then with a 2 N solution of KCl. Further details on the experimental procedure and data elaboration are reported by resin producers [30]. All chemicals were provided by Sigma-Aldrich (Milano, Italy). The relative average experimental errors, estimated by means of a statistical elaboration of repeated analyses of check standards, resulted equal to 1% for cation concentrations and 3–4% for the other parameters.

3. Results and discussion

3.1. Procedure for the selection of the most suitable sorbent and for a preliminary process optimization

The procedure for the selection the most promising sorbent for NH_4 recovery developed and applied in this work, schematically represented in Fig. 1, was articulated in the following 3 steps:

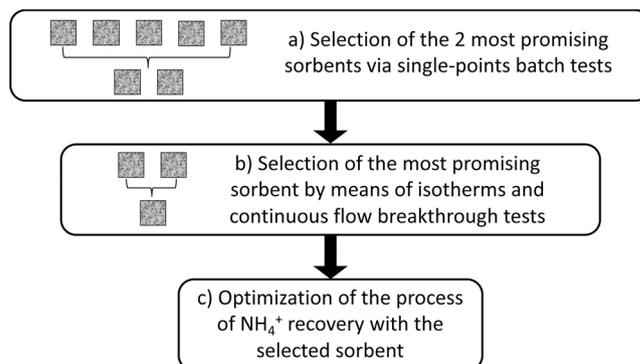


Fig. 1. Schematic representation of the proposed procedure for the selection the most promising sorbent for NH_4 recovery.

- Selection of the 2 most promising sorbents by means of single-point batch tests, conducted with both a NH_4^+ synthetic solution without competition from other cations and an actual WWTP effluent. In general, single-point tests can potentially lead to misleading results for concentrations significantly different than the one experimentally tested, depending on the shape of the isotherm. However, at the low liquid-phase equilibrium concentrations generally resulting from the application of the N concentration typical of MWW ($40 \text{ mg}_\text{N} \text{ L}^{-1}$), zeolite isotherms are typically in the linear range, where it is correct to use single-point tests for a preliminary screening between sorbent materials.
- Selection – among the 2 sorbents identified in point a) – of the most suitable one, by means of complete isotherms, conducted with both the NH_4^+ synthetic solution and the actual WWTP effluent, and continuous flow breakthrough tests, conducted with WWTP effluent.
- Preliminary optimization of the process of NH_4^+ recovery with the optimal sorbent selected in point b), by means of continuous flow breakthrough tests, conducted with at least 2 types of WWTP effluents, under different operational conditions.

3.2. Single-point batch tests for the selection of the two most promising sorbents

The single-point batch adsorption tests were aimed at selecting the two most promising materials to be further investigated by means of isotherms and breakthrough tests in step b) of the procedure. The results of the single point tests are shown in Figs. S1a (NH_4Cl solution) and S1b (Bologna WWTP effluent), Supplementary Material, in terms of NH_4 mass fraction sorbed on the solid versus NH_4 mass fraction in the liquid, at equilibrium. In the synthetic NH_4^+ solution tests (Fig. S1a), Amberlyst 15WET resulted in the best performance, and polymeric resins (Amberlyst 15WET, MAC 1 and MAC 5) in the H^+ form exhibited better performance with respect to the Na^+ form. On the contrary, Chabazite/Phillipsite resulted in higher ammonium exchange capacity in the Na^+ form ($C_{\text{S,eq}} = 9.8 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$) than in H^+ form ($C_{\text{S,eq}}$ of $4.2 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$). A possible explanation is that the HCl treatment could have decreased the Al^{3+} content in the zeolite structure and therefore the active sites available for NH_4^+ exchange [34]. Synthetic zeolite ZSM-5 showed the lowest exchange capacity. Moreover, all materials exhibited significantly lower NH_4 sorption performances in the Bologna WWTP effluent tests, due to the presence of cation competition (Table S3). Conversely, in the tests conducted with actual WWTP effluent, for both Amberlyst 15 WET and Chabazite/Phillipsite the Na^+ form resulted the best performing one (Fig. S1b). Thus, Amberlyst 15WET Na^+ ($C_{\text{S,eq}} = 18 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$ with actual effluent) and Chabazite/Phillipsite Na^+ ($C_{\text{S,eq}} = 7 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$ with actual effluent) resulted the two most promising materials to be tested by means of complete isotherms and continuous adsorption/desorption tests.

Table 1

Amberlyst A15WET and Chabazite/Phillipsite: estimates of the cation exchange capacity (CEC) and best-fitting model parameters of the interpolation with the Freundlich and Langmuir models of the isotherms conducted with NH_4Cl solution and real WWTP effluents.

Sorbent type		A15WET ^a	A15WET ^a	Ch/Ph ^b	Ch/Ph ^b	Ch/Ph ^b	Ch/Ph ^b	Ch/Ph ^b
Sorbent ionic form		Na^+	Na^+	Na^+	Na^+	K^+	Na^+	K^+
Type of water used		NH_4Cl solution	WWTP eff. ^c	NH_4Cl solution	WWTP eff. ^c	NH_4Cl solution	AnMBR eff. ^d	AnMBR eff. ^d
Langmuir model	C_{S}^{∞} ($\text{mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$)	54 ± 5	102 ± 24	30 ± 7	22 ± 2	46 ± 6	32 ± 11	38 ± 12
	K_{eq} ($\text{mL mg}_\text{N}^{-1}$)	39 ± 11	1.0 ± 0.5	21 ± 7	30 ± 13	6 ± 2	9 ± 5	6 ± 4
	R^2	0.986	0.994	0.930	0.960	0.988	0.760	0.930
Freundlich model	K_{F}	8 ± 4	0.10 ± 0.05	3.4 ± 1.8	3.1 ± 0.7	1.9 ± 0.5	1.9 ± 0.9	1.5 ± 1.2
	n	3.3 ± 1.1	1.2 ± 0.3	3.0 ± 0.9	3.2 ± 0.4	2.1 ± 0.2	2.3 ± 1.0	2.1 ± 0.7
	R^2	0.955	0.994	0.971	0.980	0.993	0.871	0.940
CEC ^e	$\text{mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$	65 ± 2		33 ± 3				
	$\text{meq g}_{\text{dry}}^{-1} \text{ resin}$	4.6 ± 0.2		2.4 ± 0.2				

^a Amberlyst A15WET. ^b Chabazite/Phillipsite. ^c Effluent of the Bologna WWTP (Table S3). ^d Effluent of the Falconara AnMBR (Table S3). ^e Cation exchange capacity, measured according to the procedure described in Section 2.5.

3.3. Adsorption isotherms and breakthrough tests for the selection of the most promising sorbent

3.3.1. Adsorption isotherms

The two adsorbents that performed best in the single-point tests (Amberlyst 15WET and Chabazite/Phillipsite) were firstly compared by means of complete isotherms performed with both the NH_4^+ synthetic solution (no cation competition) and the Bologna WWTP effluent (Table S3). Both sorbents were pre-treated in Na^+ form, which performed better than the H^+ form in the single-point tests and which is the cation for which cation exchange resins generally have the lowest affinity, therefore the one more easily displaced by NH_4^+ during the adsorption step [35]. The experimental data were interpolated with the Langmuir and Freundlich models. Table 1 shows the best-fitting model parameters and the estimated CEC of both sorbents. The experimental results and the best-fitting model interpolations are shown in Fig. 2a (Amberlyst 15WET) and 2b (Chabazite/Phillipsite). The Langmuir model resulted the best-fitting one for the isotherms conducted with Amberlyst 15WET both with NH_4Cl solution and WWTP effluent, whereas for both isotherms conducted with Chabazite/Phillipsite the Freundlich model resulted in a higher R^2 .

In the synthetic solution isotherms, Amberlyst 15WET showed a significantly higher CEC and consequently a higher NH_4^+ retention

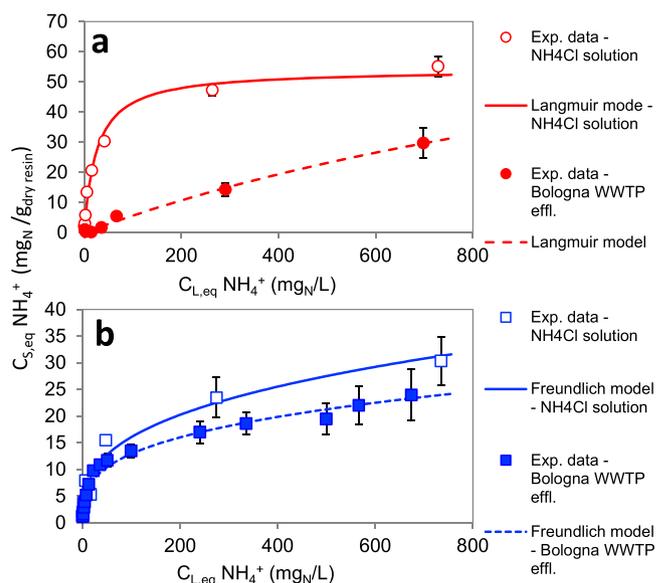


Fig. 2. Isotherms conducted with the NH_4Cl solution and with the Bologna WWTP effluent: (a) Amberlyst 15WET in Na^+ form, (b) Chabazite/Phillipsite in Na^+ form. Experimental data and best-fitting model simulations.

capacity than Chabazite/Phillipsite. However, the switch to the Bologna WWTP effluent, and the consequent competition exerted by other cations (Table S3), determined an average 70% decrease of the NH_4^+ concentration sorbed on Amberlyst 15 WET in the tested range of equilibrium liquid phase concentrations (0–730 $\text{mg}_\text{N} \text{L}^{-1}$). Nevertheless, the extrapolation of the best fitting Amberlyst 15 WET simulations (Langmuir model, Table 1 and Fig. 2a) indicates that, as a result of a much higher C_S^∞ and a much lower K_{eq} in comparison with the synthetic solution, the Amberlyst 15 WET isotherm conducted with Bologna WWTP effluent theoretically outperforms the isotherm conducted with the synthetic solution at very high liquid phase concentrations typical of other waste streams ($> 1900 \text{ mg}_\text{N} \text{L}^{-1}$). Conversely, in the case of Chabazite/Phillipsite, the switch from synthetic solution to Bologna WWTP effluent determined a much smaller drop in NH_4^+ sorption performances (21% decrease in NH_4^+ sorbed concentration, in the tested range of liquid phase concentrations). Moreover, Chabazite/Phillipsite featured a more favourable isotherm than 15WET. In particular, in the Bologna WWTP effluent tests, the NH_4^+ sorbed phase concentration - estimated according to the best fitting model for each resin - in equilibrium with 40 $\text{mg}_\text{N} \text{L}^{-1}$ (typical value in MWW) resulted equal to 9.7 $\text{mg}_\text{N} \text{g}_{\text{dry}}^{-1} \text{resin}$ for Chabazite/Phillipsite (Fig. 2b, Freundlich model), and 2.3 $\text{mg}_\text{N} \text{g}_{\text{dry}}^{-1} \text{resin}$ for Amberlyst 15WET (Fig. 2a, Langmuir model). These results suggest that Chabazite/Phillipsite features a significantly higher selectivity for NH_4^+ than Amberlyst 15WET. For both Amberlyst 15WET Na^+ and Chabazite/Phillipsite Na^+ , the experimental CEC (65 and 33 $\text{mg}_\text{N} \text{g}_{\text{dry}}^{-1} \text{resin}$, respectively) resulted in good agreement both with the values declared in the corresponding datasheets (69 and 27 $\text{mg}_\text{N} \text{g}_{\text{dry}}^{-1} \text{resin}$) and with the sorbed NH_4^+ concentration in equilibrium with an infinite concentration in the liquid in the tests conducted with NH_4Cl in the absence of cation competition (C_S^∞ , Langmuir model: 54 and 30 $\text{mg}_\text{N} \text{g}_{\text{dry}}^{-1} \text{resin}$).

3.3.2. Fluid-dynamic column characterization

Before each breakthrough test, a fluid-dynamic analysis was performed on the adsorption columns packed with the pre-selected tested sorbents (Amberlyst 15WET and Chabazite/Phillipsite, in Na^+ form). The fluid-dynamic analysis resulted in a good quality of both adsorption beds, with an average asymmetry factor of the retention time distribution curve equal to 0.44 ± 0.4 and 0.51 ± 0.05 , and an average reduced plate height equal to 46 ± 7 and 30 ± 7 for Amberlyst 15WET and Chabazite/Phillipsite, respectively. This analysis indicated that the continuous flow adsorption / desorption tests were conducted in columns characterized by an acceptable fluid-dynamic behaviour with negligible wall effects. The cumulative retention time curves and the retention time distributions obtained in the tests conducted with Chabazite/Phillipsite at 7.7 and 10.1 m h^{-1} are shown in Fig. S2, Supplementary Material.

3.3.3. Continuous breakthrough tests

The adsorption breakthrough tests aimed at comparing Amberlyst 15WET Na^+ and Chabazite/Phillipsite Na^+ were conducted with the Bologna WWTP effluent at a 10 min EBCT. The outlet normalized concentrations relative to NH_4^+ and to the other cations are shown in Fig. 3a and 3b. In the test conducted with Amberlyst 15WET, NH_4^+ was the first cation to be eluted, followed by K^+ , whereas the breakthrough of Ca^{2+} and Mg^{2+} had not started yet after 300 BVs. This result, in agreement with the isotherm conducted with actual WWTP effluent, confirms the poor selectivity of Amberlyst 15WET towards NH_4^+ . Conversely, in the test conducted with Chabazite/Phillipsite, NH_4^+ was the last cation to be eluted, confirming the high selectivity of this zeolite towards NH_4^+ observed during the isotherm tests. On the other hand, in the Chabazite/Phillipsite test the breakthrough curves of all cations occurred significantly earlier in comparison to Amberlyst 15WET, in agreement with the higher CEC of the latter material obtained from the isotherm tests (Table 1).

An overall evaluation of the isotherms and breakthrough tests led to the selection of Chabazite/Phillipsite as the most promising material for

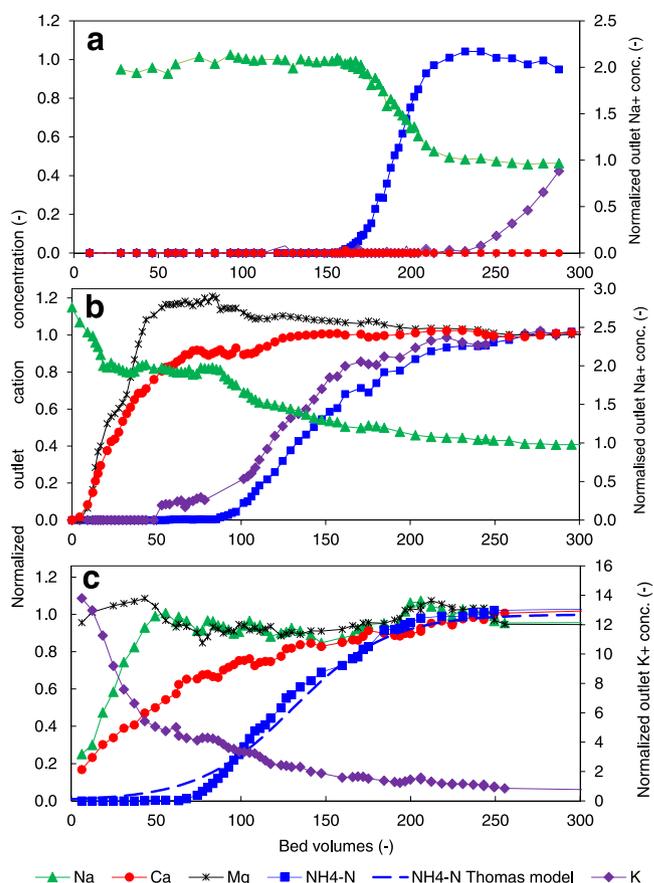


Fig. 3. Breakthrough curves of NH_4^+ and competing cations obtained at a 10-min EBCT with (a) Amberlyst 15WET Na^+ and Bologna WWTP effluent, (b) Chabazite/Phillipsite Na^+ and Bologna WWTP effluent (test BO- Na^+ -10 min, Table 2) and (c) Chabazite/Phillipsite K^+ and Falconara AnMBR effluent (test FA- K^+ -10 min-a, Table 2).

NH_4^+ recovery from WWTP effluents, on the basis of the higher selectivity for NH_4^+ and of the higher NH_4^+ sorbed concentrations obtained in equilibrium with liquid phase concentrations in the 0–40 $\text{mg}_\text{N} \text{L}^{-1}$ range, in the tests conducted with actual WWTP effluents.

The characterization of the selected sorbent provided the following results: (a) the true density of Chabazite/Phillipsite granules resulted equal to $2.256 \pm 0.003 \text{ g cm}^{-3}$, a typical value for a natural zeolite [36]; (b) the BET specific surface area resulted 109 $\text{m}^2 \text{g}^{-1}$, a relatively high value in comparison to the ones typically found in natural zeolites, in the 4–84 $\text{m}^2 \text{g}^{-1}$ range [37]; (c) the XRD pattern confirmed that the dominant crystalline phases are Chabazite (#52–0784) and Phillipsite (#39–1375) (Fig. S3, Supplementary Material); (d) the pore size distribution is broadly distributed along the 0.007–100 μm range, with an average pore size diameter of 0.12 μm , the most frequent pore diameter at 1.24 μm and an open porosity equal to 30.2%, in agreement with the values found in other natural zeolites from different deposits [36,38]. This meso-macroporosity is due to slot pores and pores located between blocks of the zeolite crystallite and other minerals in the rocks. This evaluation of pore size, limited to the 0.007–100 μm range, does not include the assessment of the typical zeolites' microporosity due to the channels present in the crystalline structure, which is in the 0.37–0.42 nm range for Chabazite and in the 0.28–0.48 nm range for Phillipsite [39].

The significantly higher selectivity of Chabazite/Phillipsite towards NH_4^+ in comparison to Amberlyst 15 WET can be explained by considering that in the case of Amberlyst 15 WET - a macroporous polymeric resin with pore sizes in the 40–80 nm range [40] - there is no steric hindrance to the diffusion of cations inside the pores. Therefore, the

resin's selectivity, based mainly on cation charge, follows the typical order reported in the literature for sulfonated cation exchange resins: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{H}^+$ [41]. Conversely, Chabazite/Phillipsite is a microporous resin, in which the size of the micro-channels plays a crucial role in determining the zeolite's selectivity towards different cations. In particular, the exchange of NH_4^+ on Chabazite/Phillipsite is not limited by steric hindrance, since its hydrated radius, equal to about 0.15 nm [42], is smaller than the typical size of the resin channels (0.37–0.42 nm for Chabazite, 0.28–0.48 nm for Phillipsite [39]); conversely, the radiuses of hydrated K^+ (0.33 nm), Na^+ (0.36 nm), Ca^{2+} (0.41 nm) and Mg^{2+} (0.43 nm) [43] are comparable to the size of the resin's microchannels, indicating that the exchange of these cations is likely to be limited by steric hindrance.

3.4. Preliminary optimization of the NH_4^+ adsorption/desorption process with the most promising sorbent

The last step of the procedure was dedicated to an optimization of the NH_4^+ recovery process with Chabazite/Phillipsite. In particular this step, articulated in isotherm and continuous flow tests, was aimed at assessing (i) the optimal cationic form of this zeolite, (ii) the process robustness, and (iii) the minimum EBCT that could be applied to the adsorption step without a significant drop in performances. Indeed, an EBCT reduction determines a reduction of the column volume required to treat a given WW flow rate, and therefore of the investment cost.

The selection of the optimal cationic form (point (i)) was conducted by means of additional isotherms aimed at comparing the NH_4^+ sorption performances obtained with the Na^+ and K^+ forms. Indeed, Na^+ is weakly bonded on cation exchange resins, which makes easy the adsorption phase but more difficult the regeneration step ([9,41]). On the other hand, a disadvantage of the use of Na-based regenerants is that the desorbed solution would contain large amounts of this cation and this would force the implementation of a NH_4^+ separation step before any reuse of the desorbed product in a fertilizer production process, since Na^+ is toxic for most crops. Conversely, K^+ has a slightly higher affinity for cation exchange resins, which could hinder the adsorption step; however, since K is beneficial for most crops, the use of a K-based regenerant leaves open the possibility to reuse the cation-rich desorbed product in a fertilizer production process, without any previous NH_4^+ separation. The reason why in the initial tests aimed at selecting the most promising sorbent (points a) and b) of the procedure; Sections 3.2 and 3.3) the different materials were not tested in the K^+ form is that cation exchange sorbents are typically used in Na^+ or H^+ forms, whereas the K^+ form represents a variation – tested only with the optimal sorbent selected under a limited number of operational conditions - that finds a justification only in the perspective of an agricultural valorisation of the desorbed product [44].

The first comparison between the Na^+ and K^+ form of Chabazite/Phillipsite was conducted with the NH_4Cl synthetic solution, i.e. in the absence of competitors. The results (Fig. 4a) show that the two forms were equivalent in the NH_4^+ concentration range typical of MWW, whereas above $100 \text{ mg}_\text{N} \text{ L}^{-1}$ in the liquid phase the K^+ form resulted in 20–40% higher adsorption performances. A further isotherm-based comparison between the Na^+ and K^+ form was conducted with the effluent of the Falconara AnMBR, characterized by a relevant saline content due to seawater intrusion (Table S3). As shown in Fig. 4b, also in the presence of relevant cation competition the two forms of Chabazite/Phillipsite resulted equivalent. On the basis of these results, the K^+ form of this zeolite was selected as the most suitable one, and KCl was selected as the regenerant for the continuous flow tests.

The results of the isotherm tests conducted with Chabazite/Phillipsite in K^+ form compare favourably with those of previous studies of ammonium removal with zeolites. In tests conducted with synthetic ammonium solutions, the sorbed concentration in equilibrium with $100 \text{ mg}_\text{N} \text{ L}^{-1}$ in the liquid resulted equal to 7–13 $\text{mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$ in studies conducted with zeolites synthesized from volcanic ash [45] or with an

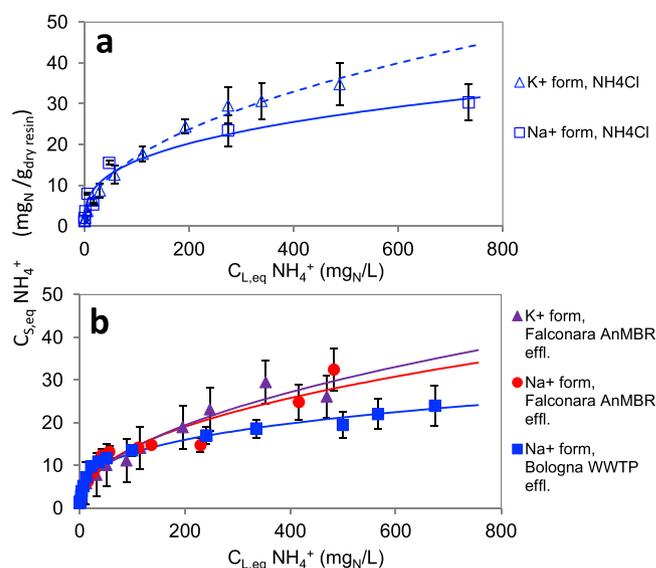


Fig. 4. Isotherms conducted with Chabazite/Phillipsite in Na^+ and K^+ form: (a) tests conducted with the NH_4Cl solution; (b) tests conducted with Bologna WWTP effluent or Falconara AnMBR effluent. All the continuous lines represent best-fitting simulations obtained with the Freundlich model.

Algerian natural bentonite [46], whereas under the same conditions Chabazite/Phillipsite K^+ resulted in $18 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$. When they switched from a synthetic solution to tap water, Gagliano et al. [45] observed at $100 \text{ mg}_\text{N} \text{ L}^{-1}$ in the liquid a 50% decrease in sorbed ammonium concentration, whereas when Chabazite/Phillipsite K^+ was tested with the saline AnMBR effluent the sorbed phase concentration dropped from 18 to $14 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$ (22% decrease). In a study conducted with Clinoptilolite and with an actual groundwater, Voccianti et al. [47] obtained a sorbed concentration equal to $4 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$ in equilibrium with $40 \text{ mg}_\text{N} \text{ L}^{-1}$ in the liquid, whereas Chabazite/Phillipsite K^+ resulted in $9 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$ in tests conducted with the saline AnMBR effluent. Conversely, higher performances were reported in studies of ammonium removal with geopolymers: in a study of ammonium removal from MWW with a metakaolin geopolymer, Luukkonen et al. [48] obtained a sorbed-phase concentration equal to $32 \text{ mg}_\text{N} \text{ g}_{\text{dry}}^{-1} \text{ resin}$ in equilibrium with $40 \text{ mg}_\text{N} \text{ L}^{-1}$ in the liquid, a value 3.5 times higher than that obtained in this work with Chabazite/Phillipsite K^+ .

The robustness of the process of NH_4^+ recovery with Chabazite/Phillipsite (point (ii)) was assessed in the first place by comparing the NH_4^+ sorption performances obtained with the Bologna WWTP effluent and the highly-saline Falconara AnMBR effluent, through both isotherms and continuous flow tests. Fig. 4b shows the comparison between these two effluents in isotherms conducted with Chabazite/Phillipsite Na^+ . Interestingly, despite the significantly higher concentration of competing cations, the test conducted with the saline AnMBR effluent resulted in a NH_4^+ sorption performance higher by 25% in average terms. The comparison between the performances obtained with the 2 types of effluents was completed by means of breakthrough tests conducted with the Bologna WWTP effluent (test BO- Na^+ -10 min, Fig. 3b and Table 2) and the Falconara AnMBR effluent (test FA- K^+ -10 min, Fig. 3c and Table 2). The change in resin form (from Na^+ to K^+), combined with the switch to a highly saline effluent, led to the same resin utilization efficiency, and to minor (3–11%) decreases of bed volumes treated and adsorption yield at the $4 \text{ mg}_\text{N} \text{ L}^{-1}$ breakpoint (Table 2). This finding is in agreement with the fact that, in the isotherm tests, neither the change from Na^+ to K^+ resin form nor the switch to a highly saline WWTP effluent led to significant changes in the sorbed NH_4^+ concentrations, in the concentration range typical of MWW (Fig. 3b).

The process robustness was further assessed through the operation of 3 repeated adsorption/desorption cycles conducted with Chabazite/

Table 2
Operating conditions and performances of the breakthrough tests conducted with Chabazite/Phillipsite in the 0.60-m column.

Test ID ^a	BO-Na ⁺ - 10 min	FA-K ⁺ - 10 min-a	FA-K ⁺ - 10 min-b	FA-K ⁺ - 10 min-c	FA-K ⁺ - 8 min	FA-K ⁺ - 6 min	FA-K ⁺ - 4 min
EBCT, adsorption (min)	10	10	10	10	8	6	4
EBCT, desorption (min)	60	60	60	60	60	60	60
Regenerant, type and conc.	NaCl 10 g L ⁻¹	KCl 100 g L ⁻¹	KCl 50 g L ⁻¹	KCl 50 g L ⁻¹	KCl 50 g L ⁻¹	KCl 50 g L ⁻¹	KCl 50 g L ⁻¹
Performances							
Bed volumes treated @BP ^b	139	122	132	126	123	126	92
NH ₄ ⁺ adsorption yield @ BP ^b	92%	89%	89%	91%	88%	87%	92%
Resin utilization efficiency @ BP ^b	83%	83%	93%	92%	88%	86%	73%
NH ₄ ⁺ recovery yield @ BP ^b	23%	78%	89%	91%	81%	87%	90%
Mean NH ₄ ⁺ + conc. in the desorbed product (mg _N L ⁻¹)	235	1243	866	967	736	951	884
NH ₄ ⁺ operating capacity (OC) @ C _{L,0} , from BT test ^c	8.4	6.0	5.4	6.2	5.9	6.1	7.3
@ BP of the BT test ^d	6.7	4.9	5.1	5.8	5.2	5.2	5.3

^a BO = Bologna WWTP effluent; FA = Falconara AnMBR effluent; the number indicates the EBCT applied during the adsorption step.

^b All the performance parameters were evaluated at a breakpoint corresponding to an average NH₄⁺ concentration in the treated effluent equal to 4 mg_N L⁻¹.

^c NH₄⁺ sorbed concentration (mg_N g_{dry}⁻¹ resin) estimated at saturation in each breakthrough test.

^d NH₄⁺ sorbed concentration (mg_N g_{dry}⁻¹ resin) estimated in each breakthrough test at the selected breakpoint.

Phillipsite K⁺ and Falconara AnMBR effluent, at a 10-min EBCT (tests FA-K⁺-10 min-a, FA-K⁺-10 min-b, FA-K⁺-10 min-c, Fig. 5 and Table 2). In these tests, zeolite regeneration was conducted with KCl 100 g L⁻¹ (test a) or 50 g L⁻¹ (tests b and c). As shown in Table 2 and Fig. 5, these repeated tests resulted in extremely stable NH₄⁺ adsorption and desorption performances. This result is confirmed by the stable values of the Thomas constants relative to the best-fitting simulation of each breakthrough test (Table S8, Supplementary Materials). Moreover, the attainment of high NH₄⁺ adsorption performances even with a saline effluent, characterized by a strong competition exerted mainly by Na⁺ cations, and the stability of the adsorption/desorption performances during 3 repeated cycles conducted with a saline effluent indicate that the process of NH₄⁺ recovery with Chabazite/Phillipsite is characterized by a high robustness, and it is therefore potentially applicable with different WW types.

Lastly, 3 breakthrough tests were conducted with the Falconara AnMBR effluent at progressively decreasing EBCTs during the adsorption step (tests FA-K⁺-8 min, tests FA-K⁺-6 min, tests FA-K⁺-4 min), in order to identify the minimum EBCT that can be applied without a significant decrease in process performances, in the perspective to optimize the investment cost. As shown in Fig. 5 and Table 2, while the tests conducted at 8 and 6 min did not present any significant drop in performances in comparison to the 3 tests conducted at 10 min, test FA-K⁺-4 min resulted in a slightly faster NH₄⁺ breakthrough curve, with a 26% decrease in the number of BVs treated at the 4 mg_N L⁻¹ BP in comparison with the average value obtained in the 10-minute tests. Six minutes was thus identified as the optimal EBCT for the adsorption step.

The attainment of high and stable ammonium removal performances during 6 repeated adsorption/desorption cycles conducted with real

effluents of different salinity and at different EBCTs in the 6–10 min range represents an important advancement towards the development of an ammonium recovery process featuring low investment costs, thanks to the EBCT reduction, and low operational costs, thanks to the selection of a low-cost natural zeolite and to the potential to re-use it over a high number of adsorption/desorption cycles. These results compare favourably with previous studies of ammonium removal from MWW with zeolites. The vast majority of the previous studies conducted with natural and synthetic zeolites under continuous flow conditions used EBCTs in the 10–30 min range [12,19,24,49]. A few attempts were made to further decrease the EBCT, primarily with NH₄⁺ synthetic solutions: in a study of ammonium removal from a synthetic WW using a zeolite synthesized from volcanic ash, Gagliano et al. [45] observed a 3-fold decrease in the time corresponding to the 10% breakpoint when the EBCT was reduced from 8 to 4 min; in addition, the resin regeneration with 1 M NaCl led to a 3-fold decrease in performances after just 1 regeneration step. In the same study, the switch from a synthetic ammonium solution to a real WW determined a major drop in process performances [45]. In a study of ammonium removal from MWW with a metakaolin geopolymer, Luukkonen et al. [48] report a drastic reduction in the time for attainment of a 50% breakpoint when the EBCT was reduced from 6 to 3 min; in addition, the geopolymer regeneration conducted with 0.1 M NaOH and 0.2 M NaCl determined a 30–50% decrease in ammonium removal between the 1st and the 3rd cycle. In a study of ammonium removal from a synthetic solution using a natural zeolite containing 75% clinoptilolite and a synthetic NaA type zeolite, Malovany et al. [50] obtained a 10% breakpoint after feeding about 100 BVs at a 5 min EBCT; however further attempts to reduce the EBCT or to switch to a real MWW were not made with these materials.

The fitting of the Thomas model to the NH₄⁺ breakthrough curves was always very good (R² = 0.983–0.993; Tables S7 and S8, Supplementary Material). This indicates that the NH₄⁺ breakthrough curve is symmetrical, as assumed by the Thomas model, and that this model can be used to extrapolate up to resin saturation experimental tests stopped before saturation, in order to estimate performance parameters such as the NH₄⁺ operating capacity and the sorbent utilization efficiency. A representative Thomas simulation of a NH₄⁺ breakthrough curve is shown in Fig. 3c, whereas the best fitting parameters are reported in Table S8, Supplementary Material.

As for the desorption step, the average NH₄⁺ concentration in the desorbed product varied in the 0.9–1.2 g_N L⁻¹ range, depending on the KCl concentration used for the desorption step. In particular, higher regenerant concentrations led to higher NH₄⁺ concentrations in the desorbed product, as the number of regenerant bed volumes required to fully recover NH₄⁺ decreased (Table 2). As shown in the representative case (test FA-K⁺-10 min-c) illustrated in Fig. S4, Supplementary

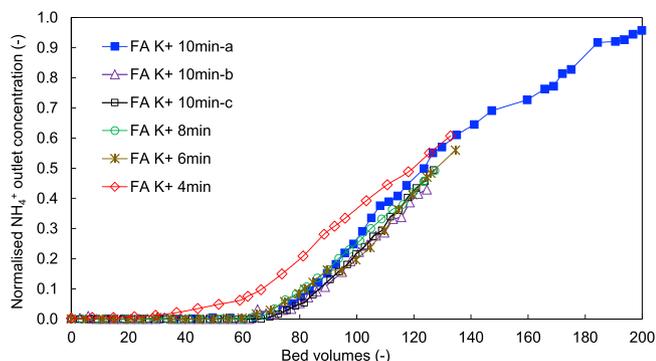


Fig. 5. NH₄⁺ breakthrough curves obtained with Falconara AnMBR effluent and Chabazite/Phillipsite in K⁺ form, during repeated cycles conducted in the 4–10 min EBCT range.

Material, the desorption breakthrough curves of the different cations confirm the relative affinities of Chabazite/Phillipsite obtained in the adsorption tests (Figs. 3b and 3c): $\text{NH}_4^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}$. This order is in agreement with that reported by [51] for pure Phillipsite ($\text{NH}_4^+ > \text{K}^+ > \text{Na}^+$). Overall, the results of the desorption tests indicate that KCl is an effective regenerant for NH_4^+ , and that further research is needed to optimize the desorption step in terms of EBCT, regenerant concentration and post-treatments aimed at making the product usable for the production of N-based fertilizers.

3.5. Ammonium Operating Capacity

The experimental data relative to the BT tests were compared in order to obtain an overall estimate of the NH_4^+ operating capacity (OC) of Chabazite/Phillipsite K^+ , i.e., the amount of N- NH_4^+ sorbed in correspondence with a given liquid phase concentration, in tests conducted with actual WW and therefore characterized by competition from other cations. The data are summarized in the last 2 rows of Table 2. The first OC estimate (OC @ $\text{C}_{\text{LO,N}}$, from BT test) was obtained by integration of the experimental curve up to resin saturation, i.e. up to the achievement of a sorbed NH_4^+ concentration in equilibrium with the inlet liquid-phase concentration of each test. For the tests that were stopped before saturation, this estimate was based on the extrapolation of the best fitting Thomas curve. The second OC estimate (OC @ BP of the BT test) was obtained by integrating the NH_4^+ breakthrough curves until the selected breakpoint. This estimate, corresponding to the actual operational conditions in a hypothetical WWTP that has to comply with a $4 \text{ mg}_\text{N} \text{ L}^{-1}$ limit in the effluent, resulted just 10–15% lower than the values estimated at saturation, confirming the high resin utilization efficiencies reported in Table 2. The average value of this latter OC at actual operational conditions, equal to $5.2 \pm 0.2 \text{ mg}_\text{N} \text{ g}_{\text{dry resin}}^{-1}$, is significantly lower than the estimate of the resin total CEC obtained in the absence of competing cations ($33 \text{ mg}_\text{N} \text{ g}_{\text{dry resin}}^{-1}$; Table 1). This result can be ascribed to two factors: (i) only 50% of the Chabazite/Phillipsite total CEC is actually used at the selected breakpoint; and (ii) despite the high selectivity of this zeolite for NH_4^+ , as a result of the high salinity of the tested effluent a not negligible fraction of the resin capacity is occupied by other cations. It should be noted that, in general, it is not possible to estimate a resin's OC at a specific breakpoint by means of isotherm tests. Indeed, in the isotherm tests the liquid and solid phases are at equilibrium, whereas in a BT test stopped at a specific breakpoint a fraction of the total resin mass – corresponding to the mass transfer zone - is not in equilibrium with the adjacent liquid.

The assessment of the total CEC of Chabazite/Phillipsite in the absence of competing cations obtained in this work ($33 \text{ mg}_\text{N} \text{ g}_{\text{dry resin}}^{-1}$) is in good agreement with the estimates reported in previous studies conducted with natural zeolites, that vary in the 34–41 $\text{mg}_\text{N} \text{ g}_{\text{dry resin}}^{-1}$ range for Chabazite [18,19], 12–52 $\text{mg}_\text{N} \text{ g}_{\text{dry resin}}^{-1}$ for Clinoptilolite [19, 23] and 16–25 $\text{mg}_\text{N} \text{ g}_{\text{dry resin}}^{-1}$ for zeolites synthesized from fly ash [25]–[27]. Similarly, the operating capacity assessed for Chabazite/Phillipsite in BT tests conducted with different WWTP effluents at the $4 \text{ mg}_\text{N} \text{ L}^{-1}$ BP is similar to the values previously reported for natural zeolites, that vary in the 3–8 $\text{mg}_\text{N} \text{ g}_{\text{dry resin}}^{-1}$ range in studies conducted with WWTP effluents [45], synthetic wastewater [50] and groundwater [47].

4. Conclusions

The proposed procedure provides a solid framework for the testing and selection of different sorbents for NH_4^+ adsorption and recovery from MWW. The application of the procedure to a range of sorbents including natural and synthetic zeolites and a cation exchange polymeric resin confirmed that batch isotherm tests – often used in the literature to compare materials for adsorption processes – need to be integrated by continuous-flow adsorption/desorption tests. Indeed, even if most observations obtained from isotherms were confirmed by the corresponding continuous flow tests, the latter allow to assess several

parameters not quantifiable by means of isotherms, such as the resin operating capacity at the selected breakpoint and the process robustness.

The selected sorbent, a natural mixture of Chabazite and Phillipsite, yielded promising NH_4^+ retention and recovery performances that resulted stable during 6 repeated adsorption / desorption cycles conducted with actual WWTP effluents in a 60-cm column, also when the WWTP effluent initially used was replaced with a highly saline one, deriving from a hotspot of seawater intrusion and featuring a stronger competition for NH_4^+ sorption exerted by other cations. The EBCT was gradually reduced down to 6 min - a value lower than the ones typically applied in previous studies - without any decrease in process performances. The selection of potassium as a regenerating agent represents an interesting solution in the perspective to produce a desorbed product to be used as a fertilizer.

This study contributes to the development of a reliable process for NH_4^+ recovery from MWW, thanks to the selection of a low-cost natural Chabazite/Phillipsite mixture and to the identification of operational conditions that allow (i) stable performances during repeated adsorption/desorption cycles, (ii) a reduction of the investment cost thanks to the low EBCT, and (iii) the production of an ammonium-rich product of high potential interest for the fertilizer industry.

CRedit authorship contribution statement

Daive Pinelli: Conceptualization, Methodology, Writing – original draft, Supervision. **Alessia Foglia:** Resources, Investigation. **Francesco Fatone:** Resources, Validation. **Elettra Papa:** Investigation. **Carla Maggetti:** Investigation, Resources, Visualization. **Sara Bovina:** Investigation. **Dario Frascari:** Writing – review & editing, Conceptualization, Supervision, Project administration, Funding acquisition.

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.

Data Availability

Research data underlying this manuscript have been published in the AMS Acta Institutional Research Repository (<http://doi.org/10.6092/unibo/amsacta/6797>).

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2022.108829](https://doi.org/10.1016/j.jece.2022.108829).

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