

Contents lists available at [ScienceDirect](https://www.sciencedirect.com/science/journal/23525541)

# Sustainable Chemistry and Pharmacy



journal homepage: [www.elsevier.com/locate/scp](https://www.elsevier.com/locate/scp)

# Recovering ammonium from real treated wastewater by zeolite packed columns: The effect of flow rate and particle diameter

Sofi[a](#page-0-0) Maria Muscarella <sup>a</sup>, Vito Armando Laudicina <sup>a</sup>, Daniele Di Trapani <sup>[b](#page-0-1)</sup>, Giorgio Mannina <sup>[b](#page-0-1), [\\*](#page-0-2)</sup>

<span id="page-0-1"></span><span id="page-0-0"></span>a Department of Agricultural, Food and Forest Sciences, University of Palermo, Viale delle Scienze, building 4, 90128, Palermo, Italy <sup>b</sup> *Department of Engineering, University of Palermo, Viale delle Scienze, building 8, 90128, Palermo, Italy*

### ARTICLE INFO

*Keywords:* Ammonium adsorption rate Ammonium adsorption kinetics Ammonium removal efficiency Wastewater ultrafiltration Circular economy

### ABSTRACT

Nitrogen (N) recovery from wastewater is a desirable way to create a (N) neutral society in view of a circular economy approach. Nitrogen recovery from wastewater by employing adsorption columns filled with zeolite can be a very attractive solution. This study assessed the effect of influent flow rates (namely, 1.6 and 2.3 L  $h^{-1}$ ) and particle diameters (namely, 0.5–1.0 and 2.0–5.0 mm) of zeolite packed in columns on recovering  $NH_4^+$  from real domestic treated wastewater (RDTWW). Findings revealed that maximum  $\mathrm{NH}_4^+$  recovery can be achieved by using zeolite with the smallest particle diameter (0.5–1.0 mm) and the highest influent flow rate  $(2.3 L h<sup>-1</sup>)$ . The maximum NH<sub>4</sub><sup>+</sup> adsorption rate was 1.2, 21 and 9.8 mg NH<sub>4</sub><sup>+</sup> kg<sup>-1</sup> h<sup>-1</sup> after 205, 32 and 35 h of operation.  $NH_4^+$  adsorption data were analysed by fitting them to both pseudofirst and pseudo-second order kinetic models. The former model best approximated  $\mathrm{NH}_4{}^+$  adsorption data. Such a result suggested that the amount of NH<sub>4</sub><sup>+</sup> adsorbed depended solely on the amount of  $\mathrm{NH_4}^+$  in contact with the zeolite surface. Results successfully established the application of zeolite-packed columns in removing  $NH_4^+$  from real domestic treated wastewater and the effects of process parameters.

### **1. Introduction**

Recovering N from treated wastewater is crucial to providing clean water for the world population [\(Naddaf,](#page-7-0) 2023), avoiding eutrophication of the aquatic environment ([Preisner,](#page-7-1) 2023) and having an alternative and sustainable source of N within a circular economy perspective [\(Guaya](#page-7-2) et al., 2018, [Mannina](#page-7-3) et al., 2021; [Muscarella](#page-7-4) et al., 2023a).

Treated wastewater holds from 0.9 to 30 mg  $L^{-1}$  of NH<sub>4</sub><sup>+</sup>, depending on the type of treatment process used and on the characteristics of the influent ([Guaya](#page-7-5) et al., 2016; [Guida](#page-7-6) et al., 2020–2021; [Pinelli](#page-7-7) et al., 2022).

Physical (e.g., air stripping, ion exchange and adsorption, reverse osmosis) chemical (e.g., chemical precipitation, electrochemical oxidation), and biological (e.g., nitrification and denitrification, anaerobic ammonium oxidation, partial nitrification) techniques can recover N from treated wastewater [\(Dong](#page-7-8) et al., 2019; de [Magalhães](#page-7-9) et al., 2022). Prominent among these are the ion exchange and adsorption processes, using low-cost industrial adsorbents that are environmentally sustainable and recyclable [\(López-Rosales](#page-7-10) et al., [2022](#page-7-10)), such as zeolite, clay, polymeric ion exchangers [\(Huang](#page-7-11) et al., 2010; Fu et al., [2020;](#page-7-12) [Muscarella](#page-7-4) et al., 2023a). Zeolites are highly porous aluminosilicate minerals with high cation adsorption capacity due to the isomorphic substitution of silicon ion (S $_1^{4+})$ with aluminium ion  $(A13+)$ , resulting in a net negative charge. The negative charges are counterbalanced by cations such as sodium

<span id="page-0-2"></span><https://doi.org/10.1016/j.scp.2024.101659>

Received 4 March 2024; Received in revised form 12 May 2024; Accepted 4 June 2024

Available online 21 June 2024<br>2352-5541/© 2024 The Authors.

<sup>\*</sup> Corresponding author. Department of Engineering, University of Palermo, Viale delle Scienze, building 8, 90128, Palermo, Italy.

*E-mail address:* [giorgio.mannina@unipa.it](mailto:giorgio.mannina@unipa.it) (G. Mannina).

Published by Elsevier B.V. This is an open access article under the CC BY license ([http://creativecommons.org/licenses/by/4.0/\)](http://creativecommons.org/licenses/by/4.0/).

(Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>), which can be exchanged by NH<sub>4</sub><sup>+</sup> [\(Sengupta](#page-7-13) et al., 2015 [Han](#page-7-14) et al.,  $2019$ ; [Muscarella](#page-7-15) et al.,  $2021$ ). Therefore, NH<sub>4</sub><sup>+</sup> enriched zeolites can be applied in agriculture to improve soil physical and chemical properties and as slow-release fertilizers within a circular economy perspective [\(Sengupta](#page-7-13) et al., 2015; [Mannina](#page-7-16) et al., 2022; [Muscarella](#page-7-4) et al., 2023a).

The ability of zeolites in the removal of  $NH_4^+$  from aqueous solution is influenced by several factors, including the homoionic forms of the zeolites ([Muscarella](#page-7-15) et al., 2021), their particle diameter [\(Huang](#page-7-11) et al., 2010), pH (Li et al., [2020\)](#page-7-17), influent  $NH_4^+$  concentration (Li et al., [2020\)](#page-7-17), retention time ([Sprynskyy](#page-7-18) et al., 2005; Tran et al., [2020](#page-7-19)), ionic competition with other cations ([Huang](#page-7-11) et al., [2010](#page-7-11); [Vocciante](#page-7-20) et al., 2018), zeolite mineralogical composition [\(Muscarella](#page-7-21) et [al.,](#page-7-12) 2023b) and temperature of the solution (Fu et al., [2020](#page-7-12)).

Huang et al. [\(2010\)](#page-7-11) studied in batch test the effects of NH<sub>4</sub><sup>+</sup> ion removal from NH<sub>4</sub><sup>+</sup>-enriched solutions (80 mg NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>) using natural zeolite particles with a diameter ranging from 0.074 to 0.3 mm and contact time ranging from 10 to 300 min. They found high  $NH_4^+$  ion removal efficiency by decreasing particle size and increasing contact time.

On the other hand, [Sprynskyy](#page-7-18) et al. (2005) investigated the NH<sub>4</sub><sup>+</sup> adsorption capacity of zeolite (clinoptilolite) on a pilot column scale under dynamic conditions using particle diameters ranging from 1.4 to 2.0 to 0.125–0.35, flow rates of 0.11, 0.36, and 0.54 L h<sup>-1</sup> and NH<sub>4</sub><sup>+</sup> enriched solution with a concentration of 100 mg L<sup>-1</sup>. Overall, their results suggested that the maximum NH<sub>4</sub><sup>+</sup> adsorption capacity of zeolite occurs by decreasing particle size and increasing flow rate. Such results are reasonable because decreasing the particle size increases the specific surface area for NH4+ adsorption, whereas increasing the flow rate increases the amount of NH<sup>4</sup> + through the column and thus in contact with the adsorbent.

However, to scale up from batch scale to real scale, pilot studies using real treated wastewater are needed to find out the most appropriate flow rate and zeolite particle size diameter to maximize NH<sub>4</sub><sup>+</sup> removal from wastewater and its adsorption by zeolite.

Moreover, to find out the mechanisms by which  $NH_4^+$  is adsorbed by zeolite, adsorption kinetics must be investigated. Indeed, by fitting experimental data to kinetic models, the nature of the interaction (physical-chemical or chemical) between zeolite and  $NH_4^+$ [\(Revellame](#page-7-22) et al., 2020) and the adsorption mechanisms (mainly ion exchange and adsorption) ([Jørgensen,](#page-7-23) 1989) can be revealed. Recently, [Muscarella](#page-7-21) et al. (2023b) fitting experimental data of NH<sub>4</sub><sup>+</sup> adsorption on natural zeolites with different mineralogical mixtures, found out that the NH<sub>4</sub><sup>+</sup>sorption occurs by two simultaneous pseudo-first-order reactions: adsorption process and ion exchange In the light of above, this study aimed to investigate, at a pilot scale, the effect of zeolite particle diameter and flow rate of real domestic treated wastewater (RDTWW) in adsorbing  $NH_4^+$ . The mass balance approach can reveal the  $NH_4^+$  adsorption efficiency of the zeolite packed in the column. This study further aimed to investigate the adsorption kinetics of the most efficient zeolite in adsorbing NH<sup>4</sup> + by fitting experimental data to pseudo-first- and second-order models.

## **2. Materials and methods**

# *2.1. Zeolites used for NH<sup>4</sup> + recovery from column pilot scale plant*

Zeolite used in the pilot scale plant was made up of 85% of clinoptilolite, 8% of cristobalite, 4% of illite, and 3% plagioclase. Clinoptilolite is a member of the heulandite group (HEU) and has the chemical formula  $(Na,K)_6Al_6Si_{30}O_{72}$ –20H<sub>2</sub>O ([Muscarella](#page-7-15) et al., [2021](#page-7-15)). It has a tetrahedral structure made up of units of  $SiO_4^4$  and  $AlO_4^{5}$ . It has a bulk density of 0.98 g cm<sup>-3</sup>, a surface area of 40  $\text{m}^2$  g<sup>-1</sup>, and a pH of 7.6. The Si/Al ratio is 4.8–5.5. The two most abundant exchangeable cations, counterbalancing the negative charges formed following the isomorphic substitution of  $Si^{4+}$  with  $Al^{3+}$ , were K<sup>+</sup> and Ca<sup>2+</sup>. Before its use, clinoptilolite was sieved to obtain particles with a 2.5–5.0 and 0.5–1.0 mm diameter, washed three times with distilled water, and dried at 105 °C.

# *2.2. NH<sup>4</sup> + recovery column pilot scale plant and tested variables*

A pilot-scale column plant filled with zeolite was constructed at the Water Resource Recovery Facility (WRRF) of Palermo University Campus ([Mannina](#page-7-24) et al., 2021a). The pilot plant specifically consisted of three polymethylmethacrylate columns, each with a height of 15 cm, an internal diameter of 5 cm, and a total volume of 0.29 L [\(Fig.](#page-2-0) 1). Each column was filled with 288 g of natural zeolite.

Zeolite was packed between two layers of cleaned quartz sand (ø 2.0–5.0 mm) to immobilise it and enable a uniform distribution of the flow over the cross-sectional region. A biological pilot plant that treated real domestic wastewater and equipped with an ultrafiltration membrane to eliminate harmful bacteria supplied the columns with RDTWW ([Mannina](#page-7-16) et al., 2022; [Cosenza](#page-7-25) et al., 2022). The RDTWW was pumped into the columns in upward flow mode using a peristaltic pump (Watson Marlow-Qdos 30 Universal). Characteristics of the RDTWW used to feed natural zeolite-packed columns are reported in [Table](#page-2-1) 1.

Three setups were tested to evaluate the effect of flow rate and particle diameter on the amount and rate of NH $_4^+$  removal by zeolite-packed columns: setup I, setup II and setup III. The setup I lasted 588.5 h, during which the flow rate through the columns packed with zeolite having a particle diameter of 2.5–5.0 mm was maintained at 2.3 L h<sup>-1</sup> per column. Setup II lasted 130.5 h; the flow rate was maintained at 2.3 L h<sup>-1</sup> per column, but the zeolite particle diameter was 0.5–1.0 mm. Setup III lasted 249.5 h, the flow rate was set at 1.6 L  $h^{-1}$ , and zeolite with a particle diameter of 0.5–1.0 mm was used. Before starting each test, the required amount of RT-DWW was accumulated in a 500 L tank to ensure a constant flow with a fixed  $\mathrm{NH}_4{}^+$  concentration.

For each test, the amount and rate of  $NH_4^+$  adsorbed by zeolite-packed columns during the test were assessed by monitoring the  $NH_4^+$  mass of the inlet and the outlet flow from the columns. The mass of  $NH_4^+$  was calculated by multiplying the concentration of NH<sub>4</sub><sup>+</sup> of the inlet and the outlet flow from the columns per column crossing time. Reported data are the average values of the three columns.

<span id="page-2-0"></span>

**Fig. 1.** Zeolite-packed columns. Each column had a height of 15 cm, an internal diameter of 5 cm, and a total volume of 0.29 L.

# <span id="page-2-1"></span>**Table 1**

Characteristics of RDTWW used to feed natural zeolite-packed columns for  $\mathrm{NH}_4^+$  removal.



## *2.3. Analytical methods*

RDTWW samples collected before and after passing through the column were filtered using membrane syringe filters with a pore size of 0.45 μm before being analysed by ion chromatography to remove contaminants and safeguard the analytical columns [\(Michalski,](#page-7-26) 2018). The concentration of NH<sub>4</sub><sup>+</sup>, as well as of Ca<sup>2+</sup>, M<sub>8</sub><sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup>, were determined by the ionic chromatograph Dionex Easion (Thermo Scientific, Milan, Italy) equipped with a Dionex IonPac CS12A (4 x 250 mm) column. The chemicals utilised were Thermo Scientific's Dionex Cation regenerant solution, Thermo Scientific TBAOH (100 mM), Dionex CS12A Eluent Concentrate, and Thermo Scientific Methanesulfonic Acid (20 mM).

## *2.4. Adsorption kinetics*

The kinetics of NH $_4^+$  adsorption was evaluated by modelling experimental data from zeolite packed column. Data were analysed by applying both pseudo-first and pseudo-second-order models. The pseudo-first order model (eq. [\(1\)\)](#page-2-2) ([Lagergren,](#page-7-27) 1898) assumes that the adsorption rate is solely dependent on the amount of  $NH_4^+$  in contact with the zeolite:

$$
q_t = q_e \left( 1 - e^{-k_1 t} \right) \tag{1}
$$

<span id="page-2-2"></span>where  $q_t$  in mg NH<sub>4</sub><sup>+</sup> L<sup>-1</sup> is the amount of NH<sub>4</sub><sup>+</sup> adsorbed by zeolite at time *t*,  $q_e$  is the equilibrium adsorption capacity (mg NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>) and  $k_1$  is the pseudo-first order monomodal constant. The latter is directly related to the adsorption rate of  $NH_4^+$  by zeolite. The higher is the  $k_1$  value, the faster is  $NH_4^+$  adsorption rate.

The pseudo-second order model is described by eq. [\(2\)](#page-3-0) (Ho et al., [1996](#page-7-28)):

(2)

$$
q_t = \frac{k_2 q_{et}^2}{1 + k_2 q e t}
$$

<span id="page-3-0"></span>where  $q_t$  (mg NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>) is the amount of NH<sub>4</sub><sup>+</sup> adsorbed at time t,  $q_e$  is the amount of NH<sub>4</sub><sup>+</sup> adsorbed at equilibrium and (mg NH4+  $L\ddot{\chi}$ 1) is the pseudo second-order rate constant and is constant related to the energy of adsorption.

The pseudo-second order model assumes a chemisorption process, i.e. an adsorption process that involves a chemical reaction and that implies the formation of a covalent bond between the molecule and one or more atoms on the surface. In this scenario, the rate of adsorption depends on the adsorption capacity rather than the concentration of  $NH_4^+$  in contact with the zeolite (Sahoo and [Prelot,](#page-7-29) [2020](#page-7-29)). The performance of the different kinetic models was evaluated through the application of different statistical parameters, such as correlation coefficient  $(R^2)$ , chi-square  $(\chi^2)$ , residual sum of squares error (SSE), and mean sum of squares error (MSE).

The kinetics have been analysed using a user-friendly UI developed based on Excel ([Wang](#page-7-30) and Guo, 2020) and Oring (Version 7.5) software program.

### **3. Results and discussion**

# *3.1. NH<sup>4</sup> + adsorption from RDTWW*

The total amount of NH<sub>4</sub><sup>+</sup> adsorbed by zeolite as a function of particle diameter and RDTWW flow rate was determined by monitoring the NH<sub>4</sub><sup>+</sup> concentration in the inlet and outlet flow from the columns. Zeolite adsorbed 11%, 49%, and 27% of NH<sub>4</sub><sup>+</sup> passed through the columns with setup I, II, and III, respectively [\(Fig.](#page-3-1) 2).

<span id="page-3-1"></span>Setup I and setup II enabled the assessment of the role of zeolite particle size in the  $NH_4^+$  adsorption; indeed, while the flow rate was maintained constant, the zeolite particle diameter was greater in setup I to setup II. It was found that the total amount of NH<sub>4</sub><sup>+</sup> adsorbed with setup I ([Fig.](#page-3-2) 3) was doubled by that adsorbed by columns with setup II [\(Fig.](#page-4-0) 4) even in less time of operation, thus suggesting that decreasing zeolite particle diameter increases the total amount of NH<sub>4</sub><sup>+</sup> adsorbed. Such a result is reasonable because, depending on the adsorption process on the specific surface area, the lower the zeolite particle size, the higher the zeolite surface area available for  $NH_4^+$  adsorption.



<span id="page-3-2"></span>**Fig. 2.** Percentage of ammonium  $\text{(NH}_4^+)$  adsorbed by zeolite packed columns with three different setups.



**Fig. 3.** Cumulative and hourly ammonium (NH<sup>4</sup> + ) adsorbed per kg of zeolite with setup I.

<span id="page-4-0"></span>

**Fig. 4.** Cumulative and hourly ammonium  $(NH_4^+)$  adsorbed per kg of zeolite with setup II.

Such findings agreed with those of de [Magalhães](#page-7-9) et al. (2022), who investigated the effect of zeolite particle diameter on NH<sub>4</sub><sup>+</sup> adsorption, found the highest amount of  $NH_4^+$  adsorbed by zeolite with the smallest particle diameter.

Besides the zeolite particle diameter, flow rate also played a key role in affecting the amount of  $\rm NH_4^+$  adsorbed by zeolite. Indeed, comparing setup II and III ([Fig.](#page-4-1) 5), the greatest amount of  $NH_4^+$  adsorbed occurred with setup III, which was characterized by a flow rate lower than that of setup II. However, more time was needed for columns with setup III compared to columns with setup II to adsorb the maximum amount of  $NH_4^+$ . Moreover, the percentage of  $NH_4^+$  adsorbed by columns with setup III was lesser than that ad-sorbed by columns with setup II ([Fig.](#page-3-1) 2). Such behaviour can be ascribed to the low amount of NH<sub>4</sub><sup>+</sup> passed through the column with setup III due to the low flow rate (see [Fig.](#page-4-1)  $5$ ).

Such findings agreed with those of  $\rm Sprynsky$  et al. (2005) who investigated NH $_4^+$  adsorption capacity of zeolite (clinoptilolite) on a pilot column scale under dynamic conditions using particle diameters ranging from 1.4 to 2.0 to 0.125–0.35, flow rates of 0.11, 0.36, and 0.54 L h<sup>-1</sup> and NH<sub>4</sub><sup>+</sup> enriched solution with a concentration of 100 mg L<sup>-1</sup>. They found that the maximum amount of NH<sub>4</sub><sup>+</sup> adsorption capacity occurs by decreasing particle size and increasing the flow rate, thus indicating that both factors play a crucial role in the adsorption process. Based on these results someone could argue that using zeolites with an even smaller diameter would be appropriate. However, this is not to be done because using particles smaller than 0.35 mm allows the formation of preferential channels or voids within the column reducing NH<sub>4</sub><sup>+</sup> adsorption [\(Sprynskyy](#page-7-18) et al., 2005).

# *3.2. Effect of zeolite particle diameter in adsorbing NH<sup>4</sup> + from RDTWW*

[Figs.](#page-3-2) 3 and 4 show the cumulative NH<sub>4</sub><sup>+</sup> adsorbed and the hourly adsorption rate per kg of zeolite under setup I and II.

As discussed above, in setup I and II, the flowrate fed to each column was maintained constant, equal to 2.3 L  $\rm h^{-1}$ , while the zeolite particle size was decreased from 2.5 – 5.0 mm to 0.5–1.0 mm to assess its role (and consequently the role of specific surface) in the  $NH_4^+$  adsorption process.

<span id="page-4-1"></span>As noticeable from data reported in [Figs.](#page-3-2) 3 and 4, the significant effect of zeolite size in the adsorption process is worth noting. Indeed, while in setup I, the cumulated NH<sub>4</sub><sup>+</sup> adsorbed reached a value close to 350 mg NH<sub>4</sub><sup>+</sup> adsorbed kg<sup>-1</sup>zeolite after 600 h of flushing [\(Fig.](#page-3-2) 3), in setup II, the cumulated  $NH_4^+$  adsorbed almost doubled, reaching a steady state value close to 350 mg NH<sub>4</sub><sup>+</sup>adsorbed kg<sup>-1</sup>zeolite after only 130 h of flushing [\(Fig.](#page-4-0) 4). In addition, the hourly (NH<sub>4</sub><sup>+</sup>) adsorbed showed significant differences in the two investigated setups. Indeed, in setup I, the hourly adsorbed (NH<sub>4</sub>+) showed an increasing trend in the first 200 h of flushing, reaching a maximum value close to 1.2 NH<sub>4</sub><sup>+</sup>adsorbed kg<sup>-1</sup>zeolite h<sup>-1</sup>. In contrast, under setup II, the hourly adsorbed (NH<sub>4</sub><sup>+</sup>) showed an increasing trend in the first 40 h of flushing, with a maximum value higher than 20 NH<sub>4</sub><sup>+</sup>adsorbed kg<sup>-1</sup>zeolite h<sup>-1</sup>, thus highlighting a



**Fig. 5.** Cumulative and hourly ammonium (NH<sup>4</sup> + ) adsorbed per kg of zeolite with setup III.

much higher adsorption rate likely related to the significant increase of zeolite specific surface under setup II. As discussed above, since  $NH_4^+$  adsorption occurs on the surface of the adsorbent material, the reduced particle size of the zeolite will increase the efficiency of the adsorption process. This result is in line with the observations of Pinelli et al. [\(2022\),](#page-7-7) who found that Chabazite/Phillipsite, characterized by lower diameter compared to other investigated sorbent materials, had a high capacity to recover  $\mathrm{NH}_4^+$  from Municipal Wastewater (MWW).

From an operational point of view, the suggestion is twofold: if the aim is the NH<sub>4</sub><sup>+</sup> removal from wastewater, it would be better to operate with a zeolite characterized by higher particle size; in contrast, if the aim is to maximize  $NH_4^+$  recovery, it would be better to use a zeolite with a lower particle size (higher specific surface).

# *3.3. Effect of flow rate in adsorbing NH<sup>4</sup> + from RTDWW*

[Fig.](#page-4-1) 5 shows the cumulative  $NH_4^+$  adsorbed and the hourly adsorption rate per kg of zeolite in setup III.

As previously mentioned, in setup III, the zeolite particle size was maintained equal to setup II (0.5–1.0 mm), while the flow rate fed to each column was decreased to  $1.63$  L  $h^{-1}$ , to assess the role of contact time in the NH<sub>4</sub><sup>+</sup> adsorption process.

From the data reported in [Fig.](#page-4-1) 5, it is worth noting that the cumulative NH<sub>4</sub><sup>+</sup> adsorbed reached a value close to 1000 mg NH<sub>4</sub><sup>+</sup> adsorbed kg $^{-1}$ zeolite after 250 h of flushing. In addition, the hourly adsorbed NH<sub>4</sub><sup>+</sup> showed an increasing trend in the first 30 h of flush-ing, reaching a maximum value close to 10 NH<sub>4</sub><sup>+</sup>adsorbed kg<sup>-1</sup>zeolite h<sup>-1</sup>. Compared to the results achieved with setup II ([Fig.](#page-4-0) 4), the decreased flow rate (corresponding to an increased contact time) increased the overall amount of the adsorbed NH<sub>4</sub><sup>+</sup>, but with a lower adsorption rate, likely related to a lower (NH $_4^+$ ) loading rate to the columns.

This behaviour was well in line with the study of [Sundhararasu](#page-7-31) et al. (2022), who found that the higher the flow rates, the greater the amount of NH<sub>4</sub><sup>+</sup> passing the adsorbent, allowing zeolite to reach saturation sooner. The results of this study fit with those of [Sundhararasu](#page-7-31) et al. (2022) and suggested that zeolite saturation with NH4+ is reached sooner by increasing the flow rate (setup II) because of the high amount of NH<sub>4</sub><sup>+</sup> passing through the adsorbent. This provides for a sharper adsorption curve. With the lower flow rate (setup III), NH<sub>4</sub><sup>+</sup> had a higher time to diffuse within zeolite pores due to the increased residence time. Therefore, (NH<sub>4</sub><sup>+</sup>) ions were allowed to approach a higher number of binding sites in the adsorbent material.

#### *3.4. Adsorption kinetics*

<span id="page-5-0"></span>The adsorption of NH<sub>4</sub><sup>+</sup> ions by zeolites was studied at different time intervals in three experimental setups ([Fig.](#page-5-0) 6). The experimental data points were studied by applying two models to study adsorption kinetics, eqs. (1) [and](#page-2-2) (2), respectively. According to the experimental results, the sorption process can be described as pseudo-first-order reactions, with a single adsorption constant  $(k_1)$  cal-culated using eq. [\(1\)](#page-2-2), suggesting a single NH<sub>4</sub><sup>+</sup> sorption mechanism. However, unlike the application of eq. (1), which provided a good fit, the application of eq. [\(2\)](#page-3-0) did not yield a satisfactory fitting [\(Table](#page-6-0) 2).



**Fig. 6.** Kinetic fitting curves of the experimental points obtained, following the application of pseudo first order model (equation [\(1\)\)](#page-2-2), to data attained with setup I (A), II (B) and III (C).

#### *S.M. Muscarella et al.*

### <span id="page-6-0"></span>**Table 2**

Parameter values obtained from applying pseudo-first and pseudo-second order to experimental data of  $NH_4^+$  adsorption by zeolite in pilot scale plant.  $R^2$ , correlation coefficient;  $\chi^2$ , chi-square; SSE, residual sum of squares error MSE, mean sum of squares error.



The experimental data showed good agreement with the proposed model. As indicated by [Muscarella](#page-7-21) et al. (2023b), the results suggest that the NH<sub>4</sub><sup>+</sup> adsorption process by zeolite involves a mechanism that can be attributed to either ion exchange or adsorption. Among these mechanisms, ion exchange appears to be the most plausible explanation.

This is because the tested zeolites, treated with RDTWW (a solution similar to a salt solution), undergo a pre-treatment process that saturates the negative charges of the zeolite with exchangeable cations. As a result, these exchangeable cations can be easily replaced by NH<sub>4</sub><sup>+</sup> ions. Moreover, the observed ion exchange mechanism in this column study may be associated with other co-existing cations competing for adsorption sites, as suggested by Jiang et al. [\(2018\).](#page-7-32) Additionally, kinetic adsorption models are essential for understanding the adsorption process, optimizing conditions, and selecting the appropriate adsorbent material to achieve desired adsorption levels in the shortest time. The presented data shows the time required for each setup to reach a plateau in terms of cumulative adsorption of NH<sub>4</sub><sup>+</sup> kg<sup>−1</sup> and the corresponding adsorption levels at that point. The plateau in the three experimental setups was reached after 589 h, 131 h, and 250 h in setups 1, 2, and 3, respectively. The first setup took the longest (589 h) to reach the plateau, with a cumulative adsorption of 350 mg NH<sub>4</sub><sup>+</sup> kg<sup>−1</sup>. On the other hand, the second setup reached the same adsorption level (350 mg  $NH_4^+$  kg $^{-1}$ ) much earlier, after only 20 h, while the third setup reached it after 45 h.

The difference in the time taken to reach the same adsorption level can be attributed to particle size and flow rate [\(Han](#page-7-14) et al., [2019](#page-7-14)). In setups II and III, zeolite with smaller particle sizes was used, providing a larger surface area than larger particles. In contrast, the setup I had slower kinetics due to the use of larger particles with a smaller surface area, resulting in a slower adsorption rate. The flow rate affects the contact time between  $NH_4^+$  and zeolite during the adsorption process. A higher flow rate can facilitate a more rapid exchange of cations on the surface, leading to faster saturation. Combining the effects of particle size and flow rate, setup II demonstrated higher efficiency in reaching the desired adsorption level earlier. This efficiency is crucial in practical applications where time and resources are critical factors.

### **4. Conclusions**

This study investigated the effect of zeolite particle diameter (0.5–1.0 mm and 2.0–5.0 mm) and influent flow rate (1.6 and  $2.3$  L  $\rm h^{-1}$ ) on NH<sub>4</sub><sup>+</sup> adsorption from real domestic treated wastewater. Findings revealed that maximum NH<sub>4</sub><sup>+</sup> recovery (49%) and adsorption rate can be achieved by using zeolite with the smallest particle diameter (0.5–1.0 mm) and the highest influent flow rate  $(2.3 L h<sup>-1</sup>)$ . The maximum NH<sub>4</sub><sup>+</sup> adsorption rate was 1.2, 21 and 9.8 mg NH<sub>4</sub><sup>+</sup> kg<sup>-1</sup> h<sup>-1</sup> after 205, 32 and 35 h of operation. NH<sub>4</sub><sup>+</sup> adsorption rate data were analysed by fitting them to both pseudo-first and pseudo-second-order kinetic models. The former bestapproximated NH<sub>4</sub><sup>+</sup> adsorption data thus suggests that the amount of NH<sub>4</sub><sup>+</sup> adsorbed depended solely on the amount of NH<sub>4</sub><sup>+</sup> in contact with the zeolite surface. The current study successfully established the application of a zeolite-packed column in the removal of NH<sup>4</sup> + from domestic wastewater and the impacts of process parameters.

#### **CRediT authorship contribution statement**

**Sofia Maria Muscarella:** Writing – original draft, Visualization, Methodology, Investigation. **Vito Armando Laudicina:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources. **Daniele Di Trapani:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources. **Giorgio Mannina:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Project administration, Funding acquisition, Formal analysis, Data curation, Conceptualization.

## **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**

The data that has been used is confidential.

### **Acknowledgements**

This work was funded by the project "Achieving wider uptake of water-smart solutions—WIDER UPTAKE" (grant agreement number: 869283) financed by the European Union's Horizon 2020 Research and Innovation Programme, in which the last author of this paper, Giorgio Mannina, is the principal investigator for the University of Palermo. The Unipa project website can be found at: <https://wideruptake.unipa.it/>.

#### **References**

<span id="page-7-25"></span>Cosenza, A., Gulhan, H., Maida, C., Mannina, G., 2022. Nutrient recovery from wastewater treatment by [ultrafiltration](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref2) membrane for water reuse in view of a circular economy [perspective.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref2) Bioresour. Technol. 363, 127929.

<span id="page-7-9"></span>de Magalhães, L.F., da Silva, G.R., Peres, A.E.C., 2022. Zeolite application in [wastewater](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref3) treatment. Adsorpt. Sci. Technol. 2022.

- <span id="page-7-8"></span>Dong, Y., Yuan, H., Zhang, R., Zhu, N., 2019. Removal of ammonia nitrogen from wastewater: a review. [Transactions](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref4) of the ASABE 62 (6), 1767–1778.
- <span id="page-7-12"></span>Fu, H., Li, Y., Yu, Z., Shen, J., Li, J., Zhang, M., Ding, T., Xu, L., Lee, S.S., 2020. [Ammonium](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref5) removal using a calcined natural zeolite modified with sodium nitrate. J. Hazard Mater. 393, [122481.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref5)
- <span id="page-7-5"></span>Guaya, D., Valderrama, C., Farran, A., Cortina, J.L., 2016. Modification of a natural zeolite with Fe (III) for [simultaneous](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref6) phosphate and ammonium removal from aqueous solutions. J. Chem. Technol. [Biotechnol.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref6) 91 (6), 1737–1746.
- <span id="page-7-2"></span>Guaya, D., [Valderrama,](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref7) C., Farran, A., Sauras, T., Cortina, J.L., 2018. Valorisation of N and P from waste water by using natural reactive hybrid sorbents: nutrients (N, P, K) release evaluation in amended soils by dynamic [experiments.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref7) Science of the total environment 612, 728–738.
- <span id="page-7-6"></span>Guida, S., Potter, C., Jefferson, B., Soares, A., 2020. [Preparation](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref8) and evaluation of zeolites for ammonium removal from municipal wastewater through ion exchange [process.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref8) Sci. Rep. 10 (1), 1–11.
- <span id="page-7-14"></span>Han, C., Yang, T., Liu, H., Yang, L., Luo, Y., 2019. [Characterizations](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref9) and mechanisms for synthesis of chitosan-coated Na–X zeolite from fly ash and as (V) adsorption study. [Environ.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref9) Sci. Pollut. Control Ser. 26, 10106–10116.
- <span id="page-7-28"></span>Ho, Y.S., Wase, D.A.J., Forster, C.F., 1996. Removal of lead ions from aqueous solution using sphagnum moss peat as [adsorbent.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref10) WaterSA 22, 219–224.
- <span id="page-7-11"></span>Huang, H., Xiao, X., Yan, B., Yang, L., 2010. [Ammonium](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref12) removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. J. Hazard Mater. 175 (1–3), 247–[252.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref12)
- <span id="page-7-32"></span>Jiang, D., Chu, B., Amano, Y., Machida, M., 2018. Removal and recovery of [phosphate](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref13) from water by Mg-laden biochar: batch and column studies. Colloids Surf. A [Physicochem.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref13) Eng. Asp. 558 (September), 429–437.
- <span id="page-7-23"></span>Jørgensen, Sven Erik, 1989. Chapter 4 - adsorption and ion exchange. In: Jørgensen, S.E., Gromiec, M.J. (Eds.), [Mathematical](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref14) Submodels in Water Quality Systems, vol 14. [Elsevier,](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref14) pp. 65–81. C.
- <span id="page-7-27"></span>Lagergren, S., 1898. About the theory of so-called adsorption of soluble substances. K. Sven. [Vetenskapsakad.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref15) Handl. 24, 1–39.
- <span id="page-7-17"></span>Li, C., Yu, Y., Zhang, Q., Zhong, H., Wang, S., 2020. Removal of ammonium from aqueous solutions using zeolite [synthesized](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref16) from electrolytic manganese residue. Int. J. [Chem.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref16) Eng. 2020.
- <span id="page-7-10"></span>López-Rosales, L., López-García, P., Benyachou, M.A., Molina-Miras, A., [Gallardo-Rodríguez,](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref17) J.J., Cerón-García, M.C., et al., 2022. Treatment of secondary urban wastewater with a low [ammonium-tolerant](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref17) marine microalga using zeolite-based adsorption. Bioresour. Technol. 359, 127490.
- <span id="page-7-3"></span>Mannina, G., Badalucco, L., Barbara, L., Cosenza, A., Di Trapani, D., Gallo, G., Laudicina, V.A., Marino, G., Muscarella, S.M., Presti, D., Helness, H., 2021. Enhancing a transition to a circular economy in the water sector: the EU project WIDER UPTAKE. Water 13 (7), 946. [https://doi.org/10.3390/w13070946.](https://doi.org/10.3390/w13070946)
- <span id="page-7-24"></span>Mannina, G., Alduina, R., Badalucco, L., Barbara, L., Capri, F.C., Cosenza, A., Di Trapani, D., Gallo, G., Laudicina, V.A., Muscarella, S.M., Presti, D., 2021a. Water resource recovery facilities (Wrrfs): the case study of palermo university (Italy). Water (Switzerland) 13, 1–19. [https://doi.org/10.3390/w13233413.](https://doi.org/10.3390/w13233413)
- <span id="page-7-16"></span>Mannina, G., Gulhan, H., Ni, B., 2022. Water reuse from wastewater treatment: the transition towards circular economy in the water sector. Bioresour. Technol. 363, 127951. [https://doi.org/10.1016/j.biortech.2022.127951.](https://doi.org/10.1016/j.biortech.2022.127951)
- <span id="page-7-26"></span>Michalski, R., 2018. Ion chromatography applications in wastewater analysis. Separations 5. [https://doi.org/10.3390/separations5010016.](https://doi.org/10.3390/separations5010016)
- <span id="page-7-15"></span>Muscarella, S.M., Badalucco, L., Cano, B., Laudicina, V.A., Mannina, G., 2021. [Ammonium](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref22) adsorption, desorption and recovery by acid and alkaline treated zeolite. [Bioresour.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref22) Technol. 341, 125812.
- <span id="page-7-4"></span>Muscarella, S.M., Badalucco, L., Laudicina, V.A., Mannina, G., 2023a. Zeolites for the nutrient recovery from wastewater. In: Current Developments in [Biotechnology](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref23) and [Bioengineering.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref23) Elsevier, pp. 95–114.
- <span id="page-7-21"></span>[Muscarella,](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref24) S.M., Laudicina, V.A., Cano, B., Badalucco, L., Conte, P., Mannina, G., 2023b. Recovering ammonium by treated and untreated zeolitic mixtures : a [comprehensive](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref24) experimental and modelling study. Microporous Mesoporous Mater. 349 (January), 112434.
- <span id="page-7-0"></span>Naddaf, M., 2023. The World Faces a Water Crisis—4 [Powerful](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref25) Charts Show How.
- <span id="page-7-7"></span>Pinelli, D., Foglia, A., Fatone, F., Papa, P., Maggetti, C., Bovina, S., Frascari, D., 2022. Ammonium recovery from municipal wastewater by ion exchange: Development and application of a procedure for sorbent selection. J. Environ. Chem. Eng. 10, 108829. <https://doi.org/10.1016/j.jece.2022.108829>.
- <span id="page-7-1"></span>Preisner, M., 2023. [Phosphorus-driven](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref27) eutrophication mitigation strategies. In: Sustainable and Circular Management of Resources and Waste towards a Green Deal. [Elsevier,](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref27) pp. 257–268.
- <span id="page-7-22"></span>Revellame, E.D., Fortela, D.L., Sharp, W., Hernandez, R., Zappi, M.E., 2020. Adsorption kinetic modeling using pseudo-first order and [pseudo-second](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref28) order rate laws: a review. Cleaner [Engineering](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref28) and Technology 1, 100032.
- <span id="page-7-29"></span>Sahoo, T.R., Prelot, B., 2020. Adsorption processes for the removal of contaminants from wastewater: the perspective role of nanomaterials and [nanotechnology.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref29) In: [Nanomaterials](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref29) for the Detection and Removal of Wastewater Pollutants. Elsevier, pp. 161–222.
- <span id="page-7-13"></span>Sengupta, S., Nawaz, T., Beaudry, J., 2015. Nitrogen and phosphorus recovery from [wastewater.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref30) Current Pollution Reports 1 (3), 155–166.
- <span id="page-7-18"></span>Sprynskyy, M., [Lebedynets,](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref31) M., Terzyk, A.P., Kowalczyk, P., Namieśnik, J., Buszewski, B., 2005. Ammonium sorption from aqueous solutions by the natural zeolite [Transcarpathian](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref31) clinoptilolite studied under dynamic conditions. J. Colloid Interface Sci. 284 (2), 408–415.
- <span id="page-7-31"></span>Sundhararasu, E., Runtti, H., Kangas, T., Pesonen, J., Lassi, U., Tuomikoski, S., 2022. Column adsorption studies for the removal of ammonium using Na-Zeolite-Based geopolymers. Resources 11, 119. [https://doi.org/10.3390/resources11120119.](https://doi.org/10.3390/resources11120119)
- <span id="page-7-19"></span>Tran, T., Le, D.A., Tuong, L.Q., Loc, H.H., Van Tan, L., 2020. Evaluation of natural zeolite as adsorbent material for the recovery of nutrients from manure [wastewater.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref33) IOP Conf. Ser. Mater. Sci. Eng. 736 (7), 072007. . IOP [Publishing.](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref33)
- <span id="page-7-20"></span>Vocciante, M., Alessandra De Folly, D., Finocchi, A., Tagliabue, M., Bellettato, M., Ferrucci, A., Ferro, S., 2018. Adsorption of ammonium on [clinoptilolite](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref34) in presence of competing cations: [Investigation](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref34) on groundwater remediation. J. Clean. Prod. 198, 480–487.
- <span id="page-7-30"></span>Wang, J., Guo, X., 2020. Adsorption kinetic models: physical meanings, [applications,](http://refhub.elsevier.com/S2352-5541(24)00234-1/sref35) and solving methods. J. Hazard Mater. 390, 122156.