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**NITROGEN RECOVERY FROM MUNICIPAL WASTEWATER THROUGH
CLINOPTILOLITE-BASED ADSORPTION FOR STRUVITE PRECIPITATION**

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Abstract: The valorization of municipal wastewater offers a promising route for recovering essential nutrients for agriculture, such as nitrogen and phosphorus. This study evaluated the adsorption of ammonium using clinoptilolite, a natural zeolite with high cation exchange capacity. Column tests achieved up to 90% NH_4^+ removal and over 80% desorption, allowing nutrient concentration for subsequent recovery. Zeolite regeneration using alkaline solution or thermal treatment enabled its reuse. The column eluate, enriched in ammonium, was then combined with magnesium and phosphate salts, enabling the precipitation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) under alkaline conditions. The resulting slow-release fertilizer contains N, P, and Mg, promoting circular economy practices and contributing to food security.

Keywords: Ammonium, Adsorption, Clinoptilolite, Struvite, Wastewater.

**RECUPERAÇÃO DE NITROGÊNIO DE EFLUENTES MUNICIPAIS POR ADSORÇÃO
COM CLINOPTILOLITA PARA PRECIPITAÇÃO DE ESTRUVITA**

Resumo: A valorização do esgoto municipal oferece uma rota promissora para a recuperação de nutrientes essenciais à agricultura, como nitrogênio e fósforo. Este estudo avaliou a adsorção de amônio utilizando clinoptilolita, uma zeólita natural com alta capacidade de troca iônica. Testes em coluna alcançaram até 90% de remoção de NH_4^+ e mais de 80% de dessorção, concentrando nutrientes para posterior recuperação. A regeneração da zeólita com solução alcalina ou tratamento térmico permitiu sua reutilização. O eluído da coluna, enriquecido em amônio, foi então combinado com sais de magnésio e fósforo, possibilitando a precipitação de estruvita ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) em meio alcalino. O fertilizante resultante, de liberação lenta, contém N, P e Mg, promovendo práticas de economia circular e contribuindo para a segurança alimentar.

Palavras-chave: Amônio, Adsorção, Clinoptilolita, Estruvita, Efluente.

1. Introduction

Brazil's reliance on imported fertilizers compromises the stability and sovereignty of its agricultural sector, especially under geopolitical or market instabilities (FAO, 2021). Recovering nutrients from urban waste has therefore emerged as a strategic and sustainable alternative, promoting circularity in agricultural systems. Reintegration of nitrogen and phosphorus into production chains helps reduce environmental burdens and supports nutrient self-sufficiency (Cordell et al., 2009).

Among these nutrients, ammoniacal nitrogen (NH_4^+) stands out for its solubility, mobility, and key role in plant nutrition. Municipal wastewater and sewage sludge from treatment plants are rich in NH_4^+ , and improper disposal may cause serious ecological and health issues. Recovering this compound allows its transformation into struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), a valuable slow-release fertilizer, which can be obtained via chemical precipitation in alkaline conditions with added magnesium and phosphate (Le Corre et al., 2009).

Clinoptilolite, a natural zeolite with high cation exchange capacity and structural selectivity, offers an efficient and low-cost medium for NH_4^+ adsorption. Its pore size is well-suited to the ammonium ion, allowing stable and selective retention, especially in column-based systems. This work aimed to recover ammoniacal nitrogen from municipal effluent using clinoptilolite adsorption followed by struvite precipitation, integrating waste valorization with sustainable fertilizer production.

2. Materials and Methods

2.1. Column Adsorption System

The nitrogen recovery system (Figure 1) consisted of a vertical glass column packed with two solid phases: a lower layer of clinoptilolite (green), responsible for ammonium adsorption, and an upper layer of sand (orange), acting as a flow disperser to prevent channeling. The raw effluent (yellow) was continuously pumped using a peristaltic pump to maintain a constant flow, allowing for interaction between the effluent and the clinoptilolite surface for NH_4^+ retention. The treated liquid (blue eluate) was collected at the outlet. After assembling the column, 100 g of clinoptilolite and 100 g of coarse sand were added, separated by cotton, and topped with 25 g of glass spheres to stabilize flow. Zeolite activation was performed with 6 mol L^{-1} NaOH, followed by rinsing with 20 L of Milli-Q water.

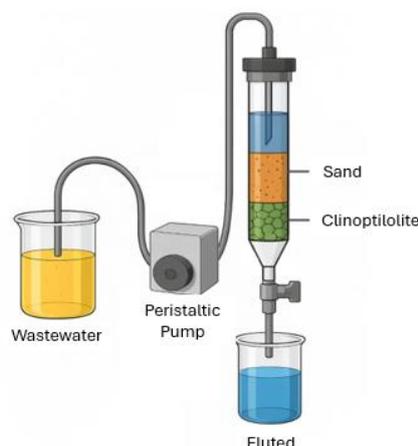


Figure 1. Nutrient recovery system using an adsorption column (Majaron, 2025).

2.2. Ammonium Adsorption Process

Adsorption was conducted by introducing 12 L of effluent into the column using a

peristaltic pump. Feeding was performed in 2 L increments to facilitate better flow control and optimal contact with the adsorbent. Effluent aliquots were collected throughout the process to evaluate the removal performance. Ammonium quantification was performed using the colorimetric method proposed by Kempers and Zweers (1986).

2.3. Ammonium Desorption and Struvite Precipitation

Two extractants were tested for ammonium recovery: NaCl and NaOH in different concentrations. Each extractor was applied in three 1 L cycles to maximize desorption. The eluates were analyzed following Kempers and Zweers (1986). The ammonium-rich solution was used for struvite precipitation by adding magnesium and phosphate at a 1.5:1.5:1 molar ratio (Mg:P:N), under alkaline conditions (pH 9.5). A white, crystalline, odorless precipitate was obtained. Characterizations were carried out by Fourier Transform Infrared Spectroscopy (FTIR) using a Bruker Vertex 70 spectrometer with ATR diamond crystal (4000–400 cm^{-1} , 4 cm^{-1} resolution), and by X-ray diffraction (XRD) using a Shimadzu LabX-6000 diffractometer (30 kV, 30 mA, $\text{CuK}\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$), with scanning from 5° to 70° (0.02° step), confirming the crystalline structure of the struvite.

3. Results and Discussion

Clinoptilolite is a natural zeolite with a microporous structure, high cation exchange capacity, and structural charge imbalances that promote selectivity for cationic species like ammonium (NH_4^+). Its affinity is enhanced by surface chemistry and the size match between NH_4^+ and its channels, resulting in strong adsorbate–matrix interactions. These features justify its selection in this study, targeting ammonium nitrogen nutrients of high agronomic value. Four adsorption cycles were conducted using 100 g of clinoptilolite in a packed column, with 2.5 L of effluent per cycle (Figure 2). The first cycle showed near-complete NH_4^+ removal, while subsequent cycles decreased to 84%, 82.7%, and 75.2%, respectively, due to progressive saturation of active sites as ammonium replaced native cations. This decline reflects typical ion exchange dynamics under increasing eluent volumes.

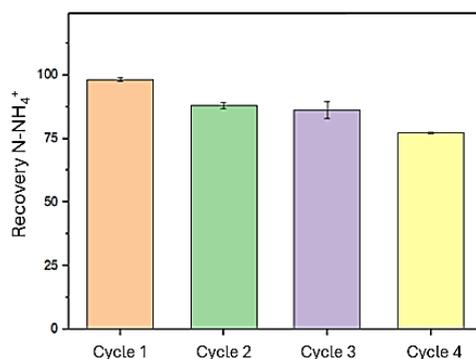


Figure 2. Ammonium removal percentages in extraction cycles.

Once saturation was reached, desorption of retained ammonium was performed using saturated NaCl and NaOH solutions to evaluate the physicochemical mechanisms involved. NaCl promoted ion exchange between Na^+ and NH_4^+ in the zeolite, while NaOH also converted NH_4^+ to NH_3 , a neutral species with low affinity for the negatively charged clinoptilolite. NaCl enabled 67.3% nitrogen recovery, whereas NaOH reached 82.9%. To reduce reagent intensity, mixed extractors (4 mol L^{-1}) with varying NaCl:NaOH ratios (4:0, 0:4, 1:3, 2:2, 3:1, 3.6:0.4) were tested. As shown in Figure 3, recovery increased with the NaOH content, reaching over 80% efficiency in higher-base treatments. The 3.6:0.4

formulation achieved a recovery of ~79.8%, similar to the highest-performing systems, but with lower NaOH usage, offering reduced risk, cost, and the need for neutralization. Results confirm that a salt-dominant ratio enables effective ionic exchange while ensuring sufficient alkalinity for the conversion of NH_4 .

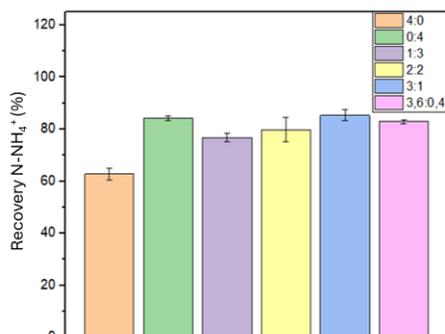


Figure 3. Percentage recovery of ammoniacal N using a variation of extractants (NaCl:NaOH).

The eluate solution enriched in ammonium was used for struvite precipitation, a slow-release fertilizer with direct agricultural applications. After passage of 25 L of primary-settler effluent through the column, the concentrated solution contained $54.16 \pm 0.14 \text{ mmol L}^{-1}$ of N-NH_4^+ , along with Mg^{2+} , PO_4^{3-} , K^+ , and Ca^{2+} (Table 1). Precipitation was induced by supplementing the solution with magnesium chloride and monobasic ammonium phosphate at a molar ratio of 1.5:1.5:1 (Mg:P:N), under a pH of 9.5, to drive crystallization while avoiding the formation of competing species, such as magnesium hydroxide.

Table 1. Chemical quantification of zeolitic column concentrate in mmol L^{-1} .

	Mg^{2+}	N-NH_4^+	P-PO_4^{3-}	K^+	Ca^{2+}
Original Wastewater	0.483 ± 0.019	2.875 ± 0.055	0.173 ± 0.013	0.387 ± 0.008	0.778 ± 0.002
Concentrated solution	3.432 ± 0.098	54.16 ± 0.142	0.188 ± 0.047	3.151 ± 0.801	4.775 ± 0.293

Precipitation occurred instantly, yielding a white, odorless solid visually consistent with struvite (Figure 4a). The process achieved a 96.5% yield based on NH_4^+ removal. X-ray diffraction analysis (Figure 4b) confirmed the presence of characteristic crystalline phases of struvite. FTIR analysis also revealed vibrational bands corresponding to phosphate and ammonium functional groups, corroborating the material's identity.

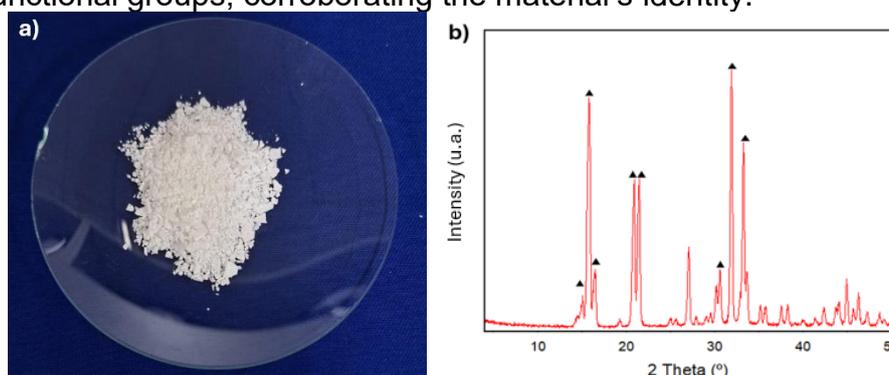


Figure 4. a) Struvite produced using a Zeolitic column and (b) XRD.

These findings demonstrate the technical feasibility of using clinoptilolite as a selective matrix for ammonium capture in column systems, as well as its effective recovery using appropriately formulated extractants. The concentration step, followed by struvite precipitation, constitutes an integrated and sustainable approach for recovering nutrients from wastewater and generating high-value fertilizers.

4. Conclusions

The results confirm the technical and environmental viability of clinoptilolite for recovering ammonium from wastewater. Selective adsorption and desorption using NaCl/NaOH proved effective, especially with mixed extractants. Struvite was precipitated with over 96% efficiency, yielding a valuable fertilizer. The process supports circular economy strategies and sustainable wastewater treatment. In Brazil, it can reduce fertilizer imports and enhance food security.

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References

- Cordell, D., Drangert, J.-O., & White, S. (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change*, 19(2), 292–305. <https://doi.org/10.1016/j.gloenvcha.2008.10.009>
- FAO – Food and Agriculture Organization of the United Nations. (2021). World fertilizer trends and outlook to 2022. <https://www.fao.org/publications>
- Le Corre, K. S., Valsami-Jones, E., Hobbs, P., & Parsons, S. A. (2009). Phosphorus recovery from wastewater by struvite crystallization: A review. *Critical Reviews in Environmental Science and Technology*, 39(6), 433–477. <https://doi.org/10.1080/10643380701640573>
- Shih, K., & Yan, W. (2016). Crystallization behavior and characterization of struvite from wastewater. *Environmental Technology*, 37(10), 1281–1290. <https://doi.org/10.1080/09593330.2015.1108320>
- Wang, S., & Peng, Y. (2010). Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*, 156(1), 11–24. <https://doi.org/10.1016/j.cej.2009.10.029>