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Scalable ammonium recovery from livestock and municipal digestates with zeolitic-rich tuffs

University of Ferrara

Alberghini, M.[1], Galamini G.[2], Faccini, B.[1] and Ferretti,G.[3]

[1]Department of Environmental and Prevention Science, University of Ferrara

[2]Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia

[3]Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara

STRUVITE Fertilisers for the Circular Economy

INTRODUCTION & AIM

Nitrogen (N) is a key nutrient for crop growth and food production, but the excessive use of synthetic fertilizers leads to environmental problems, including eutrophication and greenhouse gas (GHG) emissions. Organic fertilizers, such as those derived from anaerobic digestion (digestates), provide an alternative, yet their nutrient content can be inconsistent, complicating their proper dosage for agricultural use. Zeolites, especially chabazite-rich tuff, present an effective and sustainable method for ammonium (NH_4^+) removal from waste streams. They adsorb ammonium ions and can be reused as slow-release fertilizers, promoting improved soil health, reducing nutrient loss, and minimizing environmental impact.

This **study aims** to evaluate the effectiveness of ammonium removal from municipal solid waste and livestock digestates by a chabazite-rich tuff. It will focus on determining adsorption kinetics, performing isotherm analysis, and estimating daily and annual nitrogen recovery under realistic conditions (10 m³/day). The approach will be validated in real farm settings using chabazite-rich tuff.

METHOD

MATERIALS

Digestates:

- Swine (SD):
  - SD-S: Swine separated by screw compression;
  - SD-M: Swine microfiltered.
- Municipal Solid Waste (MD):
  - MD-R: Raw digestate;
  - MD-C: Clarified digestate by centrifugation.
- Cattle Digestates (CD-S):Separated by screw compression.

General Features: All digestates are rich in NH_4^+-N and total solids.Livestock-derived digestates show the highest concentrations of NH_4^+ and total solids (TS).CD-S (cattle digestate) also has high K^+ content.

Zeolitic Tuff:

- Source: Chabazite-rich tuff from Sorano Formation (Latera Volcanic Complex, Grosseto, Italy).
- Main Mineral: **Chabazite (68.5%)**. Other Minerals: Phillipsite, Analcime, K-feldspar, Mica, Pyroxene, and Volcanic glass.
- CEC: **2.17 meq/g** (Ca^{2+} 1.46, K^+ 0.60, Na^+ 0.07, Mg^{2+} 0.04).
- Particle Size Distribution:12.5% 5-2 mm, **60.4% 2-0.8** mm, 24.1% 0.8-0.425 mm and 3% < 0.425 mm

ADSORPTION & KINETIC TESTS

Adsorption Tests:

- **Conditions**: 12 S/L ratios, 100 mL digestate, 25°C, 24 h at 200 rpm.
- **Models**: Freundlich (multilayer, heterogeneous), Langmuir (monolayer, homogeneous).

Kinetic Tests:

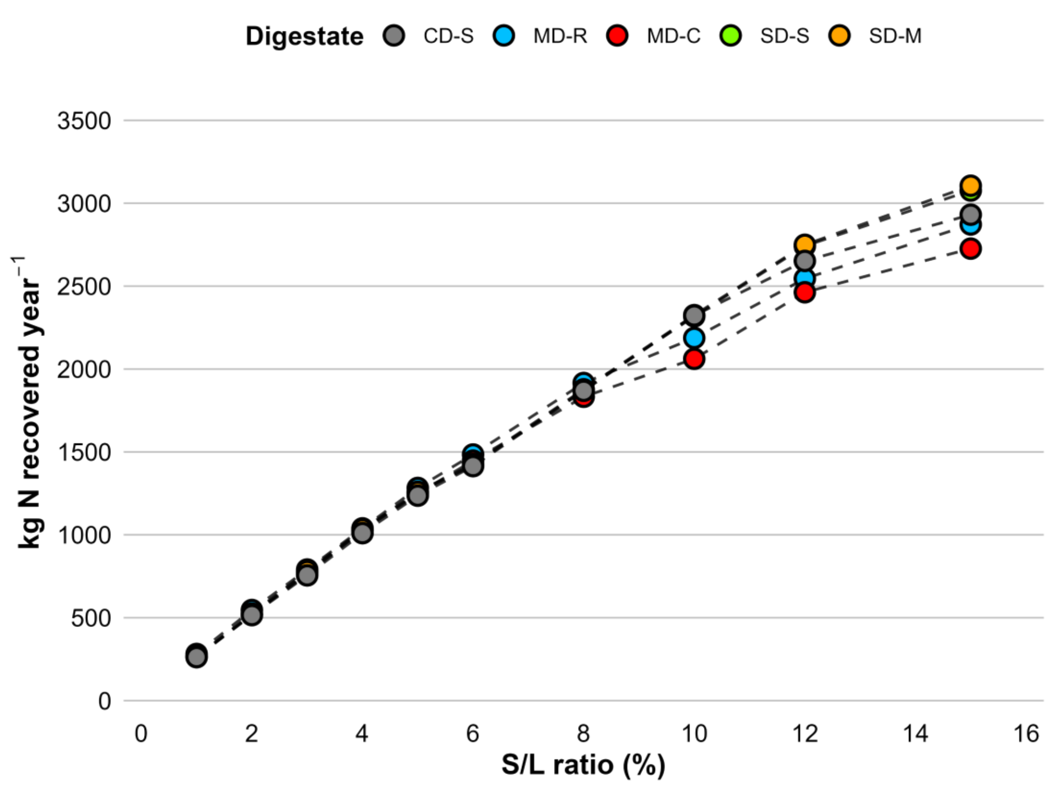
- **Conditions**: 5% S/L, 500 mL digestate, 200 rpm.
- **Time Points**: 13 (5-420 minutes).
- **Models**: Pseudo-First Order (PFO), Pseudo-Second Order (PSO), Intraparticle Diffusion (ID).

Nitrogen Recovery Estimation:

- **Model**: Continuous operation, optimal adsorption capacity, 10 m³/day digestate production.
- **Field Conditions**: Swine microfiltered digestate (S/L = 3%), 3 cycles/day, 1.5-hour cycle duration.

RESULTS & DISCUSSION

1. **Adsorption Isotherms & Thermodynamic Insights:**
   - Both Langmuir and Freundlich models fit well, indicating a combination of homogeneous and heterogeneous interactions in the adsorption process
   - .Municipal digestates (MD-C, MD-R) showed higher n and Kf values and lower RL, indicating higher adsorption capacity and more favorable interactions.
2. **Ammonium Removal Over Time:**
   - Equilibrium was reached within 90-120 minutes, faster for high-NH_4^+ livestock digestates.
   - PFO kinetics dominated, contrary to most literature that typically shows PSO.
   - Ion exchange was identified as the dominant mechanism, with rapid surface ion-exchange followed by slower intraparticle diffusion.
3. **Key Observations on Digestate Properties:**
   - Physical-chemical properties (Total Solids, K^+ content) strongly influenced NH_4^+ removal efficiency.
   - Pre-treatment (clarification, microfiltration) improved adsorption efficiency, leading to faster equilibrium and better NH_4^+ removal.
4. **Scalability of Nitrogen Recovery:**
   - Farm-scale model: Up to 3000 kg N/year recoverable from livestock digestates with lower recovery but higher removal efficiency for MSW digestates.
   - Field data: Zeolite loading of 11 g NH_4^+/kg zeolite, estimated 715 kg N/year nitrogen recovery using current batch setup.



CONCLUSION

The chabazite-rich zeolite proved effective in NH_4^+ recovery from digestates, with better performance in livestock digestates and rapid kinetics. The digestate composition and pre-treatment strongly influence adsorption efficiency and NH_4^+ removal. A farm-scale test confirmed process feasibility, with an estimated 715 kg N/year recovery, and the spent zeolite could be used as a slow-release nitrogen fertilizer, contributing to a circular nutrient management system.

FUTURE WORK

Future works will focus on continuing field tests to optimize the system for continuous-flow operation, aiming to enhance nitrogen recovery and overall process efficiency.