Use of natural zeolites for abatement of ammonium in animal slurries and waste waters

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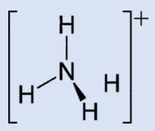
Ammonium



- Nutritive for plants
- Nitrogen source for protein biosynthesis (along with Nitrates)
- Used as a fertiliser

If N is exceeding crops requirements?

POLLUTION
- Aquifer
- Eutrophication

Abatement needed!

Zeolite can be the solution!

Zeolites: aluminosilicate minerals whit **natural microporous structure** that can accommodate a wide variety of **cations**, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others positive ions that are rather loosely held and **can readily be exchanged for others in a contact solution, such as Ammonium.**

How does it work?

Semi-continuous system:

Ammonia solution recirculated through micro punctured vessel in which zeolite* was laid.

After 24h contact, reaches equilibrium:

Abatement: 70.8%

Ammonium sorbed: **7.8 mg/g of zeolite**

Is zeolite saturated in ammonium?

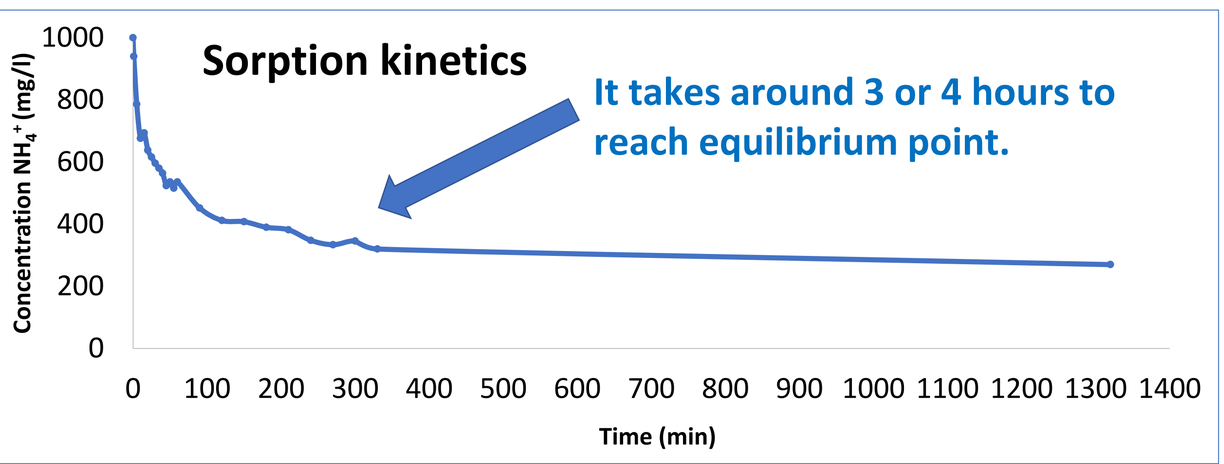
* Natural zeolite – Clinoptilolite 90-95%, Cristobalite 0-5%, Tridymite 0-5%

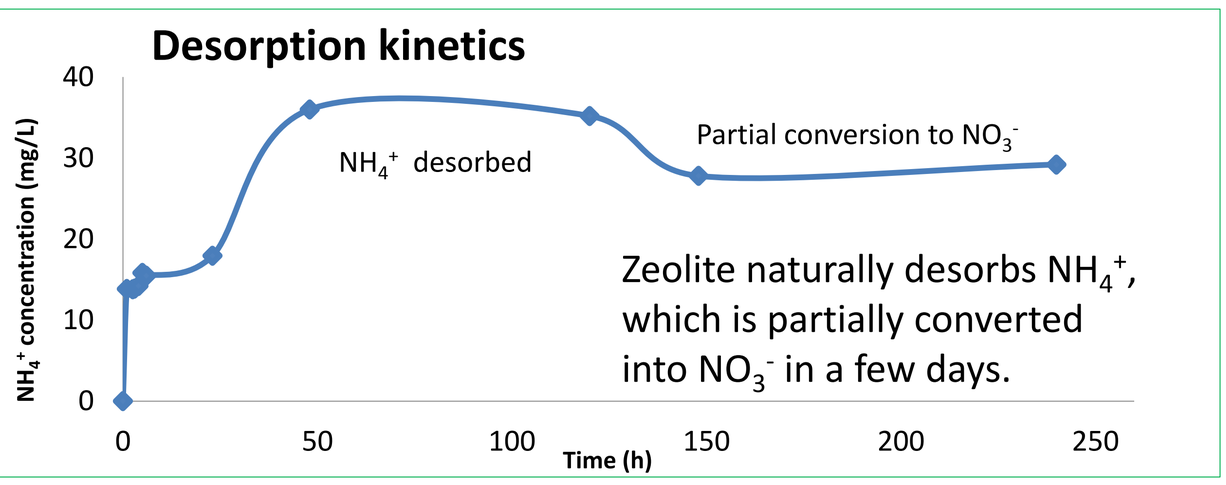
Zeolite was put again in contact with new NH_4^+ solution (1000 mg/l NH_4^+) many times, pushing it to subsequent equilibriums to evaluate saturation point:

After 6 cycles zeolite stopped sorbing:
Saturation point = 20.24 mg/g.
To improve abatement, equilibrium beetween [ammonium] and [zeolites cations] must be forced to make zeolite sorb again beyond it's «stabilisation» point.

Exchange: How fast?

To evaluate kinetics, NH_4^+ concentration was observed in a 24h time at different intervals. The first hour shows fast sorption ratios and concentration was checked in 5 minutes intervals. Further intervals are way more distant because of the slow kinetics going on with sorption.





Sorption: How is influenced?

Zeolite was tested in different conditions to evaluate the influence of:

1. Concentration
2. NH_4^+ absolute quantity
3. Volume
4. pH

Concentration	Absolute quantity	Volume	pH	Results	
Variating	Constant	*Variating*	Constant	Increasing concentration	Poorly increasing sorption
Constant	*Variating*	*Variating*	Constant	Increasing absolute quantity	Highly increasing sorpion
Variating	*Variating*	Constant	Constant	Increasing volume	Sorption constant
Constant	Constant	Constant	*Variating*	Best pH	8 ÷ 9

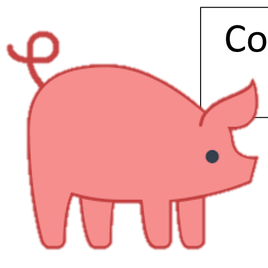
Higher ammonium quantity → **Higher zeolite sorption (11 mg/g)**

Best pH conditions → **Between 8 and 9**

Zeolite works better when NH_4^+ quantity is high, and continues its performance even after first sorption. It's better to leave zeolite in contact with solution for a long time, at a pH between 8 and 9.

How does it work in real situations?

Animal slurries (pigs)



Conc NH_4^+ (mg/l) ~ 4000
pH = 8.4

→ Abatement: 82% - 12.2 mg/g

Why so good? → High NH_4^+ quantity, Ideal pH

Less zeolite is going to be used

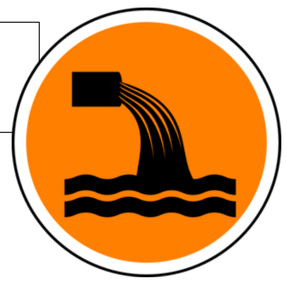
Waste waters (anthropic source)

Conc NH_4^+ (mg/l) ~ 23.3
pH = 7.8

→ Abatment: 66% - 2.8 mg/g

Why so bad? → Low NH_4^+ quantity, Bad pH

More zeolite is going to be used



Conclusions

Zeolites:

- **Good ammonium sorbers**
- **Natural, non-pollutant materials**
- **Low cost**
- **Can be re-utilised as agricoltural ammendants**

NH_4^+ is slowly released and converted into NO_3^-

Zeolite can give plants the nitrogen needed without polluting aquifers or soil.