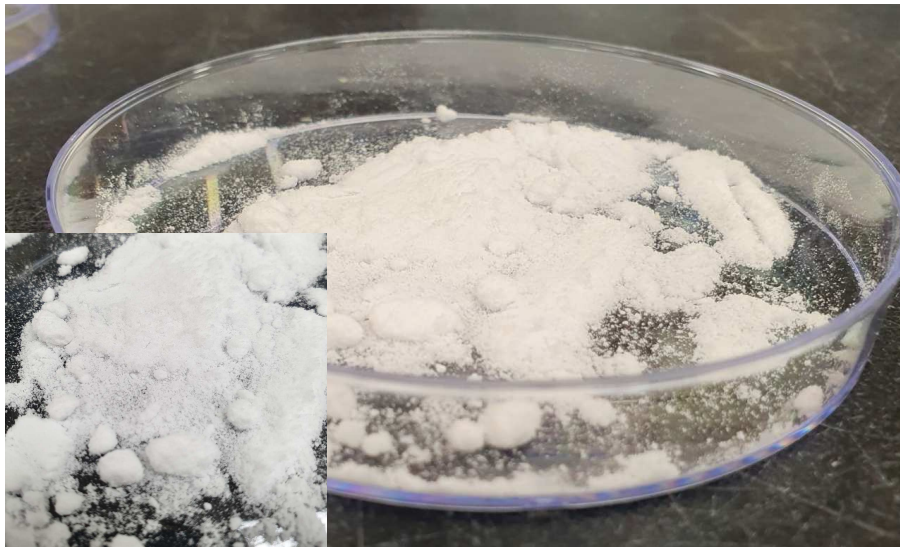


Harvesting high-purity ammonium salt
from wastewater
via membrane contact and
solvent-driven fractional crystallization



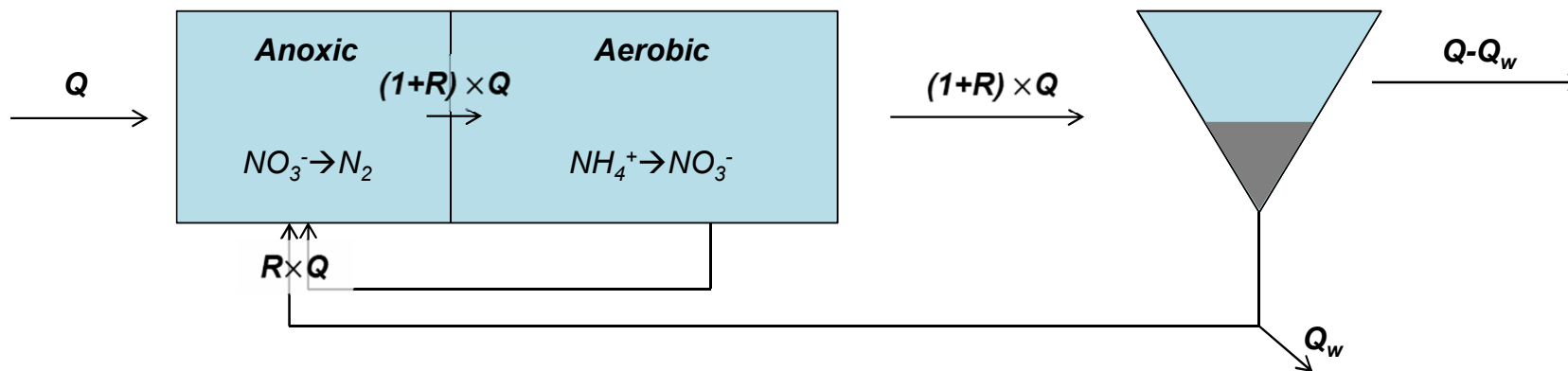
Nitrogen (N) in wastewater – treatment needs

- Eutrophication problem; ammonia (NH_3) toxicity; health impact by nitrate (NO_3^-)
- ~ 50 mg N/L in domestic wastewater (sewage) → < 20 mg/L discharge limit (S. Korea)
- Most Korean wastewater treatment plants adopt biological N removal process



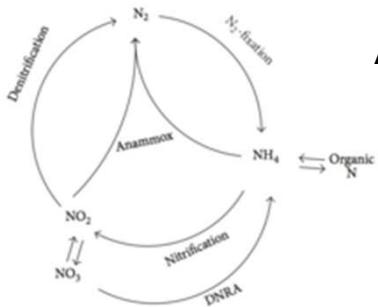
How to achieve enhanced N removal?

Preanoxic denitrification [e.g., Modified Ludzack-Ettinger (MLE) process]



- If 100% efficiency in each segment, removal efficiency = $R/(1+R) \times 100$ (%)
 - Reactor size increases by a factor of $(1+R)$
 - Energy ++ for aeration & pumping
- NH_4^+ [N(-III); high value] \rightarrow NO_3^- [N(+V); lower value] \rightarrow N_2 [N(0); no value]

N removal from wastewater – suggested alternatives for sewage



Anammox: $\text{NO}_2^- + \text{NH}_4^+ \rightarrow \text{N}_2$

- 1-2 yrs for reactor setup
- Operational challenges
- No potential for N utilization



Struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$)

formation

- $\text{NH}_4^+ : \text{Mg}^{2+} : \text{PO}_4^{3-} = 1:1:1$ ratio (molar)
- Impurities



Ion exchange (+ IX resin regen for NH_4^+ recovery)

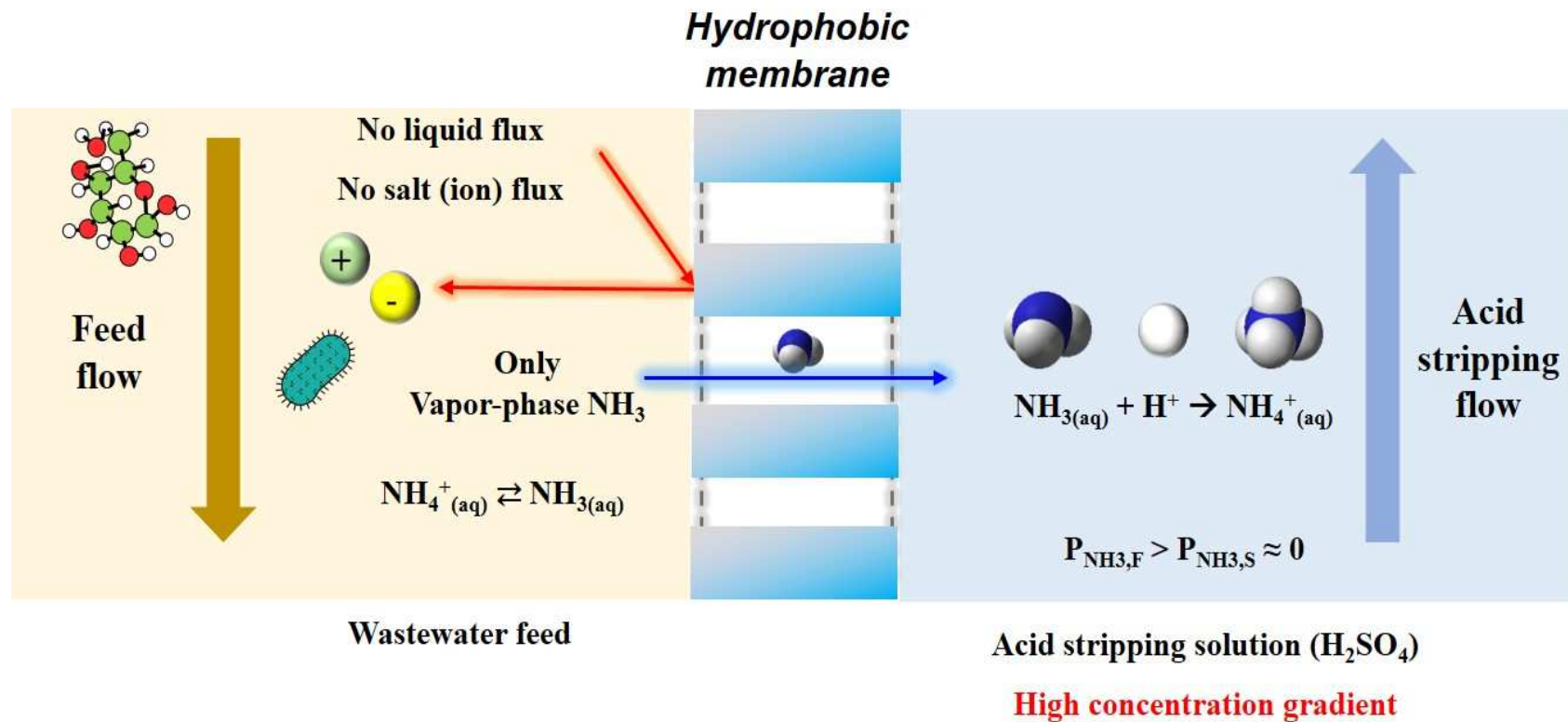
- Cost & environ. impacts (brine for regen)
- Coexistence of other cations in regen solution



Ammonia stripping

- High cost, limited efficiency
- Scaling issue

Ammonia extraction from sewage using membrane contactor

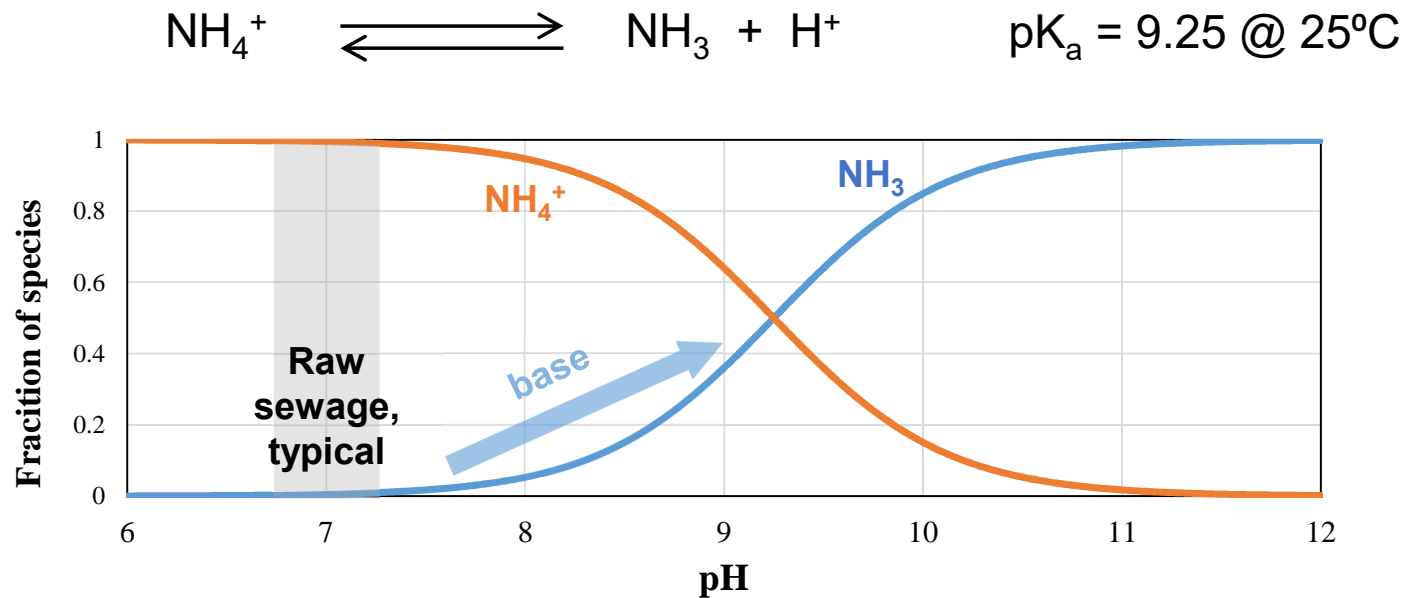


- **Complete rejection** of liquid water-carrying impurities → high purity product
- Feed → strip flux ensured as long as the strip solution pH is low enough
- Holds generic advantages of membrane processes: scalability, low areal footprint

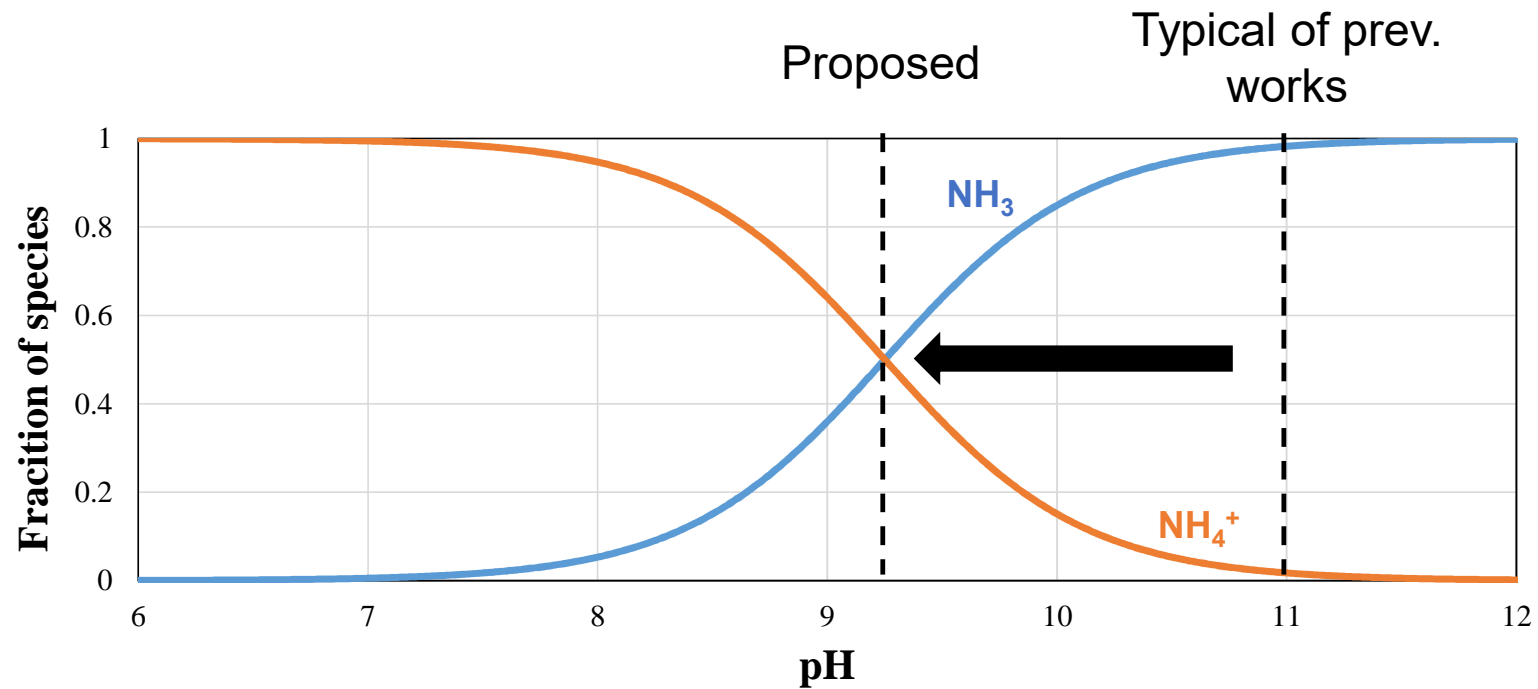
Challenge I – chemical cost

- For reasonable $\text{NH}_3\text{-N}$ flux, base should be added to the feed solution (sewage)

Does it make sense to spend chemicals to raise pH of a massive amount of sewage??



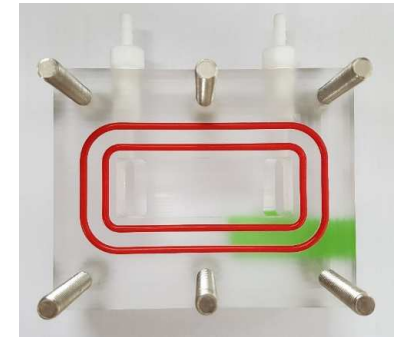
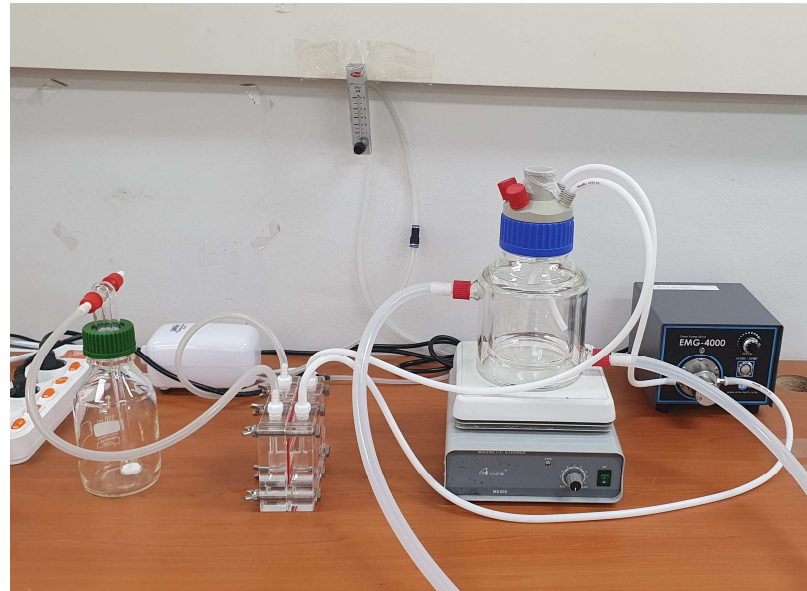
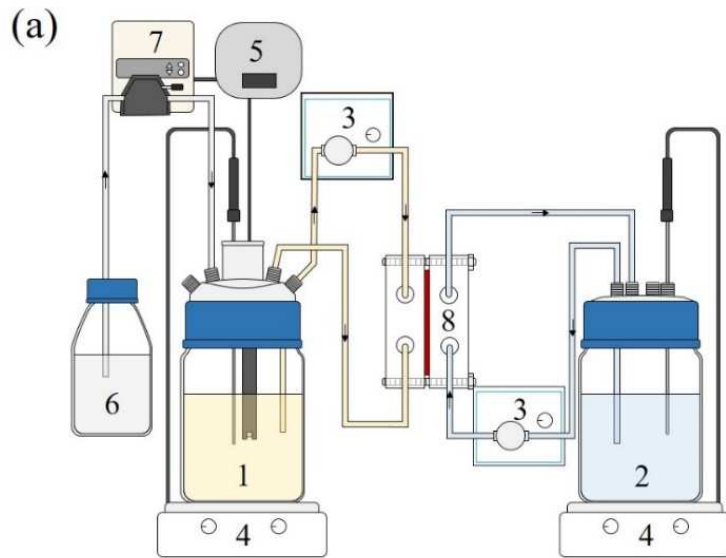
A simple idea: What if we apply lower pH_{feed} ?



- We may get some loss in kinetics but instead we get chemical cost savings
- **How much loss? vs. How much benefit?**

Experimental setup

DCMD (direct contact membrane distillation) system

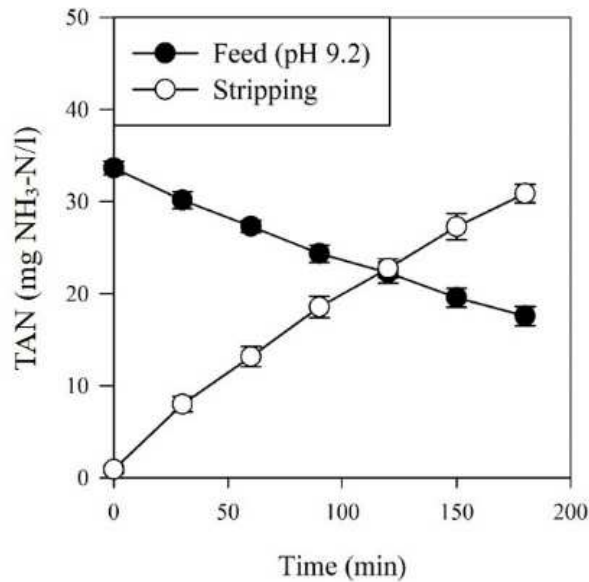


- Used **real sewage** as a feed, 0.1 N H₂SO₄ as a stripping solution
- Polyvinylidene fluoride (PVDF) membrane
- pH_{feed} maintained @ 9.2 or 11.0

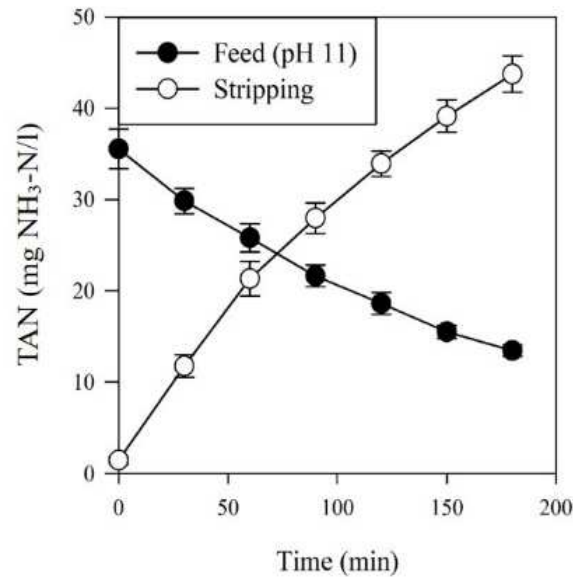
3-hr experiments

*slope = rate const.

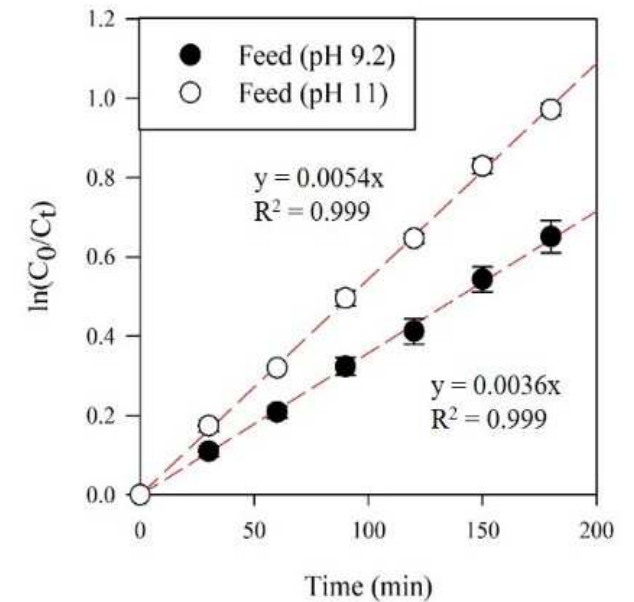
$\text{pH}_{\text{feed}} = 9.2$



$\text{pH}_{\text{feed}} = 11.0$



pH 9.2 vs. 11.0
(linearized plot*)

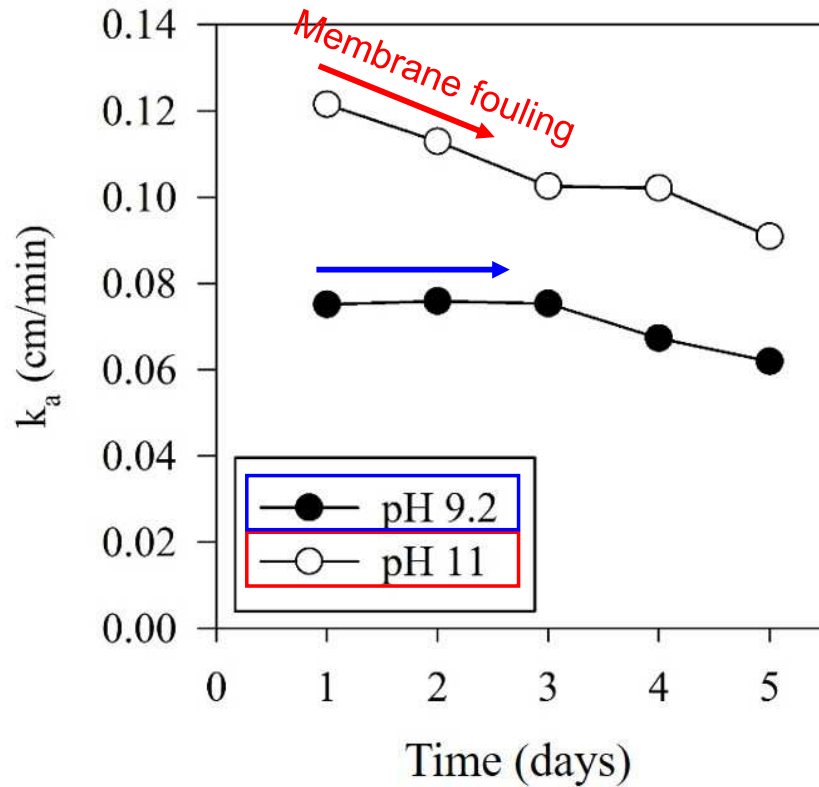


- **Only 25% loss in kinetics by pH_{feed} 11.0 \rightarrow 9.2 (@ 30 °C)**

Remember that ammonia fraction calculation tells the loss should be 38%

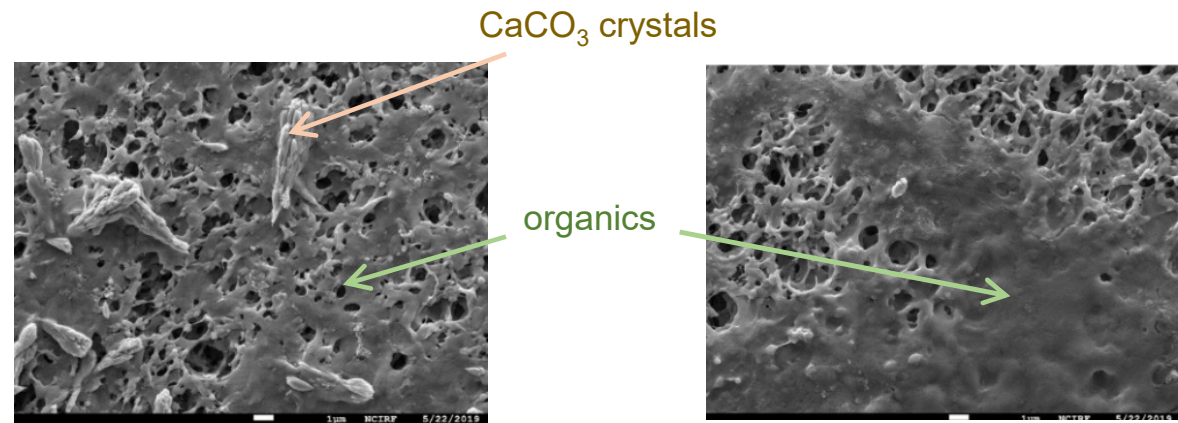
$$\alpha_{\text{NH}_3} = [\text{NH}_3]/([\text{NH}_3]+[\text{NH}_4^+]) = 0.61 \text{ @ pH}=9.2 \text{ vs. } \alpha_{\text{NH}_3} = 0.98 \text{ @ pH } 11.0; (0.98-0.61)/0.98 \times 100 = 38\%$$

5-d experiments



k_a = apparent mass transfer coeff.

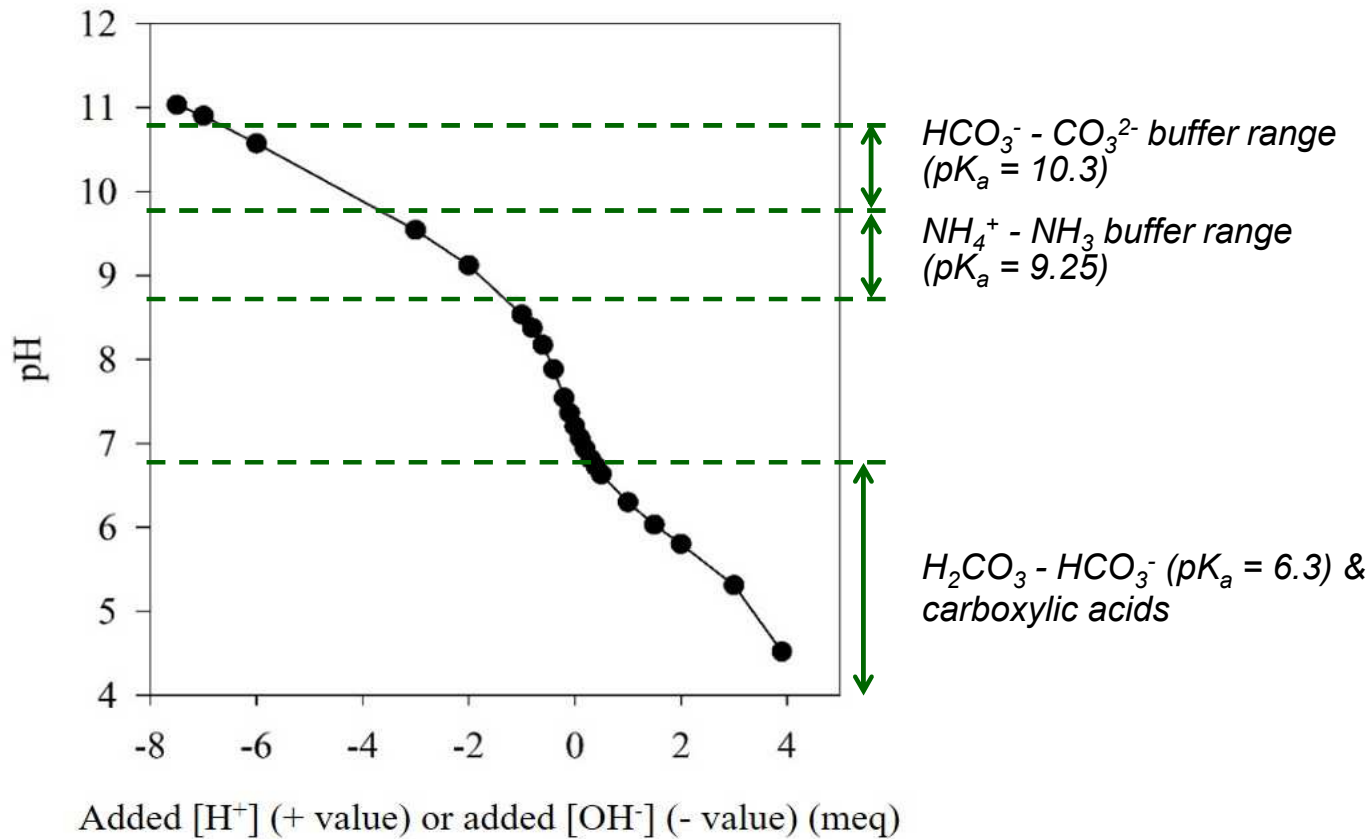
- Smaller rate gap b/w $\text{pH}_{\text{feed}} = 9.2$ & 11.0 at longer operation period
- Low pH_{feed} much less prone to inorganic fouling



SEM image, $\text{pH}_{\text{feed}} = 11.0$

SEM image, $\text{pH}_{\text{feed}} = 9.2$

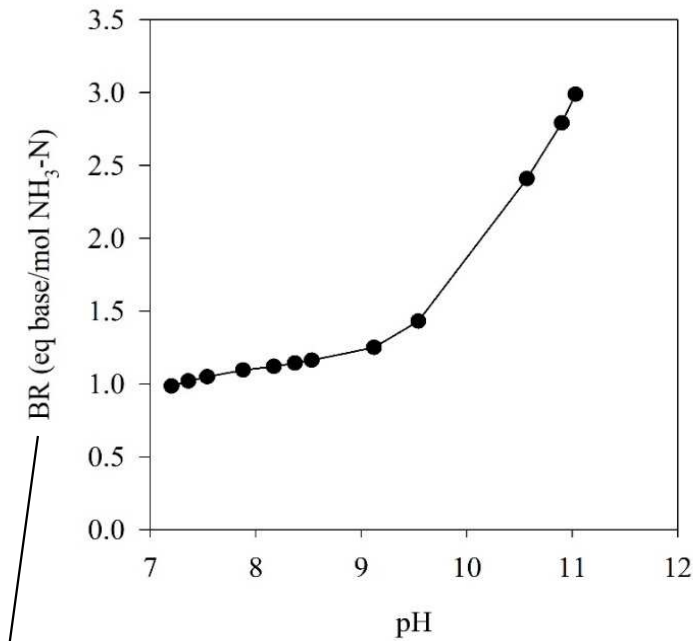
Sewage pH titration



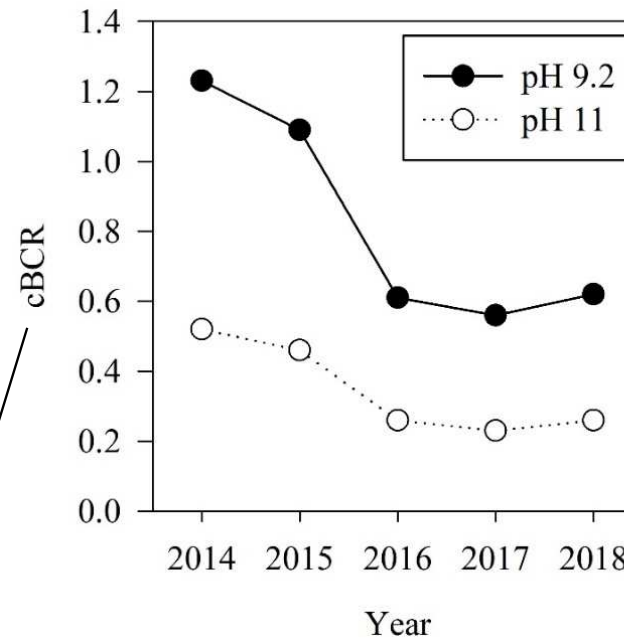
Titration path from raw sewage (pH ~7) to pH 11.0

- pH ~7 → ~8.7: no significant buffer, **low base consumption**
- pH ~8.7 → ~9.7: base consumed to **deprotonate the one we want to**
- pH ~9.7 → 11.0: base mostly consumed to **deprotonate HCO_3^-** , etc.

Chemical cost is affordable



base requirement.
100% NH₄-N recovery assumed



Benefit-cost ratio for chemicals.
(price of NH₃) / (cost of base as Ca(OH)₂)
100% NH₄-N recovery assumed

cf)
pH 9.2
2021 cBCR = 1.07

- **1.25 eq base / mol NH₃-N @ pH_{feed} = 9.2** cf) 2.99 eq base/mol NH₃-N @ pH_{feed} = 11.0
- **Can be net-profitable** in terms of benefit of chemical recovery vs. chemical cost

■ Rate is enough @ $\text{pH}_{\text{feed}} = 9.2$

Using the mass transfer coefficient we measured, assuming sewage $\text{NH}_3\text{-N}$ conc. of 55 mg N/L & applying a typical value of membrane packing density, we calculate:

$$\begin{aligned} \frac{\text{Membrane module volume}}{\text{Sewage (feed) flowrate}} &= \frac{V_M}{Q_F} = 3.9 \text{ min} \quad (50\% \text{ removal}) \\ &= 12.9 \text{ min} \quad (90\% \text{ removal}) \end{aligned}$$

cf) biological N removal (current)

$$\text{HRT} = \frac{\text{effective volume of reactor}}{\text{Sewage flowrate}} = \frac{V_{\text{eff}}}{Q_F} = 5 \sim 15 \text{ h}$$

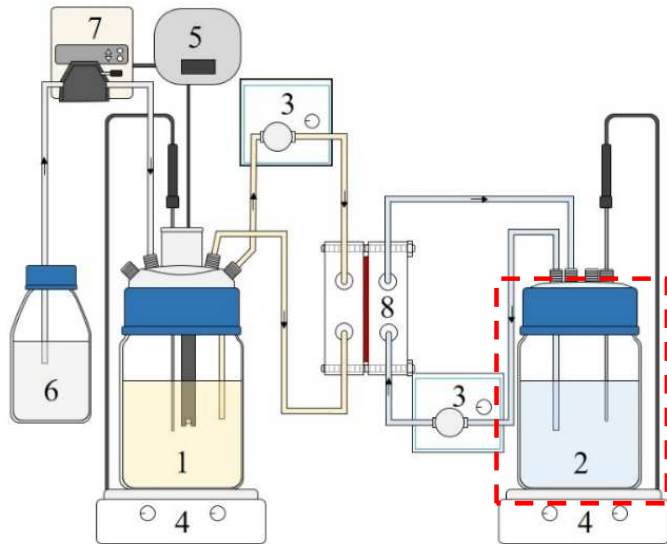
typical range of removal efficiency = 50-65%

Challenge II – product usability

- Salt of NH_4^+ + acid anion (e.g., $(\text{NH}_4)_2\text{SO}_4$) → fertilizer
- Product obtained in the form of aqueous solution → difficulty in handling & transportation

<연도별, 비종별 생산 실적>

(단위 : 천톤)

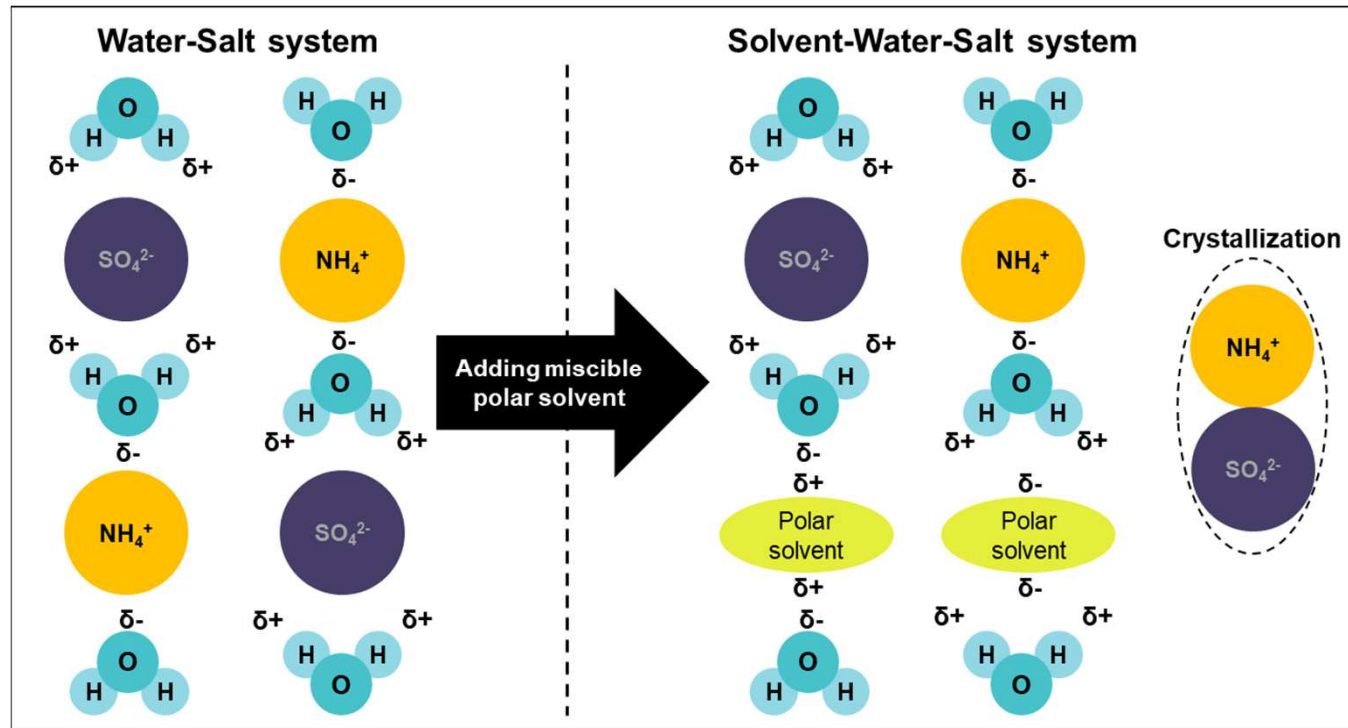


| 구 분 | 1994년 | 1997년 | 2002년 | 2003년 |
|---------|-------|-------|-------|-------|
| 요 소 | 904 | 900 | 360 | 234 |
| 황산암모늄 | 480 | 511 | 537 | 521 |
| 석회질소 | - | - | - | - |
| 복 합 비 료 | 2,717 | 2,321 | 2,265 | 2,434 |
| 인산질비료 | 171 | 132 | 65 | 56 |
| 가리질비료 | 67 | 119 | 74 | 70 |
| 합 계 | 4,339 | 3,983 | 3,301 | 3,315 |

자료출처 : 한국비료공업협회

Solvent-driven fractional crystallization (SDFC)

- Very rapid crystallization
- High crystallization efficiency

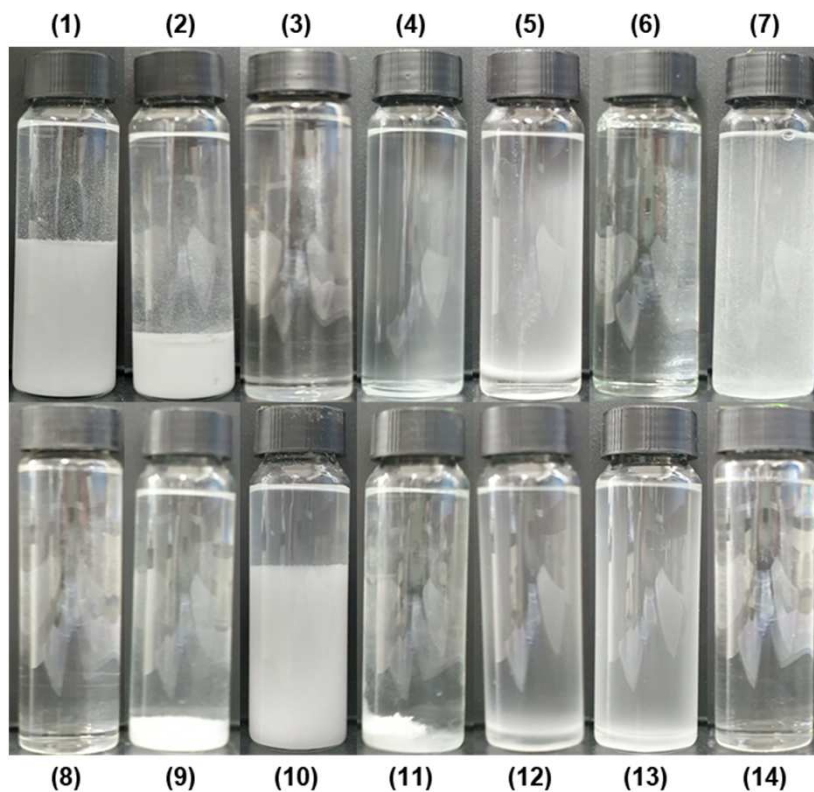
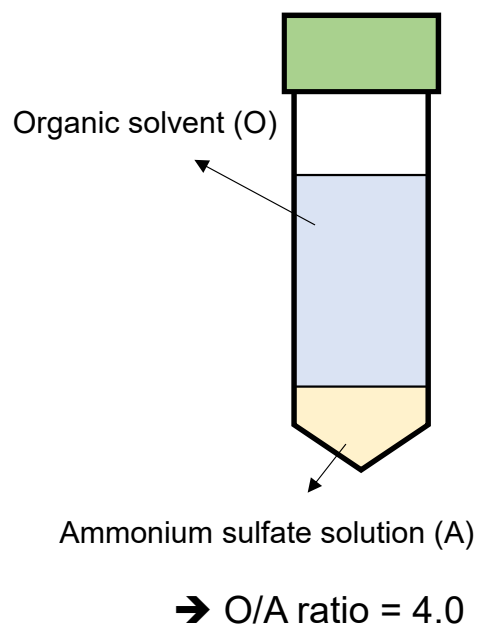


Candidate solvents

| | Surface tension (dyn/cm, 20 °C) | Viscosity (cp, 25 °C) | Vapor pressure (mmHg, 20 °C) | Dipole moment (D) | Dielectric constant (20 °C) | Polarity | Specific heat (cal/mol /°C) | IDLH (ppm) | OES-TWA (ppm) | OES-STEL (ppm) | Odor threshold (ppm) | POCP |
|---------------------------|------------------------------------|--------------------------|---------------------------------|----------------------|--------------------------------|----------|--------------------------------|---------------|------------------|-------------------|-------------------------|------|
| Methanol | 22.6 | 0.6 | 103 | 1.7 | 32.6 | 76.2 | 19.5 | 25,000 | 200 | 250 | 6,000 | 12.3 |
| Ethanol | 22.3 | 1.08 | 45.7 | 1.7 | 22.4 | 65.4 | 27 | - | 1,000 | - | 6,000 | 27 |
| n-propanol | 23.7 | 1.72 | 13.4 | 1.7 | 20.1 | 61.7 | 34 | 4,000 | 200 | 250 | 45 | 45 |
| i-propanol | 21.7 | 2 | 35.1 | 1.66 | 18.3 | 54.6 | 37 | 20,000 | 400 | 500 | 60 | 15 |
| n-butanol | 24.6 | 3 | 4.8 | 1.66 | 18.2 | 60.2 | 41 | 8,000 | 50 | 75 | 80 | 40 |
| Ethylene glycol | 46.5 | 20 | 0.12 | 2.31 | 37.7 | 79.0 | 35 | - | 60 | 125 | - | - |
| Diethylene glycol | 48.5 | 34 | 0.019 | 2.31 | 31.7 | 71.3 | 58.4 | - | - | - | - | - |
| Diethyl ether | 17 | 0.24 | 462 | 1.3 | 4.3 | 11.7 | 40 | 19,000 | 400 | 500 | 1 | 60 |
| 1,4-dioxane | 40 | 1.3 | 32 | 0.4 | 2.21 | 16.4 | 36 | 200 | 25 | 100 | 170 | - |
| Dimethyl formamide | 35 | 0.82 | 3.8 | 3.8 | 36.7 | 40.4 | 36 | 3,500 | 10 | 20 | 100 | - |
| Acetone | 23.3 | 0.33 | 194 | 2.9 | 20.6 | 35.5 | 30 | 20,000 | 750 | 1,500 | 300 | 17.8 |
| Acetonitrile | 29.1 | 0.38 | 71 | 3.2 | 37.5 | 46 | 22 | 4,000 | 40 | 60 | 40 | - |
| Tetrahydro furan | 28 | 0.55 | 133 | 1.75 | 7.6 | 21 | 36 | - | 100 | 200 | 30 | 133 |
| Acetic acid | 27.4 | 1.13 | 13 | 1.7 | 6.2 | 64.8 | 29.4 | 1,000 | 10 | 15 | 2 | - |

Polarity, polarity relative to water at 100; IDLH (immediately dangerous to life or health), a maximum vapor concentration from which a person can escape within 30 min without irreversible health damage or effects that would impair their ability to escape; OES (occupational exposure standard), exposure to a solvent in the air at which there is no indication that injury is caused to people, even if it takes place on a day-after-day basis; OES-TWA (occupational exposure standard – 8 h time-weighted average); OES-STEL (occupational exposure standard – 15 min short-term exposure limit); POCP (photochemical ozone creation potential), POCP relative to ethylene at 100 and the very stable organics at 0; Ref. (reference)

Solvent screening

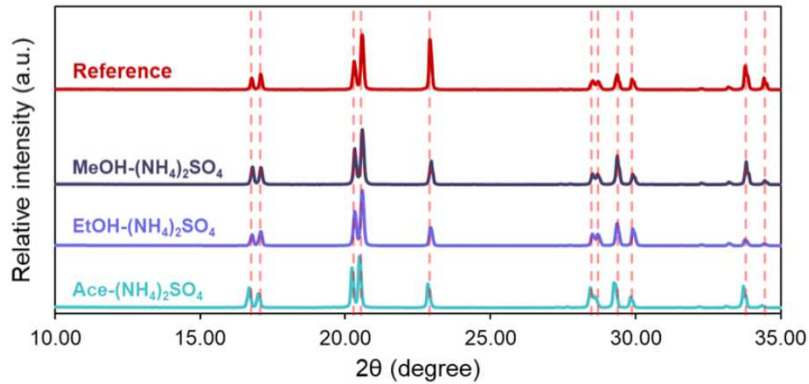


| | Solvent | Yield | Crystallization Efficiency (%) |
|----|-------------------|-------|--------------------------------|
| 1 | Methanol | ● | 83.05 ± 0.39 |
| 2 | Ethanol | ● | 91.21 ± 0.41 |
| 3 | n-Propanol | × | - |
| 4 | i-Propanol | ▲ | - |
| 5 | n-Butanol | ▲ | - |
| 6 | Ethylene glycol | × | - |
| 7 | Diethylene glycol | ▲ | - |
| 8 | Diethyl ether | × | - |
| 9 | 1,4-Dioxane | ● | 94.08 ± 5.58 |
| 10 | Dimethylformamide | ● | 96.35 ± 0.61 |
| 11 | Acetone | ● | 97.82 ± 2.63 |
| 12 | Acetonitrile | ▲ | - |
| 13 | Tetrahydrofuran | ▲ | - |
| 14 | Acetic acid | × | - |

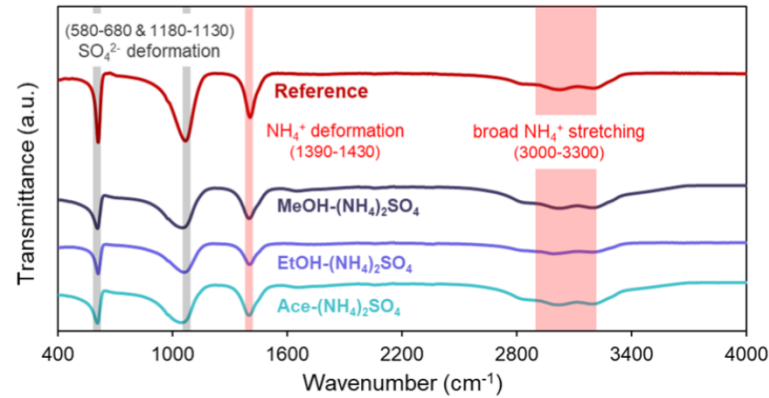
● : crystals were observed
 ▲ : crystals were produced, but not separated
 × : Nothing observed

Crystal analysis & crystallization rate

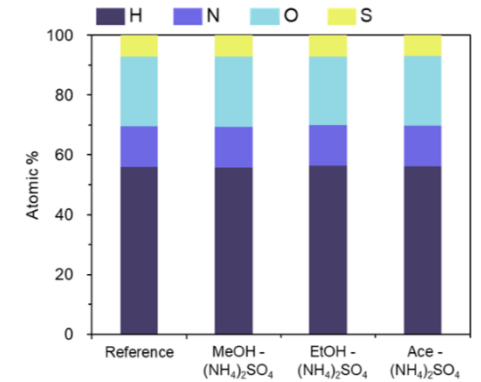
XRD spectra



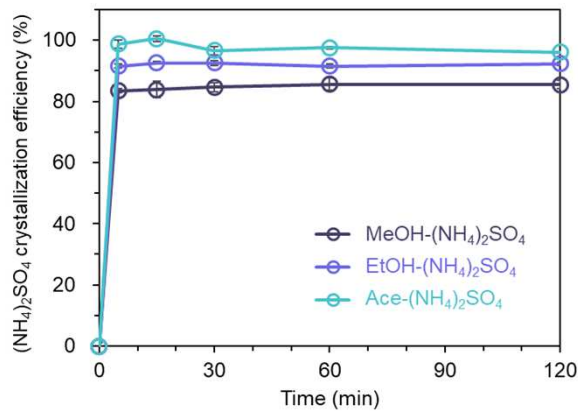
FT-IR spectra



Elemental composition



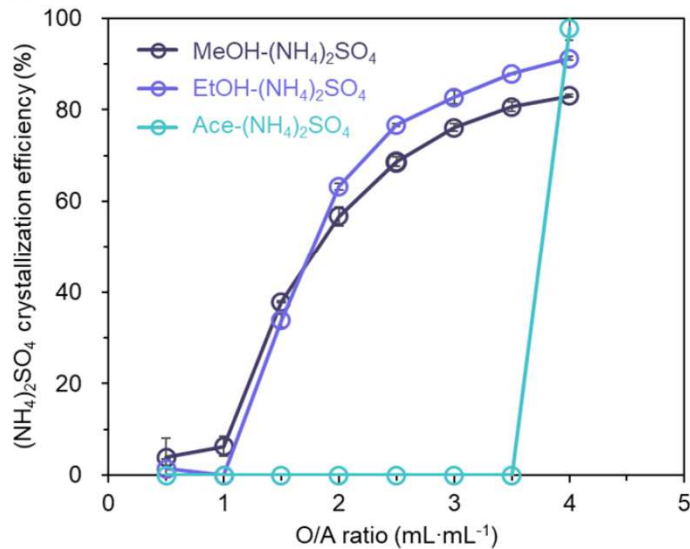
Crystallization rate



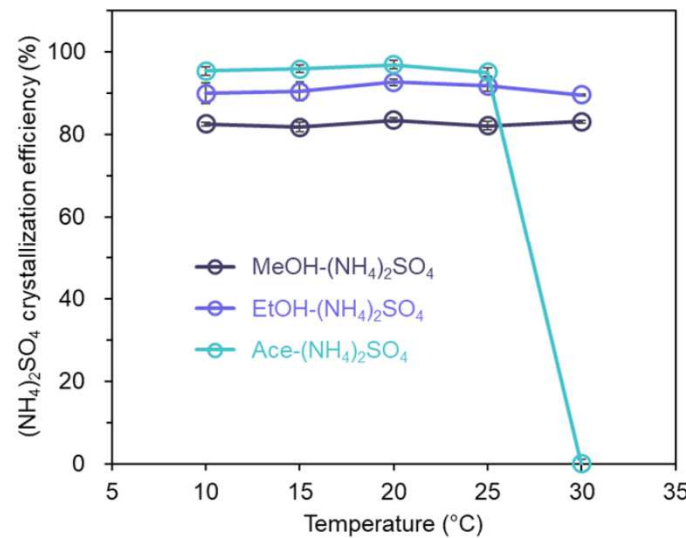
- XRD, FT-IR, elemental analysis all confirm the crystals are (NH₄)₂SO₄ (exact match with the reference)
- Crystallization completed within 5 min @ 25 °C – very rapid

Effect of mixture conditions: O/A ratio, temperature, initial aqueous $(\text{NH}_4)_2\text{SO}_4$ conc.

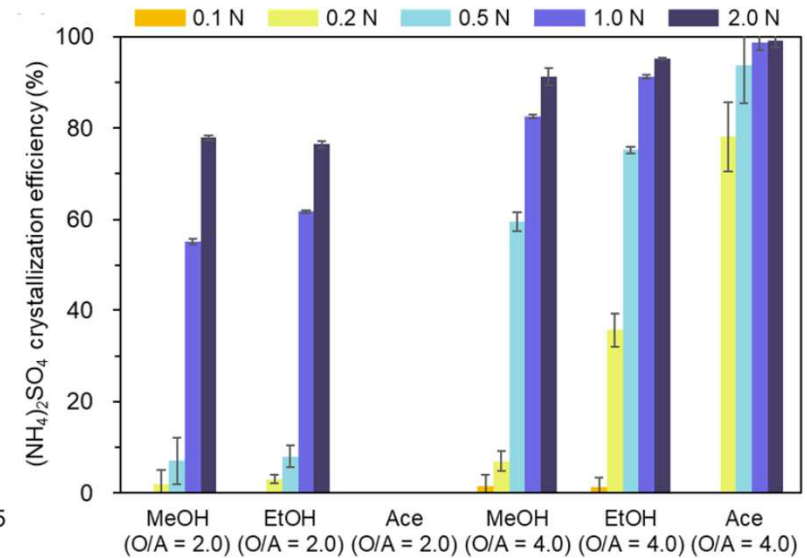
O/A ratio effect



Temperature effect



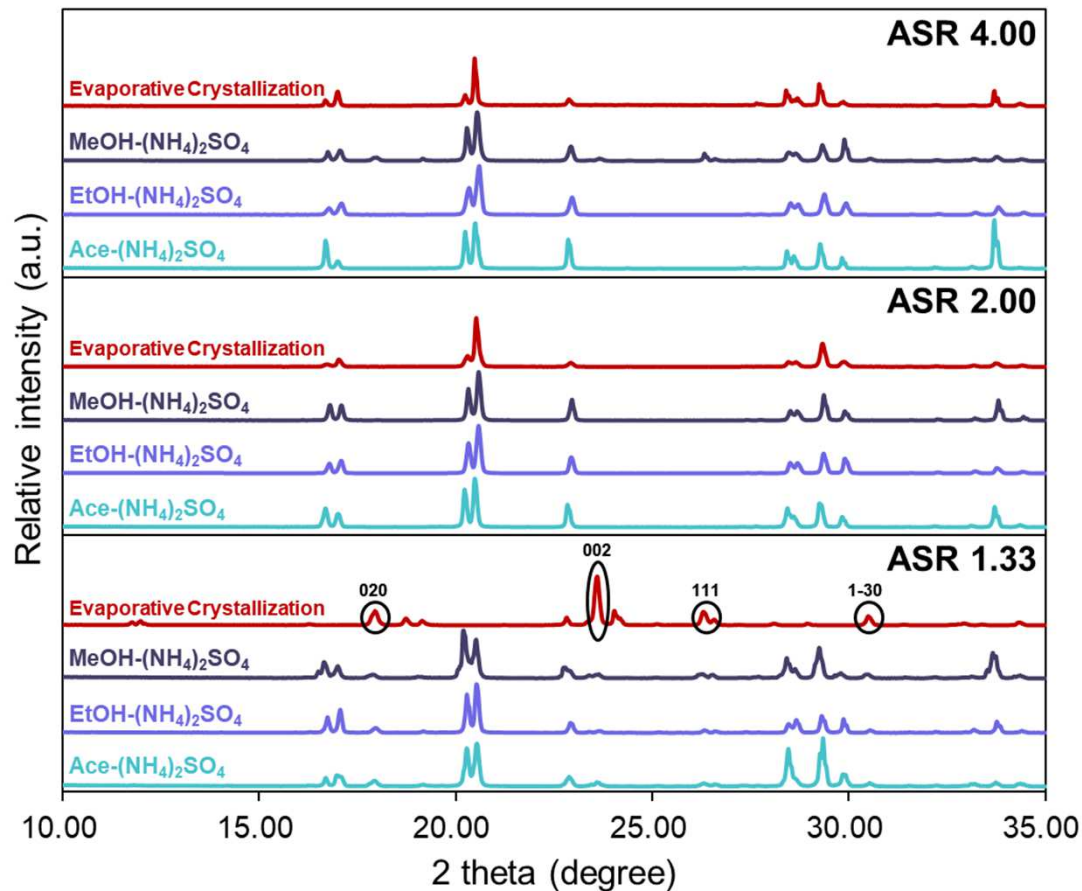
Initial aqueous $(\text{NH}_4)_2\text{SO}_4$ concentration effect



- Acetone very sensitive to O/A ratio & temperature
- Initial aqueous $(\text{NH}_4)_2\text{SO}_4$ concentration important for all solvents
(∴ salt dissolved in excess of saturation concentration precipitates)

Crystals obtained at different ammonium-to-sulfate (ASR) ratio

X-ray diffraction (XRD) spectra



$(\text{NH}_4)_2\text{SO}_4$ -- salt of ammonium & sulfate at 2:1 molar ratio

Solvent-driven fractional crystallization:

Always produces pure $(\text{NH}_4)_2\text{SO}_4$

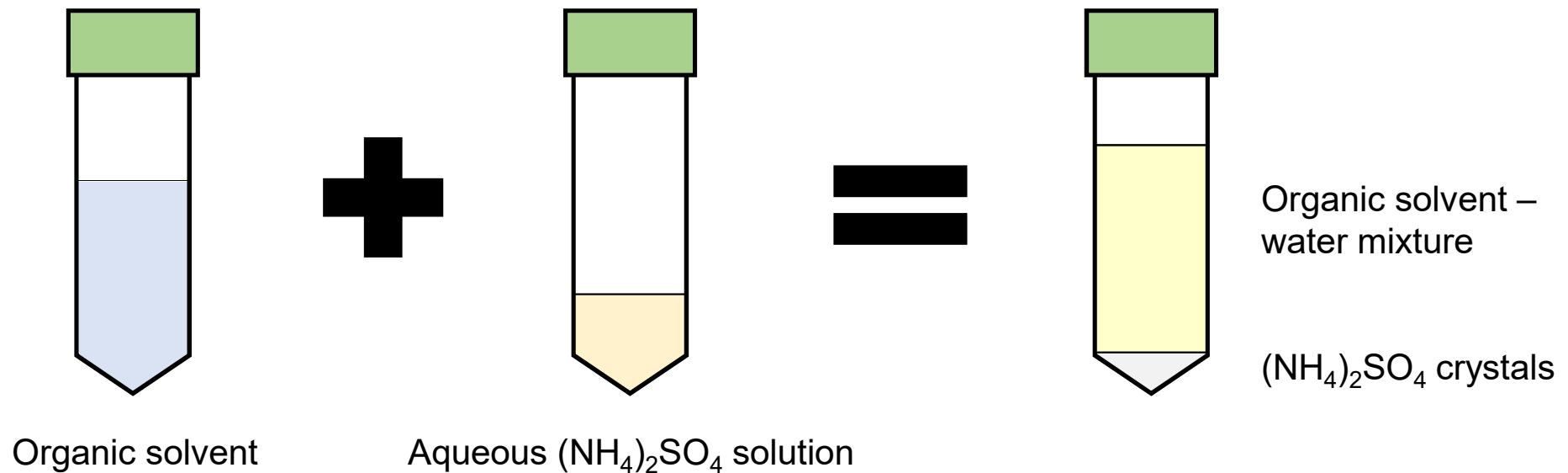
vs.

Evaporative crystallization:

Significant production of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ at ASR lower than 2:1

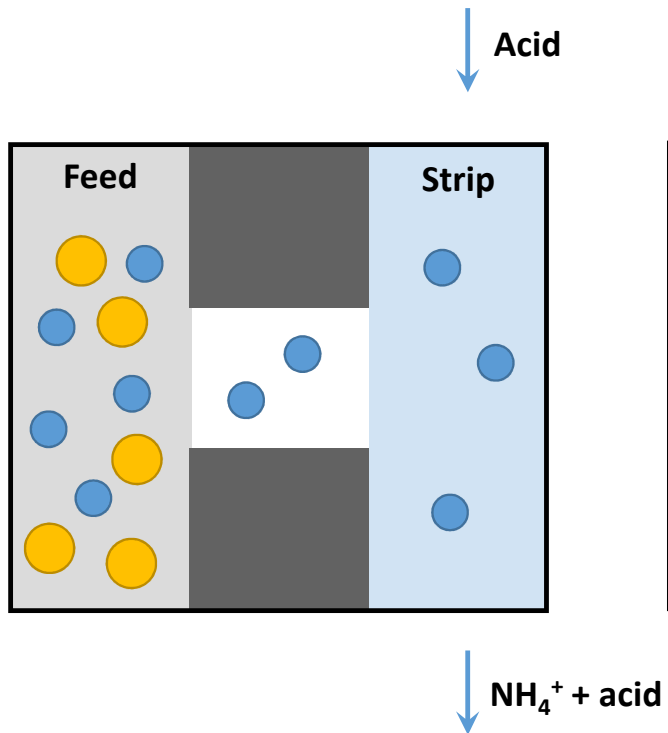
Challenge III – solvent reuse

- Crystals obtained by mixing the aqueous $(\text{NH}_4)_2\text{SO}_4$ solution with an organic solvent
- High cost of organic solvents – how can they be reused?

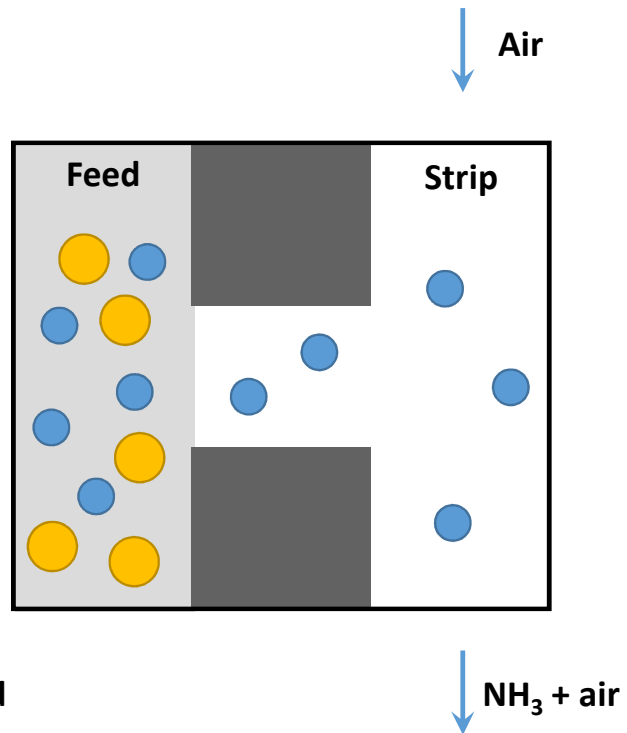


Variability in the stripping method

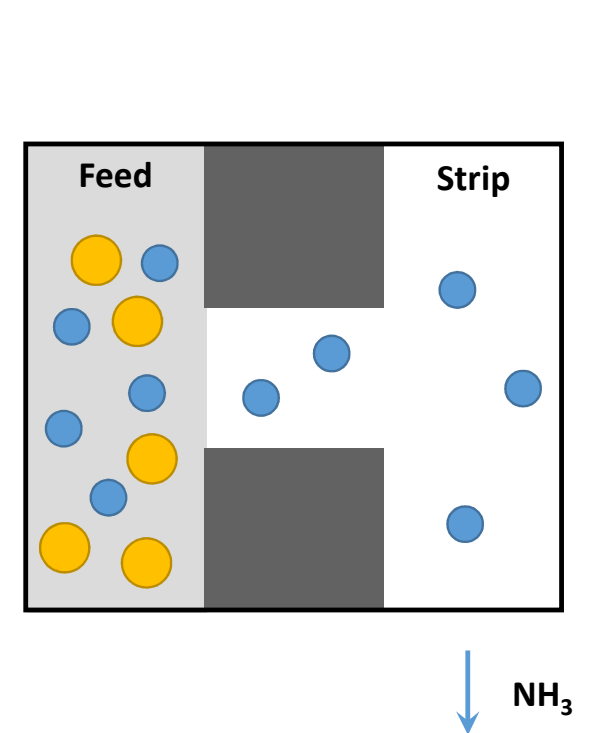
Liquid-Liquid

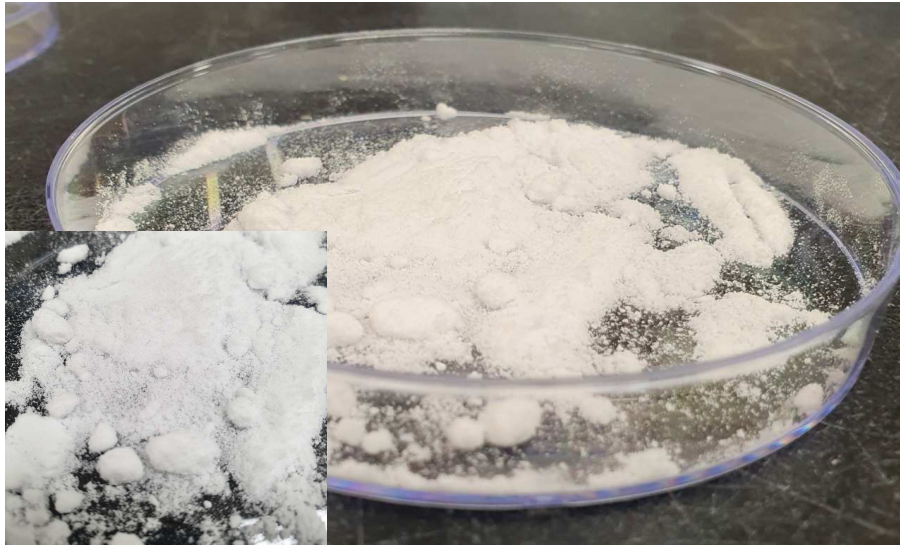


Liquid-Air



Liquid- Vacuum





Takeaway

- It may be economically feasible (or beneficial) to recover ammonia from sewage using membrane contactor

It is not the volume, but the pH buffering capacity that matters!

- Solvent-driven fractional crystallization allows obtaining pure $(\text{NH}_4)_2\text{SO}_4$ crystals from aqueous ammonium sulfate solutions
- By combining liquid-gas membrane contact with solvent-driven fractional crystallization, it is possible to harvest ammonia in solid form from wastewater without consumption of organic solvents

