# Co-Removal of Energetics and Oxyanions via *In Situ* Coupling of Catalytic and Enzymatic Destructions: A Solution to Ammunition Wastewater Treatment

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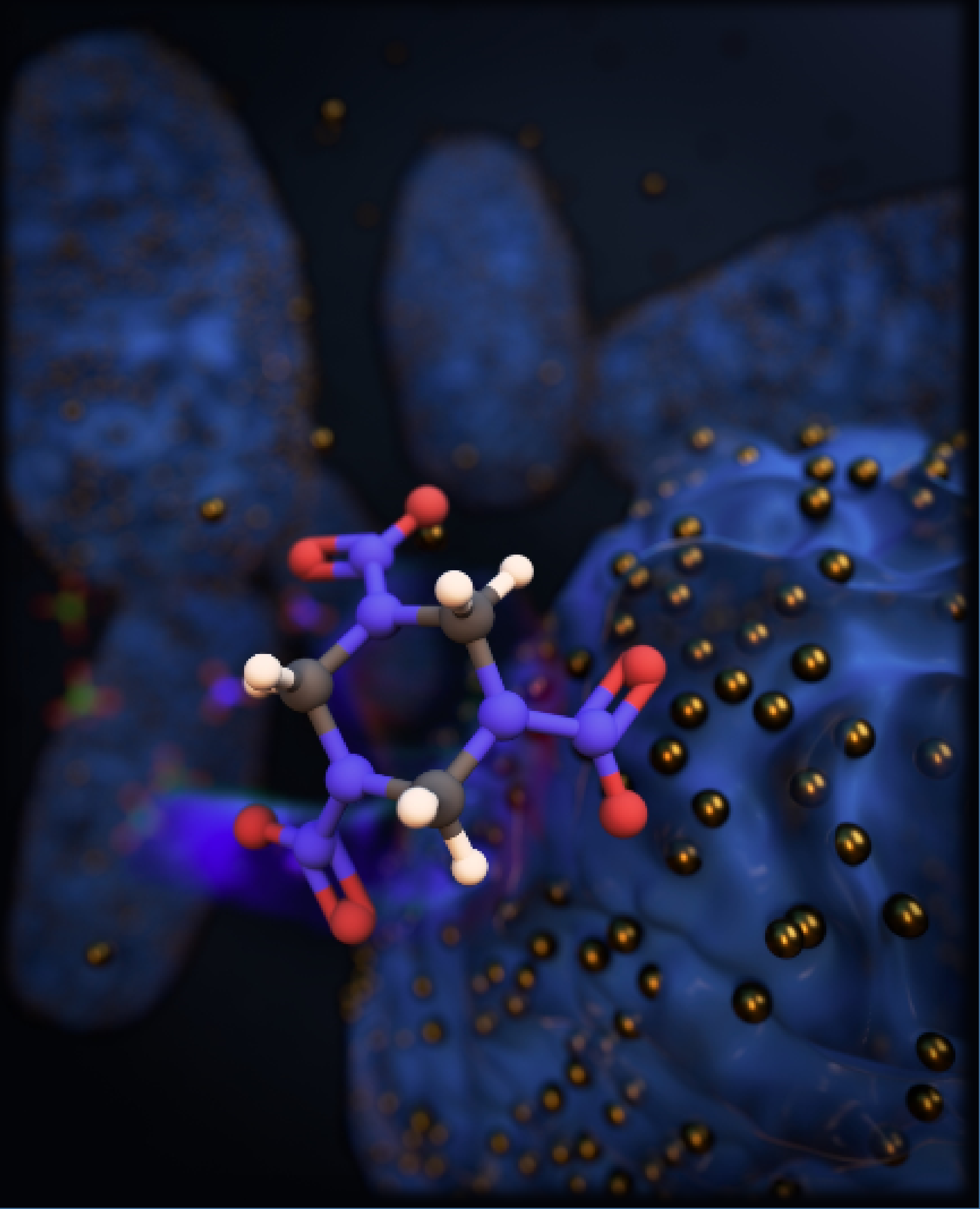
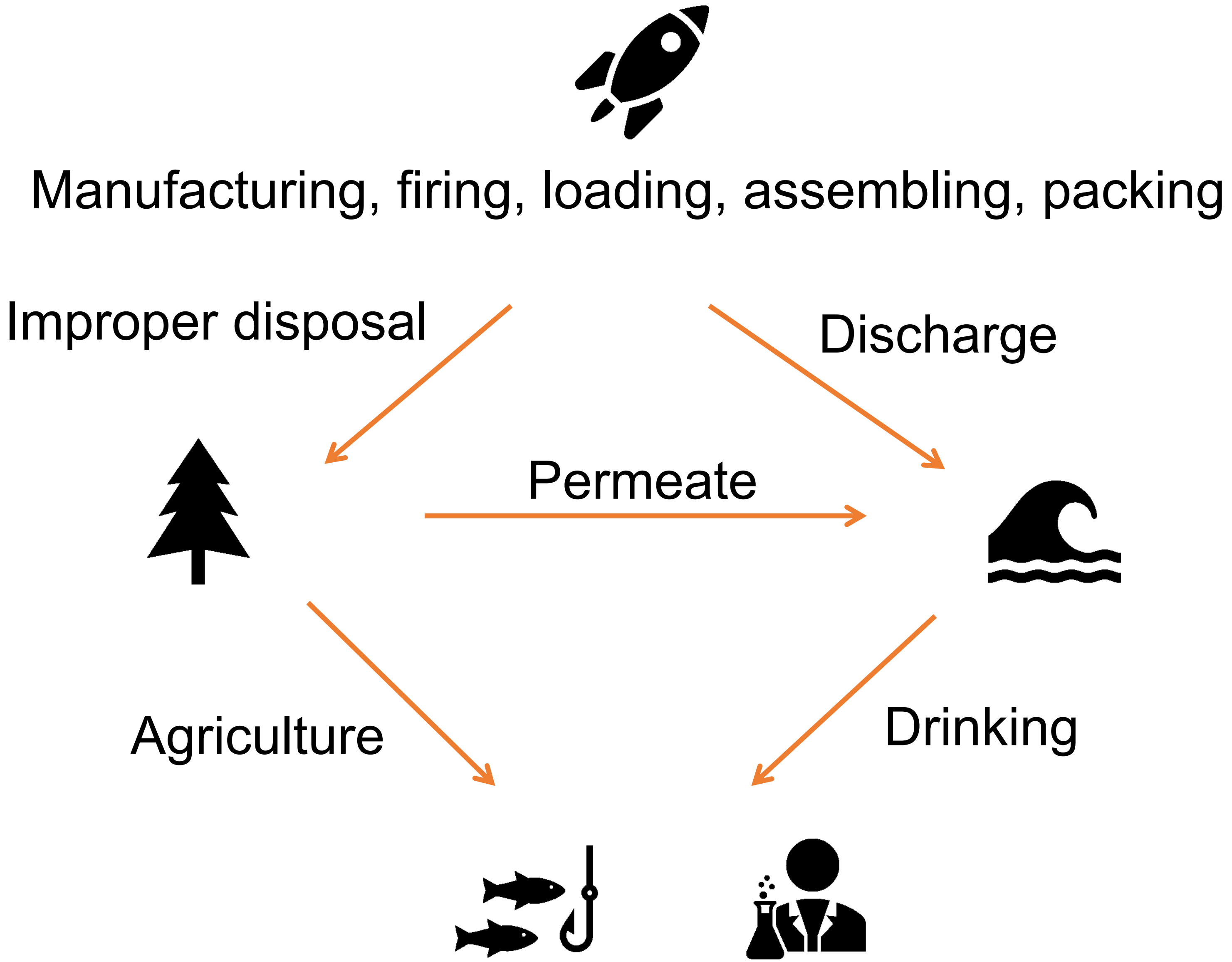
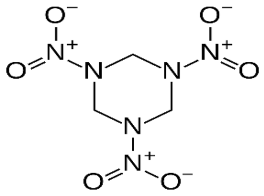
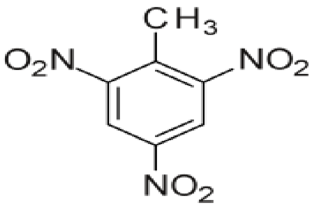
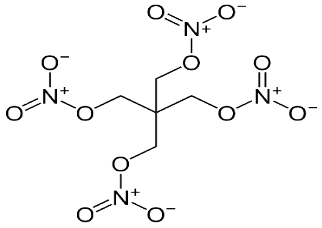


# BACKGROUND ON ENERGETICS





# RISKS FROM IMPORTANT ENERGETICS

| | Structures | Risk |
| --- | --- | --- |
| Nitroamines ($R_2N\text{-}NO_2$) |  **RDX** 1,3,5-Trinitro-1,3,5-triazinane | Carcinogenic<br>Targets the nervous system |
| Nitroaromatics ($R\text{-}NO_2$) |  **TNT** 2,4,6-trinitrotoluene | Causes papilloma and carcinoma<br>Targets reproductive system |
| Nitrate esters ($R\text{-}O\text{-}NO_2$) |  **PETN** Pentaerythritol tetranitrate | Toxic to aquatic organisms |

## Perchlorate

Propellants

Food Packaging

Thyroid inhibition
Lung toxicity
EPA: 1-18 ppb (GAO 2010)
Groundwater: 4-500000 ppb (GAO 2010)
Ammunition wastewater: 200 ppm (Oh *et al.*, 2006)

## Nitrate

Gunpowder

Fertilizer

Infants methemoglobinemia
EPA:10 ppm N (EPA MCL)
Groundwater:10-30 ppm N (Townsend et al., 2003)
Ammunition wastewater: 114.3 ppm (Oh *et al.*, 2006)

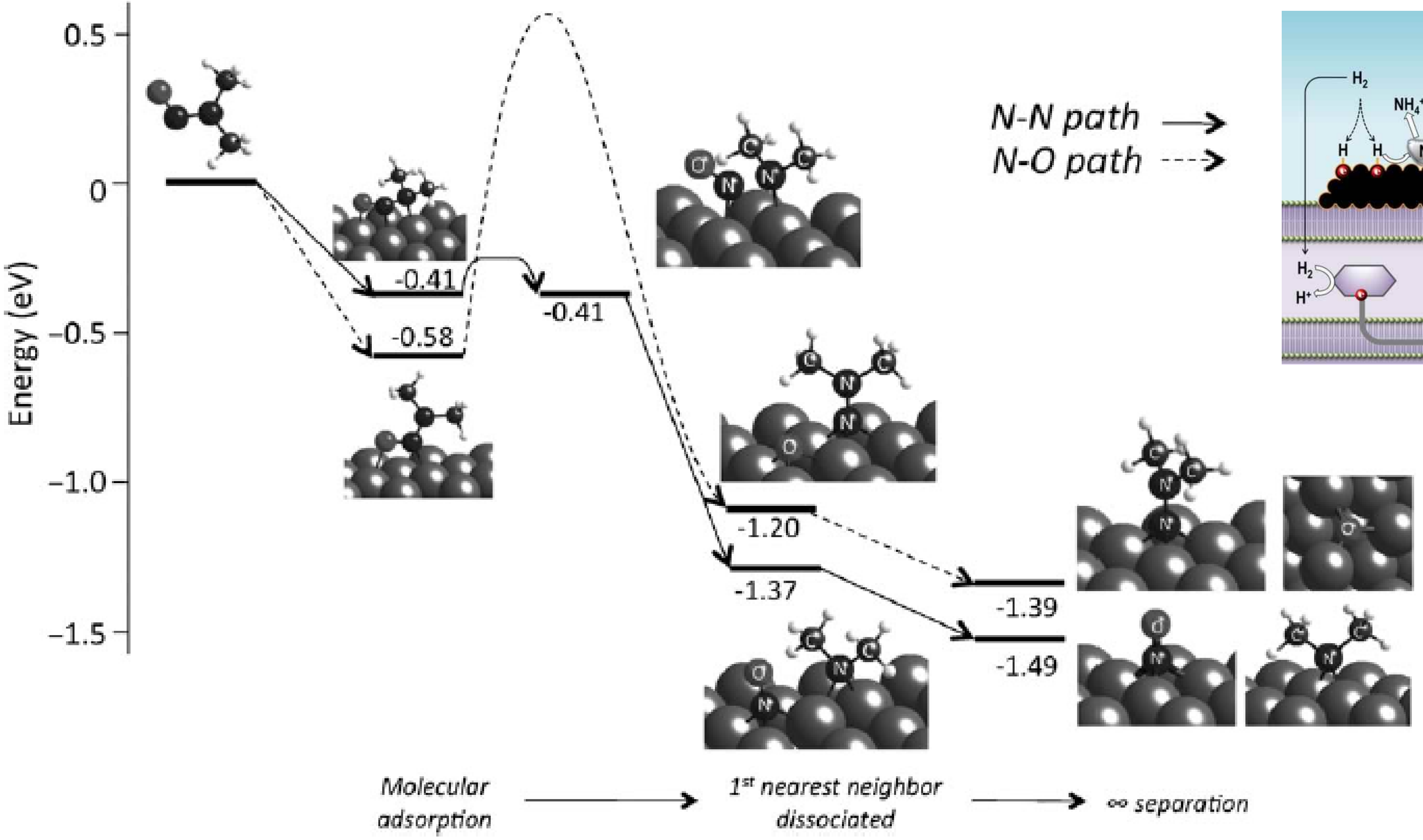
# CURRENT ROADBLOCKS TO TREATMENT

- **PHYSICAL APPROACHES:**
  - **Carbon adsorption** — Secondary pollution
- **BIOLOGICAL APPROACHES:**
  - **Anaerobic Fluidized Bed Reactor**
  - **Phytoremediation by Vetiver glass**
  
  Low rates
- **CHEMICAL APPROACHES:**
  - **Fenton reagent**
  - **Photoelectrocatalysis**
  
  High energy input
  - **Zero-valent iron** — Used-iron disposal
  - **Metal catalysis** — Not in continuous-flow mode

## Three Roadblocks

1. Low biodegradability
2. Secondary contamination
3. Simultaneously removal of the explosives and oxyanions in continuous flow mode

# Abiotic Solution – Pd Catalysis



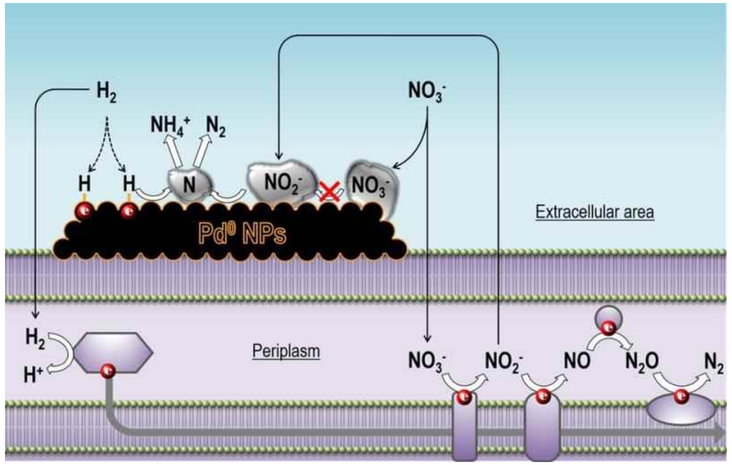
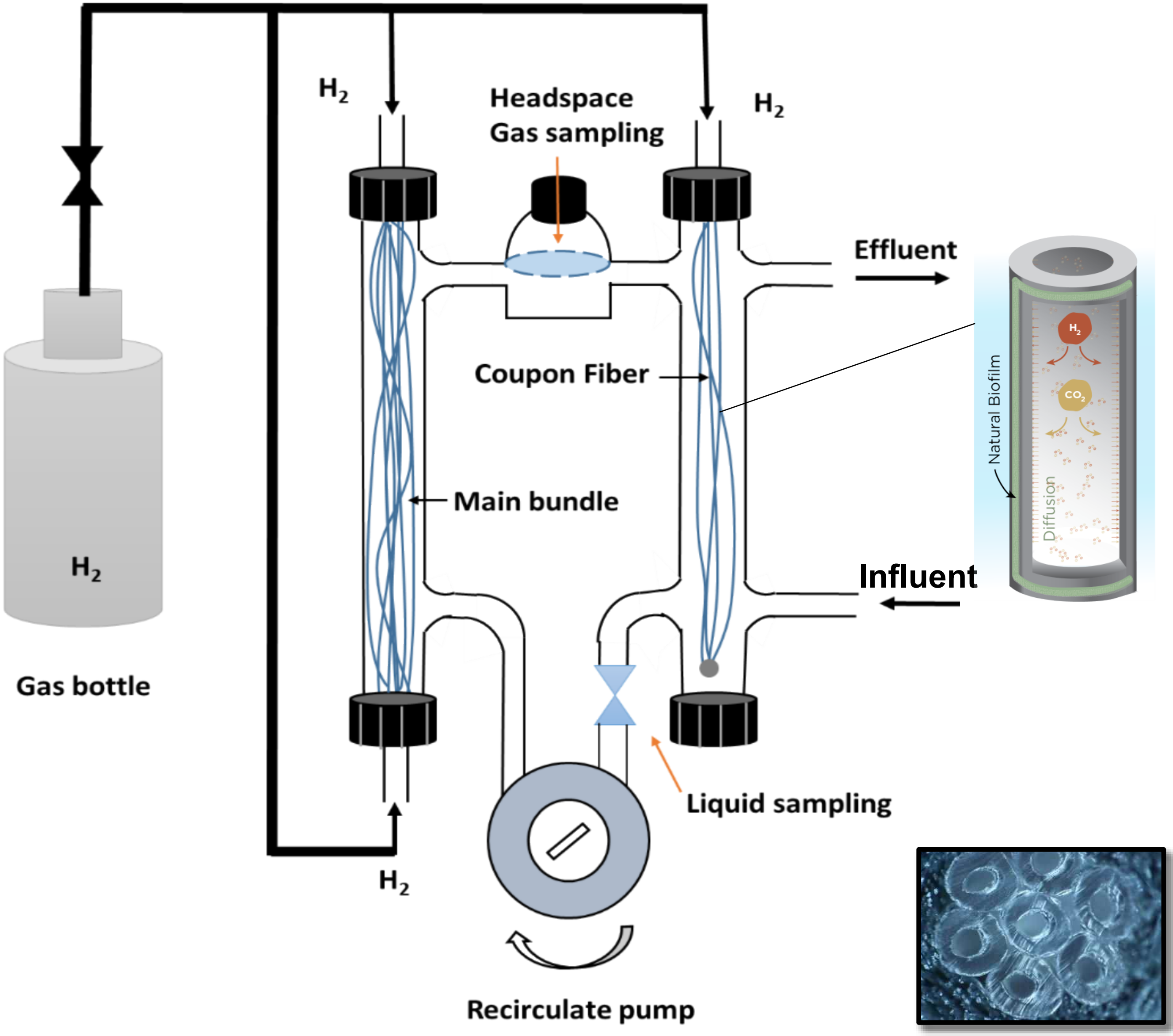
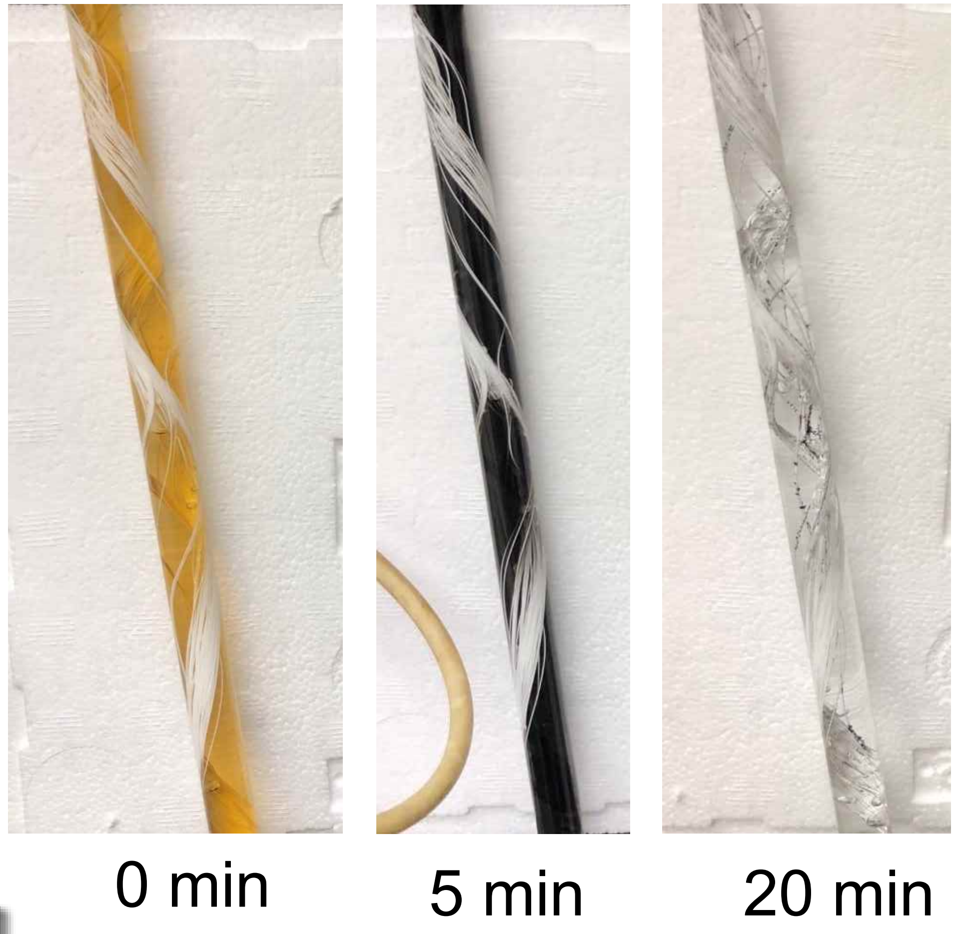



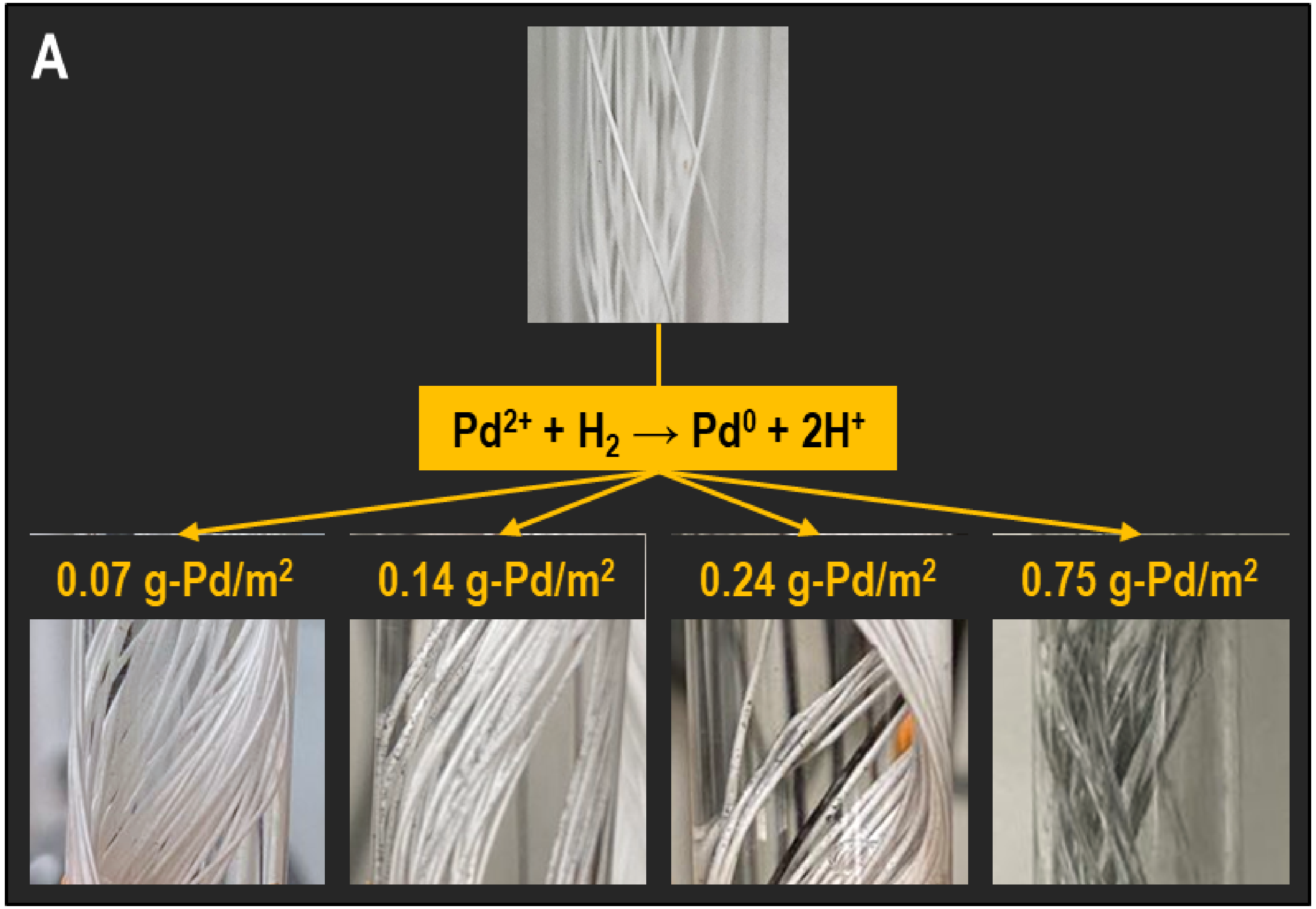

**Figure 3.** Calculated NDMA dissociation pathways on Pd.

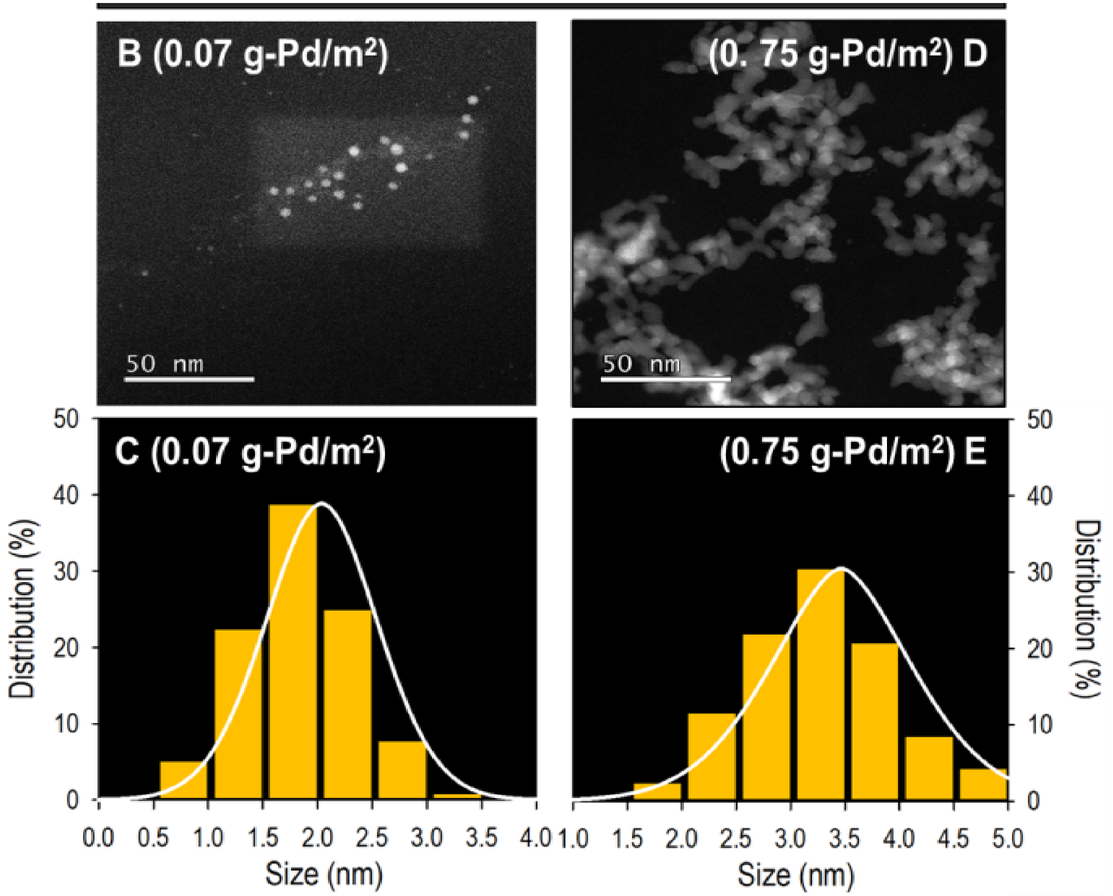
# Abiotic Solution – Membrane Catalyst-film Reactor (MCfR)



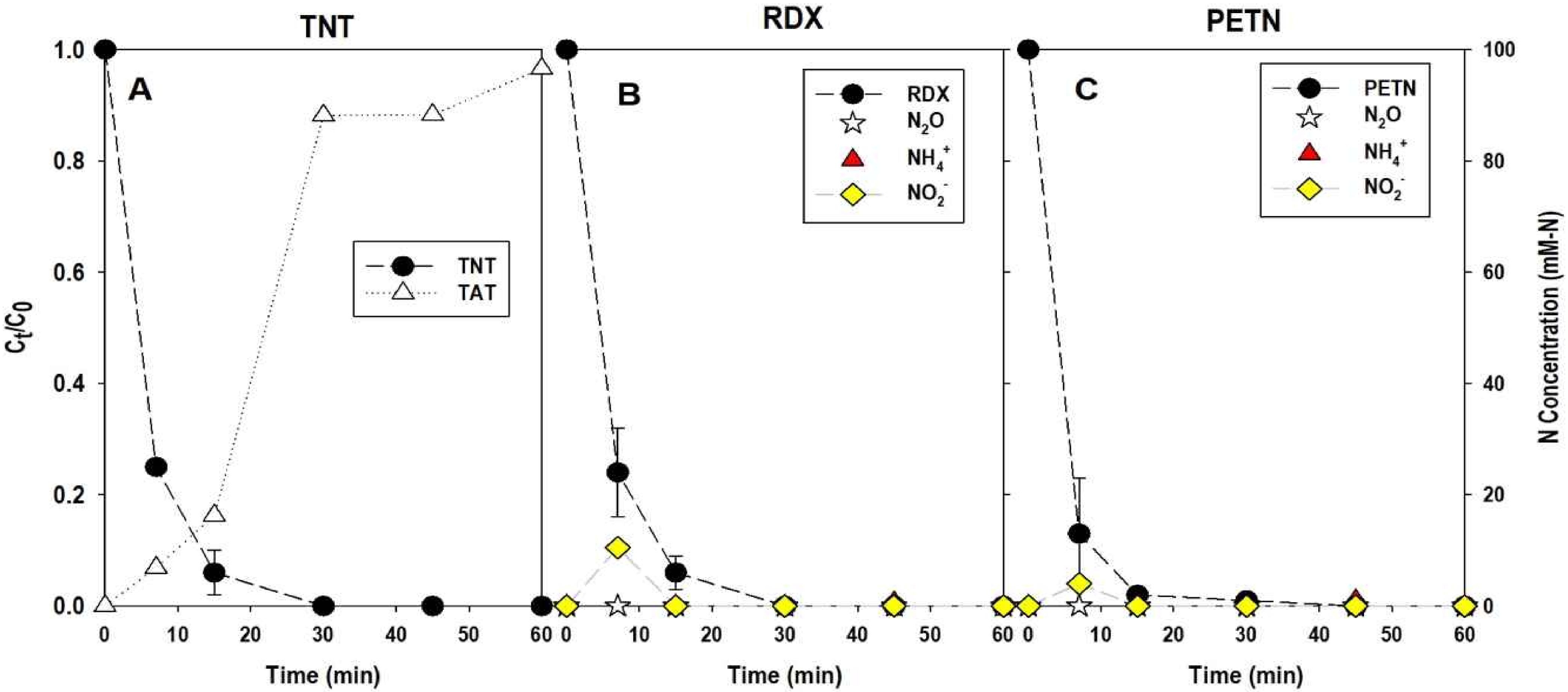
# Abiotic Solution – Catalyst-film Characterization




- The $H_2$-based MCfR formed catalysis-activity Pd nanoparticles of size 2 – 5 mM.

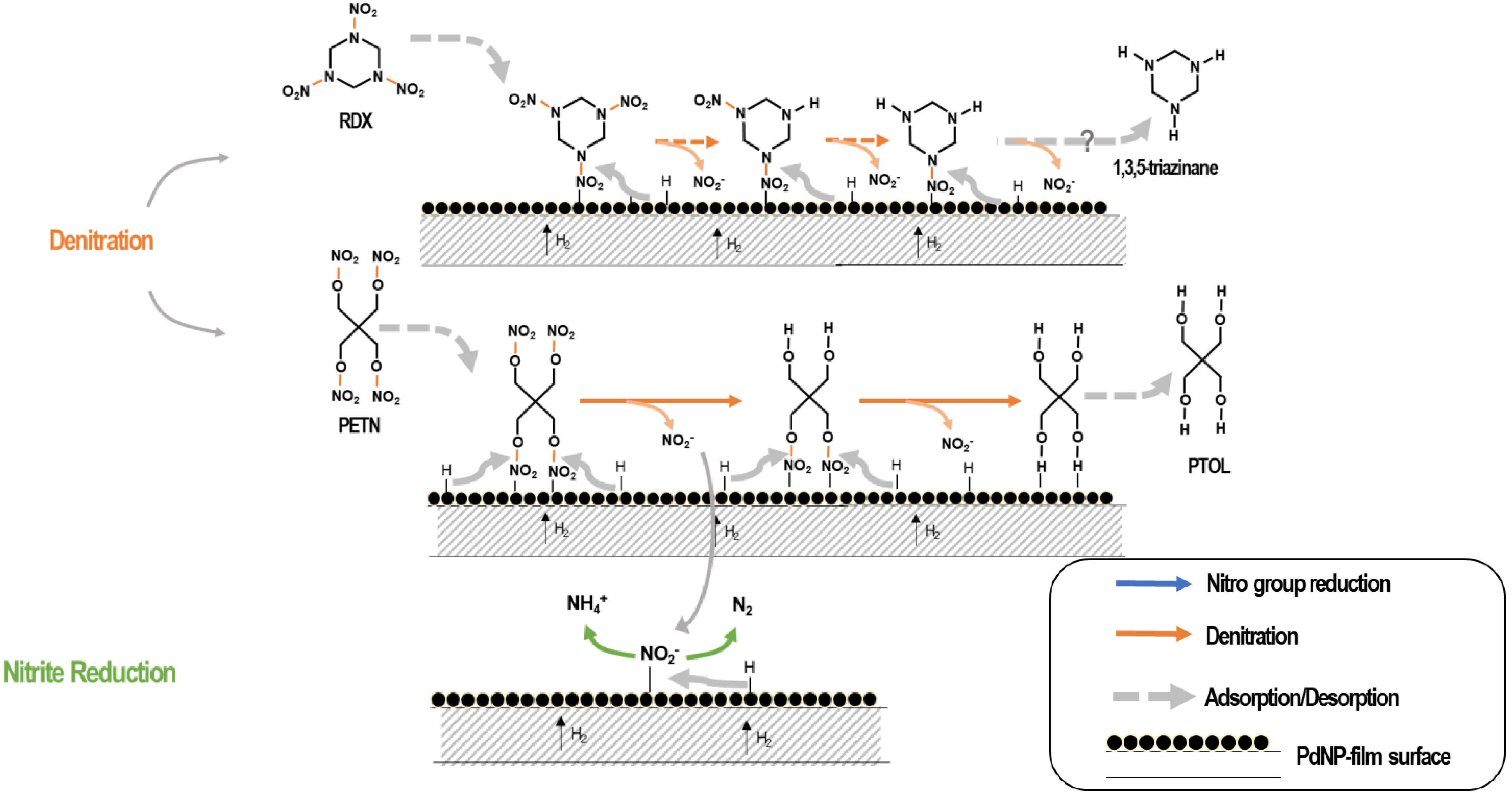
# Abiotic Solution – Results for Energetics Removal




- TNT, RDX, and PETN were rapidly reduced and removed.
- Only small, but transient $NO_2^-$ accumulation
- High selectivity to $N_2$

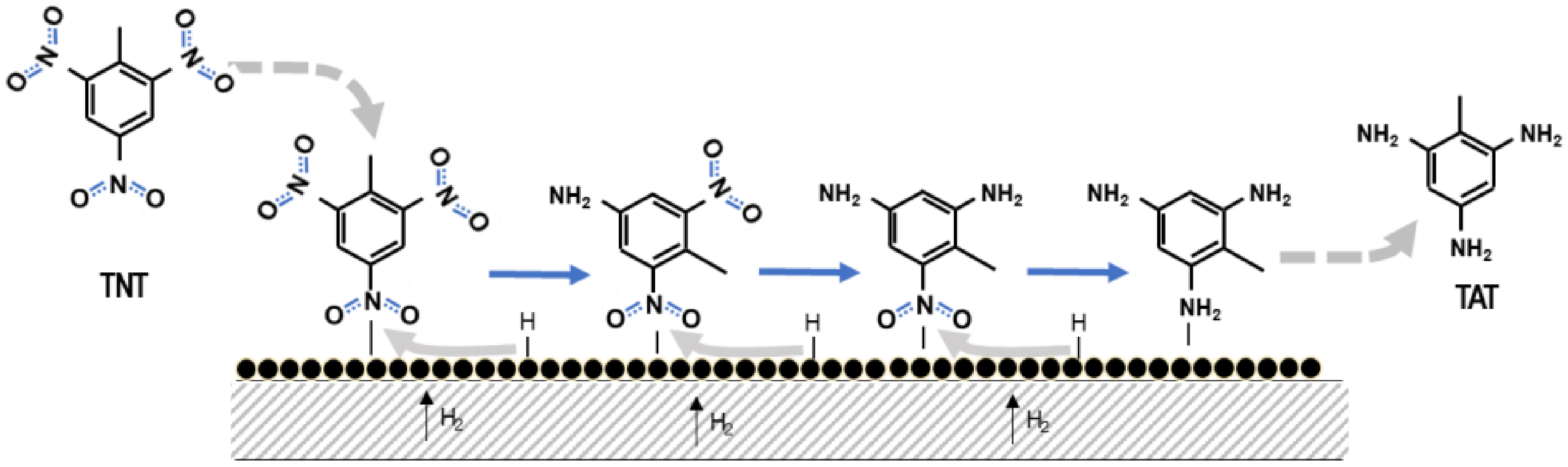
1. Biodegradable
2. **No secondary contamination** ✓
3. Simultaneous removal

# Abiotic Solution - Mechanisms



# Abiotic Solution - Mechanisms

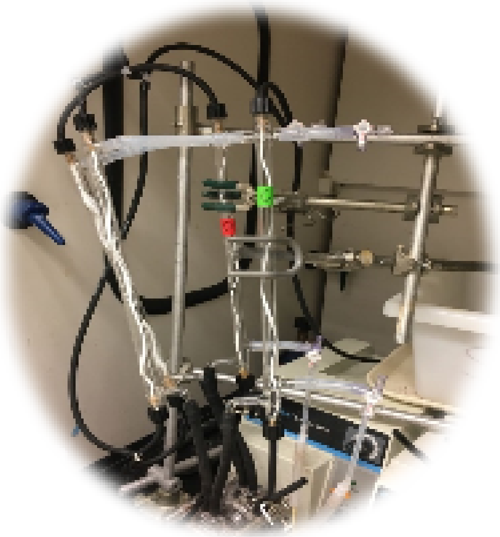
Nitroaromatic Reduction

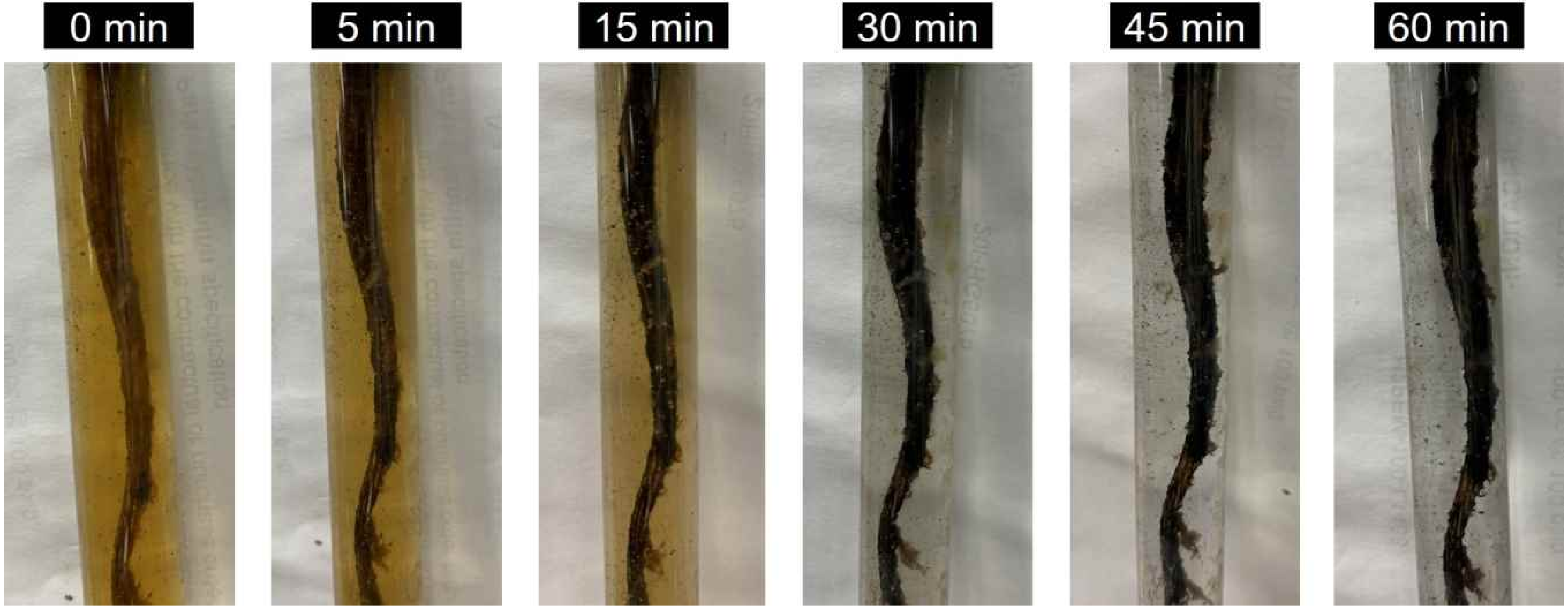



- Pd catalyzed RDX, TNT, and PETN reductions that transformed them to biodegradable products

1. **Biodegradable** ✓
2. **No secondary contamination** ✓
3. Simultaneous removal

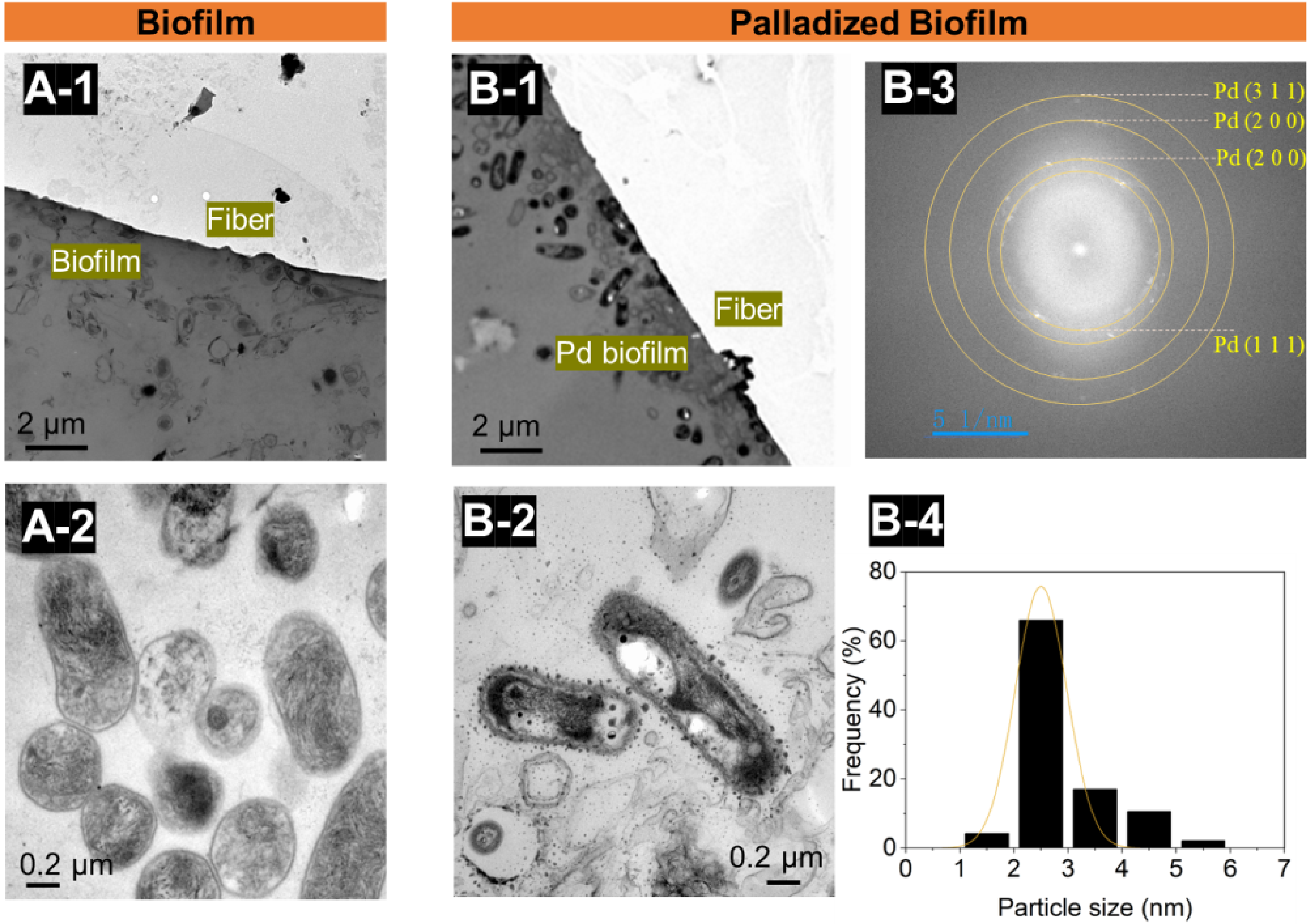
# Biotic Solution – Deposition of Pd NPs in the Biofilm






- Pd deposition in the biofilm combines catalysis and biodegradation

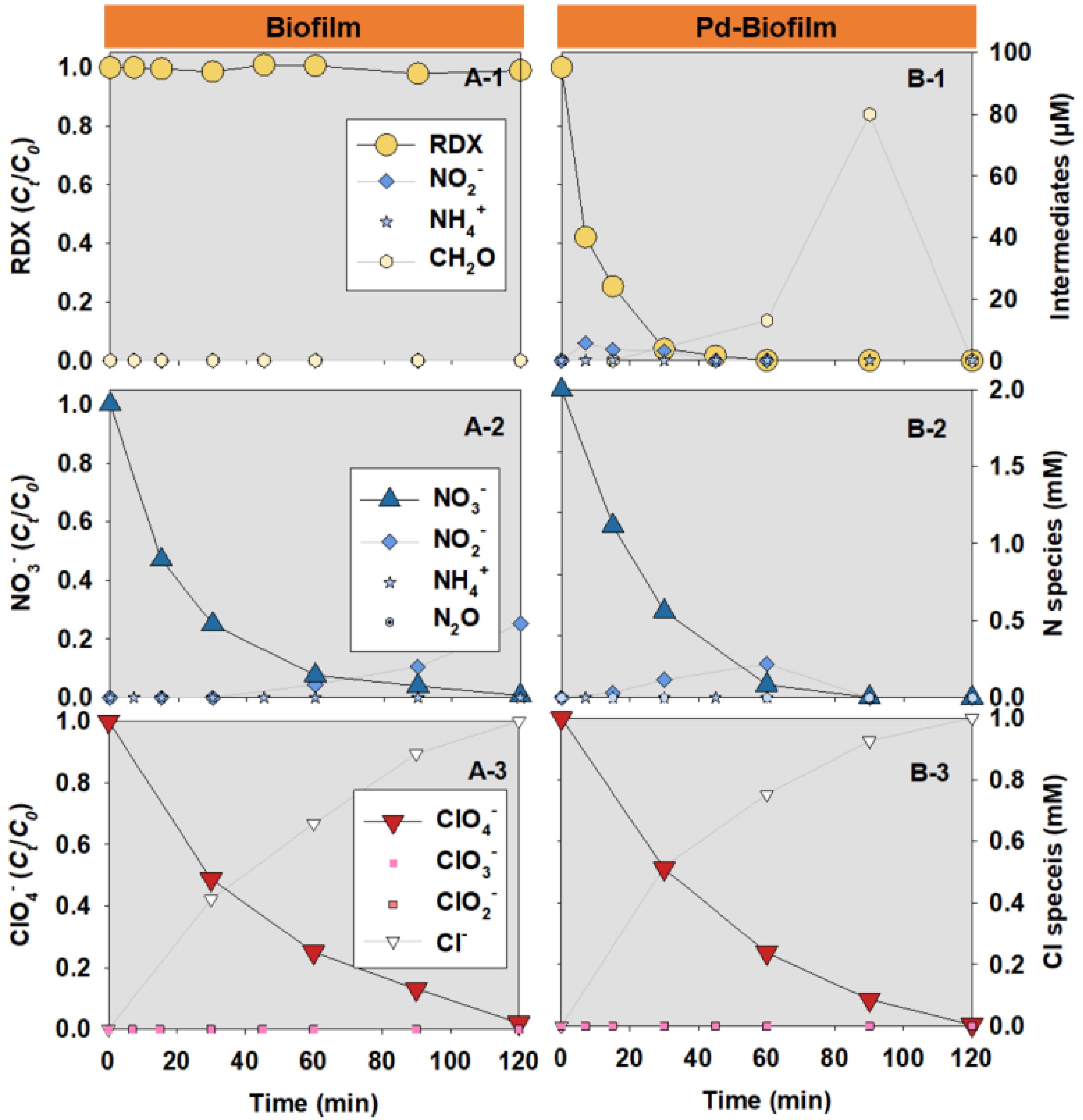
# Biotic Solution - Biofilm Characterization



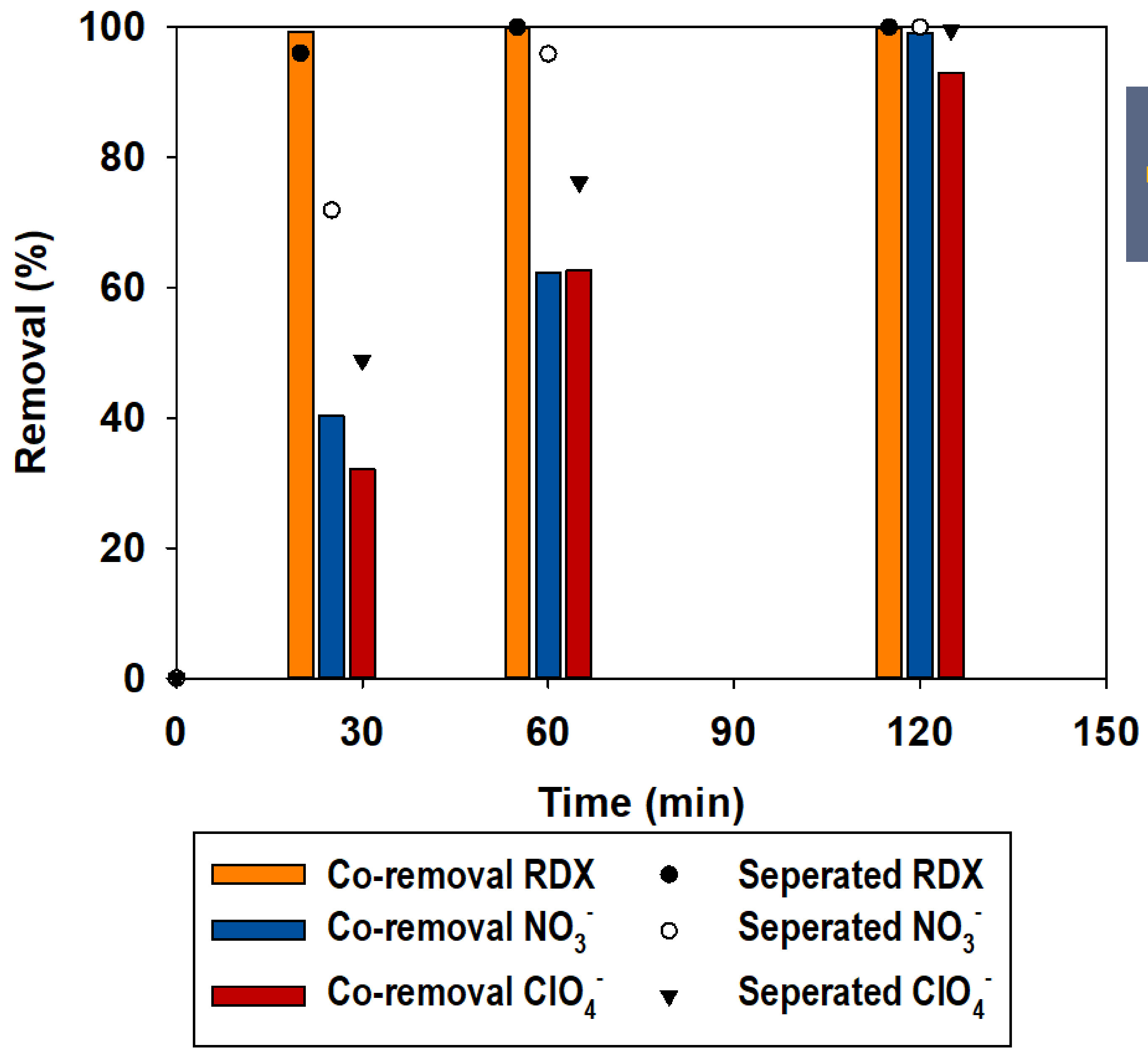

- Biofilm act as supporter to form smaller sized Pd nanoparticles

# Biotic Solution - Results for RDX, $NO_3^-$, and $ClO_4^-$

## Separate tests



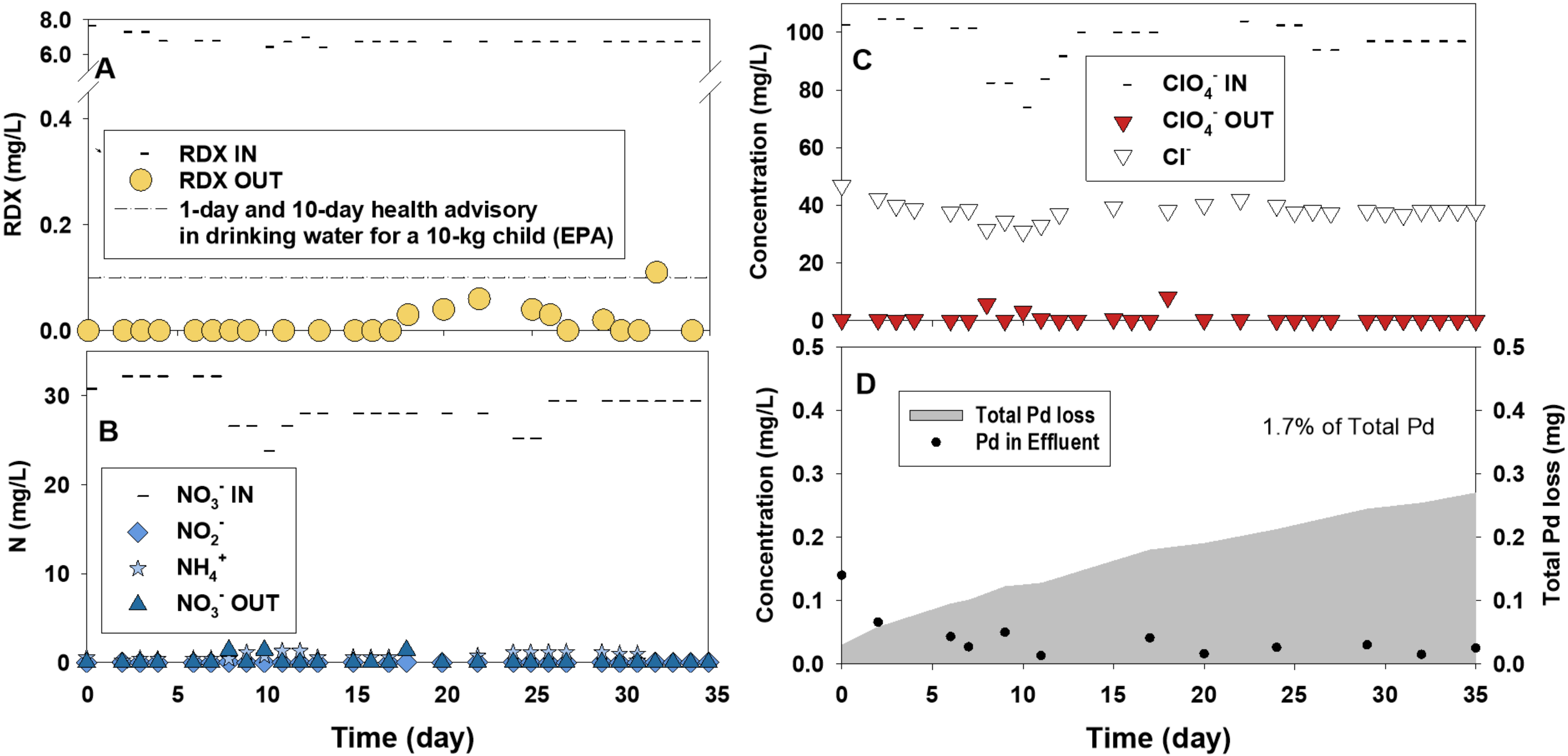

- Pd catalyzed RDX denitration
- Biofilm reduces both oxyanions, including $NO_2^-$ from the denitration




- Co-removal of RDX, $NO_3^-$, and $ClO_4^-$

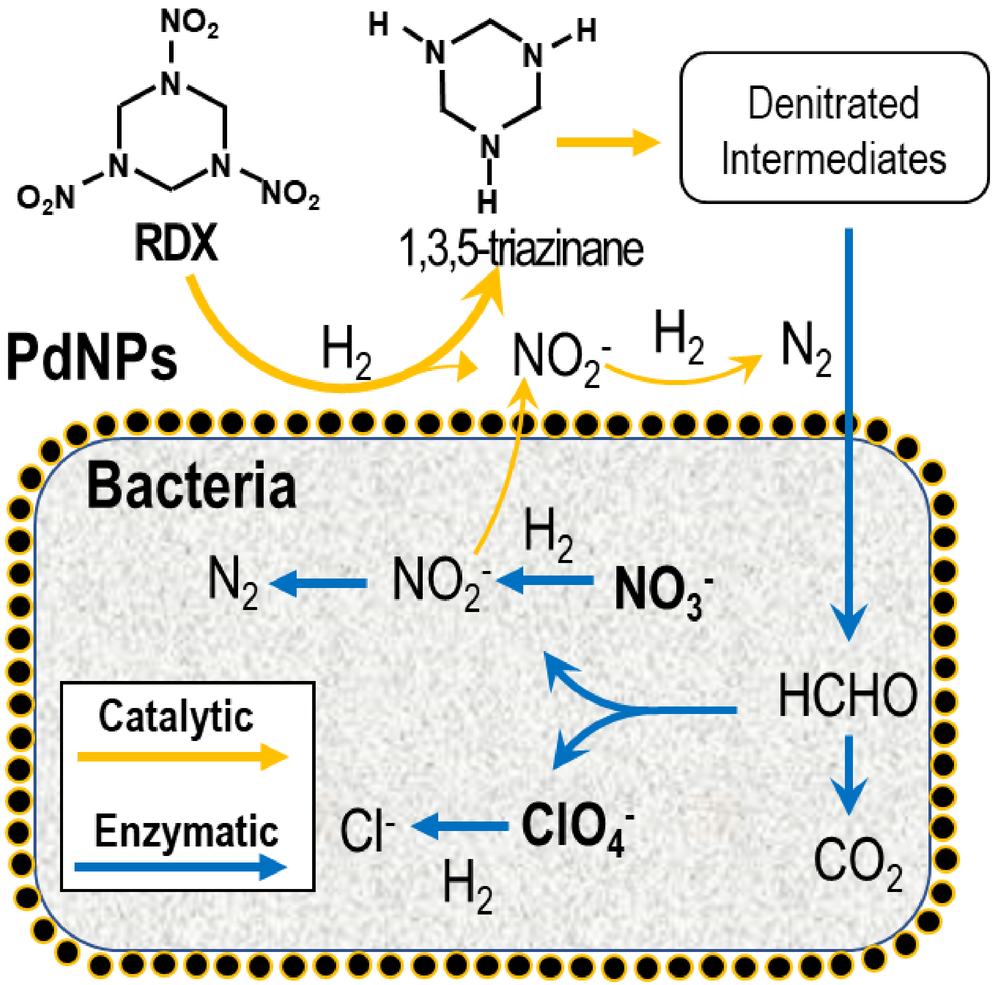
1. **Biodegradable** ✓
2. **No secondary contamination** ✓
3. **Simultaneous removal** ✓

# Biotic Solution – Results for Continuous Co-removal




**RDX, $NO_3^-$, and $ClO_4^-$ removed continuously. Minimal loss of Pd NPs.**

# Co-Removal of Energetics and Oxyanions via *In Situ* Coupling of Catalytic and Enzymatic Destructions: A Solution to Ammunition Wastewater Treatment





Zheng et al. *ES&T* (2023)

1. **Biodegradable** ✓
2. **No secondary contamination** ✓
3. **Simultaneous removal** ✓

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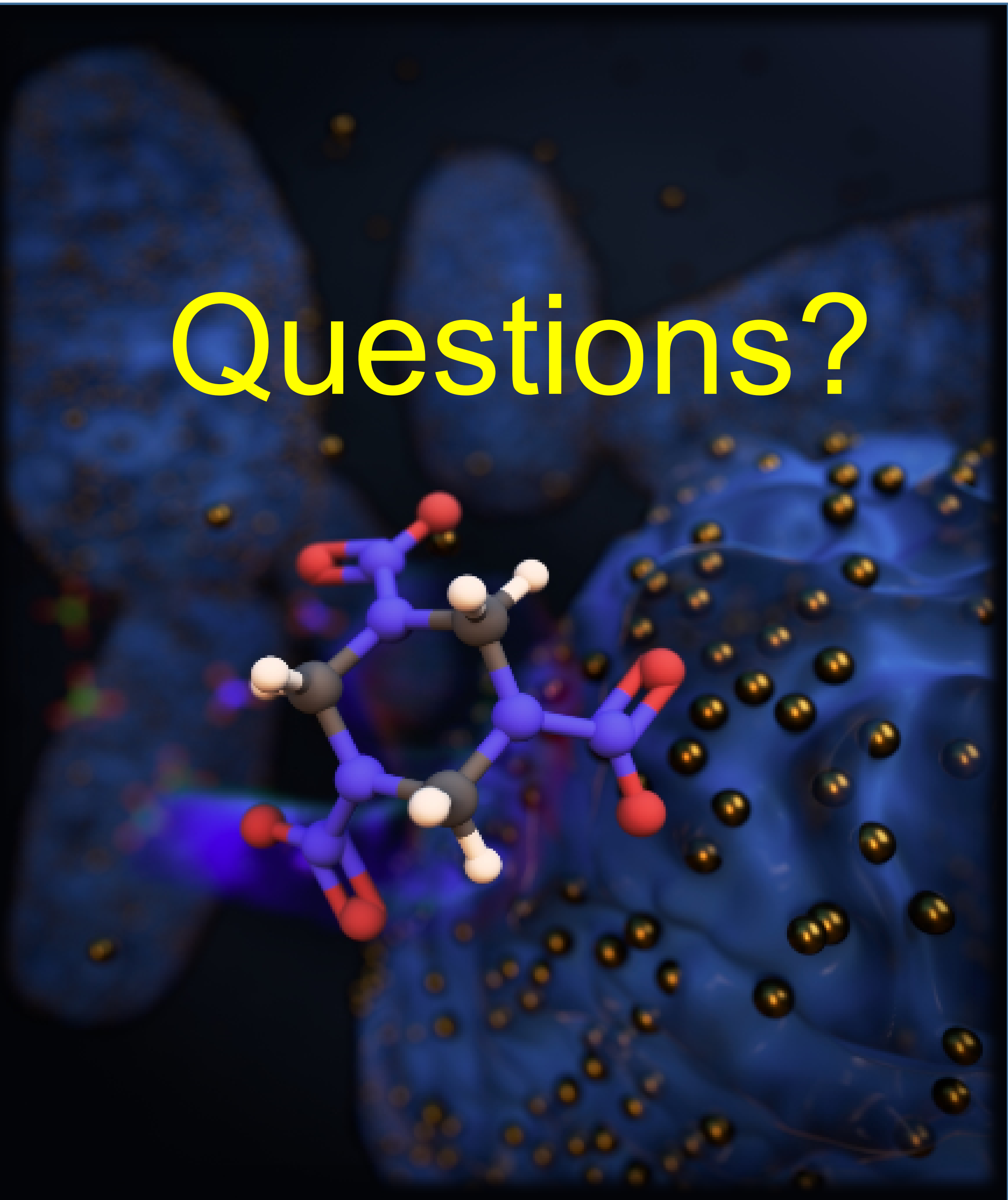


# Extra Pages

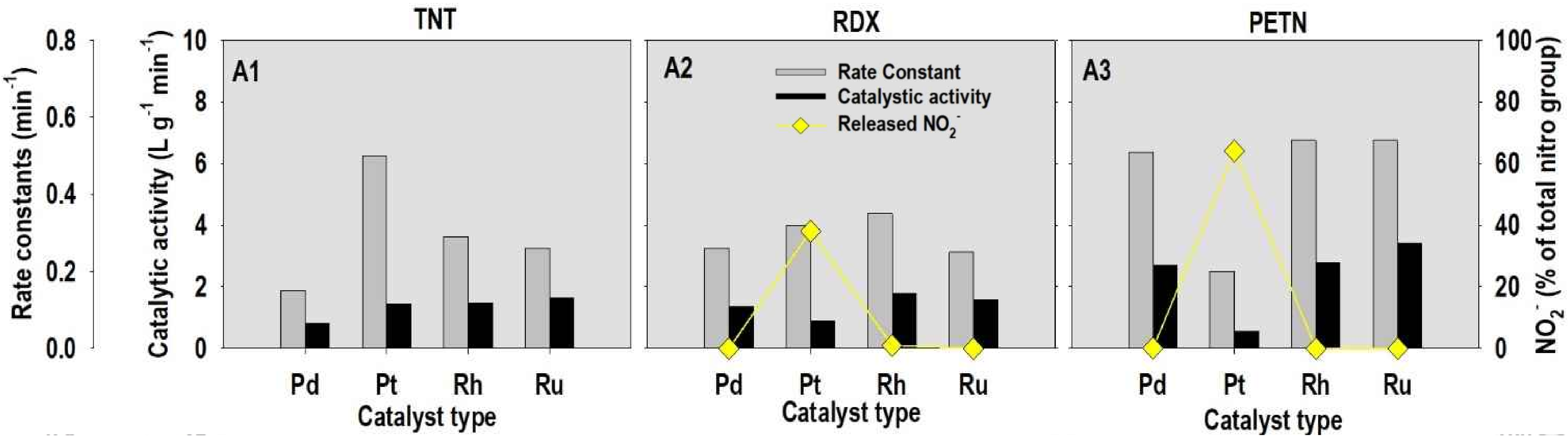
## References Cited


- Zheng, C., C. Zhou, Y. Luo, M. Long, X. Long, S., Yang, Y. Bi, D. Zhou, and B. E. Rittmann (2023). Co-removal of energetics and oxyanions via *in situ* coupling of catalytic and enzymatic destructions: a solution to ammunition-wastewater treatment. Environ. Sci. Technol. 57: 666-673.

- Zhou, C., Wang, Z., Ontiveros-Valencia, A., Long, M., Lai, C. Y., Zhao, H. P., ... & Rittmann, B. E. (2017). Coupling of Pd nanoparticles and denitrifying biofilm promotes H2-based nitrate removal with greater selectivity towards N2. *Applied Catalysis B: Environmental*, *206*, 461-470.

- Ranea, V. A., Strathmann, T. J., Shapley, J. R., & Schneider, W. F. (2011). DFT Comparison of N-Nitrosodimethylamine Decomposition Pathways Over Ni and Pd. *ChemCatChem*, *3*(5), 898-903.

# Abiotic Solution - Results




- Four NPs catalyzed the reduction of TNT, RDX, and PETN
- Pd was selected as example catalysts as it had the highest nitrite reduction rates

# Application of $H_2$-based membrane biofilm reactor

## ARoNite™

***A***utotrophic – an organism capable of making organic molecules from inorganic sources. Examples are plants, algae, some bacteria

***R***eduction – Chemical reaction in which an electron is gained

***o***f - **Nitrate** (or Chromium, Selenium and other compounds)

| Location | Contaminant | Dates | System configuration | Significant Outcome |
|---|---|---|---|---|
| La Puente, CA | Groundwater $ClO_4^-$ | ~2003 | Pilot module | AwwaRF Report by MWH, early system design info. |
| Modesto (Grayson) | Groundwater $NO_3^-$ | 9/06 – 6/11 | Pilot module | Multiple fiber and module construction improvements, CDPH data collected |
| Lake Arrowhead | Tertiary effluent $NO_3^-$ | 3/07-11/07 | Pilot module | WateReuse Report by Trussell |
| San Bernardino | Groundwater $NO_3^-$, $ClO_4^-$ | 3/08 - 1/09 | Pilot module | Flow maldistribution limit performance, ESTCP with CDM reauthorized |
| Glendale, AZ | Groundwater $NO_3^-$ | 4/08 - 2/09 | Pilot module | WRF Report by CH2MHill, positive comparison to IX and heterotrophic systems |
| Rancho Cordova | Groundwater $ClO_4^-$ | 9/08 – 11/10 | Pilot module | Successfully treat 14 ppm to <4 ppb |
| Rancho Cordova | Groundwater $ClO_4^-$ | 10/08 – 11/10 | Commercial module | Develop and test larger modules |
| Ojai, CA | Tertiary effluent $NO_3^-$ | 2/10 – 12/10 | Commercial module | Tested multitude of large modules in one system |
| Rialto, CA | Groundwater $NO_3^-$, $ClO_4^-$ | 5/11 – 2/12 | Commercial module | ESTCP project with CDM based on improvements in commercial module |
| Burbank, CA | Groundwater $NO_3^-$, Cr(VI) | 6/11 - 11/12 | Commercial module | Tested low ppb Cr(VI) removal |
| Rancho Cucamonga | Groundwater $NO_3^-$ | 11/11 – 1/13 | Commercial module | 1st commercial-scale system, gained regulatory approval for DW in CA |