# Magnetically Recoverable & Reusable NanoComposites

## for Treating Vessel Discharges

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The views expressed in this presentation are the author's own and not those of the U.S. Merchant Marine Academy, the Maritime Administration, the Department of Transportation or the United States Government



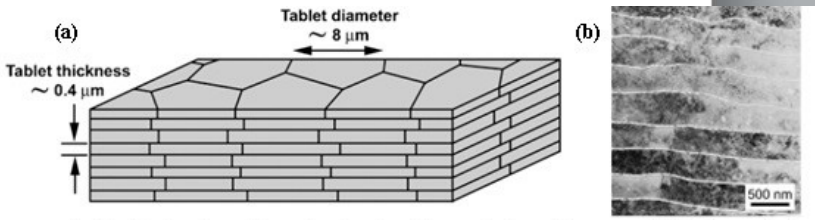
# Research Goal

To use magnetic separation based technology for treating vessel discharges via the development of **low-cost**, **eco-friendly**, **easily recoverable**, **reusable**, and **highly functional** nanocomposites

# NanoComposites

- Multiphase solid with at least one phase being nano-scaled (<100 nm)
- **Nano = Size dependent new properties**
- Synergistic/hybrid properties of the components
- **Natural nanocomposites: bones, teeth & sea shells**

https://en.wikipedia.org/wiki/Mollusc_shell




*(a) An illustration of the microstructural organization of nacre and (b) a transmission electron micrograph depicting the "brick-and-mortar" arrangement of the aragonite tablets and the organic interfacial layers in nacre. Both images adapted from Barthelat et al. (2007)*

http://umich.edu/~acemrl/NewFiles/Bio-inspiredECC.html

# Shipping, Vessel Discharges & MARPOL Regulations

## Shipping & World Economy

- 90% of world's food, products, and energy
- **Safer, greener & more efficient**
- > $649 billion to U.S. GDP
- **Increased demand for waterway transportation**

## Large Amounts of Vessel Discharges

- **Bilge water (lowest space)**
- Ballast water (stability)
- **Deck runoff**
- Grey & Black water (shower, sinks, laundry facilities)

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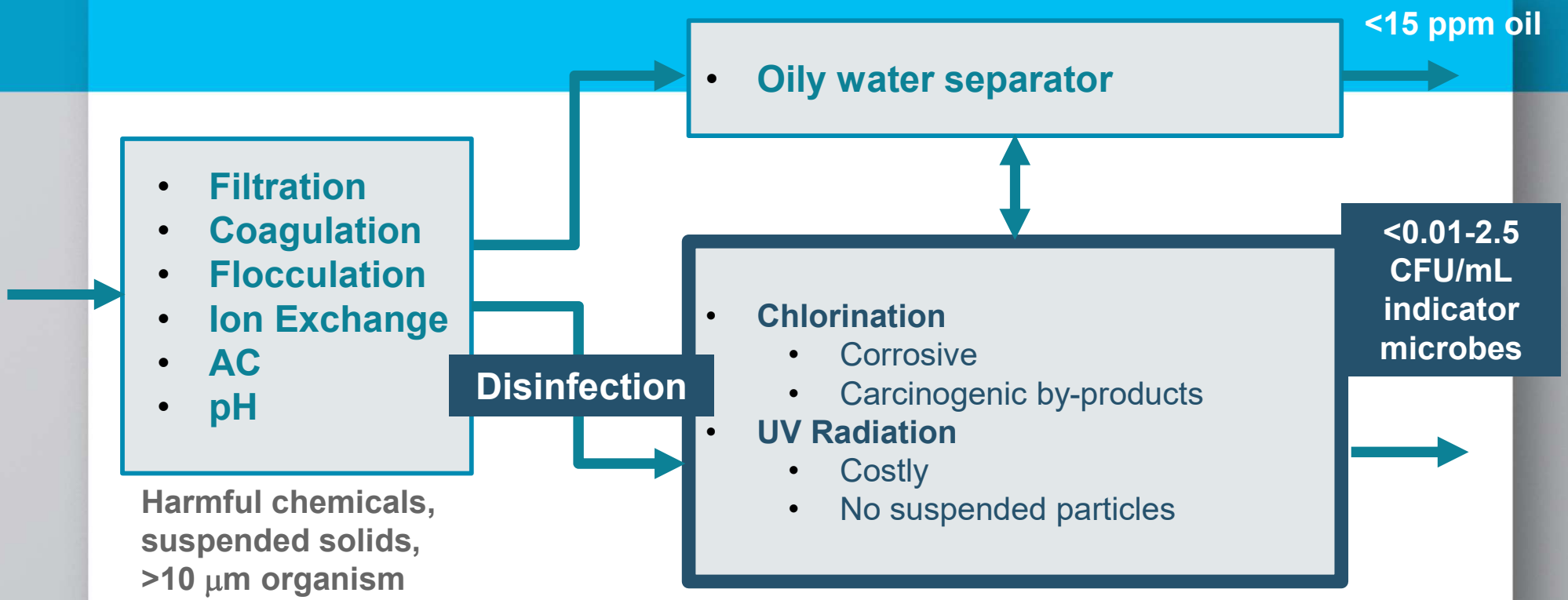
# Shipping, Vessel Discharges & MARPOL Regulations

| Pollutants | MARPOL (IMO) | Sources |
|---|---|---|
| **Oily water** | <15 ppm oil<br>(73/78, 83) | • Bilges<br>• Accidental spills<br>• Grey water |
| **Invasive microbes, pathogens** | **Indicator Microbes**<br>**< 0.01-2.5 cfu/mL**<br>(2004, 2017-Ballast, 73/78) | • Ballast water<br>• Black & grey water<br>• Oily water |
| **Harmful chemicals, suspended solids,**<br>**>10 mm organisms** | No visible solids<br>No detectable organisms<br>(2004, 2017-Ballast, 73/78) | • Antifouling paints<br>• Cathodic protection<br>• All other wastes/wastewaters |
| **$SO_x$, $NO_x$**<br>**$CO_2$** | % S in fuel < 0.50 % (1997, 2020)<br>50% reduction by 2050 rel. 2008 | • Combustion Exhaust |

# Current Water Treatment Technology



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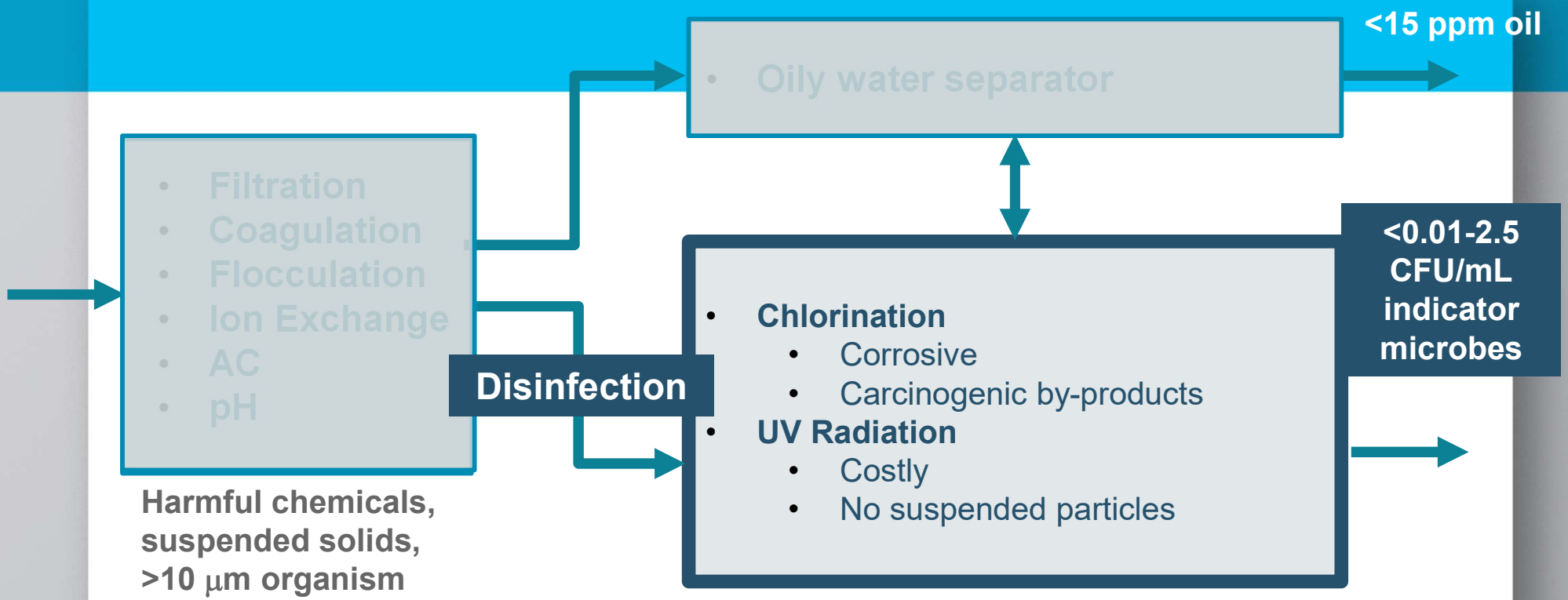
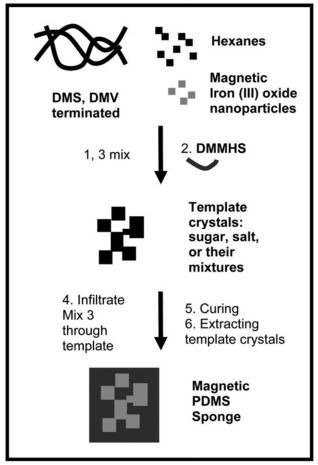


# Magnetic Separation Based on Nanocomposites

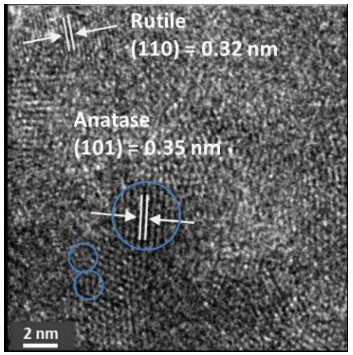
## – A Promising Technology

- Rapid recovery
  - reusability
  - 2nd pollution elimination
- No contact action
- Not affected by ship's motion
- Synergistic
  - highly magnetic
  - additional functionalities

### Magnetic PDMS sponge




### $TiO_2$ based magnetic nanocomposite





**P.Y. Furlan**, B.M. Ackerman, M. E. Melcer, S. E. Perez*J Ship Prod Des* **2017**, 33 (03): 227–236

M. Keeley, K. Kisslinger, C. Adamson, **P.Y. Furlan** *J. Mar. Sci. Eng.* **2021**, *9*(9), 943

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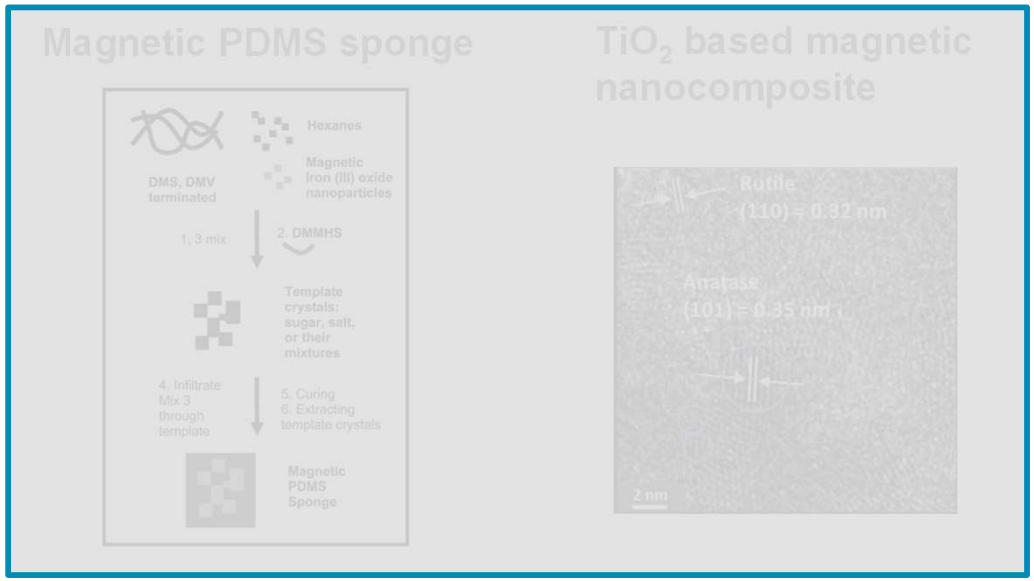


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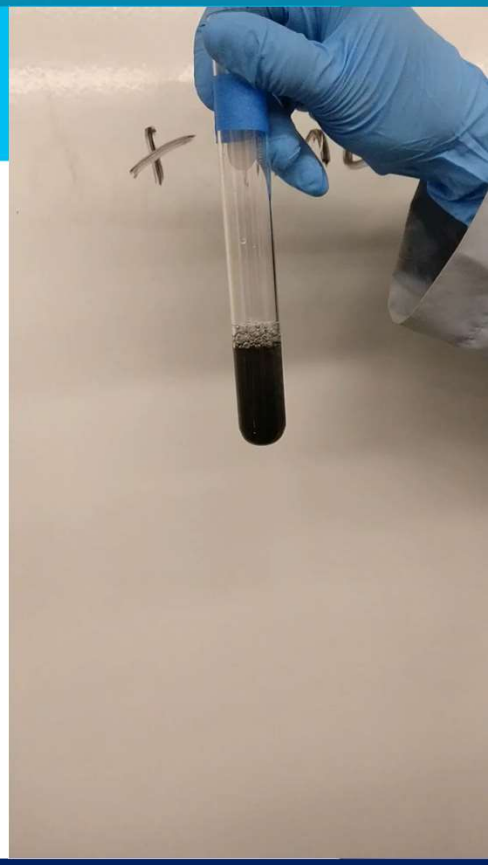
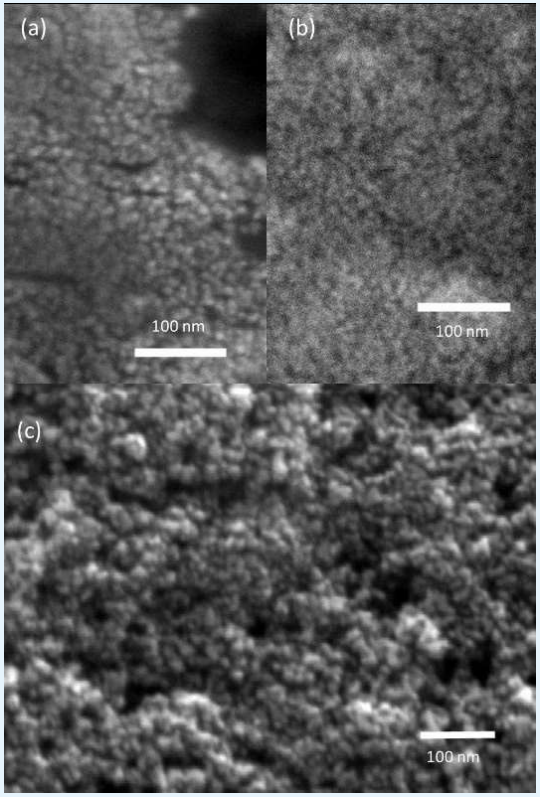


# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

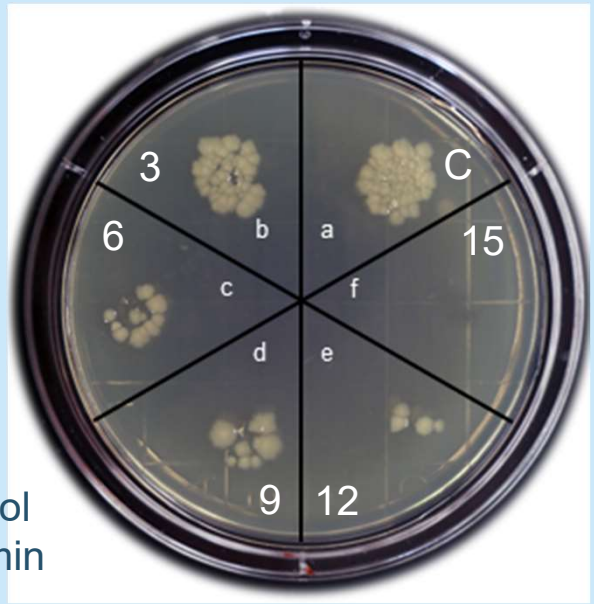



| Component | Functionality |
|---|---|
| $Fe_3O_4$ MNPs (10-16 nm) | • Highly magnetic<br>• Large surface area for intimate binding to AC |
| Activated Carbon (AC, 20 μm) | • Superior absorption ability<br>• Host and spacer for MNPs & AgNPs |
| Ag NPs (10-12 nm) (Ag source - 560,000 metric tons) | • Strong antimicrobial activity to bacteria, fungi, algae, viruses<br>• Low toxicity toward humans<br>• EPA recommends <0.1 ppm Ag in drinking water |

**P.Y. Furlan,** A.J. Fisher, A.Y. Furlan, M.E. Melcer, D.W. Shinn, and J.B. Warren *Inventions*, **2017**, 2, 10.
**P.Y. Furlan,** A.J. Fisher, M.E. Melcer, A.Y. Furlan, and J.B. Warren *J. Chem. Educ*, **2017**, 94(4), 488-493.

# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

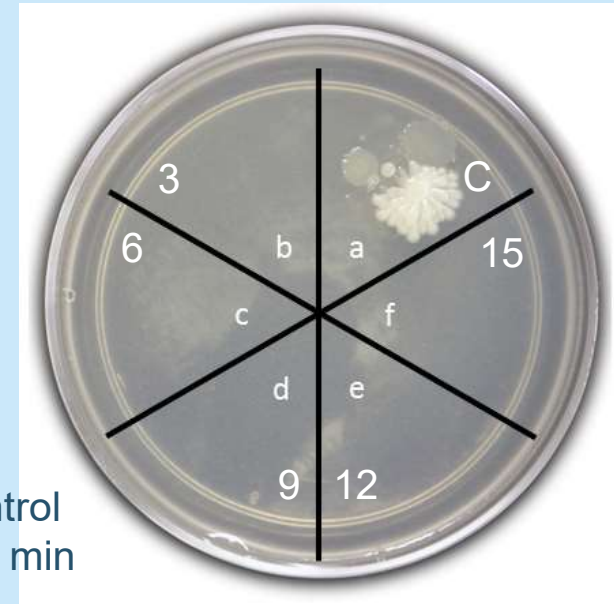
- 0.5 g MACAg (0.15%Ag)
- Killed 2x10$^6$ cfu in 15 min
- 0.01 ppm Ag release by AA




C= Control
Time in min

cfu = colony-forming unit

- 0.5 g MACAg (0.22%Ag)
- Removed all 10$^5$ viable microbes from Long Island Sound Surface Water in 3 min



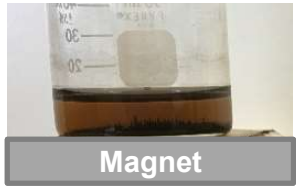

C= Control
Time in min

# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Major Concerns

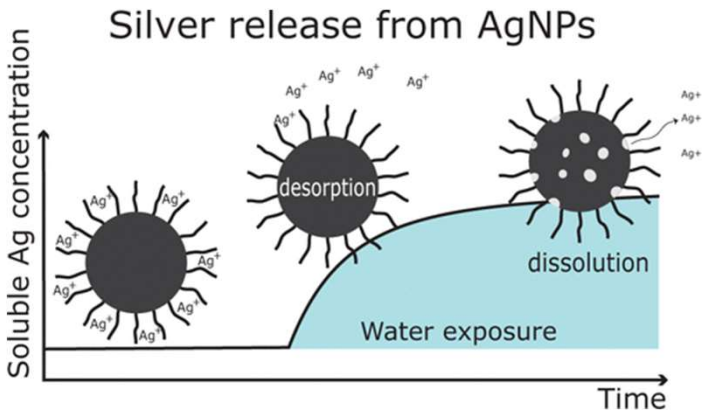
### Oxidation of Magnetite

$$2\ Fe_3O_4 + \tfrac{1}{2}\ O_2 \rightarrow 3\ Fe_2O_3$$




**After 1 min Sonication**

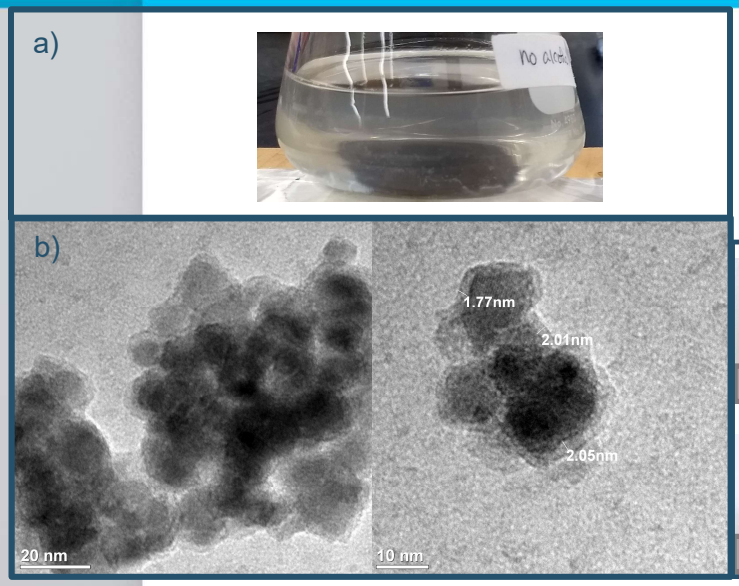
### Ag Release > 0.1 ppm




J. Dobias, R. Bernier-Latmani, *Environ. Sci. Technol.* 2013, 47, 9, 4140−4146

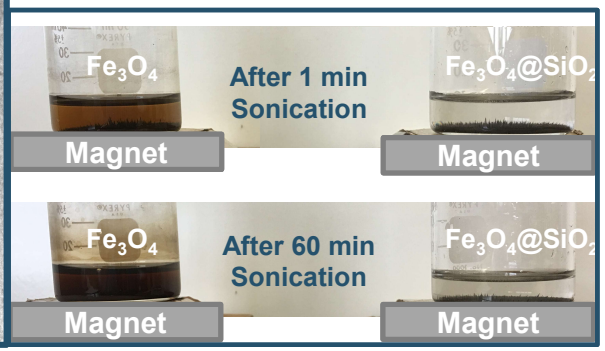
# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

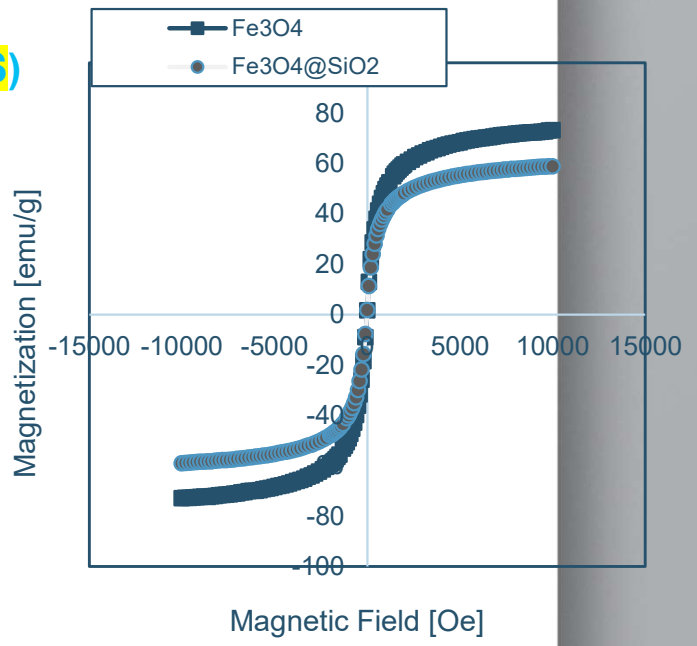
## Simple and Green Procedure for Forming Silica Shells




TEOS (tetraethoxysilane)

$Fe_3O_4$ ⟶ $Fe_3O_4@SiO_2$ (MS)




**P.Y. Furlan**, A.Y. Furlan, K. Kisslinger, M. Melcer, D. Shinn, J. Warren,
*ACS Sustainable Chem. Eng.* **2019**, 7, 18, 15578−15584

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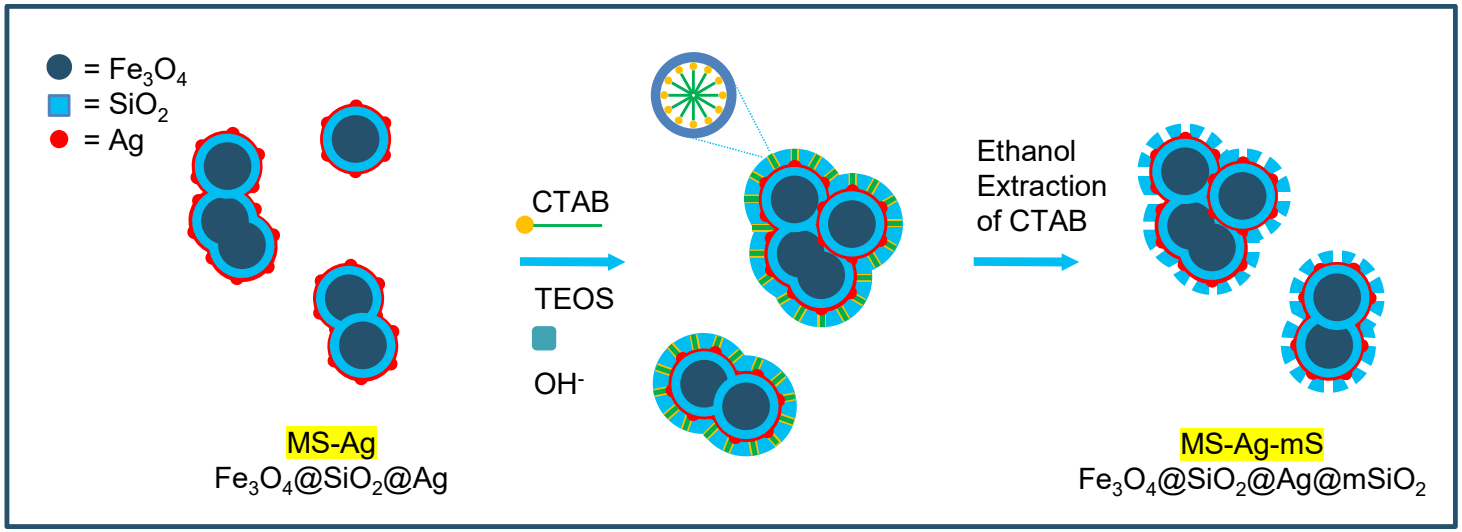
# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Novel Core-Multishell Approach

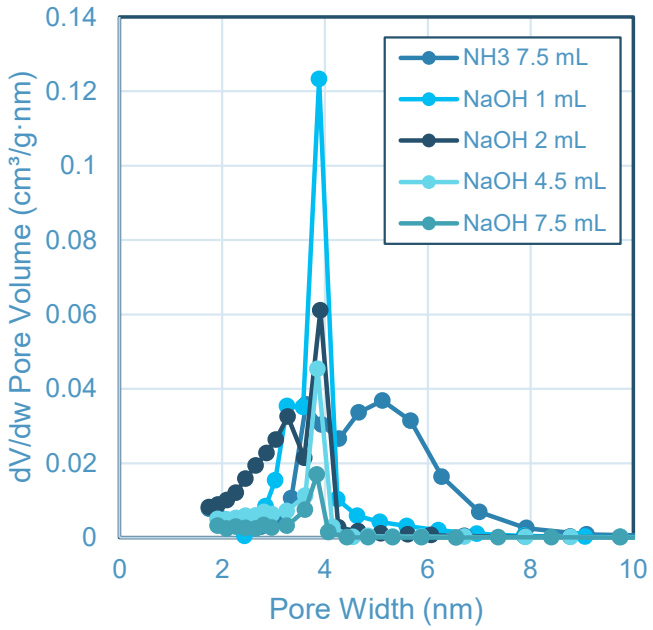

Cetyltrimethylammonium bromide (CTAB, ~2nm long)

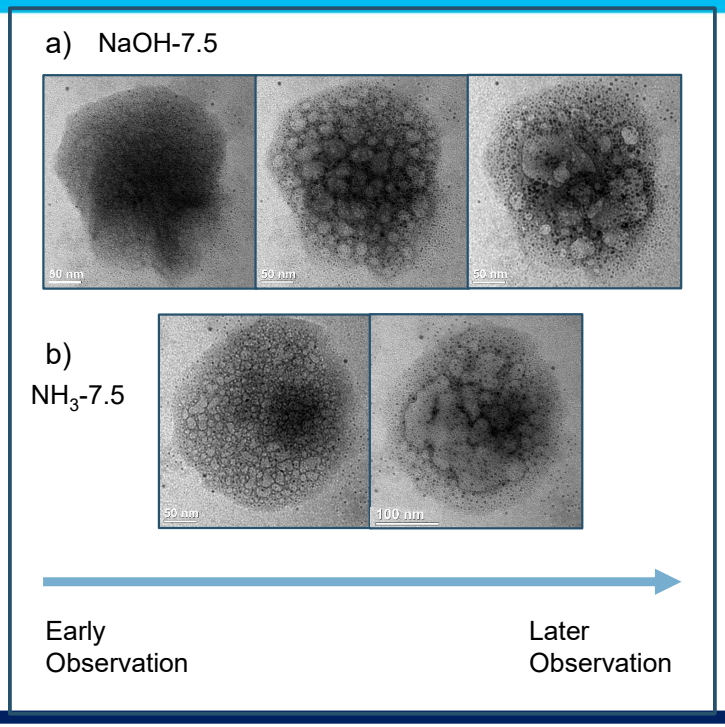



**P.Y. Furlan**, A.Y. Furlan, K. Kisslinger, M. Melcer *ACS Appl. Mater. Interfaces* **2021**, 13, 40, 47972−47986

# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## BET Results & TEM Images using an 80 kev e-Beam



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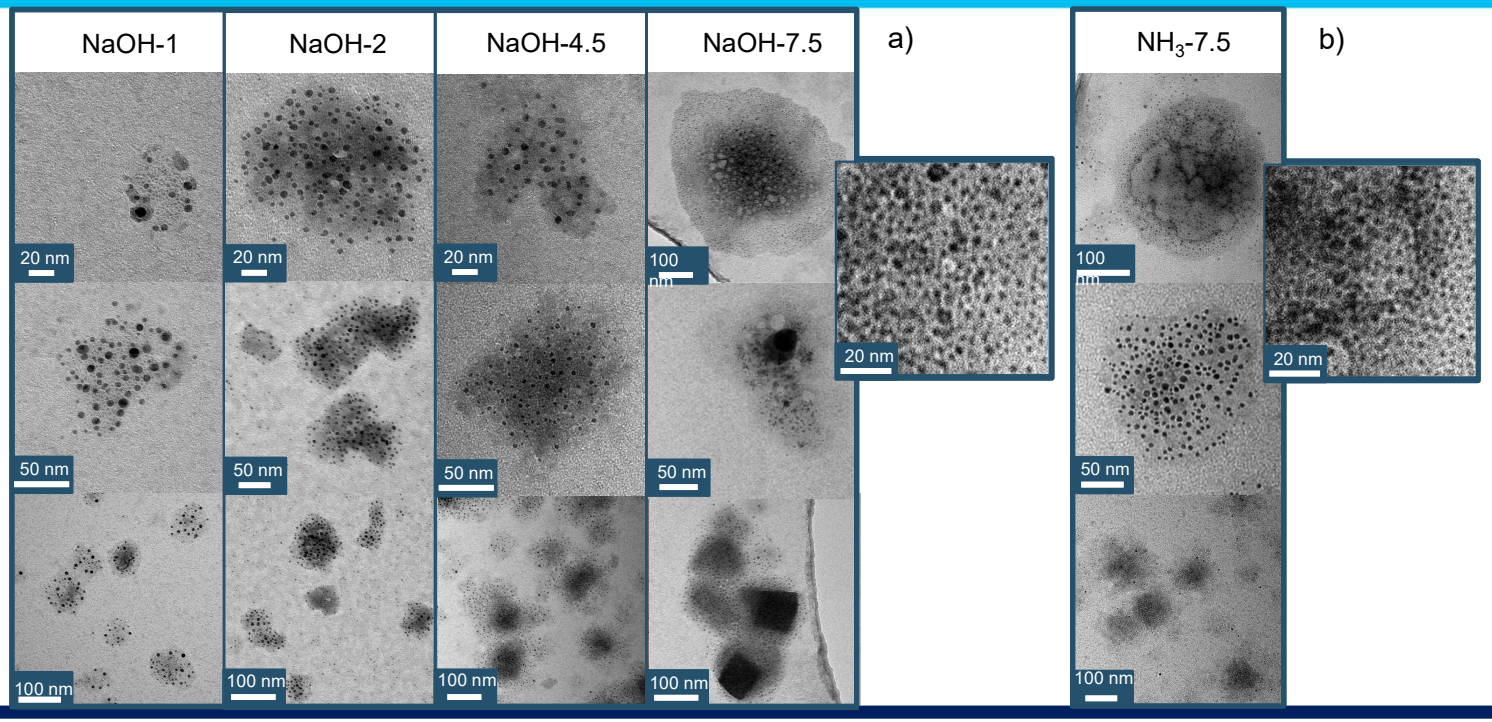
## Transmission Electron Microscope (TEM) Images using an 80 kev e-Beam



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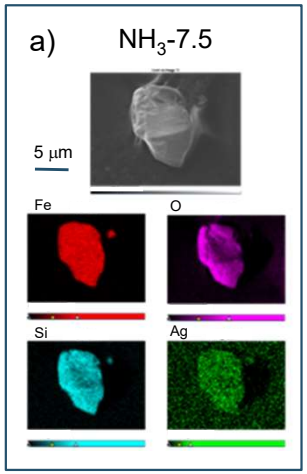
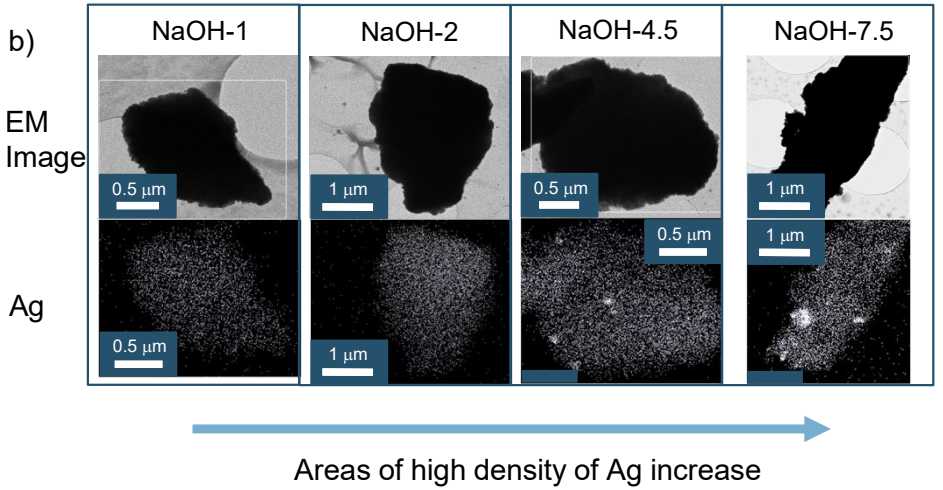
## Energy Dispersive Spectroscopy (EDS) Elemental Maps

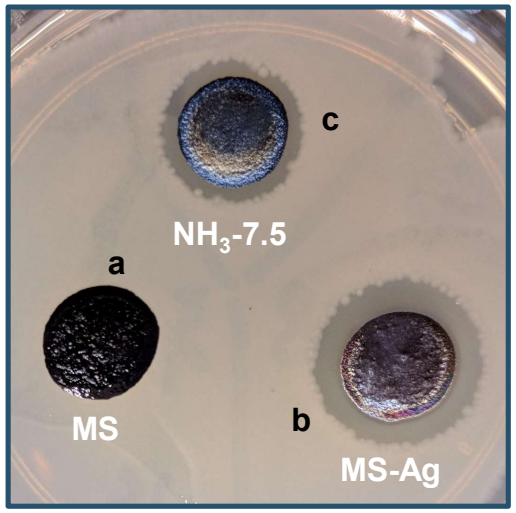


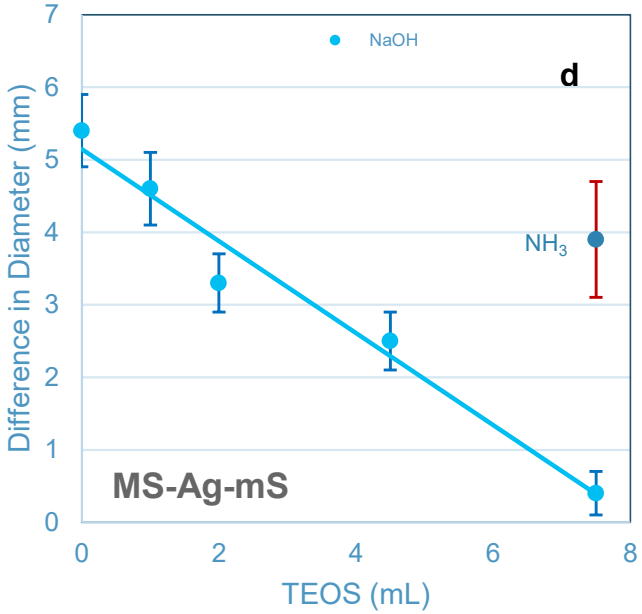



# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Results of the Diameter of Inhibition Zone

100 μL 5x10$^7$ cfu/mL *E. coli* culture
25 mg/25 μL sample
(cfu = colony-forming unit)



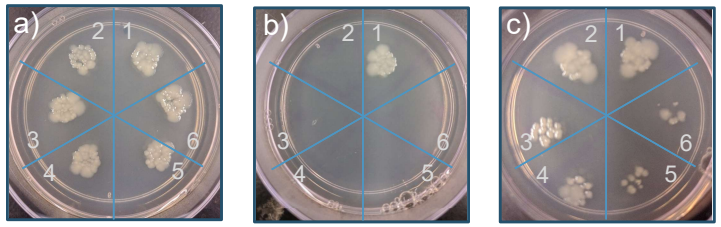



# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Antimicrobial Activities against *E. coli*

**Shaking Test:** 5 mg in 1 mL culture. Sampling every 3 min. Plate results of $10^4$ cfu/mL *E. coli* culture.

MS | MS-Ag | $NH_3$-7.5




**Reusability Test:** 3 repeated cycles, each 15 min shaking. Plate results of $10^4$ cfu/mL *E.coli* culture.

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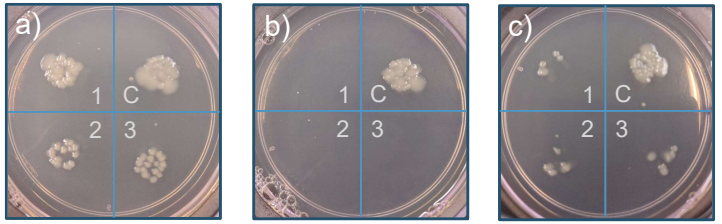


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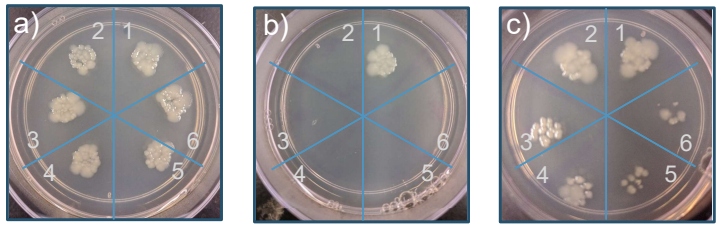


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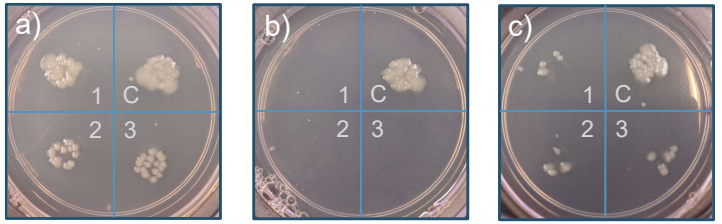


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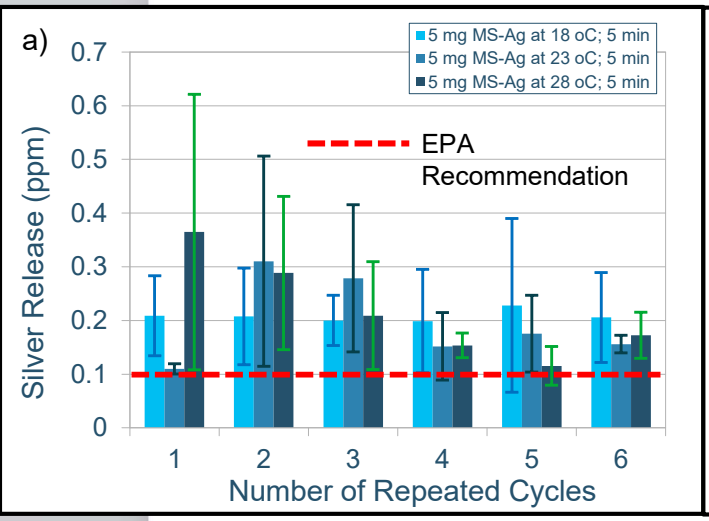
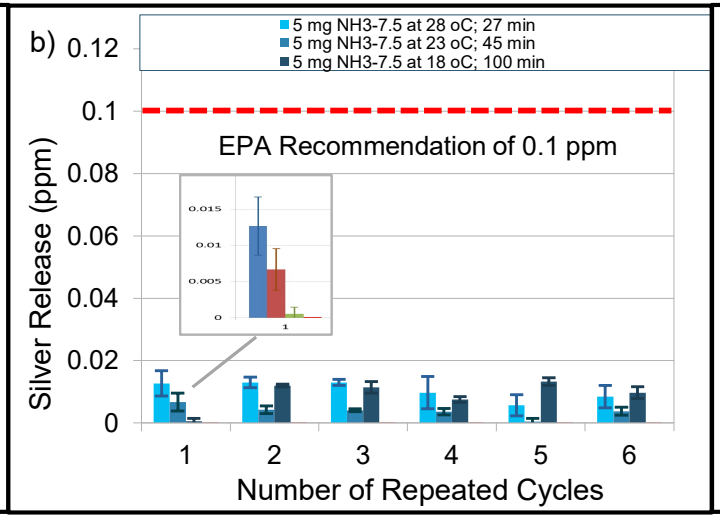
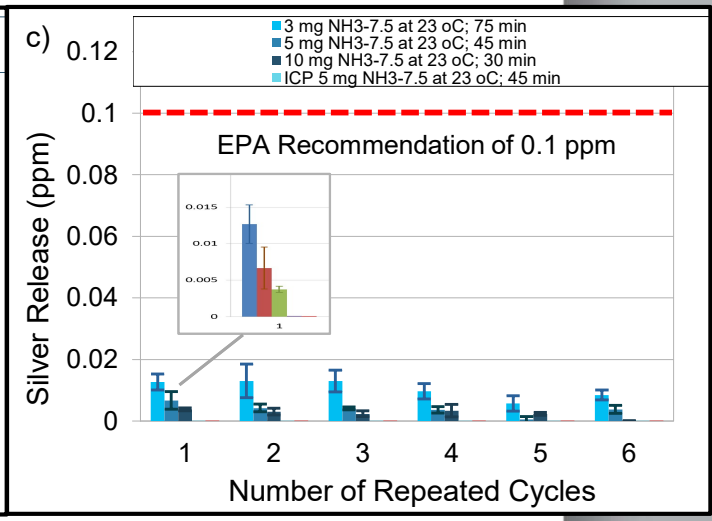
# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Silver Release Profile by AA Spectroscopy & ICP-MS

*4-Log Reduction in Viable E. coli Counts*





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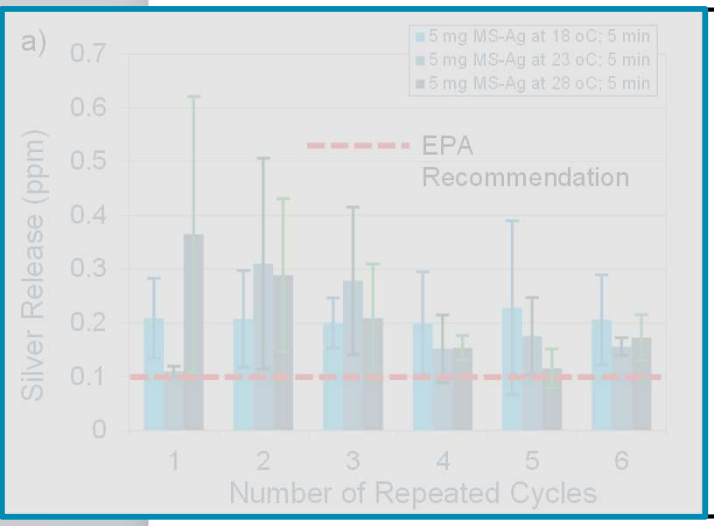
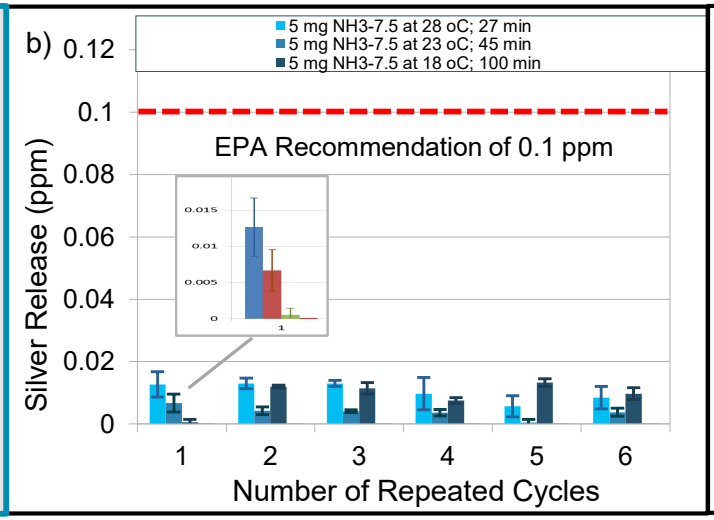
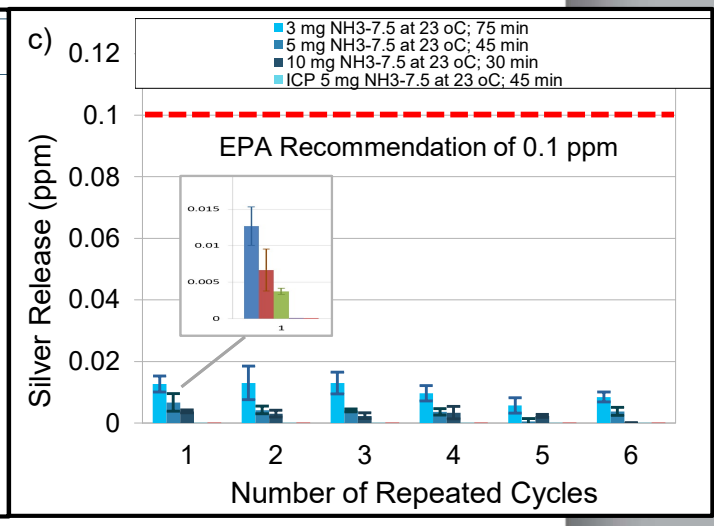
# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Silver Release Profile by AA Spectroscopy & ICP-MS

*4-Log Reduction in Viable E. coli Counts*



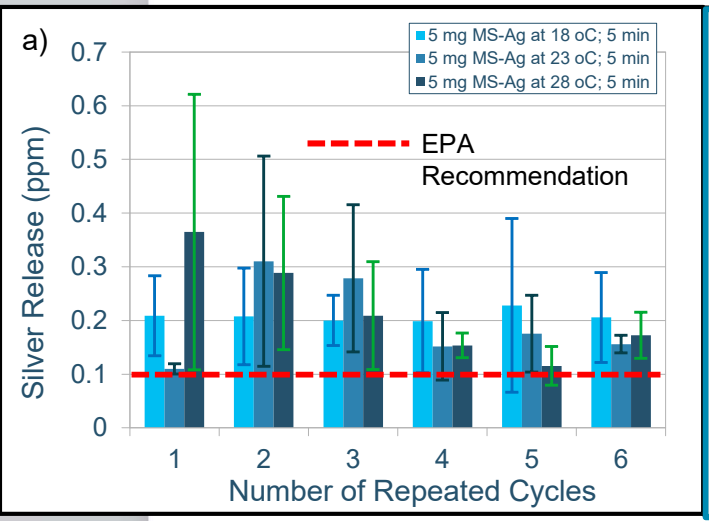



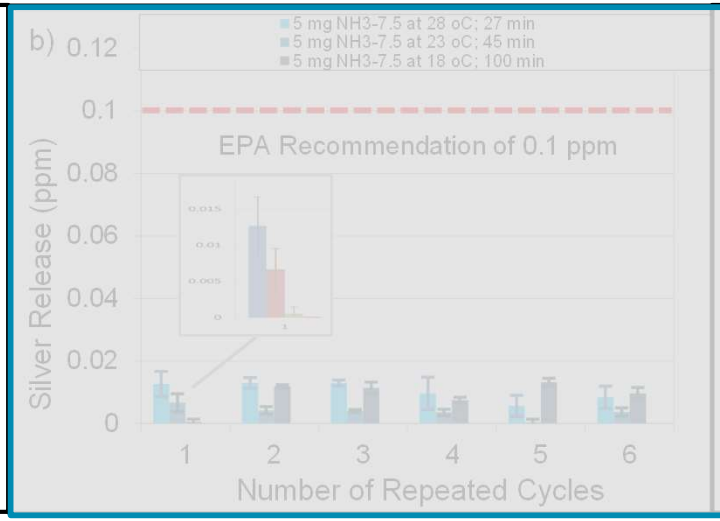



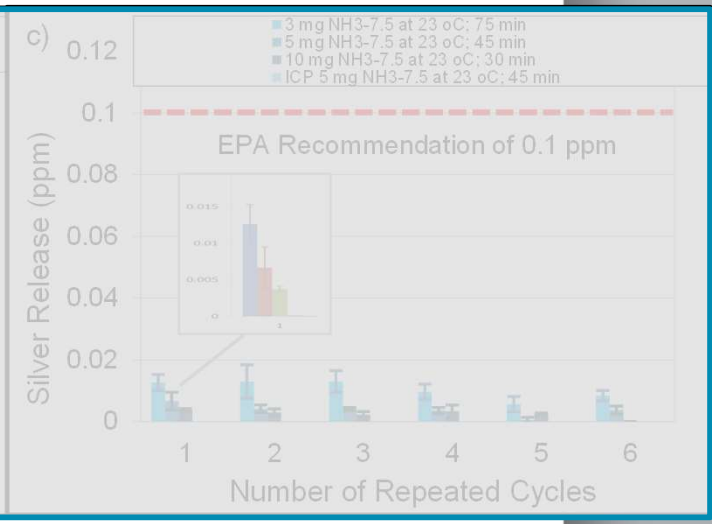
# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Silver Release Profile by AA Spectroscopy & ICP-MS

*4-Log Reduction in Viable E. coli Counts*





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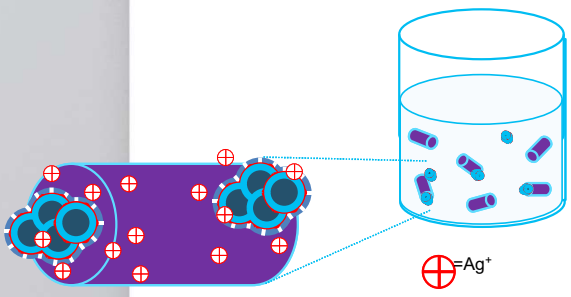
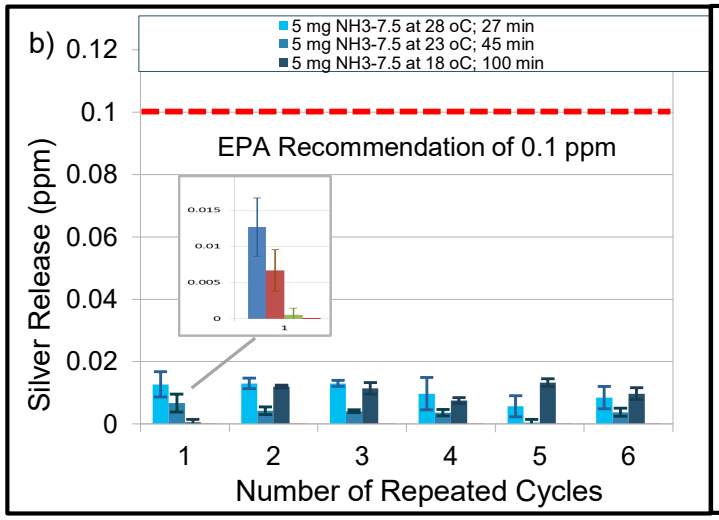
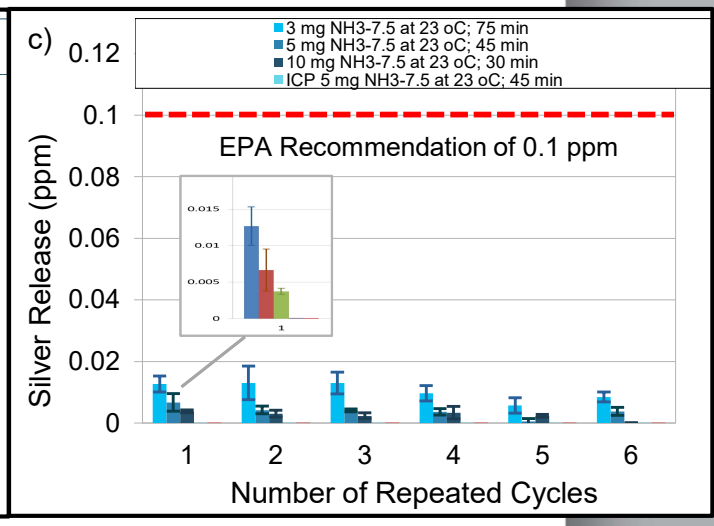
# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Silver Release Profile by AA Spectroscopy & ICP-MS




*4-Log Reduction in Viable E. coli Counts*

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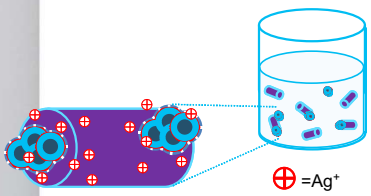
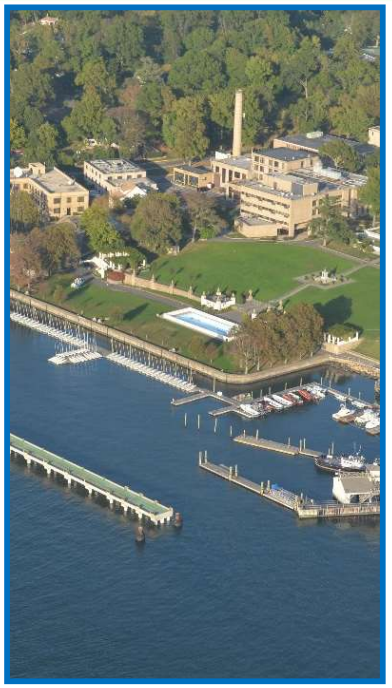
# Reusable Magnetic AgNPs-Based Nanocomposites for Water Disinfection

## Disinfection of Long Island Sound Surface Water




**Treating** LISS water collected in Sept. at 23-24°C by 1 mg/mL of a) $NH_3$-7.5 b) NaOH-2

United States Merchant Marine Academy
Maritime Administration of the United States of America
Department of Transportation

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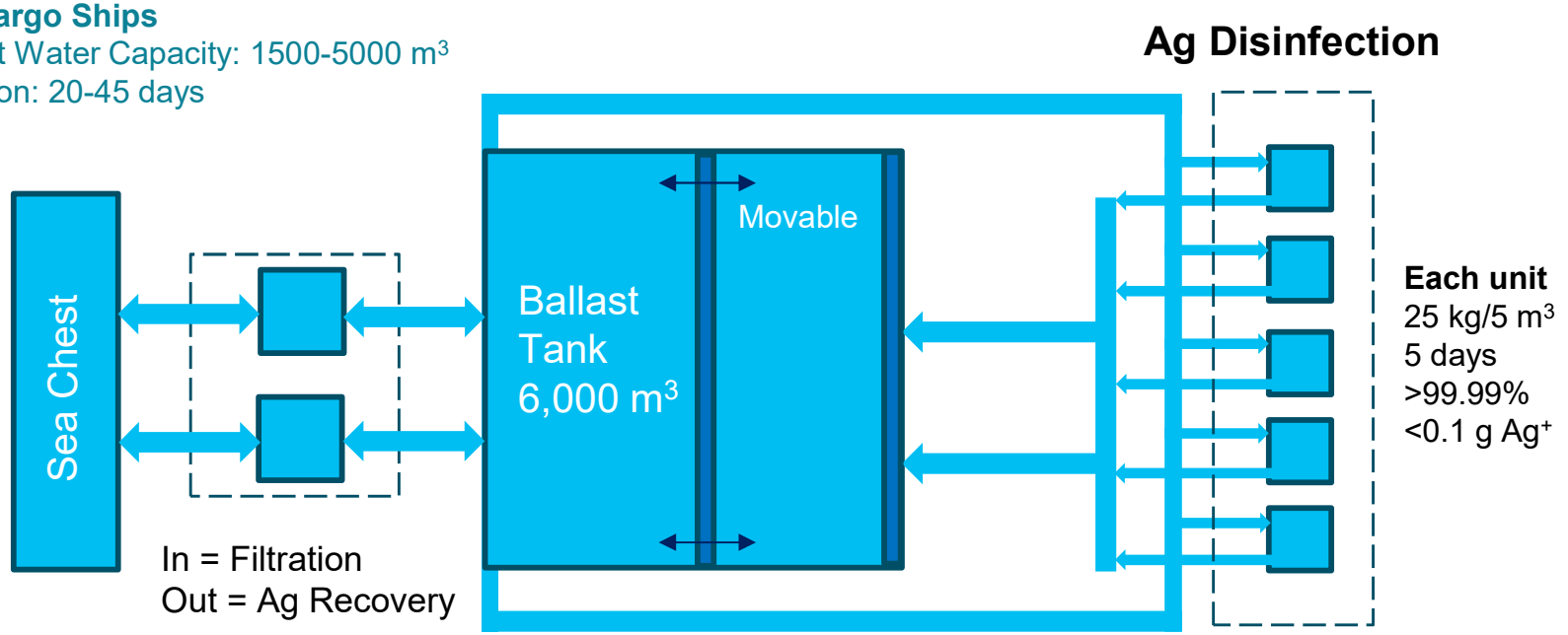
## Ballast Water Treatment System – Ag Nanocomposite Units

**For Cargo Ships**
Ballast Water Capacity: 1500-5000 $m^3$
Duration: 20-45 days



# Conclusion

## Via nanotechnology, magnetic functional nanocomposites

### Simple

Common Chemicals/Facilities

### Recoverable

Highly magnetic for easy & rapid recovery

### Stable

Highly oxidation resistant

### Synergistic

Highly Functional (e.g. antimicrobial)

### Tailorable

Highly tunable structures

### Green

Highly eco-friendly w/ minimum chemical release

## Promising green & low cost technology for treating vessel discharges such as disinfecting ballast water

# Acknowlegement



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## THANKS!

# Any questions?

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