

# Functionalized Mesoporous Carbon Fibers for Effective Recovery of Rare Earth Elements from the Acidic Extract of End-of-Life Magnet Scrap

**WP22-S1-3463**

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<b>14. ABSTRACT</b> To develop functionalized mesoporous carbon fiber (MCF) materials that can be used in solid-liquid separation systems for effective extraction, concentration, and purification of REEs from electronic and industrial wastes. Specific research objectives: To develop ligand-assisted extraction technology of REEs from NdFeB powder as a model system for magnet scrap. To develop MCF materials with tunable pore size, pore structure, and surface functionalities using diblockcopolymer templates. To develop new organic-ligand functionalized MCF materials using post-synthesis methods. Target ligands include diglycolamide (DGA), and diethylenetriaminepentaacetic acid (DTPA). To elucidate the molecular, nano, and micro scale interactions and binding mechanisms of REEs with organic ligands and MCF materials by using advanced spectroscopic characterizations.					
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# Project Team

- **Dr. Dien Li** (Savannah River National Laboratory)  
Expertise: Porous and nano materials, extraction and separation of critical metals and contaminants, remediation of waste streams.
- **Dr. Yuanzhi Tang** (Georgia Institute of Technology)  
Expertise: Molecular-level characterization of critical metals in complex matrices, environmental geochemistry, spectroscopy.
- **Dr. Guoliang Liu** (Virginia Polytechnic Institute and State University)  
Expertise: Mesoporous carbon materials, polymer chemistry, coordination chemistry.



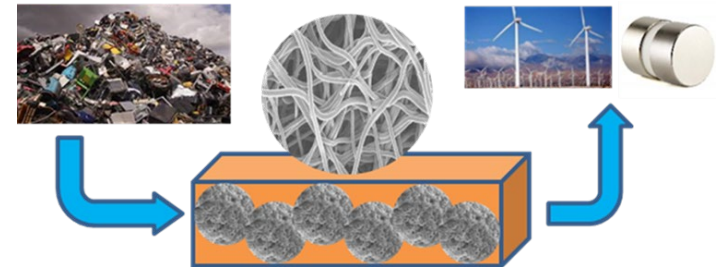
## Background

- **Performance period:** November 1, 2021 – October 31, 2022.
  
- **Response to SON:** To develop a framework and provide initial laboratory scale tools for securing critical minerals and rare earth elements (REEs) by recovery, recycling, and reuse in DoD weapons systems and platforms.
  
- **Problem statement:**
  - ◆ REEs are critical for high-technology and clean energy industries.
  - ◆ The US relies heavily on international supplies of REEs.
  - ◆ Current hydrometallurgical technologies for REE extraction are energy intensive and costly, have low REE recovery rate, and produce toxic wastes.
  - ◆ There are urgent needs for the exploration of alternative resources and sustainable technologies for domestic REE production.
  - ◆ There are large amounts of hazardous electronic and industrial wastes (e.g., NdFeB magnet scrap, electronic devices), posing high environmental risks while requiring high cost for proper management.
  - ◆ Electronic and industrial wastes contain high REE content and can serve as alternative feedstocks for domestic REE recovery.

## Technical Objectives

- **Overarching objective:**

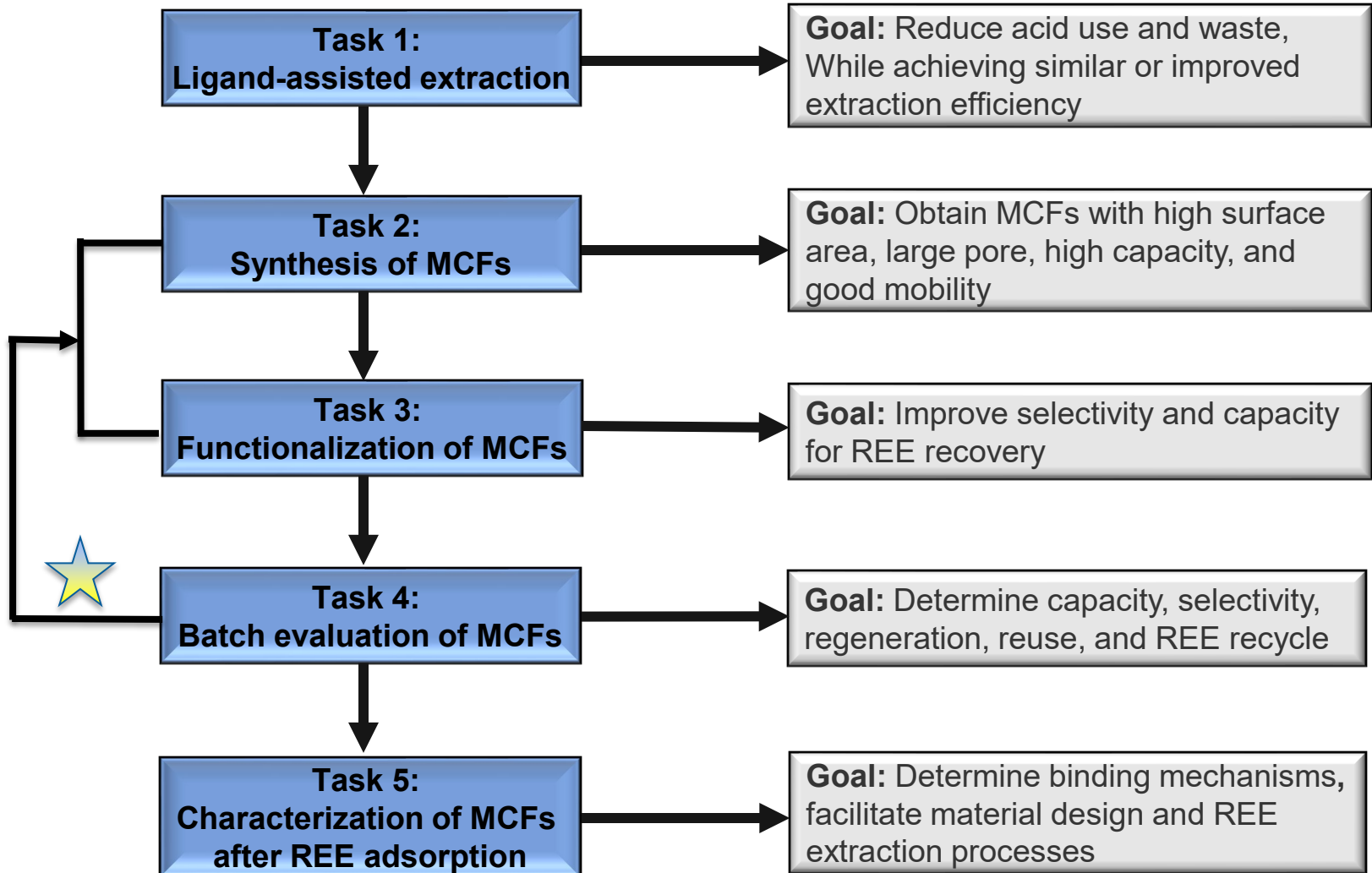
To develop functionalized mesoporous carbon fiber (MCF) materials that can be used in solid-liquid separation systems for effective extraction, concentration, and purification of REEs from electronic and industrial wastes.



- **Specific research objectives:**

- ◆ To develop ligand-assisted extraction technology of REEs from NdFeB powder as a model system for magnet scrap.
- ◆ To develop MCF materials with tunable pore size, pore structure, and surface functionalities using diblock copolymer templates.
- ◆ To develop new organic-ligand functionalized MCF materials using post-synthesis methods. Target ligands include diglycolamide (DGA), and diethylenetriaminepentaacetic acid (DTPA).
- ◆ To elucidate the molecular, nano, and micro scale interactions and binding mechanisms of REEs with organic ligands and MCF materials by using advanced spectroscopic characterizations.

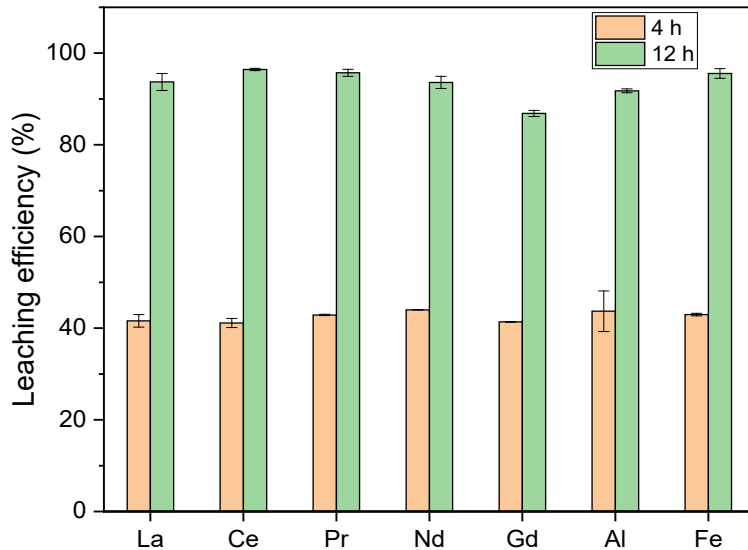
# Technical Approach



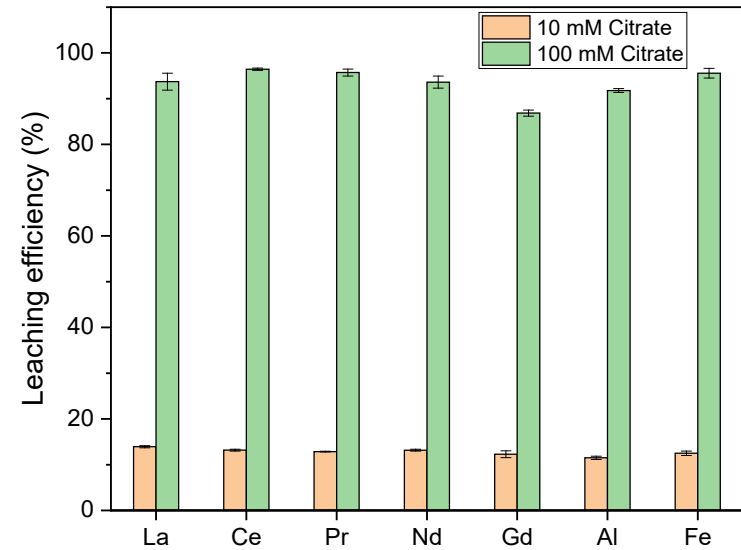
# Results

- **Citrate ligand assisted extraction of REEs from NdFeB powder (Task 1)**

- ◆ NdFeB powder was used as a model system.
- ◆ Cheap and biodegradable citrate was used as an environmentally friendly ligand.
- ◆ HCl was used to adjust pH.
- ◆ The impacts of reaction time, citrate concentration, and solution pH were studied.



**Extraction efficiency VS reaction time**  
(100 mM citrate, pH 2, liquid/solid 200 mL/g, 200 rpm)

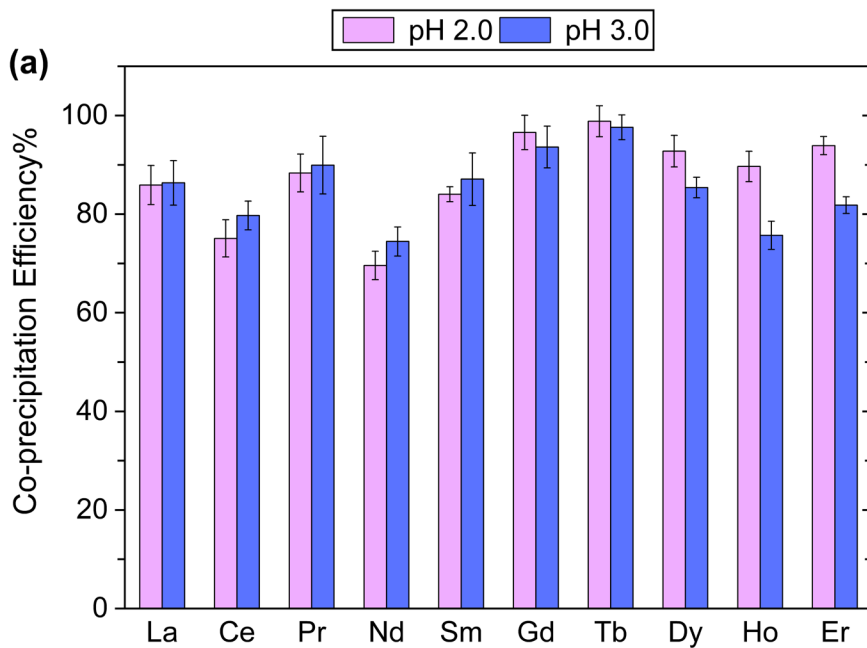


**Extraction efficiency VS citrate concentration**  
(pH 2, liquid/solid ratio 200 mL/g, 12 h, 200 rpm)

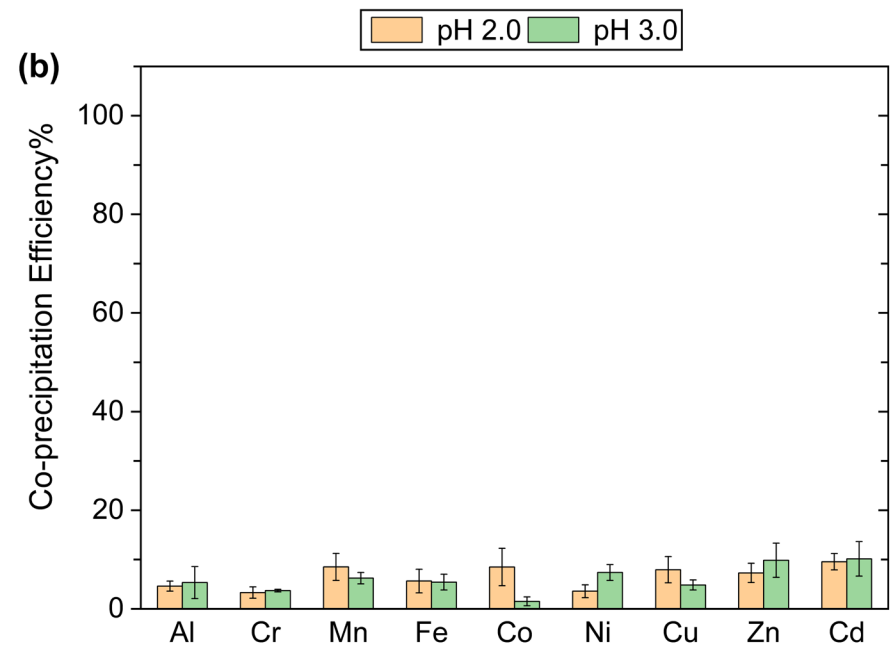
# Results

- **Oxalate assisted separation of REEs from other impurity metals (Task 1)**

- ◆ **Purpose:** To separate REEs from other impurity metals
- ◆ **Method:** Ca salt and sodium oxalate were added to the citrate extraction solution.
- ◆ **Final product:** Ca/REE-oxalate co-precipitate with minimal amount of other metal impurities.



(a) Co-precipitation efficiency of REEs



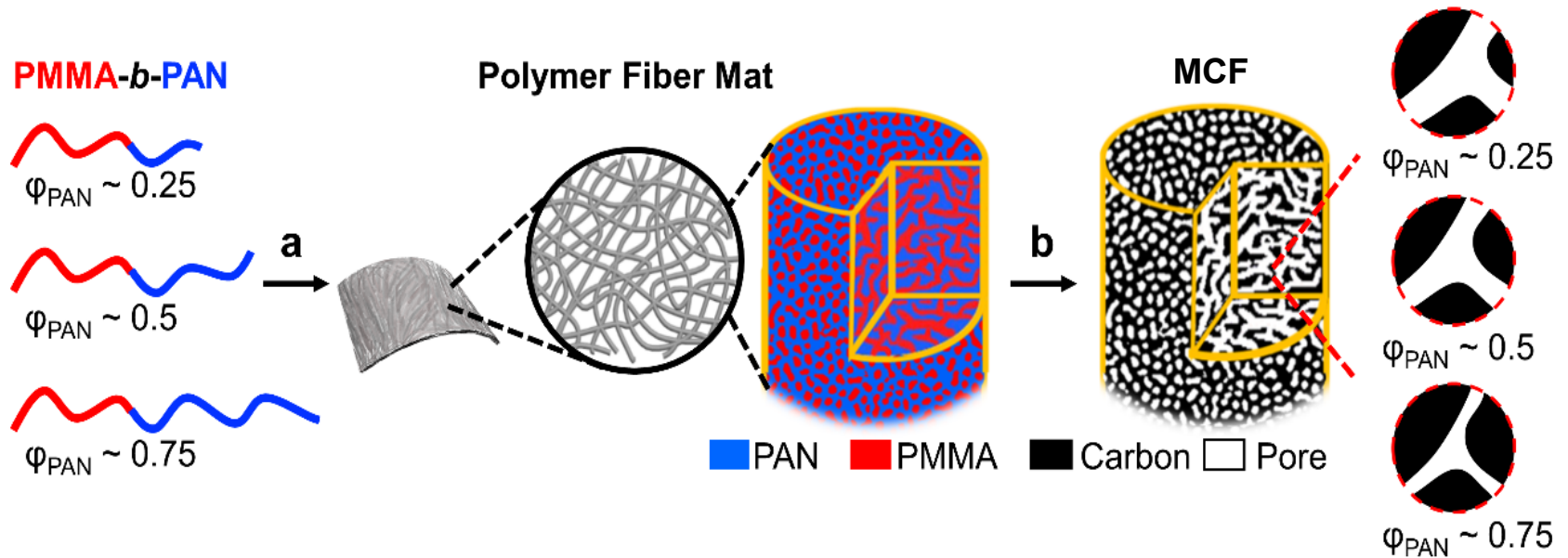
(b) Co-precipitation efficiency of other metals

**Experimental conditions:** pH 2 or 3, 10 mM Ca<sup>2+</sup>, 20 mM oxalate, 30 minutes

# Results

- **MCF material for REE recovery (Tasks 2, 4, and 5)**

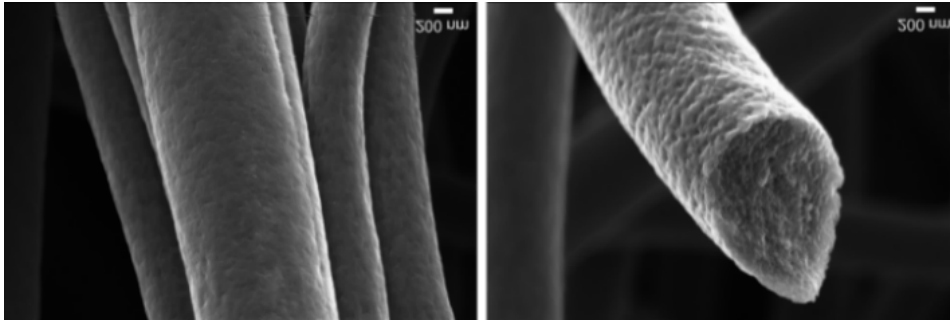
- ◆ Polymethyl methacrylate–block–polyacrylonitrile co-polymer (PMMA-*b*-PAN) was used as a template.
- ◆ PMMA-*b*-PAN solution was electrospun into a fiber mat.
- ◆ After phase-separation, polymer fibers are oxidized and carbonized into porous carbon fibers.
- ◆ The block copolymer composition controls the pore size, surface area, and ion diffusion.



**Schematic illustration of MCF synthesis**

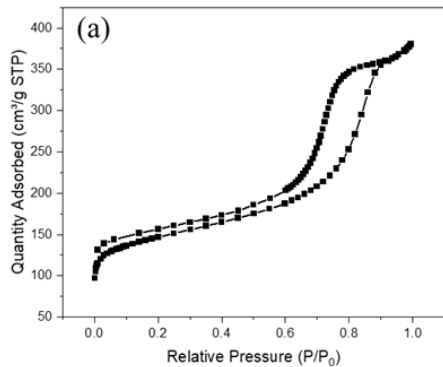
# Results

- MCF material for REE recovery (Tasks 2, 4, and 5)

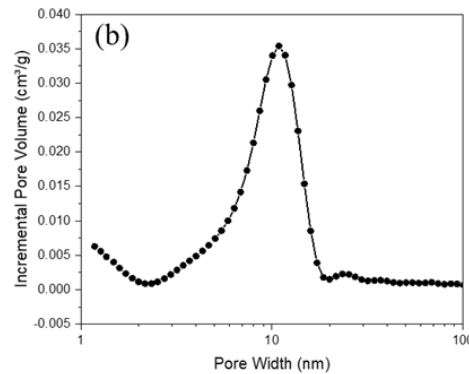


Scanning electron microscopy (SEM) images

MCFs: like sponge, 3D pore connection

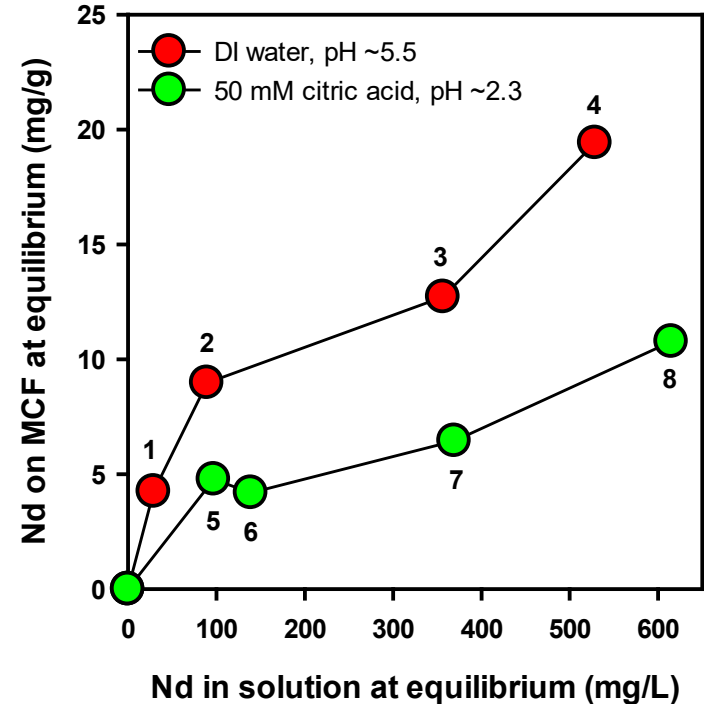


(a) N<sub>2</sub> sorption isotherms



(b) Pore size distribution

Pore size: 10.9 nm; Surface area: 540 m<sup>2</sup>/g

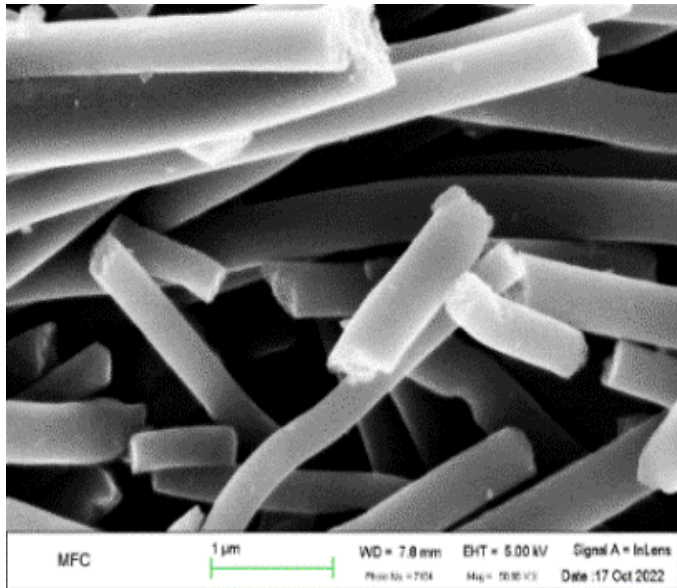


Nd adsorption onto MCF in DI water and 50 mM citric acid simulant

Reaction time: 24 hours  
Solid/liquid ratio: 10 g/L

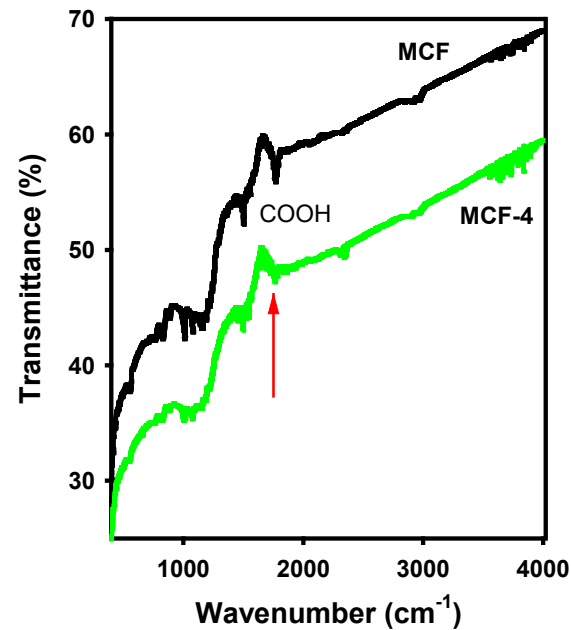
# Results

- MCF material for REE recovery (Tasks 2, 4, and 5)



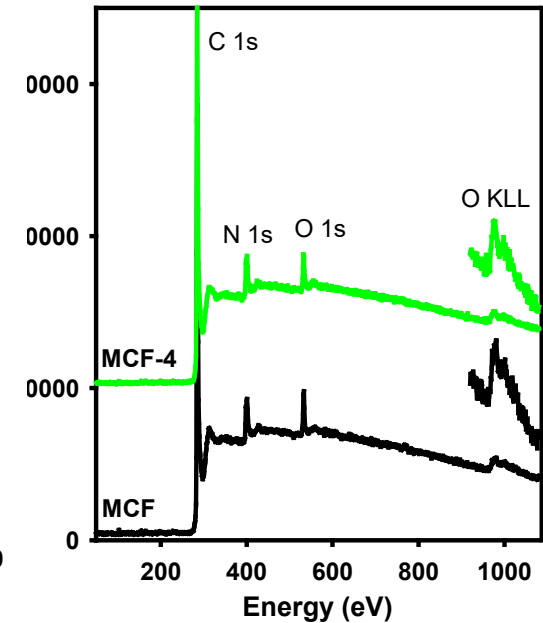
**SEM images of MCFs after Nd adsorption**

MCFs were stable after Nd adsorption, and the fiber texture and pore structure remained well



**FTIR spectra of MCFs before and after Nd adsorption**

The FTIR peak for C=O decreased significantly after Nd adsorption

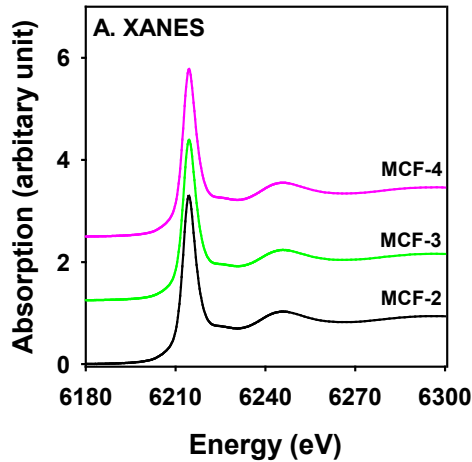


**XPS spectra of MCFs before and after Nd adsorption**

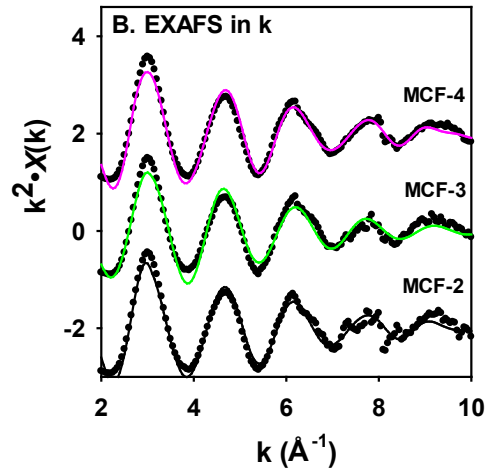
The surface chemistry of MCFs remained similar after Nd adsorption

# Results

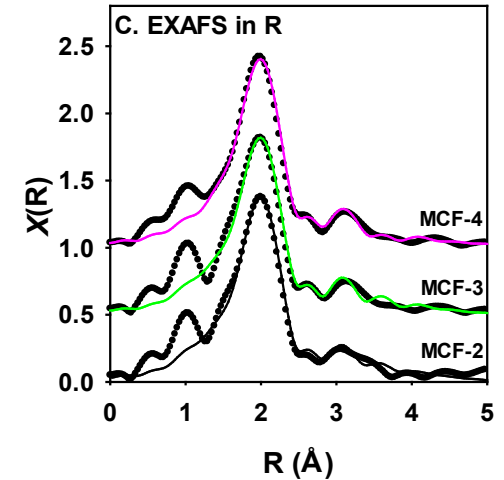
- **MCF material for REE recovery (Tasks 2, 4, and 5)**
  - ◆ **Molecular binding of Nd with MCFs**



**Nd L<sub>3</sub>-edge X-ray absorption near-edge structure (XANES) spectra**



**Nd L<sub>3</sub>-edge extended X-ray absorption fine structure (EXAFS) spectra**

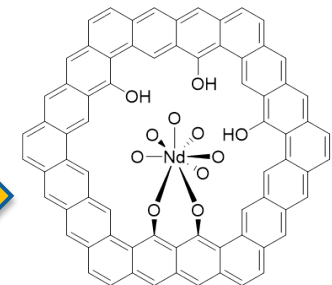


Nd speciation: Nd<sup>3+</sup>



**Nd L<sub>3</sub>-edge EXAFS fitting data**

Paths	Distance (Å)	Coord #
Nd-O	2.51±0.05	8.6±0.1
Nd-C	3.67±0.02	2.7±0.4

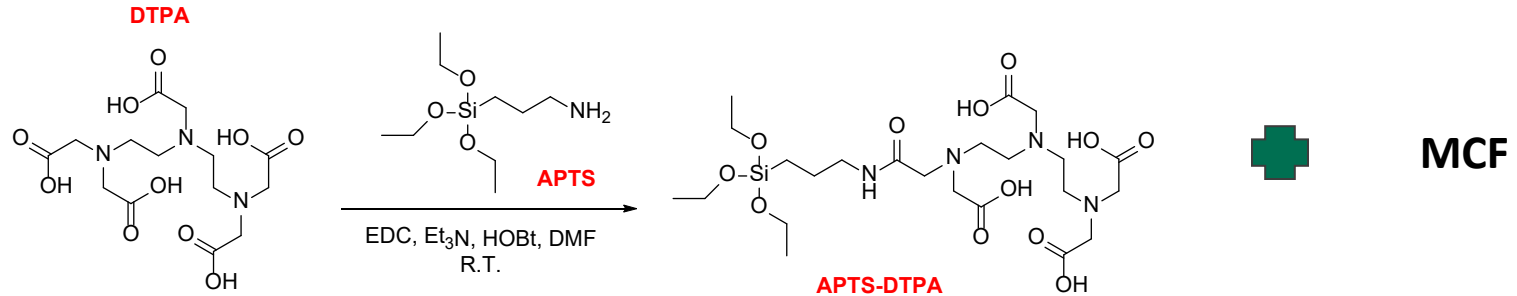


**Nd binding mechanism with MCFs**

# Results

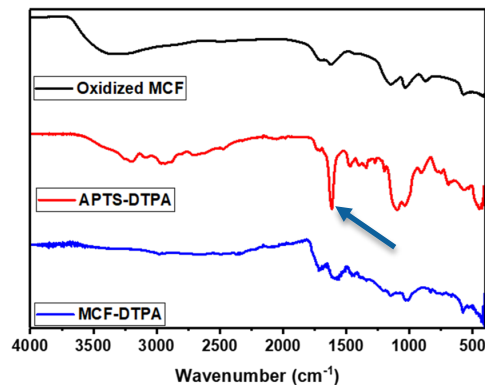
## Organic ligand functionalized MCF material (Tasks 3 and 4)

- ◆ **Functionalization methods:** Two-step post-synthetic methods were used. Diglycolamide (DGA), and diethylenetriaminepentaacetic acid (DTPA); 3-Aminopropyl)triethoxysilane (APTS).



### Functionalization of DTPA onto MCFs

#### ◆ FTIR Characterization



#### ◆ REE recovery from a real citrate extraction solution of NdFeB powder

	Nd recovery rate, %	Nd capacity, mg/g
MCF	0	0
MCF-DTPA	23.5	16.5
	Pr recovery rate, %	Pr capacity, mg/g
MCF	0	0
MCF-DTPA	23.9	2.5

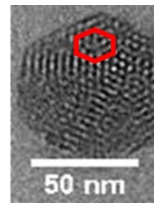
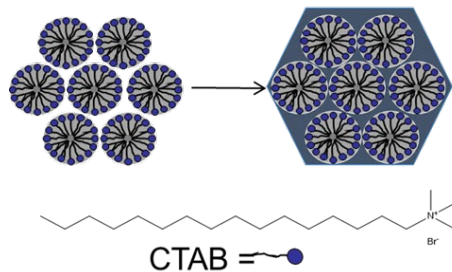
- ◆ **Challenges:** The pore structure of MCF was damaged due to harsh oxidation step, thus the performance for REEs recovery was compromised.

# Results

## Organic ligand functionalized mesoporous silica (Tasks 3 and 4)

### ◆ Synthesis of magnetic mesoporous silica (MMS)

- Cetyltrimethylammonium bromide (CTAB) template.
- The presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

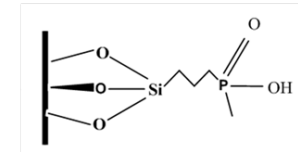


MCM-41

### Functionalization of MMS

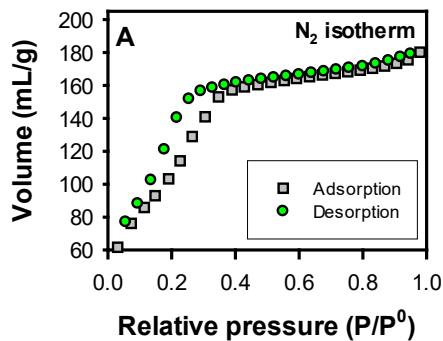
A post-synthetic method  
Phosphonate (PP)  
Polyethyleneimine (PEI)

#### Phosphonate (PP) Functionalization

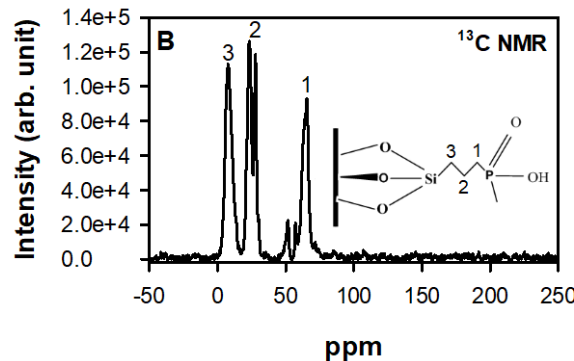


3-(trihydroxysilyl) propyl methylphosphonate

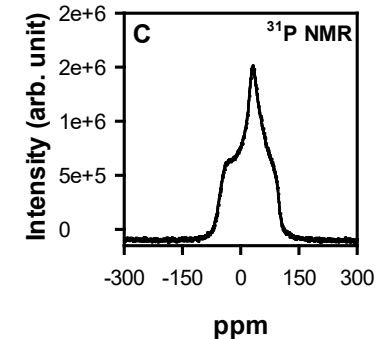
### ◆ Characterization of phosphonate functionalized MMS/MS



N<sub>2</sub> sorption isotherms



<sup>13</sup>C CPMAS NMR spectrum

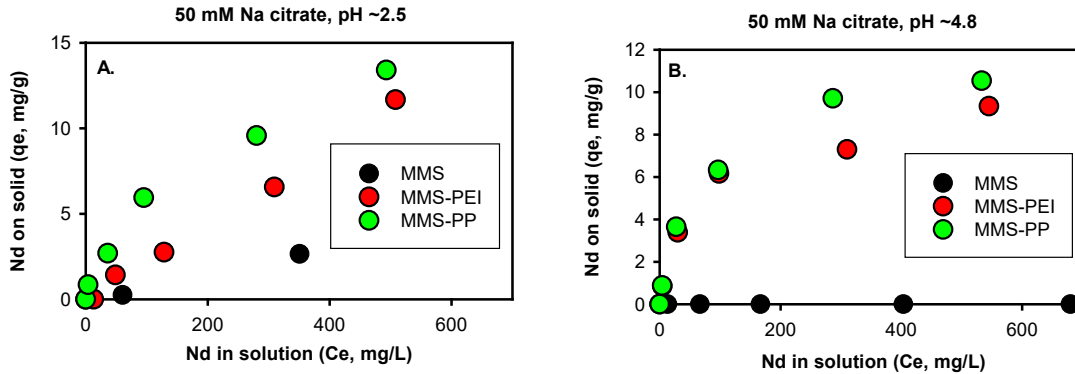


<sup>31</sup>P CPMAS NMR spectrum

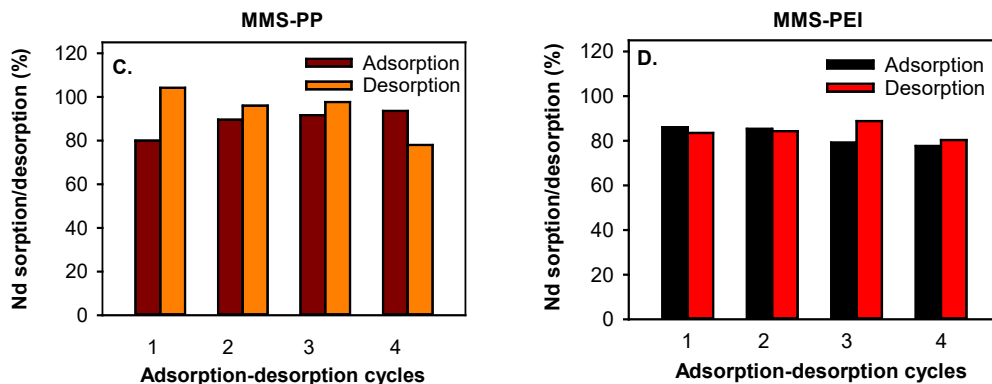
# Results

## Organic ligand functionalized mesoporous silica (Tasks 3 and 4)

### ◆ Nd recovery from a citrate simulant



### Nd adsorption isotherms

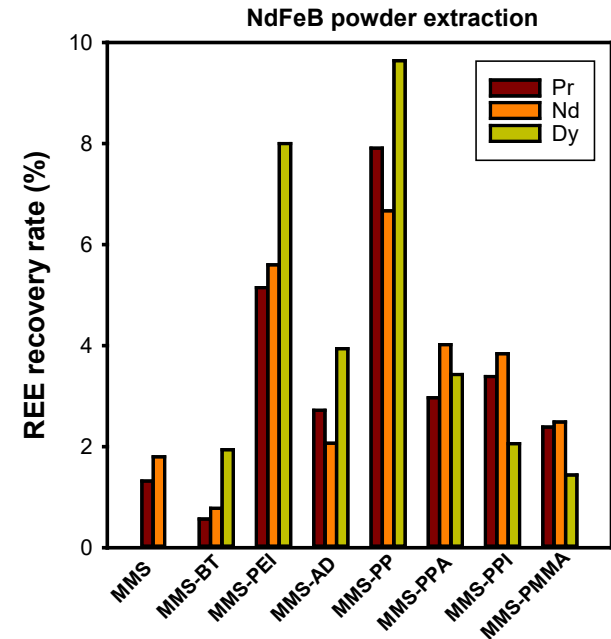


### Nd adsorption and desorption for four cycles:

**Adsorption:**  $5 \times 10^{-4}$  M Nd in 50 mM citrate, pH 2.5, 30 mins

**Desorption:** 1M HCl, 30 mins

### ◇ REE recovery from a real citrate extraction solution of NdFeB powder



**BT:** Benzoylthiourea

**AD:** Polyaryloamidoxime

**PPA:** Phosphonate-amino

**PPI:** Poly(propylenimine) dendrimer

**PAMAM:** Poly(amidoamine) dendrimer

## Next Steps

- One immediate Next Step is to develop a new oxidation method for the MCF material. We have been testing several methods for the oxidation step and should be able to develop a fully executable oxidation method within 6 months. Then, we can prepare new functionalized MCF materials of improved REE recovery.

## Technology Transfer

- Proprietary material IP will be protected via patent applications.
- Non-proprietary data will be presented at domestic conferences and published on peer-reviewed journals.
- Research data will be shared with other DoD/DOE research labs.
- Collaboration with DoD laboratories will be sought to demonstrate the technology for real magnet wastes.
- Knowledge gained from this research will help other researchers to develop advanced materials for critical metal extraction from waste streams.
- An enterprise entity will be set up or a private partner will be sought to commercialize the advanced materials and separation technology.

## Key Points

- Biodegradable organic ligands can assist REE extraction, and significantly reduce mineral acid use and acidic waste generation.
- Mesoporous carbon fibers have large surface areas and 3D interconnective pores for high REE recovery efficiency. Organic ligand functionalization can further improve REE recovery rate and capacity. The functionalized mesoporous materials can be regenerated for reuse and REE recycling.
- The advanced mesoporous materials can be potentially applied in solid-liquid separation systems so that we can recover REEs from electronic and industrial wastes in an environmentally friendly manner, and meanwhile, to off-set the maintenance and remediation cost of the existing solid waste streams.

## Future Research

- **Demonstration of proof-of-concept for future funding:**
  - ◆ Ligand-assisted extraction technology was environmentally friendly for REE extraction from NdFeB powder.
  - ◆ Mesoporous carbon fiber (MCF) of tunable surface area, pore size, pore structure and functionalities was synthesized.
  - ◆ Organic ligand functionalization significantly improved REE extraction selectivity and capacity.
  - ◆ The advanced mesoporous materials were regenerated for reuse and REE recycling.
  
- **General scope of future research:**

To develop novel functionalized porous materials as a new solid-liquid separation platform for effective recovery and separation of REEs from magnet scrap, and other electronic and industrial wastes.

# Future Research

- **Planned approach:** To use combined rational material design, theoretical computation and machine learning, advanced molecular-level characterization, and robust engineering processes to address this complex system. This combined approach will significantly improve the design of new materials and our understanding of the driving forces for efficient REE separation.

- ◆ **Continued technical approach for experimental work**

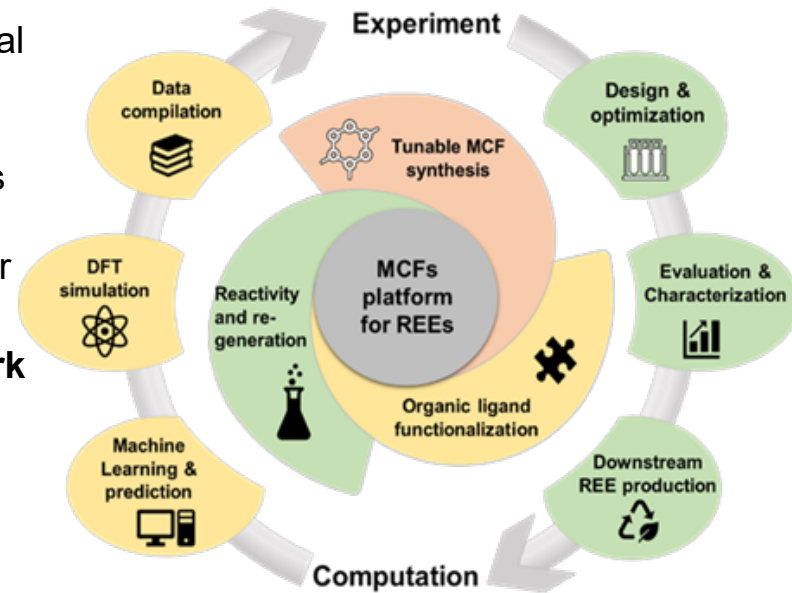
- Ligand-assisted extraction
- Synthesis and organic ligand functionalization
- Materials performance evaluation
- Molecular-level understanding of REE-ligand interactions.

- ◆ **Theoretical computation and machine learning** to improve material designs.

- ◆ **Robust engineering process design and upscale** to address the complex separation system from wastes.

- **Benefits to achieve:**

- ◆ Recover and produce REEs in the US using environmentally-friendly technologies.
- ◆ Offset the maintenance and remediation cost of electronic and industrial wastes.
- ◆ Reduce the generation of new wastes and the associated remediation cost.



## Publications

- Dien Li, Yuanzhi Tang, Guoliang Liu, Functionalized mesoporous carbon and silica for effective recovery of rare earth elements from NdFeB magnet scrap, DoD SERDP-ESTCP Symposium 2022, Arlington, Virginia, Nov 29-Dec 02, 2022.

## S1-3463: Functionalized Mesoporous Carbon for Effective Recovery of Rare Earth Elements from the Acidic Extract of End-of-Life Magnet Scrap

**Performers:** Dien Li, Yuanzhi Tang, Guoliang Liu

### Technology Focus

- To develop advanced materials and processes for environmentally friendly extraction and effective recovery of REEs from electronic and industrial waste.

### Research Objectives

- To develop ligand-assisted extraction technology of REEs from NdFeB powder.
- To develop mesoporous carbon fiber (MCF) materials with tunable pore size, pore structure, surface functionalities using diblock copolymer templates.
- To develop new organic-ligand functionalized MCF materials using post-synthesis methods. Target ligands include diglycolamide (DGA), and diethylenetriaminepentaacetic acid (DTPA).
- To elucidate the molecular interaction and binding mechanisms of REEs with organic ligands and MCF materials, vis advanced spectroscopic measurements.

### Project Progress and Results

- Environmentally friendly ligand assisted extraction technology was developed for REE extraction from electronic wastes.
- Tunable MCF materials were synthesized using PMMA-b-PAN block co-polymer template.
- Organic ligand functionalization onto MCF significantly improved REE extraction selectivity and capacity.
- The advanced mesoporous materials can be regenerated for reuse and REE harvest.

### Technology Transition

- Patent applications to protect IP information.
- Conference presentation and peer-review publications for no-IP data.
- Collaboration with DoD labs or partners to demonstrate the technology for real DoD magnet wastes.
- Planned outreach efforts to potential end-users.

