Final Abstract

Final Report Approved on October 16, 2024

M.L. 2020 Project Abstract

For the Period Ending June 30, 2024

Project Title: Minerals and Water: Demonstration of Three Sulfate Reduction Technology Applications

Project Manager: Meijun Cai

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Funding Source:

Fiscal Year:

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 20a3

Appropriation Amount: $300,000

Amount Spent: $299,947

Amount Remaining: $53

Sound bite of Project Outcomes and Results

This project developed three sulfate reduction technologies—biological reduction, chemical precipitation, and ion exchange—through lab and field pilot testing. These methods reduce sulfate levels in industrial and municipal wastewater from 150 to over 3,000 mg/L to below 10 mg/L, protecting Minnesota's wild rice and ensuring environmental

Overall Project Outcome and Results

Minnesota has enforced a sulfate concentration limit of 10 mg/L for wild rice waters. Achieving this typically requires reverse osmosis, which is costly for industries and small municipalities. This project aimed to identify cost-effective technologies for sulfate treatment. Three technologies—biological reduction, chemical precipitation, and ion exchange— were developed and tested through laboratory and pilot studies to assess feasibility, operational parameters, and process optimization.

A biological treatment system, coupled with sulfide immobilization, treated wastewater with sulfate concentrations of 200-3,000 mg/L and varying characteristics (e.g. sulfate concentration, organic content, and hardness) under different operating conditions (e.g., flow rate, substrate dosing, and sulfur recovery methods), reducing sulfate levels to 20-30 mg/L at optimized operation conditions. Effluents from the biological treatment were further treated with chemical precipitation technology to meet the sulfate limit for wild rice water.

Chemical precipitation technology used barium chloride to react with sulfate, producing barite sediment to remove sulfate from water. This process was tested with two types of wastewater at a flow rate of 1-1.5 gallons per minute for about four months, reducing sulfate from 150-400 mg/L to 10-150 mg/L. Process parameters were refined for different water types and target effluent concentrations. Testing also indicated that this process could simultaneously remove sulfate and phosphate.

Ion exchange was tested using novel peat lignin-derived materials and a sulfate-selective strong base anion exchange (SBA) resin. The peat lignin material performed best at pH 4.75, while the SBA resin was most effective at pH 8.3, achieving a breakthrough capacity of 144 mg/g, removing sulfate to below 1 mg/L. Chloride levels were controlled at 230 mg/L, ensuring compliance with Minnesota regulations for recreational waters.

These findings provide guidelines for designing and operating plant-scale sulfate treatment systems.

Project Results Use and Dissemination

This project has produced materials of interest to a wide variety of stakeholders, including the researchers, the city councils, wastewater treatment plant operators, and the community. Among these products are presentations, posters, and publications. Sulfate treatment research results were presented at conferences (Minnesota Water Resources conference, The Society for Mining, Metallurgy & Exploration conference, and the International Mine Water Association conference, American Water Works Association, 2023 Water Network Virtual Poster Symposium) and department seminars at other universities (e.g. Moreover). NRRI organized a webinar on Sulfate Remediation Technologies for stakeholders including public agencies, industries, municipalities, tribal entities, and communities.

Environment and Natural Resources Trust Fund

M.L. 2020 Approved Final Report

General Information

Date: November 18, 2024

ID Number: 2020-083

Staff Lead: Mike Campana

Project Title: Minerals and Water: Demonstration of Three Sulfate Reduction Technology Applications

Project Budget: $300,000

Project Manager Information

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Project Reporting

Final Report Approved: October 16, 2024

Reporting Status: Project Completed

Date of Last Action: October 16, 2024

Project Completion: June 30, 2024

Legal Information

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 20a3

Appropriation Language: The appropriation in Laws 2019, First Special Session chapter 4, article 2, section 2, subdivision 8, paragraph (c), Sauk River Dam Removal and Rock Rapids Replacement, in the amount of $2,768,000, no longer needed for its original purpose is transferred as follows:

(3) $750,000 is transferred to the Board of Regents of the University of Minnesota for academic and applied research through the MnDRIVE program at the Natural Resources Research Institute to develop and demonstrate technologies that enhance the long-term health and management of Minnesota's mineral and water resources. Of this amount,

$300,000 is to support demonstration of three sulfate reduction technologies for improved water quality, and $450,000 is for continued characterization of Minnesota iron resources and for developing next-generation technologies and iron products. This research must be conducted in consultation with the Mineral Coordinating Committee established under Minnesota Statutes, section 93.0015;

(d) Transfers and Availability
The transfers under this subdivision are effective June 30, 2021, and the transferred amounts are available until June 30, 2023.

M.L. 2022, Chp. 94, Sec. 2, Subd. 19 Carryforward; Extenstions, (b) The availability of the transfers for the following projects is extended to June 30, 2024: (3) Laws of 2021 First Special Session, chapter 6, article 5, section 2, subdivision 20, paragraph (a), clause (3), Applied Research in State Mineral and Water Resources

Appropriation End Date: June 30, 2024

Narrative

Project Summary: Applied research and demonstration of three sulfate reduction in Minnesota waters

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

Sulfate concentration is a challenge across the state due to a restrictive water quality standard for sulfate of 10mg/L in wild rice waters. Meeting this or a modified water quality standard is a special challenge, especially in systems with relatively low (<300 mg/L) sulfate concentrations. Existing technologies (e.g., reverse osmosis; ultrafiltration) can achieve this standard, but are expensive and generate significant waste products. New tools are required to provide economically viable technologies in support of Minnesota's industries and wastewater treatment facilities. NRRI has tested several technologies for reducing sulfate in water bodies, including chemical precipitation technology via barite precipitation, microbial treatment, and development of novel carbon-based sorption materials. This project will test the effectiveness of sulfate reduction technologies and assess economic costs associated with their deployment.

What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.

On the basis of this past funding, NRRI is proceeding to pilot three technologies for reducing sulfate in water bodies: chemical precipitation; microbial treatment, and novel carbon-based materials to absorb sulfate ion. Two trailer-based pilot systems have been constructed to deploy the chemical precipitation system and a microbial treatment system. These will be deployed in tandem for demonstration at regional sites to determine effectiveness and quantify costs in real-world applications. The novel carbon sorbent materials will be evaluated first in the laboratory using pit lake water samples and will be piloted when the proper activity is achieved.

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

Technologies to reduce sulfate in Minnesota's waters that are both effective and affordable for municipal and industrial water treatment challenges offer new tools to manage and remediate impacts on regional water resources. Demonstration of these approaches in different combinations should provide options for a range of sulfate challenges.

Project Location

What is the best scale for describing where your work will take place?

Statewide

What is the best scale to describe the area impacted by your work?

Statewide

When will the work impact occur?

In the Future

Activities and Milestones

Activity 1: Minerals and Water: Demonstration of Three Sulfate Reduction Technology Applications

Activity Budget: $300,000

Activity Description:

A trailer-based chemical treatment pilot system will be deployed in a wastewater treatment plant to reduce sulfate concentrations to desired levels. The facility treats domestic wastewater using pit lake water as the drinking water source. A trailer-based biological system will be operated in the NRRI facility over winter by transporting water from the field to the facility. The treated water will be collected and used as the influent for the trailer-based chemical treatment process. The performance of the treatment systems will be evaluated through water chemistry, operational parameters, and waste management. A series of laboratory tests will be conducted to remove sulfate anions from the same mining pit lake water using functional carbon materials with introduced anion exchange properties. The performance of the functional carbon materials will be evaluated using equilibrium and column tests. The water chemistry, ability to lower the concentration of sulfate anions in the presence of competing anions (selectivity) as well as breakthrough capacity will be measured and reported. Costs associated with each treatment system will be documented to estimate operational costs.

Activity Milestones:

Description	Approximate Completion Date
Milestone 1: Deploy the trailer based pilot systems on the site	June 30, 2022
Milestone 2: Completion of the field pilot trial of the chemical treatment process	June 30, 2023
Milestone 3: Performance evaluation of biological treatment system to reduce sulfate concentration from a minepit	June 30, 2023
Milestone 4: Performance evaluation of the functional carbon materials with anion exchange properties to remove	June 30, 2023

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Rolf Weberg	Natural Resources Research Institute, UMD	NRRI Executive Director, Dr. Rolf Weberg, who is on the Minerals Coordinating Committee, will review project progress for comment and potential collaboration at regularly scheduled Minerals Coordinating Committee meetings	No

Dissemination

Describe your plans for dissemination, presentation, documentation, or sharing of data, results, samples, physical collections, and other products and how they will follow ENRTF Acknowledgement Requirements and Guidelines.
We anticipate building partnerships with the agencies and industrial partners during our field pilot trial and lab tests. The results will be shared with the partners to seek suggestions and recommendations for the applications of the treatment systems in the real world. The research findings will be disseminated to the public, agencies and industry through reports, workshops and conference presentations that will acknowledge the ENRTF funding of the project.

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?
With funds from 2016 and 2019 Minnesota Legislative investment, Industry, and internal funding, NRRI sulfate team has successfully demonstrated three sulfate reduction technologies in the laboratory; one trailer based system has been deployed for field pilot trials. Lessons learned from the past and ongoing tests will refine the system process and material development for wide applications in industrial and natural environments. Application of the permanent university trust fund is another potential source to bridge any funding gaps.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineli gible	% Bene fits	# FTE	Class ified Staff?	$ Amount	$ Amount Spent	$ Amount Remaining
Personnel										
George Hudak		Research Group Leader			25.09%	0.02		$501	-	-
Meijun Cai		Project manager and lead of chemical treatment project			25.09%	0.34		$37,729	-	-
Chan Lan Chun		Lead of biological treatment project			25.09%	0.1		$14,590	-	-
Lucinda Johnson		Part of the project management team			25.09%	0.02		$4,557	-	-
Adrian Hanson		Technical advisor			25.09%	0.3		$7,013	-	-
Shashi Rao		Co-lead of chemical treatment project			25.09%	0.08		$9,456	-	-
Igor Kolomitsyn		Lead of material modification project			25.09%	0.2		$25,216	-	-
Erik Hendrickson		Lab technician for material modification project			22.3%	0.22		$15,074	-	-
Sara Post		Field operation of the chemical treatment project			22.3%	0.8		$5,467	-	-
Jeff Kinkel		Mechanical Engineer			25.09%	0.06		$8,167	-	-
Jack Grochowski		Mechanical Engineer			25.09%	0.1		$10,963	-	-
Jerald Henneck		Lab technician			22.3%	0.2		$16,378	-	-
Matthew Mlinar		Mlinar will provide project management support and serve as a part of the project management team for this grant			25.09%	0.04		$5,235	-	-
Anthony Masching		Mechanical maintenance			22.3%	0.1		$7,570	-	-
TBD Field Tech, temp/casual		Field operation of the chemical treatment project			6.91%	0.2		$7,488	-	-
Undergraduate Researcher		Lab and field support			0%	0.32		$7,546	-	-
Matthew Berens		Field operation for the biological treatment project			17.28%	0.6		$36,814	-	-
Summer Graduate Student		Laboratory support			18.96%	0.02		$128	-	-

TBD Researcher 1		Field operation for the biological treatment project			22.3%	0.4		$19,825	-	-
Patrick Schoff		Principal Investigator			25.09%	0.01		$300	-	-
							Sub Total	**$240,017**	**$240,017**	**-**
Contracts and Services										
							Sub Total	**-**	**-**	**-**
Equipment, Tools, and Supplies										
	Tools and Supplies	Supplies for the system modification or site connection	Including pumps, pipes, tanks, valves, pressure meters, and any possible changes to be made to the pilot system					$18,000	$18,000	-
	Tools and Supplies	Laboratory and chemical supplies	Lab supplies, bottles, vials, chemicals, gloves, filter membrane, pipet, and other supplies that may be needed during laboratory work					$15,957	$15,904	$53
							Sub Total	**$33,957**	**$33,904**	**$53**
Capital Expenditures										
		Potentiostat	Used for electrochemical analysis to monitor biological sulfate reduction and redox mediator during the biological sulfate treatment.	X				$8,030	$8,030	-
							Sub Total	**$8,030**	**$8,030**	**-**
Acquisitions and Stewardship										
							Sub Total	**-**	**-**	**-**
Travel In Minnesota										

	Miles/ Meals/ Lodging	Field visit (15 times/month) *5 month* total miles per trip (~154 miles) = $6,462. Additional money for sample dropping to the external lab, travel from Duluth to Coleraine facility	Travel needed between Duluth and Coleraine NRRI sites to perform testing and transporting samples. GSA rates will be used while traveling.					$2,019	$2,019	-
							Sub Total	**$2,019**	**$2,019**	**-**
Travel Outside Minnesota										
							Sub Total	**-**	**-**	**-**
Printing and Publication										
							Sub Total	**-**	**-**	**-**
Other Expenses										
		External lab measurement	External lab measurement for samples					$5,958	$5,958	-
		Data plan	Data plan for remotely access the control panels, and the data plan for onsite video cameras	X				$1,500	$1,500	-
		Electricity	Cost of electricity for the field pilot trial occurring at a remote site off campus					$8,519	$8,519	-
							Sub Total	**$15,977**	**$15,977**	**-**
							Grand Total	**$300,000**	**$299,947**	**$53**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
Capital Expenditures		Potentiostat	The biological treatment used in the project is a biofiltration integrated with electrochemical cells which stimulate and sustain biological sulfate reduction. For the treatment system, the potentiostat is used as an electric instrument that controls the cell potential and measures variable current as an essential component of the system. This will be also used to conduct electrochemical analysis for redox active chemicals in the treatment system through the life of the instrument. **Additional Explanation :** The Potentiostat purchased with the project will continue to be used for the water treatment in relation to sulfate reduction and its associated processes in the lab and field.
Other Expenses		Data plan	The site is located in a remote location (60 miles away) where no Wi-Fi is available. Cellular data will be the only way for remote access. The remote access allows controlling the system remotely, therefore reducing the field visit times and keep the system run smoothly.

Non ENRTF Funds

Category	Specific Source	Use	Status	$ Amount	$ Amount Spent	$ Amount Remaining
State						
			State Sub Total	-	-	-
Non-State						
			Non State Sub Total	-	-	-
			Funds Total	-	-	-

Attachments

Required Attachments

Visual Component

File: 04d4de42-0d5.pdf

Alternate Text for Visual Component

The graphics describe the sulfate remediation technologies and the municipal treatment mobile systems....

Supplemental Attachments

Capital Project Questionnaire, Budget Supplements, Support Letter, Photos, Media, Other

Title	File
Background Check	015f5e9e-370.pdf
Institutional Letter	c85d0358-602.pdf
Article published	052cd56f-4f3.pdf
old 1-page visual component	c7617a8b-f33.pdf

Difference between Proposal and Work Plan

Describe changes from Proposal to Work Plan Stage

Minor editing

Additional Acknowledgements and Conditions:

The following are acknowledgements and conditions beyond those already included in the above workplan:

Do you understand and acknowledge the ENRTF repayment requirements if the use of capital equipment changes?

Yes

Do you agree travel expenses must follow the "Commissioner's Plan" promulgated by the Commissioner of Management of Budget or, for University of Minnesota projects, the University of Minnesota plan?

Yes, I understand the Commissioner's Plan applies.

Does your project have potential for royalties, copyrights, patents, sale of products and assets, or revenue generation?

Yes

Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10?

Yes

Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF?

No

Does your project include original, hypothesis-driven research?

No

Does the organization have a fiscal agent for this project?

Yes, Sponsored Projects Administration

Work Plan Amendments

Amendment ID	Request Type	Changes made on the following pages	Explanation & justification for Amendment Request (word limit 75)	Date Submitted	Approved	Date of LCCMR Action
1	Amendment Request	• Budget - Personnel • Budget - Capital, Equipment, Tools, and Supplies	We are requesting the capital equipment line item to be increased by $30 and to decrease the TBD Researcher 1 effort by $30 to account for the increased equipment cost. At the time of budget estimation, the cost of equipment was $8,000, but later increased due to the increased cost in materials for the equipment. The scope of work will remain the same.	April 29, 2022	Yes	May 4, 2022
2	Amendment Request	• Activities and Milestones	The activity task of deploying two trailer-based pilot systems (a biological reactor and a chemical treatment system) at one mining pit lake is changed to two tasks in two different locations because • The wastewater plant has similar sulfate levels as the pit lake water and provides better utility connections and equipment security. • The second test is performed in the NRRI facility to protect the equipment in cold temperatures and keep the tests running over winter.	October 14, 2022	Yes	October 17, 2022
3	Completion Date	Previous Completion Date: 06/30/2023 New Completion Date: 06/30/2024	Project delays resulted from: 1) delays in completion of the carbon-based sulfate absorption study due to loss of lab personnel; 2) the biological treatment system was completed in fall, 2022 delaying experiments and results; 3) the indoor pilot trial proposed in October 22 and subsequently approved is currently being set up. The proposed time extension will be used to complete the indoor trial	May 26, 2023	Yes	May 26, 2023

			and complete the carbon-based sulfate absorption study.			
4	Amendment Request	• Budget • Budget - Professional / Technical Contracts • Budget - Capital, Equipment, Tools, and Supplies • Budget - Travel and Conferences • Budget - Other	- Removing contract/service costs because services were no longer needed. - Decreased travel budget because pilot testing was conducted at the NRRI facility instead of the usual field sites, allowing for a cost-savings - Decreased shipping because less shipping was needed than originally estimated. - Increased lab measurement costs due to increased costs due to inflation. - Dataplan increased due to inflation - Increased electricity due to underestimating original costs	September 27, 2023	Yes	October 12, 2023
5	Amendment Request	• Budget • Attachments • Other • Budget - Other • Budget - Personnel • Budget - Capital, Equipment, Tools, and Supplies • Budget - Travel and Conferences	There was an increase in personnel time needed to complete tasks. Shipping costs were removed because it was no longer needed. Decrease in lab supplies, travel, lab services, and date plan. Electricity charges were higher than anticipated. Hudak has retired and requesting for Patrick Schoff to replace his PI role. M. Cai remains the project manager.	October 7, 2024	Yes	October 8, 2024

Status Update Reporting

Final Status Update August 14, 2024

Date Submitted: October 7, 2024

Date Approved: October 8, 2024

Overall Update

During the last semi-annual phase of this project, a pilot test of the biological and chemical precipitation train system was conducted over 2.5 months using wastewater from WLSSD. Comprehensive water quality data were collected to assess changes in chemical properties and explore the feasibility of integrating ion exchange technology into the system. Lab testing results informed the development of isotherms to evaluate the affinity of various anions when using a commercially available resin for sulfate and chloride removal.

Over the three-year project, multiple pilot tests were performed on chemical and biological treatment processes to achieve target sulfate concentrations for industrial and municipal wastewater. The biological treatment, utilizing anaerobic reduction and iron/hydrogen peroxide oxidation, effectively treated sulfate concentrations ranging from 200 to 3,000 mg/L, immobilizing sulfide and allowing for scaling based on removal rates. Chemical precipitation with barium chloride and ferric chloride reduced sulfate levels below 10 mg/L while demonstrating simultaneous removal of sulfate and phosphate. Additionally, peat lignin-derived anion exchange materials and commercial resins successfully reduced sulfate levels from 365 mg/L to below 1 mg/L, while complying with chloride regulations. All findings have been compiled into a comprehensive final report.

Activity 1

In the final phase of this project, the project team tested sulfate reduction using a train treatment system. Wastewater from WLSSD was first processed through the biological system for pilot testing. The effluent was collected and stored in totes, then transferred to the chemical precipitation system when a sufficient amount was available for pilot testing. Approximately 3,000 gallons of wastewater were hauled from WLSSD to the NRRI facility over 2.5 months. Comprehensive water quality data were collected through the different treatment systems to monitor changes and evaluate the potential for integrating a third treatment technology: ion exchange.

We have completed the equilibrium isotherm assessment of the commercially available strong base anion exchange resin (HW-300™) using an equilibrium between sulfate and bicarbonate anions. Our results confirmed the following affinity relationship: $SO_4^{2-} > Cl^- > HCO_3^-$. This data aligned with the resin's behavior observed during column experiments.

From 2021 to 2024, the project team conducted various field and laboratory tests for sulfate treatment, both in standalone systems and in treatment trains, aimed at reducing sulfate levels to below 10 ppm. The team successfully identified the optimal process and operational parameters and selected and developed the most effective resins for the treatment.

(This activity marked as complete as of this status update)

Dissemination

Cai, M., S. Post, S. Rao, C.L. Chun, L. Johnson, and G. Hudak (2024): Low-concentration sulfate removal from wastewater with barite precipitation technology. – In: Kleinmann, B., Skousen, J., Wolkersdorfer, Ch.: West Virginia Mine Drainage Task Force Symposium & 15th International Mine Water Association Congress. – p. 65 – 67; Morgantown, WV, USA (International Mine Water Association).

Status Update Reporting

Status Update April 1, 2024

Date Submitted: October 7, 2024

Date Approved: October 8, 2024

Overall Update

Pilot testing was conducted separately for the biological and chemical precipitation processes using WLSSD wastewater with concentrations of around 250-350 ppm of sulfate. The biological treatment reduced the sulfate concentrations to 20 ppm under various operation conditions. Effluent and influent from the biological sulfate treatment have been collected and chemically analyzed to assess their compatibility with the integration with ion exchange technology in the train treatment system. We successfully demonstrated that bicarbonate anion can be used as a regenerant with a combination of sodium chloride effectively controlling the concentration of chloride anion in the effluent. The tests for the chemical precipitation process were conducted for 8 weeks, to assess the potential changes of chemical dosage amount and process parameters, and to investigate the feasibility of simultaneous removal of sulfate and phosphate without any process changes to the system design.

Activity 1

The active biological sulfate treatment system was modified to retain more biomass for increased water treatment capacity. It effectively treated industrial and municipal wastewater with varying characteristics (e.g. sulfate concentration, organic content, and hardness) under different operating conditions (e.g., flow rate, substrate dosing, and sulfur recovery methods), reducing sulfate levels to 20-30 ppm at certain operation conditions.
Pilot testing of the chemical precipitation treatment process was conducted at 1 gallon/minute for 8 weeks. Without any process changes, the system can successfully reduce sulfate from around 300 ppm to below 50 ppm and phosphate from around 10 ppm to below 1 ppm.
Peat-derived anion exchange material showed high affinity for bicarbonate anions with the affinity relationships as follows: oxalate > acetate > bicarbonate > sulfate > chloride. We found that the sodium bicarbonate can effectively regenerate the exhausted anion exchange material, reducing chloride concentration in the effluent to 0 ppm at low pH. This suggests that peat-derived anion exchange material can be used to treat sulfate in acid mine drainage scenarios.
Chemical analysis of influent and effluent water after the biological system indicated the potential for further sulfate treatment using a train treatment system, achieving 10 ppm sulfate concentration in effluent.

Dissemination

1. Post, S., S. Rao, M. Cai, L. Johnson, C. L. Chun, and G. Hudak (2023). Pilot Trials of Sulfate Reduction in Municipal Wastewater by Chemical Precipitation Technology, 2023 Minnesota Water Resources Conference, October 18, 2023.
2. Showcase of the chemical precipitation pilot system to the general public in NRRI's open house, September 16, 2023.

Status Update Reporting

Status Update October 1, 2023

Date Submitted: September 27, 2023

Date Approved: October 12, 2023

Overall Update

During this bi-annual period, the trailer-based biological sulfate treatment was tested to treat wastewater with concentrations of over 800 ppm of sulfate. The biological treatment reduced the sulfate concentrations to 100 ppm under various operation conditions. Effluent from the biological sulfate treatment has been collected to be used for the other treatment systems: chemical precipitation and ion exchange.

The team communicated with the Western Lake Superior Sanitary District (WLSSD), which expressed concerns about potential effluent backflow with high sulfate concentrations affecting upstream wild rice sites. Due to space constraints for field pilot testing, pilot testing in the NRRI facility will be conducted by transferring water from WLSSD. The necessary drainage permits from WLSSD and the town authority have been received, and water collection and transportation protocols have been developed.

The sulfate treatment by ion exchange has been assessed with two materials: modified peat lignin ion exchange and sulfate-selective anion exchange resin. In the laboratory-scale column test, it was demonstrated that the sulfate-selective anion exchange resin effectively lowered sulfate concentrations from 375 ppm to 10 ppm while maintaining chloride concentrations in the effluent below 230 ppm, thus meeting the standards for class 2 waters as defined by the state of Minnesota.

Activity 1

The trailer-based active biological system effectively reduced sulfate in industrial wastewater from >800 ppm to 100 ppm under various operating conditions including flow rate, substrate dosing, and sulfur recovery methods. To improve the treatment capacity, the bioreactor configuration was modified to accommodate the retention of more biomass for a greater volume of water treatment. It will be reoperated to treat the same industrial wastewater and another wastewater that has different characteristics.

Lab testing was conducted to set up the operational parameters such as mixing rates, dosage rates, and concurrent removal of sulfate and phosphate for the upcoming summer pilot testing with WLSSD wastewater. Meanwhile, the team engaged WLSSD in discussions about the requirements for pilot testing at the NRRI facility, involving the water transportation protocols, and drainage permits.

Two sulfate ion exchange technologies, including modified peat lignin ion exchange and sulfate-selective anion exchange resin, were assessed using lab column testing. The latter consistently achieved a breakthrough capacity of 144 mg/g and reduced sulfate from 375 ppm to 10 ppm, while keeping chloride concentrations under 230 ppm, meeting Minnesota standards for class 2 waters. This study demonstrates effective sulfate removal, even with high influent concentrations.

Dissemination

Cai, MJ. (presenter), S. Post (co-presenter), S. Rao, L. Johnson, C.L. Chun and G. Hudak (2023). Sulfate Removal of a Mining Pit Lake by Chemical Precipitation Technology, Minnesota Society for Mining, Metallurgy & Exploration, Virginia MN, April 18, 2023.

Sulfate Remediation Webinar, Potential Cost-Effective Sulfate Remediation Technologies for Minnesota, online (78 attendees), March 17, 2023

Yemets, S., and I. Kolomitsyn (2023). Peat Derived Anion Exchange Materials for Sulfate Remediation in Mine Pit Water. Poster presentation, 2023 Water Network Virtual Poster Symposium, April 19, 2023. U of M Water Network, University of Minnesota. https://stateofwater.d.umn.edu/water-symposium.

Yemets, S., and I. Kolomitsyn, I (2023). Peat Derived Anion Exchange Materials for Sulfate Remediation in Mine Pit Water. Poster presentation, NRRI's Annual Poster Session, April 26, 2023. Natural Resources Research Institute, UMD.

Status Update Reporting

Status Update April 1, 2023

Date Submitted: April 9, 2023

Date Approved: April 26, 2023

Overall Update

Field pilot testing was performed at the Aurora Wastewater Treatment Plant for two months to define operation processes to treat sulfate and reduce sulfate levels from 200 – 350 ppm to desired concentrations using chemical precipitation technology. With the amendment on project activity, a trailer-based active biological system has been utilized for demonstrating the concept that a train of three different sulfate treatment technologies can be combined to effectively treat aqueous sulfate. We found that sulfate reduction technology by strong base anion exchange technology should be used as a secondary treatment after sulfate concentration is reduced to 250 ppm. Other options involving ion exchange technology are being currently investigated.

Activity 1

A field pilot trial of sulfate removal by chemical precipitation technology was continuously conducted at the Aurora wastewater treatment plant for two months (late July to late September). Wastewater and tap water were tested and the sulfate levels were reduced from 200-350 ppm to targeted concentrations (10, 50, 100 and 150 ppm). Operation parameters were defined to determine strategies for the commercial application of this technology.

A trailer-based active biological system was transported to the NRRI facility and has been operating with sulfate-rich wastewater over the winter. The performance of the treatment system has been evaluated based on water chemistry and operational parameters. Effluent from the biological treatment continues to be collected at amounts sufficient for the chemical treatment process and laboratory column tests.

Another sulfate reduction technology that involves modified peat lignin strong base ion exchange material was evaluated. The batch testing conducted using St. James Pit Lake and synthetic water found that the loading capacity of peat lignin-derived ion exchange material is 60 mg/g and 100 mg/g correspondingly. We demonstrated that the sulfate anion can be effectively replaced with chloride anion and the optimum concentration of sulfate in the influent should be 250 ppm or less.

Dissemination

Cai, MJ., Barr Engineering, “Sulfate Reduction by Chemical Precipitation in Municipal Wastewater,” online, (November 30, 2022).

Cai, MJ., West Lake Superior Sanitary District (WLSSD), “Sulfate Reduction by Chemical Precipitation in Municipal Wastewater,” Duluth, Minnesota, United States. (December 9, 2022).

Chun, C. L., Department Seminar of Civil, Environmental, & Construction Engineering, "Sulfate in freshwater ecosystem: Biogeochemical stressor and integrated sulfur remediation," Texas Tech University, Lubbock, Texas, United States. (October 24, 2022).

Lucinda Johnson, Minnesota Ground Water Association, ‘Developing Technologies for Mitigating Sulfate in Minnesota’s Waters’, Brooklyn Center, MN, (November 17, 2022).

Status Update Reporting

Status Update October 1, 2022

Date Submitted: October 14, 2022

Date Approved: October 17, 2022

Overall Update

The chemical treatment team has met with MPCA, DNR, the city of Aurora, and the Aurora Wastewater Treatment Plant staff to discuss the sulfate reduction work plan for St. James Pit Lake water. The Aurora wastewater treatment facility has been selected as the field pilot trial site using the trailer-based chemical system because 1) the wastewater source comes from the pit lake, and 2) the facility provides better utility connections and trailer security. The test start date was set for late July. The biological team performed lab-scale continuous tests to evaluate the conditions of chemical and mechanical parameters for the development of a pilot-scale treatment system. For the third sulfate removal technology – ion exchange, the team has produced four different peat lignin-derived materials to be used for sulfate removal.

Activity 1

NRRI team worked with MPCA and DNR to set up the test plan of using a trailer-based chemical treatment system to treat sulfate in the Aurora wastewater treatment facility. With the approval from the City of Aurora and the facility, the test started in late July. NRRI completed the documents with the city and the facility, trained the staff, listed operation conditions, and produced field operation and sample collection/measurement procedures. Flow-through biological sulfate treatment reactors operated in various conditions including sulfur loading, flow rate, and delivery methods of substrate and water chemistry to gain scalable design and operation parameters for the development of a pilot-scale treatment system. Additionally, the sulfur-containing byproduct materials generated from the biological treatment reactors have been characterized to evaluate the stability of sulfur in byproducts and develop waste management plans with resource recovery. NRRI synthesized four different peat lignin-derived strong base anion exchange materials to be tested in terms of selectivity and activity to remove sulfate from the St. James Pit Lake water. Additionally, NRRI scaled up a synthetic protocol and additionally synthesized 5 gallons of the most promising peat lignin-derived strong base anion exchange material.

Dissemination

1. Matthew Berens (presenter), Randy Kolka, and Chan Lan Chun, Development of an electrochemical bioreactor to treat sulfate-laden wastewater. Gordon Research Conference Environmental Science: Water, Holderness, NH, June 19-24, 2022 (Poster).
2. Matthew Berens, Randy Kolka, and Chan Lan Chun (presenter), Development of an electrochemical bioreactor for sulfur recovery from sulfate-laden wastewater. 2022 Association of Environmental Engineering and Science Professors (AEESP) Research and Education Conference, St. Louis, MO, June 27-29, 2022 (Oral).

Status Update Reporting

Status Update April 1, 2022

Date Submitted: April 29, 2022

Date Approved: May 4, 2022

Overall Update

The project comprises demonstration of three sulfate treatment technologies; biological treatment, chemical precipitation, ion exchange using modified peat materials. The biological and chemical treatment technologies are planned for demonstration in field pilot trials. The St. James Pit Lake in Aurora has been selected as pilot site. This pit lake has a sulfate concentration between 350-450 mg/L and the rising water level must be reduced regularly to prevent flooding in the community. In 2021, invasive zebra mussel veligers were detected in this water body. In order to treat this water, NRRI is working with the DNR and the MPCA to determine a safe way to treat sulfate without spreading veligers. Lab trials for the biological process are being pursued to determine parameters. Peat-based ion exchange materials have been prepared for testing.

Lab batch tests are being performed using synthesized mining water through batch- and flow-through electrochemical bioreactors. Around 95% of sulfate would be reduced using proper soil media. For ion exchange technology, a chemical treatment process has been developed to convert peat materials to be H-form lignin, the precursor of the ion exchange material for sulfate reduction. Three gallons of H-form of peat lignin have been synthesized through this process.

Activity 1

St. James Pit Lake located in Aurora was selected as the field pilot testing site for the biological and chemical treatments. The discovery of zebra mussel veligers in 2021 increased the risks of water sampling and treatment. The project team is working with the Department of Natural Resources (DNR) and the Minnesota Pollution Control Agency (MPCA) to create a work plan to support field pilot testing of the chemical and biological systems this summer.

Meanwhile, synthesized mine pit water is being employed in the laboratory to evaluate biological treatment system efficacy in batch and flow-through electrochemical bioreactors. Sulfate concentrations appear to be reduced by 95% over a 30 day period when a soil media with high iron and low organic carbon is used. To create the ion exchange material, peat is treated chemically to produce H-form lignin via a newly developed procedure. Three gallons of modified peat ion exchange material have been prepared for testing in similar water samples.

Dissemination

We currently do not have a dissemination update.