

## Resilient Reclaimed Land And Water Systems 2021 Workshop





### **Extended Abstracts**

Tuesday, December 14, 2021

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### **Resilient Reclaimed Land And Water Systems Research**

### Identifying Knowledge Gaps

As the world moves towards a low-carbon energy future, legacies of current and past energy technologies remain a serious concern. Reclamation and restoration of land and water after generations of utilization will be important for our future, with many issues to address. Research in the Resilient Reclaimed Land and Water Systems theme addresses a systemic approach to energy production and delivery and the environment. Our research is composed of multiple projects across 4 faculties and 7 departments. Three research clusters were formed based on our team's assessment of gaps in current knowledge. These research clusters are 1) materials synthesis and development for utilization in land and water reclamation, 2) land and water approaches for reclamation of process water, and 3) reclamation success indicators, criteria and policy for energy systems.

#### **Developing Solutions**

Adsorption is one of the most efficient ways to remove pollutants from contaminated land and water. Low cost and high efficiency adsorbents would increase economic efficiency, which is especially beneficial to large scale land and water reclamation approaches.

- 14 graduate students, post doctoral fellows and research associates
- 8 novel materials investigated including multiple types of biochar
- Materials are natural or industry by-products, which have low to no cost
- Identified at least 3 novel materials with potential to remove inorganic or organic compounds from soil and water and be scaled up for production in the next few years
- Development of clean energy and mining processes with minimal environmental footprints

Process water is a highly complex mixture of salts, metals, ammonia and organic compounds. The complex matrix of process water, its toxicity to organisms and recalcitrance of its constituents require treatment using conventional and advanced processes for safe release to the environment.

- 20 graduate students, post doctoral fellows and research associates
- 4 main treatment processes investigated: catalytic oxidation, photodegradation, electro-oxidation and biological including biofiltration
- Potential greater in combination and as part of passive treatment systems for process water
- Development of processes and policies for safe release of process water into the environment

Reclamation, an important step in the design and transition of energy systems, aims to return disturbed land and water systems to former or other productive uses and ensure their long term resilience. Quantitative measures of reclamation success are required to achieve diverse end land uses from agriculture, recreation and urban to natural areas.

- 16 graduate students, post doctoral fellows and research associates
- Biophysical, behavioral and community, and economic indicators investigated
- Biophysical indicators can tell us much about ecosystem function; reclamation success also dependent on socio-economic and community indicators
- Development of science based indicators to address the needs of stakeholders and the public and contribute to criteria and policy

Over 60 peer reviewed scientific papers have been published, over 216 presentations given to diverse audiences, and media coverage provided from radio interviews and podcasts to articles in industry publications and newspapers. Our faculty and highly qualified personnel have received over 57 awards and scholarships. Our graduate students have gone on to higher degrees and work in consulting and industry and most post doctoral fellows have secured faculty positions.

### Integration And Scaling Up

The next stage in the research program will focus on integrating the best novel adsorbents and processes for soil and water remediation at the pilot scale. The goal is to address the energy industry's need for cost effective and sustainable treatment systems for soil and water, which will result in productive and safe landscapes for communities, current and future. Scaling up tests the ability of technologies to be produced at a capacity suitable for implementation by industry. Collaborative and multidisciplinary projects are underway and partnerships being developed. The initial approach is testing materials, processes and indicators in mesocosms, leading to the development of a smart, efficient field scale constructed treatment wetland.

Goals of the Future Energy Systems (FES) Resilient Reclaimed Land and Water Systems theme are:

- Integrate biological, physical, chemical, social, political and economic aspects of land and water reclamation systems and disseminate results widely;
- Develop and pilot several options for land and water reclamation for legacy, current and future energy systems; and
- Evaluate, modify and develop land and water reclamation criteria for energy systems and determine their acceptability among stakeholders.

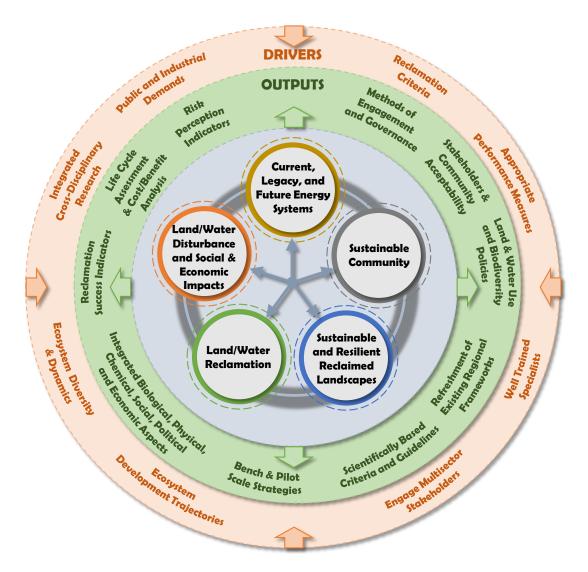


Figure 1. Schematic of the theme drivers and outputs.

### **Adsorbents Synthesis And Development For Reclamation**

### 1. Progress In Biochar And Hydrochar Syntheses For Soil And Water Remediation

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Biochar and hydrochar are carbon-rich materials synthesized from waste biomass via pyrolysis and hydrothermal carbonization, respectively. They can be used as adsorbents for soil and water remediation because of their excellent properties, such as having a high specific surface area, well-developed pores, high oxidative recalcitrance and a high abundance of surface functional groups. However, we have a poor understanding of how these properties are affected by feedstock type, and process conditions such as production temperature. Understanding such effects is a first step that would guide our selection of biochar and hydrochar for a given purpose, such as for water remediation.

We evaluated the effect of feedstock types, thermochemical conversion methods and process conditions on biochar and hydrochar properties and contaminant removal capacities from synthetic wastewater. The feedstocks were selected mainly based on local availability while temperatures were selected to represent low, medium and high for the different thermochemical conversion methods. Relative to conventional pyrolysis, microwave heating was selected as an energy-efficient method, while hydrothermal carbonization was selected because it can handle dry and wet feedstocks. The contaminants of interest were cadmium, copper, nickel, lead and ammonium.

We have produced > 100 biochars using conventional and microwave-assisted pyrolysis and > 50 hydrochars using hydrothermal carbonization. The biochars and hydrochars have been activated, comprehensively characterized and evaluated for heavy metal removal through adsorption-desorption-kinetic studies.

The major outcomes are that (1) feedstock type, thermochemical conversion process and process conditions are crucial in designing carbon-rich materials; (2) biochars are better heavy metal adsorbents than hydrochars; (3) feedstock type drives biochar properties more than process conditions such as production temperature and purging gas type; (4) canola straw biochars are best for removing heavy metals in wastewater; (5) high surface area does not always result to a high heavy metal adsorption by biochars and hydrochars; (6) minerals and dissolved elements in biochars and hydrochars significantly contribute to heavy metal removal; (7) process parameters such as operating time and energy consumption can be optimized by properly selecting a thermochemical conversion method; and (8) contaminated biochars can be reclaimed using reagents such as hydrochloric acid (0.1 mol L<sup>-1</sup>) but not water.

Our next steps are to construct a wetland using the most promising biochar, evaluate the performance of biochar as an adsorbent under real-life conditions, using real wastewater and evaluate the fate of contaminants on spent biochars, when used as a soil conditioner or disposed in landfills.

### 2. Carbon-Based Materials As Adsorbents

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In Alberta, more than 170 billion barrels of oil in deposits account for one of the largest oil deposits in the world. The extraction of bitumen from sand and clay using the Clarke caustic hot water extraction process is responsible for the generation of large volumes of oil sands process water (OSPW) that are stored in tailing ponds. The tailing ponds have become a concern due to their potential of leaching into groundwater and toxic effects. The OSPW is a complex alkaline mixture that includes organic and inorganic pollutants, including naphthenic acids (NAs) and metals such as chromium (Cr), copper (Cu), lead (Pb), and selenium (Se), all of which can be effectively removed from OSPW using adsorption. Two carbon-based materials were produced to the date to target pollutants in OSPW: carbon xerogel (CX) and sludge-based biochars (SBBs).

The CX is effective in targeting large compounds, such as NAs because this synthesized material has mesoporous characteristics, high surface area, and controllable pore size. The CXs were produced based on a sol-gel preparation technique involving the polycondensation of formaldehyde and resorcinol. The adsorptive performance of CX produced at pH 5.5 was evaluated for the adsorption of model compounds of NAs and acid-extractable fractions (AEFs) and NAs in real OSPW. The adsorption capacity for model compounds was higher than AEFs and NAs: 61 to 87 mg g<sup>-1</sup> for model compounds, 15 and 7.8 mg g<sup>-1</sup> for AEFs and NAs, respectively. This was expected because the adsorption of model compound does not account for the competitive adsorption and complexity of OSPW. Nonetheless, the application of CX as adsorbent in the adsorption of organic matter (AEFs and NAs) from real OSPW was outstanding, achieving about 90 % removal for NAs and 75 % removal for AEFs.

The application of SBBs is effective in targeting specific pollutants because some production and activation techniques can yield high surface area, and abundance of surface functional groups. To target Cr, Cu, Pb, and Se in real OSPW, two biochar composites were studied: biochar/iron oxide composite and biochar/chitosan composite. Both chitosan and iron oxide composites provided good characteristics to the sludge biochar and high removal of metals: 80 to 98 % and 84 to 97 % for biochar/iron oxide and biochar/chitosan composites, respectively. The main difference between these biochars is the adsorption mechanism. The adsorption was maximized because of a large increase in the surface area and pore volume for both biochars, but the biochar/iron oxide composite also added important functional groups to the biochar surface, which played an important role in the adsorption of metals.

These carbon-based materials have potential to be applied in the adsorption of pollutants from OSPW in continuous treatment (i.e. fixed-bed columns) or in pit lakes as a semi-passive treatment method. Some of the knowledge gaps include the evaluation of carbon-based materials as adsorbents in continuous systems, production of biochar to target naphthenic acids, and the evaluation of carbon xerogel for the adsorption of metals from OSPW.

### 3. Poultry Feather Keratin Derived Biopolymers

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Developed keratin biopolymers (KBPs) showed great effectiveness for the removal of metals from energy simulated synthetic wastewater. Therefore, the adsorption performances of developed KBPs were evaluated under the influence of process parameters (pH, temperature, and contact time). The pH of the aqueous media is the most important parameter governing metal adsorption by sorbent's surface. The pH has influence on the ionization of solute metal ions and sorbent's surface sites, hence, affecting the sorption efficiencies. The effect of temperature on sorption phenomena can also not be neglected, as suggested that the sorption efficiencies increase with the increase in temperature. The kinetics performance of test sorbent is also important aspect to be considered, thus, determining the minimum time to reach sorption equilibrium.

Here, we describe sorption behaviour of KBPs (KBP-I, KBP-IV, KBP-V) and optimization of process parameters such as pH, temperature, and contact time on adsorption. The results revealed that pH change (5.5 and 8.5) had no significant influence on adsorption of metals. For adsorption analysis at two incubation temperature (30 °C and 45 °C) ranges of multi-metal synthetic wastewater, the KBP-I and KBP- IV had shown high adsorption efficiencies for (Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, V<sup>V</sup>, Cr<sup>VI</sup> and As<sup>III</sup>) at lower temperature 30 °C, while the KBP-V revealed the high adsorption results for divalent cations at higher temperature 40 °C. However, KBPs achieved maximum adsorption of metals within one hour of equilibrium. The multi-functional character of hybrid sorbent enhances sorption efficiencies. The hybrid sorbent (KBP-IX) prepared by mixing the (KBP-IV and KBP-V) displayed the higher sorption affinities towards the divalent cations and oxyanions removal from synthetic wastewater.

At last, the sorbents are regenerated, and the regeneration of sorbent involves the desorption of heavy metals from metal-loaded sorbents. Based on the desorption results of this study, 2 molarity (M) hydrogen chloride (HCl) found to be an effective desorbing eluent recovering 84 % of Cobalt (Co<sup>2+</sup>), 100 % of Nickel (Ni<sup>2+</sup>), 100 % of Cadmium (Cd<sup>2+</sup>), 82 % of Vanadium (V<sup>V</sup>) and 50 % of Chromium (Cr<sup>VI</sup>) from KBP-I, KBP-IV and KBP-V. The KBPs were also applied for the removal of inorganics and organics from field-collected wastewaters (oil sand processed affected water, OSPW), and the results concluded that KBP-VII removed 84 % of Strontium, 87 % of Barium and all KBPs (KBP-I, KBP-IV, KBP-V, and KBP-VII) removed 40-50 % of naphthenic acids from OSPW.

### 4. Potential Of Nano Humus For Reclamation

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Coal is mined for energy generation around the world, producing large amounts of waste and extensive disturbances to soil health and vegetation. Heavy metals enter the environment through coal industry activities before being transmitted to the food chain. Reclaiming post mining sites covered by sandy soils with low nutrient and high heavy metal concentrations for agricultural uses is very challenging. Using coal waste derived humic substances as soil amendments may enhance soil reclamation outcomes due to their great potential as a soil conditioner, plant growth biostimulator, and heavy metal adsorbent.

This research was undertaken in three greenhouse and laboratory experiments at the University of Alberta that ran for three months each, and two field experiments on a former underground coal mine (Shendong mining area) in China that ran for two years. The overall objective was to assess potential of a coal waste derived humic substance product called nano humus as a soil amendment for mined sandy soils in combination with other materials.

Direct application of nano humus at the beginning of each growing season at 150 g m<sup>-2</sup> was a suitable reclamation strategy. The beneficial effect of nano humus was expressed in year two in the field. As a soil conditioner, nano humus positively changed most soil variables, particularly soil cation exchange capacity (38 %), total organic carbon (36 %), and available nitrogen, phosphorus, and potassium (20 to 92 %). As a plant growth biostimulator, nano humus significantly enhanced the total biomass of alfalfa (*Medicago ruthenica*) by 749 %, barley (*Hordeum vulgare*) by 250 %, and sea buckthorn (*Fructus hippophae*) by 147 %. As a heavy metal adsorbent, nano humus reduced 18 % of soil cadmium and 3 % of arsenic from contaminated soils after two years; nano humus removed approximately 90 % of toxic metals after 15 minutes. Beneficial effects were more pronounced with combined fertilizer and arbuscular mycorrhizal fungi than with sole applications of each.

Our findings confirmed the great application potential of nano humus in coal mine reclamation. The pronounced performance of combined applications with other inputs provided insights for future reclamation strategies. The comparison of biological effects of humic products from different origins and their efficacy in mesocosms to treat industrial process water that contains multiple organic and inorganic toxic elements needs to be addressed in future research. Pilot scale research is then needed to ascertain their applications by Alberta industries.

### 5. Evaluation Of Adsorption Of Naphthenic Acids Onto Different Types Of Materials

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In northern Alberta, Canada, large volumes of oil sand process water (OSPW) are generated by the bitumen extraction process from oil sands by applying hot alkaline water. OSPW is a complex alkaline mixture that includes organic and inorganic constituents. The OSPW is stored in tailing ponds. The potential environmental risks of the contaminants in OSPW and the potential seepage risk of stored OSPW cause environmental concerns. The naphthenic acids (NAs) present in OSPW have been proved to be one of the contributors to the acute toxicity of OSPW. Studies have reported the seepage of OSPW into groundwater and surface water. However, more studies are needed to be developed focusing on the adsorption and desorption process of NAs by natural reclamation materials and tailing materials. The role of the adsorption process in the transport of the NAs also needs to be investigated. The main aim of this project is to evaluate the adsorption behavior of NAs related to OSPW onto different types of materials. Besides, the assessment of the leaching potential of target pollutants will also be performed. The results should be used as a good guidance for helping the in-field management and application of these reclamation and tailing materials.

The specific objectives of this project are to: 1) evaluate the transport of NAs in different materials; 2) study the adsorption kinetics and isotherm for targeted pollutant in the adsorption process; 3) determine the adsorption mechanisms for targeted pollutants; 4) investigate the characteristics of different materials and the correlation with adsorption process; and 5) assess the leaching potential of the target pollutants from different materials.

All the raw materials were prepared by the air-dry process and then crushed and sieved by 2 mm mesh. Preliminary experiments have been done in batch scale tests with OSPW as the targeted contaminant solution. Several different concentrations for adsorbents, and different contact time have been applied. All experiments were run in the shaker with rotation speed at 200 rpm under room temperature. The separation process included two steps: centrifugation at 7000 rpm for 10 min and then filtration with 0.2 µm Nylon filter. Preliminary results have shown the removal of classical NAs by all kinds of materials. The kinetics and isotherm study experiments have been accomplished with single NAs model compound. Further works will focus on the adsorption and desorption study with the mixture of NAs model compounds and the real OSPW as well as the characterization for materials before and after adsorption experiments.

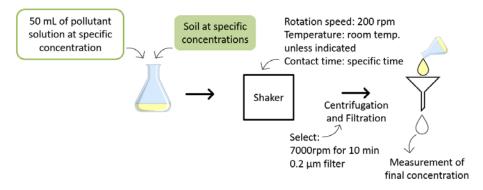


Figure 1. The scheme of batch scale adsorption experiments.

### Land And Water Approaches To Reclamation Of Process Water

### 6. Catalytic Oxidation Of Naphthenic Acids In Oil Sands Process Water

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We studied four methods for the removal of naphthenic acids (NAs) in oil sands process water (OSPW), including catalytic ozonation technology, catalytic peroxymonosulfate (PMS) technology, photocatalytic technology, and photocatalytic Fenton technology.

Firstly, we applied iron and carbon materials for the catalytic ozonation of NAs. Iron oxyhydroxide (FeOOH)-derived materials are abundant in nature and easily synthesized in the laboratory. Our results showed that the addition of ferric oxyhydroxide catalyst increased the degradation rate of model NA compound 1-adamantanecarboxylic acid (ACA). We also investigated the use of carbon xerogels and granular activated carbon (GAC) as catalysts for the catalytic ozonation. Compared with GAC, carbon xerogels were mesoporous materials with well controlled pore size. Carbon xerogels synthesized at pH 5.5 were more efficient than those synthesized at pH 6.9. The first order rate constant normalized by surface area of carbon materials shows that carbon xerogels exhibited higher removal ability compared with GAC. Secondly, ozone can be used to active PMS into sulphate radical without residual chemical. Our results showed that ozone/PMS could effectively degrade ACA compared to single ozonation. Sludge based biochar iron oxide composite was also used to activate PMS. Sludge-based biochar can be generated from sewage sludge, thus reducing the threat to the environment. The sludge-based biochar iron oxide catalyst was effective in the activation of PMS and degradation of ACA. Thirdly, solarbased zinc oxide (ZnO) photocatalyst and visible light driven bismuth tungstate (Bi<sub>2</sub>WO<sub>6</sub>) based semiconductor photocatalysts with strong light absorption, rapid separation of photo-generated charge carriers were applied for the photocatalytic treatment of OSPW. More than 99 % NAs were degraded after ZnO-based solar photocatalysis, while aromatic organics were reduced by 98 % with ZnO. Our results also showed that classical-NAs and heteroatom-NAs were completely removed and oxidized-NAs were partially removed by  $Bi_2WO_6$  based semiconductor photocatalyst.

We also investigated the use of photocatalytic Fenton technology for NA degradation. Ferric citrate was used as homogeneous catalyst. Ferric citrate is a naturally available iron complex. Our results showed that ferric citrate possessed excellent visible light absorption ability and the photochemical reactions of ferric citrate could produce both iron ions (Fe<sup>2+</sup>) and hydrogen peroxide in situ, Fenton reagent, which could non-selectively degrade NAs of OSPW. The addition of ferric citrate could effectively treat OSPW and induce a self-regenerate photo-Fenton process for the treatment of OSPW using visible light. Prussian blue/polyvinylidene (PVDF) catalytic membrane have been used as heterogeneous catalyst. Prussian blue/PVDF catalytic membrane was widely used with cheap price and could be easily synthesized in laboratory. In the future, the developed materials can be coated on a mesh or nanosphere or nanofiber, then put it on the top of the pit lake or wetlands for simultaneous oxidation of methane and NAs.

### 7. Treatment Of Oil Sands Process Water By Electrochemical Oxidation

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Electrochemical oxidation as an alternative water treatment technique is attracting huge interest as an effective remediation process for the degradation and mineralization of organic fractions of oil sands process water (OSPW). The distinguish characteristics of this technology including high energy efficiency, effectiveness, and versatility as well as excellent conductivity of the OSPW make this technology very exciting for the remediation of OSPW. Besides, it is a clean technology since chemical addition is not required and sludge is not generated after treatment. Herein, we investigated electrooxidation using low-cost electrode materials (graphite plate and dimensional stable anode (DSA)) and high oxidation potential electrode (boron doped diamond electrode (BDD)) for the degradation and mineralization of dissolved organic carbon in real OSPW.

The effect of operating parameters, especially current density on the degradation of different classes of organics in OSPW was studied. The potential and feasibility of coupling electrooxidation with biological treatment were also examined. The low-cost electrode – graphite plate and DSA showed poor to average degradation of naphthenic acids (NAs), acid extracted fraction (AEF) and chemical oxygen demand (COD) at relatively high current densities (10 and 20 mA cm<sup>-2</sup>), whereas very poor degradation with no mineralization was observed at lower current density (0.5 – 5 mA cm<sup>-2</sup>). The clear limitation of treatment of OSPW by electrooxidation with graphite and DSA electrodes was the poor degradation of dissolved organics which results in residual toxicity in the treated OSPW as well as corrosion of graphite electrode even at low current density. The treatment of OSPW by BDD electrode showed complete degradation of NAs and polycyclic aromatic carbons (PACs) with excellent mineralization of the dissolved organic carbon (up to 87 % in 2 h of treatment) in the OSPW, even at low current densities. Additionally, the use of BDD electrolysis for the OSPW treatment at low current densities (1.25 – 5 mA cm<sup>-2</sup>) showed very low energy consumption (< 15 kWh) after 2 h of treatment, indicating the exciting potential and effectiveness of this technique.

The main challenges of electrooxidation with BDD are the expensive cost of a unit BDD electrode (~ \$26,000 m<sup>-2</sup>) which make scale up very difficult and the possible formation of low concentration of chlorinated byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs). Post-treatment of the effluents of the electrooxidation treated OSPW by biological treatment showed tremendous enhancement in the degradation of NAs, COD removal as well as reduction in acute toxicity, proving the potential of coupling electrooxidation with biological treatment.

Future research works will address the scale up reactors, including stacked electrochemical reactors (containing several unit cells), in-pipe electrochemical reactors where treatment will be conducted during the transport of OSPW to the tailings ponds, and solar powered scale up reactors. The potential of scale up reactors coupling electrooxidation with biological treatments such biofiltration, wetlands and membrane bioreactors will be investigated for the treatment of OSPW.

### 8. Enhancing The Photodegradation Of Pollutants In Water

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In the field of water treatment, photoreactions are widely applied to decompose contaminants due to the abundant light resource, relative lower cost, and less toxic residuals. If the light energy is used sufficiently, it is a key issue when applying the photolysis in the water treatment process. To improve the efficiency of the degradation via photodegradation, some traditional methods have been well studied, such as heterogeneous photocatalysis with semiconductors and sensitizer. However, those traditional methods require supporting facilities and follow-up steps, resulting in some limitations in practical scenarios. More efficient and low-cost methods for enhancing the photoreaction efficiency without adding processing cost is necessary. Our research focused on two aspects to enhance the efficiency without using catalysts: one is the application of surface microlenses (MLs), and the other is the utilization of natural photosensitizers.

Surface MLs were fabricated from the surface droplets obtained from a solvent exchange process followed with in-situ polymerization. The surface MLs had strong focus effect and were highly tunable due to the flexible conditions of solvent exchange. On the first step, we chose an organic dye as the model compound to optimize the performance of surface MLs in the photodegradation. We found that the random MLs on a homogeneous hydrophobic substrate achieved higher photodegradation efficiency when they had higher surface coverage and larger median size. Meanwhile, the MLs array made on a pre-patterned substrate was more effective in enhancing the photodegradation compared to random MLs. The phenomena were also proven by optical simulations. Furthermore, we developed the fabrication method to immobilize the surface MLs onto the inner surface of glass bottles, enabling larger scale treatment. The MLs-decorated bottles showed obvious enhancement in the photodegradation of the organic dye and other three types of real pollutants (sulfadiazine, sulfamethoxazole, and norfloxacin). Therefore, the surface MLs is a potential method to improve the efficiency of photoreactions and save the required energy in water treatment, which is universal in different process.

Naturally existing inorganic photosensitizer in oil sands process water (OSPW) for indirect photolysis was explored in our research. OSPW inorganic fraction (OSPW-IF) was found to accelerate the noncatalytic photolysis of naphthenic acids (NAs) in OSPW by 96 %. Therefore, the photodegradation of a NA model compound, 1-adamantanecarboxylic acid (ACA), was chosen to study the enhanced photodegradation of NAs by OSPW-IF. By using free radical scavengers, nitrate was identified to be the photosensitizer in OSPW-IF that promoted the indirect photolysis of ACA. In the presence of nitrate, both hydroxyl radicals (·OH) and reactive nitrogen species were generated in the light treatment process. Our results also suggested that ·OH was the dominant reactive species for the degradation of ACA. The possible pathways of the nitrate-enhanced photodegradation of ACA were analyzed with an ultra-performance liquid chromatography coupled with a single quadrupole mass spectrometry (UPLC-MS), and ten possible by-products were identified. This study demonstrated that the photolysis of NAs in OSPW due to the presence of natural photosensitizers and nitrate could act as a natural photosensitizer for the remediation of OSPW by the photo-oxidation process.

### 9. Biofiltration And Biological Processes For The Treatment Of Oil Sands Process Water

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Adopting nature-based solutions for the reclamation of oil sands process water (OSPW) is of significant interest, which requires a thorough understanding of biological processes occurring within the treatment systems. In this research, fixed bed biofilters were established to study the OSPW remediation whereas laboratory-based pit lake systems were constructed to decipher the fate of dissolved organics in a lake ecosystem.

For biofiltration, raw and pre-treated OSPW were used as influent and degradation of naphthenic acids (NAs), aromatics, and other organics was investigated. In sand-based biofilters, the removal of classical NAs was limited to ~35 % in the raw OSPW which was increased to ~90 % when ozonation pretreatment was carried out upon continuous circulation of OSPW for 23 days. Aerobic, facultative, and anaerobic microbial communities were observed at top, middle and bottom of the biofilters, whereas transcriptome analysis indicated the enrichment of genes involved in benzoate degradation and beta-oxidation pathways. On the other hand, petroleum coke-based biofilters displayed slightly lower removal of classical NAs (~20 %) over a period of 15 days, which was mainly attributed to the only abundance of anaerobic bacterial communities at all depths of the biofilters. Further, the anaerobic digestion of dissolved organics was coupled with methanogenesis in a syntrophic mechanism. Upon transition from anoxic to oxic conditions, the removal of classical NAs was enhanced to ~33 %; nevertheless, most of the oxygen was consumed by methylotrophs dominating the top layer of petroleum coke.

For the pit lake systems, settling of tailings deposits along with the mobility of NAs, toxic ions, and metals were investigated under oxic and anoxic conditions. In the first few weeks, some physicochemical parameters (turbidity, phosphate) reached a stable state sharply as part of natural acclimation process. Briefly, more than 10 cm of tailings' consolidation was recorded at the end of 6<sup>th</sup> month. On the contrary, the concentration of acute toxic compounds mainly NAs and acid extractable fraction was increased in capping water, which was likely due to the release of tailings' pore water. The ammonium ion  $(NH_4^{+1})$ concentration and pH were increased, which indicates the possible degradation of polyacrylamide. Sodium (Na<sup>+</sup>) and Chloride (Cl<sup>-</sup>) concentrations were also increased, representing increase in salinity over time. On the contrary, calcium ion (Ca<sup>2+</sup>) concentration was decreased which could be due to the precipitation effect. Sulfate ion (SO<sub>4</sub><sup>-2</sup>) concentration did not change and suggests the poor dissociation of alum. Lastly, the concentration of toxic metals namely strontium (Sr), boron (B) and silicon (Si) in the lake water did not change over time. The off-gases composition indicated a large fraction of carbon dioxide (CO<sub>2</sub>) and only traces of methane (CH<sub>4</sub>). The bacterial communities were mostly aerobic in the capping water and anaerobic in the tailings' deposits. In conclusion, although toxic compounds fraction is increased in capping water, the mobility of several metals/ions is apparently reduced temporally. This signifies the efficacy of permanent aquatic storage structure (PASS) treatment for the demonstration pit lake project.

### 10. Water Characterisation And By-Product Identification

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Oil sand process water (OSPW) could potentially cause adverse impact to the environment when discharged into the environment untreated or without a proper treatment. Therefore, it would be beneficial to identify the fraction that is most likely to be responsible for the OSPW toxicity. Moreover, the fractions of the organic component of the OSPW could provide insight into the fractions that are resilience or more favorable to degradation by advance oxidation processes. Oxidation treatment could effectively remove the organics from OSPW. However, by-products that are potentially more harmful than the parent compounds can be formed after oxidation treatment. Therefore, the identification of by-products can assist in the understanding of the chemistry of the treatment process, thus helping to optimize the treatment process. Multiple parameters are also often monitored to determine the effectiveness of the treatment and thus by establishing the correlation between the monitored parameters could potentially reduce the monitored parameters.

The isolated organic and inorganic fractions were tested for their toxicity and the organic fractions were further fractionated into 20 different fractions and their reactivities towards ozonation and ferrate oxidation were tested. The by-products for photo-based and sulphur-based oxidation were identified and the reaction pathway was proposed. The correlation between gas chromatography and liquid chromatography analytical method was also statically established.

Our results showed that the organic fraction was found to be the potential fraction of OSPW that was responsible for its toxicity. Ozonation favored the degradation of aromatic and oxygenated naphthenic acids (NAs) while ferrate favored the degradation of classical and aliphatic NAs. Hydroxyl radical was found to be the main reactive species for the degradation of NAs for most treatment processes, resulting in the formation of both more oxygenated organics and non-polar organics. Good correlation ( $R^2 > 0.99$ ) was observed between the solid phase microextraction organics, neutral organics, and NAs measurements.

Correlations between more analytical techniques particularly techniques that can be applied on site to monitor the treatment performances will be established in the future. In addition, the correlation between chemical indicators with toxicity indicators would also be established, so that the on-site monitoring parameter could be used as a gauge for the toxicity of the treated water. The mass balance from the treatment of organics in real process water will also be investigated to understand the fundamental of the treatment processes of OSPW.

### Measures Of Reclamation Success

## 11. Poly(N-isopropylacrylamide)-co-acrylic Acid-based Etalon Sensors For Real-Time Environmental Monitoring

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Real-time monitoring of water quality is important for industrial and household purposes. Several natural and anthropogenic activities can disrupt the water quality of natural sources. The traditional methods for monitoring water from lakes, rivers, and other sources involve laboratory setups that consume a significant amount of time, cost, and labor. Hence low cost, simple, portable, rapid, and sensitive water quality monitoring sensors are of high interest.

In this work, we used a sensor (etalon), originally developed by our group, made from a layer of poly(Nisopropyl acrylamide)-co-acrylic acid microgel sandwiched between two gold layers on a glass substrate. The microgel layer can swell/shrink in the presence of specific chemical species, resulting in changes in the etalon's optical properties and visual color. As such, we constructed a Raspberry Pibased system that can continuously track the color changes utilizing simple lighting and camera components. Alternatively, the color changes can be monitored using a reflectance probe setup that can provide reflectance peaks that shift with color changes; this information can also be used for analysis of species of interest in water samples. Several water samples were analyzed: laboratory tap water, North Saskatchewan river water, Kananaskis river water, Bow river water, Sylvan lake water, Elbow lake water, and Forgetmenot pond water. Water samples were passed over etalons, which provided a realtime response that yielded a signal plateau within 30 min. Then the water samples were spiked with 100 ppm of sodium chloride (NaCl), which we used as an initial "model contaminant". The etalon instantly provided a sharp rise in the signal signifying potential contamination. All the water from different sources showed a similar phenomenon confirming the potential applicability of the etalon sensor for natural water quality monitoring. A single etalon sensor was used in the above experiments demonstrating that this sensor can be reused over a long time. The other application for real-time monitoring was to detect and quantify lead ions (Pb<sup>2+</sup>), mercury (Hg<sup>+</sup>), and chromium Cr<sup>3+</sup> in water. In this case, the acrylic acid contents of the microgel were 0, 10, 20, and 30 % respectively. All four different etalons were introduced in the 0-2000 ppb of the above-mentioned heavy metals. Interestingly, the various etalons behaved differently in response to the respective heavy metals. For example, an increase in the reflectance peak shift was observed for Pb<sup>2+</sup> where a decrease in the signal was detected for Cr<sup>3+</sup>. A moderate to no increase in the signal was seen for Hg<sup>+</sup>. These observations allow the etalons to potentially selectively detect and quantify Pb<sup>2+</sup>, Hg<sup>+</sup>, and Cr<sup>3+</sup> in water.

However, there are some further experiments to be done to optimize the sensor for heavy metal detection in more complex matrices. The selectivity of the sensor has to be determined in presence of potential interfering ions and finally in industrial water and wastewater samples. Furthermore, in terms of scaling up the etalon sensor to be applicable in industrial and household use, the sensor setup should incorporate a data analysis and visualization interface and/or a user friendly smartphone interface to analyze the images and finally provide the respective results.

### 12. Biophysical Indicators For Reclamation Success

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Reclamation of a disturbed ecosystem is complex, requiring a comprehensive multi-trophic level understanding of the ecosystem, and clearly defined reclamation goals with quantitative endpoints and achievable targets to reclaim ecosystem structure, composition and function. Current reclamation criteria often rely on a few soil and vegetation indicators, often assessed separately from each other. More detailed success indicators may be needed when ecological complexity and integrity are expected to be restored. Effective biophysical indicators of reclamation success need to be simple to assess, while providing information about structure, composition and function of the ecosystem, and be sensitive to ecosystem changes.

The aim of this research is to identify the most appropriate biophysical indicators for tracking ecosystem trajectories and endpoint targets for reclamation of different land use types (forest, agricultural, grassland) and disturbance ages (short term < 5 years, mid term 5-20 years, long term > 20 years). Field studies, modelling and meta-analyses are approaches being applied to answer these questions. Based on field studies in southern and central Alberta, it appears that sodium adsorption ratio for sodium and electrical conductivity for some salt ions can be effective indicators of soil quality on reclaimed sites. but their effectiveness depends on soil depth and ecoregion. These indicators were not directly tied to vegetation success. Quantifying soil quality is important in land reclamation to ensure that designed soil covers and underlying substrates support plant productivity and diversity. Soil quality scoring functions were used to generate metrics of soil cover design, such as the volume of soil materials required to supply adequate plant nutrients, support plant rooting structure, retain or transmit water. The study revealed soil quality scoring functions can be useful for quantitatively defining equivalent capability functions for reclaimed soils which are based on different soil chemical (pH, organic carbon, nitrogen) and physical (texture, water holding capacity, bulk density) indicators. Another study has found soil invertebrates, in particular Oribatid mites, to be effective indicators of reclamation success though this is dependent on sampling timing. Soil invertebrates were most effective as indicators when sampling in May or September in aspen parkland.

The outcomes of this research program may have significant implications in reclamation planning and focusing on gaps and avenues for research to advance our understanding. However further studies are required to determine the effect of soil type and climate on biophysical indicators and interactions among indicators for reclamation success. This research will inform regulatory guidelines and policy and lead to development of scientifically based criteria.

### 13. Behavioural And Community Success Indicators For Reclamation

### Maggie Cascadden<sup>1</sup>, Kylie Heales<sup>1</sup>, Shandra Pandey<sup>1,2</sup> and Dev Jennings<sup>1</sup>

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Reclamation measures commonly look to biophysical indicators to know if reclamation is successful. However, it is important that the reclamation project is socially acceptable. It is not only beneficial but imperative to consider how stakeholders and communities are impacted by reclamation because these people are impacted by resource extraction and reclamation operations. Understanding what behavioural and community indicators of success are will help projects be properly assessed and help us better understand how to do reclamation that is acceptable to those who are most impacted.

There are four main streams of research associated with this project. The first project is a review paper of behaviour success indicators identified by scholars. This project has yielded a better understanding of how behaviour success indicators have been historically approached (Figure 1). The other three projects can be mapped onto these approaches, which are delineated by their degree of formalization vs. customization and the degree to which the engagement is with a consolidated group. The second project is a group-based experiment that tested the impact of engagement format on group decisions. Two engagement formats were tested: a one-way, informative town hall engagement, and a collaborative, co-design engagement. We found that the latter, co-design form of engagement, resulted in better environmental and social outcomes. In a preliminary follow-up study, we also found that evidence that violating the group's decision results in lower trust and group cohesion scores, but this appears to be less pronounced for groups that were engaged via codesign.

The third project is about collaboration across disciplines. Dev Jennings and Maggie Cascadden, along with Andrew Hoffman from the University of Michigan, wrote a book chapter theorizing the process through which sustainability scientists and corporate teams might be able to work together and agree on sustainability action. Even when they have common goals, sustainability scientists and corporate teams have very different perspectives on how to best achieve those goals. We theorize what we call the TRI Model, with TRI standing for translating, resistance, and integration. The book chapter will be published in The Handbook of Business Sustainability in 2022.

The first three projects hold a basic assumption that there is stability in the institutions, organizations, and stakeholders that are involved with the project. However, reclamation occurs as a project ends,

which means that these things may be eroding or closing while reclamation is ongoing. The final project is a case study of the Village of Wabamun's response to the closure of nearby coal power plants and mines. The purpose of this project is to provide insights in to how a community may be able to cope with closures, and the project may provide insight into how to assess behavioural and community success of reclamation projects when the institutions and organizations that indicators are based on are eroding or closing. This project is at the preliminary stage and will be the focus of Maggie Cascadden's doctoral thesis work.

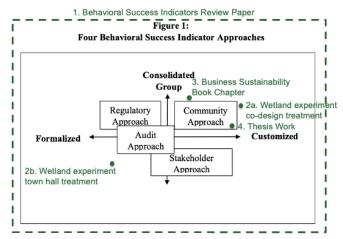


Figure 1. Four main projects

### 14. Life Cycle Assessment (LCA)

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The purpose of the Life Cycle Assessment (LCA) of Novel Materials project is designed to compare the environmental impact of the production and use of two families of novel materials being developed by University of Alberta scientists to help remediate oil sands process water (OPSW): biochar and chicken feathers. The LCA takes in account all material, chemical and energetic inputs of each process step in the manufacture of novel materials, as well as all waste heat, effluent, gas and other outputs of the manufacturing process. The LCA can calculate the total environmental impact of each novel material, and can then compare one novel material to another quantitatively. This research can allow decision makers to use these quantitative values for measuring the environmental impact of a novel material prior to its scale up and use, effectively allowing for the mitigation of some of the unintended consequences of a manufacturing process prior to commitment.

Thus far, we have conducted interviews with the biochar and keratin filaments novel material labs. From these interviews we generated LCA maps which outlined all of the manufacturing steps for each process. and the inputs and outputs for each step. Once these maps were confirmed for accuracy, we then acquired further information about the specific equipment used so that we could calculate more precise energy inputs. We then built the front end of the LCA model using OpenLCA software, and began researching the correct database to connect to the front end of our model in order to actually run the LCA. We determined that the best database for our needs would be Ecolnvent, as it has data from North America, and includes the breadth of data that we needed to capture electrical, chemical, transportation, water, and various other inputs and outputs needed for our study. This past year, we have made major progress on the time consuming task of disconnecting our front end LCA model from our previous databases, then reconnecting it to the new EcoInvent database. We have now made a list of gaps that must be filled in order to make our LCA model fully functional. Our next steps are to (1) fill these model gaps by conducting extensive literature reviews on the impacts of inputs or outputs not present in our new database, (2) build these custom inputs and outputs, and (3) further research into quantification of specific outputs for specific steps such as nitrogen and carbon dioxide. Once these steps have been completed, we will be able to run the LCA model, generate environmental scores, perform comparisons of novel materials, and move forward with further pitch experiments.

The second major component of this research involves pitch experiments to decision makers in government and industry. While currently in the development phase, this part of the research project will increase understanding of what information about novel materials makes decision makers more likely to invest in them, allowing us to then increase the likelihood that some of these novel materials will be scaled up and adopted at an industrial scale.

## 15. A Dynamic Economic Analysis Of Oil Sands Process-Affected Water (OSPW) Treatment Alternatives In Alberta

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Alberta's oil sands are the world's 3<sup>rd</sup> largest proven oil reserve. About half of current extraction is by open pit mining, which generates oil sands process water (OSPW), a complex mixture of solids, residual bitumen, inorganics, and organic constituents. As part of their obligations, oil sands companies must treat the OSPWs before they are released into the environment. However, there are still unanswered questions around this objective as there is no certainty about the abatement costs and the quality standards for the treated OSPW. To address these issues, this study aims to construct an optimization model of the oil sands to identify cost effective abatement approaches, the optimal treatment time for OSPW, and the sensitivity of these costs to various factors including water quality standards.

The proposed model will include three different periods of time (i.e. production, regulation, and post regulation), where companies can decide to treat the OSPW or continue accumulating in their facilities. To analyze the implications of these decisions we will model and track the water and OSPW cycle in the mine, as well as the concentration of different components (i.e. naphthenic acids, total dissolved solids, and chloride) and the costs of implementing different active and passive treatment technologies. The model was built using the information available from the Alberta Energy Regulator (AER) and the Canada's Oils Sands Innovation Alliance (COSIA), as well as partnerships with chemical engineers and reclamation experts.

The model will be implemented for a "virtual" mine, where the objective will be to minimize the sum of the discounted costs of different bundle of technologies to find cost effective treatment approaches. Among the constraints in the model, which include the water and chemical balance, we will also account for the different attributes for each technology as they will have direct implications in the technology cost function. The results will be compared to a base scenario where the companies use only a pit lake, which could be affected by the amount of net precipitation, fresh water and the release of pore water trapped in the fine fluid tailings. Currently, the model includes cost functions for wetlands and membrane bioreactor. We model the acute and chronic concentration limits as this allows us to understand the implications of different regulatory standards on the abatement cost.

Our preliminary results show that the cost of implementing wetlands or membrane bioreactors vary between 31 and 142 million dollars, depending on different assumptions regarding the effectiveness of the treatment and the requirement for the pit lake at closure time. The model also shows that costs and the decision to do early OSPW treatment are very sensitive to the water quality standard selected by the regulator. The impact of quality standards on costs outlines the trade-offs that arise for regulators in selecting standards that are feasible while also protecting the environment and ensuring that reclamation will take place in the expected time. Future research will aim to expand the number of technologies and the parameters analyzed in the model.