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Theme Goals

The goals of the Future Energy Systems (FES) theme on Resilient Reclaimed Land and Water Systems 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.

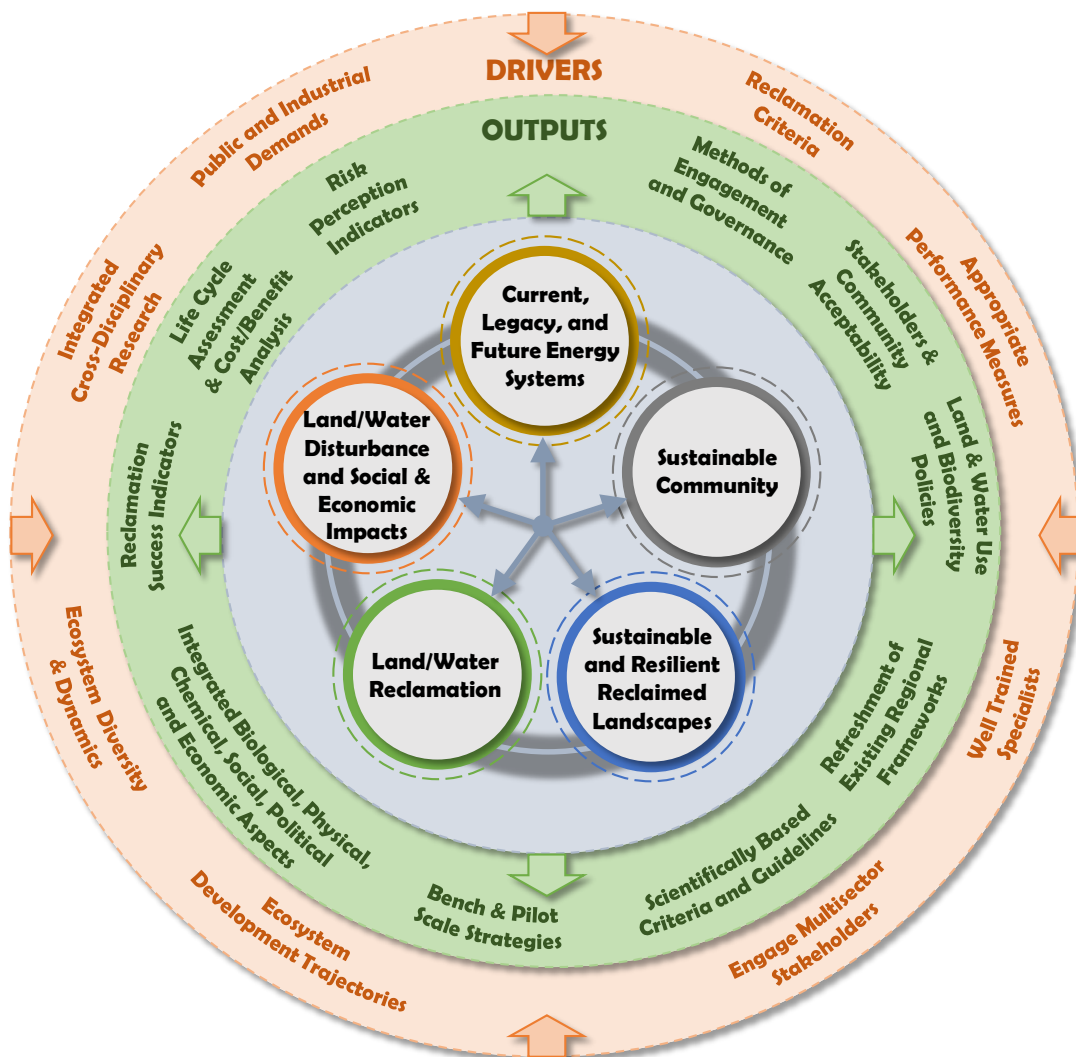


Figure 1. Schematic of the theme drivers and outputs.

Material Synthesis And Development For Reclamation Session

1. Feather Keratin Derived Sorbents For The Treatment Of Wastewater Produced During Energy Generation Processes

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Water and energy infrastructures are interdependent as energy is essential for water extraction, desalination and transportation. The energy industry also requires water for resource exploitation (fossil fuels), energy conversion processes (refining), electricity generation (thermoelectric, hydropower, and renewable technologies) and transportation. Water dependency of energy generation systems including renewable energy resources pollute water. Water pollution due to inorganic (heavy metals) and organic contaminants is a threatening issue because of their acute toxicities and carcinogenic nature. Efforts are being made to control energy-related water pollution. Among the conventional technologies (biological, chemical, and electrochemical) for wastewater treatment, adsorption is more effective, economical and environment friendly. Recently, the adsorbents containing natural polymers have been developed and among them keratin derived biopolymers have gained attention because of its potential use for wastewater treatment.

The objective of this study is to develop the keratin derived biopolymers (KBPs) and evaluate their applicability for a range of inorganic contaminants in industrial simulated synthetic wastewater. Here in, eight keratin derived biopolymers were developed to sequester the toxic trace elements from synthetic wastewater. Chemical modifications of biopolymers affect their physical and chemical characteristics, hence, enhancing the sorption of contaminants from wastewaters. KBP-I (processed chicken feathers), KBP-II (acid modified), KBP-III and KBP-IV (modified with ionic liquids), KBP-V (amine modified), KBP-VI and KBP-VII (POSS modified) and KBP-VIII (sodium sulfite modified) were characterised for their surface morphology, structural integrity, functional group changes, crystallinity behaviour, surface area and pore size distribution through scanning electron microscope, thermogravimetric analysis, differential scanning calorimetry, Fourier-transform infrared spectroscopy, X-ray diffraction and Brunauer–Emmett–Teller analysis. The results of characterization studies support the chemical modification of the developed KBPs indicating the denaturation of keratin structures that is beneficial in enhancing the surface functionality for the adsorption of contaminants. Developed biopolymers were then tested against synthetic wastewater at pH = 7.5 and ionic strength $I = 0.05$, spiked with nine transition and redox sensitive elements ($100 \mu\text{g L}^{-1}$ each). The results are highly promising with very high sorption affinity of metals towards biopolymers. Among the eight biopolymers, KBP-I removed 87–93 % of As and Cd, KBP-IV removed 80–85 % of Cu and VV, KBP-V removed 60–90 % of Co, Ni and Zn, whereas KBP-VI removed 95 % of CrVI. On an optimistic approach, the developed KBPs of this project open diverse possibilities in eliminating the inorganic contaminants from energy-related wastewaters.

2. Evaluation Of Adsorption Of Organic And Inorganic Compounds Related To OSPW Onto Different Types Of Soils

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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 bring environmental concerns in oil sand industries. The naphthenic acids (NAs) present in OSPW have been proved to be one of the contributors to the acute toxicity of OSPW. Meanwhile, heavy metal ions are recognized as the most toxic inorganic pollutants that can exist in soils. Several studies have already studied 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 organic contaminants and heavy metals by natural soils. The role of the adsorption and desorption process in the migration or transport of the OSPW related contaminants needs to be investigated deeply. The main purpose of this project is to evaluate the adsorption and desorption behavior of organic and inorganic compounds present in OSPW by using six types of natural soils (Figure 1.) and build up a relationship between the uptake of pollutant by soil and the soil properties. Based on the evaluation, the assessment of the leaching potential of target pollutant should also be performed. The results should be used as a good guidance for predicting the transport and environmental fate of contaminants in the soils.

The specific objectives of this project are to: 1) evaluate the transport of target pollutants (e.g. organic model compounds and metals) in natural soils; 2) determine the adsorption mechanisms for targeted pollutants; 3) investigate the characteristics of the soils and the correlation with adsorption or desorption process; 4) study the effects of some significant parameters on adsorption process by soils in column test; 5) determine the impact of other contaminants in OSPW on the adsorption of target pollutants by soils; and 6) assess the leaching potential of target pollutants from the soils.

Preliminary experiments have been conducted in batch scale tests and the scheme is showing in Figure 1. OSPW was used as the targeted contaminant solution for preliminary experiments. Several different concentrations for soils as adsorbents, and different contact time have been applied as attempts. All preliminary 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 0.45 μm filter. Measurements used in preliminary stage include total organic carbon (TOC) analysis, site frequency spectrum (SFS) analysis, time-of-flight (TOF) analysis and inductively coupled plasma mass spectrometry (ICP-MS) analysis. Based on the preliminary results, it has been observed the occurrences of adsorption for all soils. Further works will be the adsorption and desorption kinetics and isotherm study by batch experiments. The column tests will be designed based on batch experiment results.

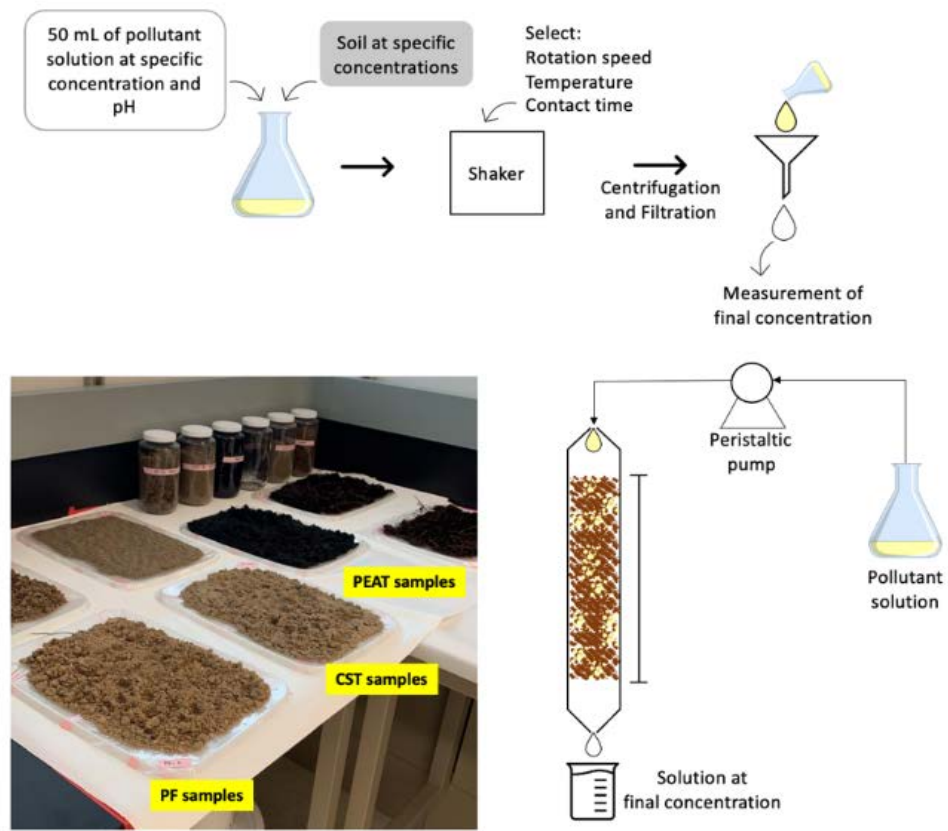


Figure 1. Diagram of soil column experiments.

3. Nano Humus In Coal Mine Reclamation

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Excessive release of heavy metals may pose a significant risk to the environment and public health. Soil and water can be contaminated with heavy metals from many industrial activities, such as coal mining. Conventional methods of treating heavy metals are usually high energy requirements, low efficiency, and expensive. Therefore, developing an efficient, rapid, and cost-effectively method for heavy metal remediation is critical. Nano Humus is a coal-derived humic substance product. The main component of nano humus, humic substance, are natural organic compounds and considered the most reactive organic carbon fraction. Nano humus features a large pore volume which provides a relatively higher surface area and unique electrical properties. It has chemically reactive functional groups which could enhance the metal adsorption. It is cost effective as the raw materials (coal) can be achieved on coal mine sites at low costs. Owing to these characteristics, nano humus has a high potential in removing heavy metal contaminants.

The primary objective of this study was to investigate the use of nano humus in the removal of cadmium (Cd(II)) and zinc (Zn(II)) from artificial metal contaminated water. The effects of initial metal concentration and contact time were also studied. A batch sorption experiment was conducted at room temperature to evaluate the sorption properties of the studied material nano humus. Heavy metal solutions were prepared from cadmium and zinc salts at 5 different concentrations, from 25 to 125 mg L⁻¹ (pH at 7). A volume of 20 ml single elemental solutions was added to 0.02g of nano humus. Then, the mixtures were placed on a shaker for 24 hours to reach equilibrium.

Isotherm data of Cd(II) and Zn(II) fitted well for the Freundlich model, indicating multilayer adsorption dominated for nano humus. Adsorption of metal ions is dependent on their initial concentrations and contact time at neutral pH. After treatment, the levels of metal ions were observed to decrease by 83.1 - 99.6 % for Cd(II) and 57.6 - 98.3 % for Zn(II). The percentage removal decreased with the increase in the initial concentration. The order of affinity which represents the adsorption capacity decreased in the order of Cd(II) > Zn(II). The effect of contact time on the Cd(II) adsorption at different time intervals of 15 min, 30 min, 1 hr, 3 hr, 6 hr, 9 hr, 24 hr showed that 89.1 % of Cd(II) in the solution was adsorbed in 15 minutes and the removal gradually reached at 92.8 % with the increase of contact time. Nano humus appears to be a promising adsorbent for the removal of Cd(II) and Zn(II) ions from water. The use of nano humus may reduce remediation costs resulting from the utilization of low cost humic products derived from coal in treating contaminated soil or water. Further studies could be conducted on investigating the effect of various solution pH, different nano humus dose, and other metal ions.

4. Cadmium Stability In Spent Biochar In Electrolyte Solutions And Soils

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Industrial wastewater, such as oil sands process water (OSPW), usually contains various potentially toxic elements (PTEs). Biochar is a stabilized carbon made from organic waste material through pyrolysis. It is considered both as a soil amendment and a promising and economical adsorbent for wastewater treatment. After wastewater treatment, biochar becomes contaminated with PTEs and is called spent biochar. Spent biochar has reuse potential in activities (e.g., land reclamation), which can simultaneously reduce its storage in landfills and sequester carbon.

To safely reuse spent biochar in soil applications, we need to improve our understanding of the potential stability of adsorbed PTEs on the biochar. Cadmium (Cd) is a representative PTE to study because average Cd concentration in OSPW exceeds the standards of heavy metals for the protection of aquatic life in Environmental Quality Guidelines for Alberta Surface Waters more than other PTEs such as lead, cobalt, and zinc. Therefore, this research evaluates the desorption and stability of Cd in different types of spent biochars.

The biochars with high adsorption capacity and disparate properties were selected for this experiment based on the results in our previous study. Wheat straw and manure pellet biochars were produced at 700 °C with or without steam activation. Then an adsorption experiment investigated the effects of feedstock type and steam activation on Cd adsorption. The adsorption isotherms and maximum adsorption capacity (Q_{max}) were obtained.

Spent biochars with different Cd contamination levels (0, 60 and 80 % of Q_{max}) are produced based on the adsorption isotherms and used in desorption and incubation experiments to determine the effects of contamination level on the stability of Cd in spent biochar. The desorption experiment determines how stable Cd is on different spent biochars in electrolyte solutions with different pH.

The incubation experiment investigates how the environmental behavior of biochar-adsorbed Cd is in spent biochar amended soils. A sandy soil (pH = 7.3, organic carbon (OC) % = 4 %, sand = 84 %, clay = 6.8 %) and a clayey soil (pH = 6.5, OC % = 5 %, sand = 20 %, clay = 30 %) are selected to investigate the effect of soil texture. The potential mechanisms that may induce desorption in the incubation are 1) Cd tends to desorb from spent biochar to reach equilibrium between biochar and soil solution; 2) the desorbed Cd may be adsorbed by soil mineral from the soil solution; 3) adsorbed by and complexed with organic matter; or 4) precipitated with anions (e.g., carbonate, phosphate). The distribution of Cd in the soil-biochar system may change over time. The amount of extractable Cd can be an effective indicator to determine the stability of Cd in a soil-biochar system since the strength of each bonding is different. Therefore, bioavailable Cd and geochemical reactive Cd are extracted at day 3, day 30, and day 60 during the incubation. This study investigates the factors that influence the stability of Cd in spent biochar, which would help determine the conditions of reusing spent biochar in soil application in the future.

5. Development Of Hydrochar For The Treatment Of Oil Sands Process Water

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Oil sands mining generates a large amount of process water, and without proper management the process water can pose a threat to both the environment and human health because it contains life threatening contaminants. An example is lead(II), which negatively affects human health including causing brain disorder in children if ingested or inhaled. By effectively treating the oil sands process water before discharging to the environment, environmental and health impacts can be ameliorated.

Adsorption can be a suitable method to treat process water and the use of hydrochar (a solid by-product of hydrothermal carbonization of biomass) as an adsorbent can be a cost-effective and environmentally friendly approach because of notable properties of hydrochars such as the abundance of surface functional groups. How feedstock type and production conditions such as temperature used for feedstock conversion would affect hydrochar properties and lead(II) adsorption is not well known. Therefore, we evaluated the effect of four feedstocks (canola straw, manure pellet, sawdust, wheat straw) and three conversion temperatures (180, 240, 300 °C) on (1) the physical and chemical properties of hydrochars, and (2) lead(II) removal from synthetic wastewater by hydrochars. We explored the associated mechanisms of lead(II) removal by (1) studying surface properties of the hydrochars before and after lead adsorption, and (2) exploring relationships between hydrochar properties and maximum lead(II) adsorption capacity.

Functional group abundance and yield of hydrochar production depended on feedstock type and decreased with increasing temperature due to loss of volatiles associated with biomass hydrolysis during hydrothermal conversion. Specific surface area was generally low with a maximum of 30.6 m² g⁻¹ for sawdust hydrochar produced at 240 °C. With a few exceptions, lead(II) removal by the hydrochars was less than 25 % due to the effect of pH and inorganic minerals. Lead(II) adsorption depended on feedstock type and conversion temperature, highest for canola straw hydrochars and lowest for those derived from sawdust. X-ray diffractogram of hydrochars before and after lead(II) adsorption was not significantly different suggesting that lead(II) did not precipitate on the hydrochars. Maximum lead(II) adsorption capacity of the hydrochars was strongly correlated ($R^2 = 0.9$) with atomic hydrogen:carbon ratio suggesting that lead(II) was adsorbed through metal- π interaction. We conclude that feedstock type and temperature used for hydrochar production affected hydrochar properties and played a key role in lead(II) adsorption. We recommend that hydrochars be activated to increase their adsorption capacities for lead(II) removal in wastewater.

Land And Water Approaches To Reclamation Of Process Water Session

6. Z-Scheme Plasmonic Ag Decorated NiO/Bi₂WO₆ Hybrids For Enhanced Photocatalytic Treatment Of Naphthenic Acids In Real Oil Sands Process Water Under Simulated Solar Irradiation

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Recovering bitumen through a caustic hot water extraction method in northern Alberta produces large volumes of oil sands process water (OSPW). Due to the industry's zero discharge approach, more than 10^6 m³ OSPW are currently impounded in tailings ponds, waiting for remediation due to environmental and health concerns. Assessment of OSPW toxicity has shown that OSPW could induce acute and chronic toxicity to both prokaryotes and eukaryotes. Organic compounds, especially naphthenic acids (NAs), are suggested to be the main cause of OSPW toxicity. Advanced oxidation processes (AOPs) have demonstrated to be effective for NAs removal and toxicity reduction. However, the main disadvantages of traditional AOPs are their high cost due to high energy and consumable chemicals. Utilization of solar energy and reusable catalyst are the benefits of photocatalytic AOPs technology and can be seen as a green alternative to the traditional AOPs. Studies on photocatalytic treatment of OSPW have been mainly conducted using TiO₂. However, the weak visible light absorption has been one of the critical limitations of TiO₂ photocatalysis against its application in the field of water treatment as UV light is only 3-5 % in the whole solar spectrum. Therefore, in this study, heterojunction photocatalysts Bi₂WO₆/NiO/Ag, which could be activated by visible light, were prepared by hydrothermal method. The prepared catalysts were characterized to obtain their structural, textural, chemical and optical properties and tested for the treatment of real OSPW under simulated solar irradiation. For the treatment of OSPW, the NAs were detected by using ultra performance liquid chromatography-time-of flight mass spectrometry (UPLC-TOFMS) with ion mobility spectrometry (IMS). Hydroxyl radical and superoxide radical were identified during the photocatalytic process by scavenger experiments and electron paramagnetic resonance (EPR). The improved degradation rate (88.75 %) of classical NAs in OSPW by Bi₂WO₆/NiO/Ag could be ascribed to the unique Z-scheme electron transfer among NiO, Ag and Bi₂WO₆, particularly surface plasmon resonance and local electric field near Ag. Through this study, a novel and efficient NAs photocatalytic degradation process is expected to be developed and will provide valuable information for the treatment of NAs by engineered passive solar-based approaches.

7. Solar-Activated Zinc Oxide Photocatalysis

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Being a huge process water stream resulting from oil sands refining, oil sands process water (OSPW) has been the subject of many studies on wastewater treatment. The toxicity of OSPW to the ecosystem has been well documented. The non-zero discharge approach on OSPW has resulted in the continuous storage of this water stream in large oil sands tailings ponds constructed across the active oil sands fields in Canada. Naphthenic acids (NAs) have been identified as main acid components of OSPW and major contributors to its toxicity. NAs degradation via biodegradation has been determined to be slow and ineffective as the NAs are considerably toxic to microbial community needed for the degradation. Another class of organic compounds identified as contributing to OSPW toxicity are the dissolved aromatic compounds. Thus, effective degradation of NAs and aromatic organics in OSPW is significant towards reducing its toxicity. Oil sands processing into valuable refined products draws a lot on freshwater which makes the reclamation and reuse of OSPW an move at reducing freshwater demand by the oil sands processing industry. Efficient degradation of NAs and other dissolved organic substance in OSPW is an important step towards the effective reclamation and safe reuse of OSPW. Various advanced oxidation processes (AOPs) have been demonstrated as promising OSPW treatment methods. Among these AOPs, photocatalytic treatment is gaining increased research interest due to its considerable effectiveness, superior environmental friendliness and relatively low cost, among other positive features. Hence, this project is focusing on assessing zinc oxide (ZnO) as an environmentally benign chemical substance for passive, low-energy and effective photocatalytic degradation of dissolved organics in OSPW towards cost-effective reclamation and safe reuse of OSPW.

In this work, the performance and efficiency of ZnO as a photocatalyst for the degradation of NAs and aromatic compounds in OSPW under solar radiation was investigated. Initial experiments were conducted with commercial ZnO in suspension in OSPW under simulated solar radiation (277.92 W m^{-2}). Samples were taken at intervals for concentration and toxicity change analyses. The nanoparticles appear to be efficient in degrading NAs and aromatic organic substances in OSPW. With 1g/L of ZnO and solar irradiance of 277.92 W m^{-2} , $>99\%$ of initial 65.7 mg L^{-1} NAs was degraded after 4 hours of reaction. The aromatic organics were almost completely degraded within the same time period. The photocatalytic degradation of NAs was modeled with pseudo first-order kinetics, with an overall rate constant of $k_{\text{apparent}} = 6.81 \times 10^{-7} \text{ m}^2 \text{ J}^{-1}$. Toxicity change assessment of the treated OSPW using Microtox indicated 47.8% and 52.7% reductions in toxicity for 5 and 15 minutes of exposures, respectively. The results indicate that solar-activated ZnO photocatalysis can be potentially applied as a treatment method for OSPW.

8. Degradation Of Oil Sands Process Water By Continuous-Flow Packed Bed Electrode Reactor

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Electro-oxidation has been used for organic wastewater reclamation for a period of time. It has some outstanding advantages such as simple operation, no additional chemicals needed, and no secondary sludge generated compared with other methods. However, the traditional electrolytic reactor uses a two-dimensional electrode structure, which means the organics must transfer to the interface before reaction. Besides, as the specific area of the two-dimensional electrode is relatively small, improving the mass transfer and reaction efficiency is one of the hotspots in the electro-oxidation study.

In this project, a Packed Bed Electrode Reactor (PBER) was adopted to degrade the organics in oil sands process water (OSPW). Spherical electrode materials were added between the anode and cathode to form a new working electrode. Under the electric field, packed particles were charged and polarized, which could be regarded as micro electrolytic cells. The organics on the electrode surface could be oxidized step by step until they were completely degraded into water and carbon dioxide. Using PBER, the reaction rate and efficiency become much higher because the mass transfer distance is reduced, and the specific electrode area is increased significantly.

The main body of PBER is made of acrylic (Figure 1). Titanium plates (10×10 cm) were selected as the anode and cathode. The material packed is Spherical Activated Carbon (SAC). The OSPW flowed through the reactor continuously by a peristaltic pump. Before electrolysis, the SAC must be pre-treated for 48 hours until nearly saturation to eliminate the effect of adsorption. Three operational parameters, including flow rate (5, 10, 20, 30 mL min⁻¹), electrode space (4, 5, 6, 7 cm), and cell voltage (5, 7.5, 10, 12.5 V), were investigated to assess their effects on the OSPW degradation.

The flow rate determined the OSPW retention time in PBER. The results revealed that the slower the flow rate, the better the treatment performance. At 5 mL min⁻¹ of flow rate, 60 % of chemical oxygen demand (COD) and 50 % total organic carbon (TOC) were removed. The electrode space not only affected the electric field intensity but also determined the packed volume of SAC. With the increase of electrode space, the organics removal rates increased, and then were reduced. The best removal rate was achieved at 6 cm, where up to 61 % of COD and 54 % of TOC were removed. The cell voltage affected the electrode reaction rate directly, and due to the side reactions, the current efficiency and energy consumption were also affected. The organics removal rate was improved by increasing the cell voltage, but only 10% improvement was achieved. However, bubbles and corrosion were observed on the anode and cathode surface when the cell voltage was over 12.5 V, indicating that the side reaction was too strong. Furthermore, the treatment effect of the 2-D electrode and PBER under optimal conditions was compared. Based on the results, PBER can improve the treatment of real OSPW treatment. The COD and TOC removal rates of PBER were 5-6 times higher than those in the 2-D system, while the energy consumption of PBER was much lower.

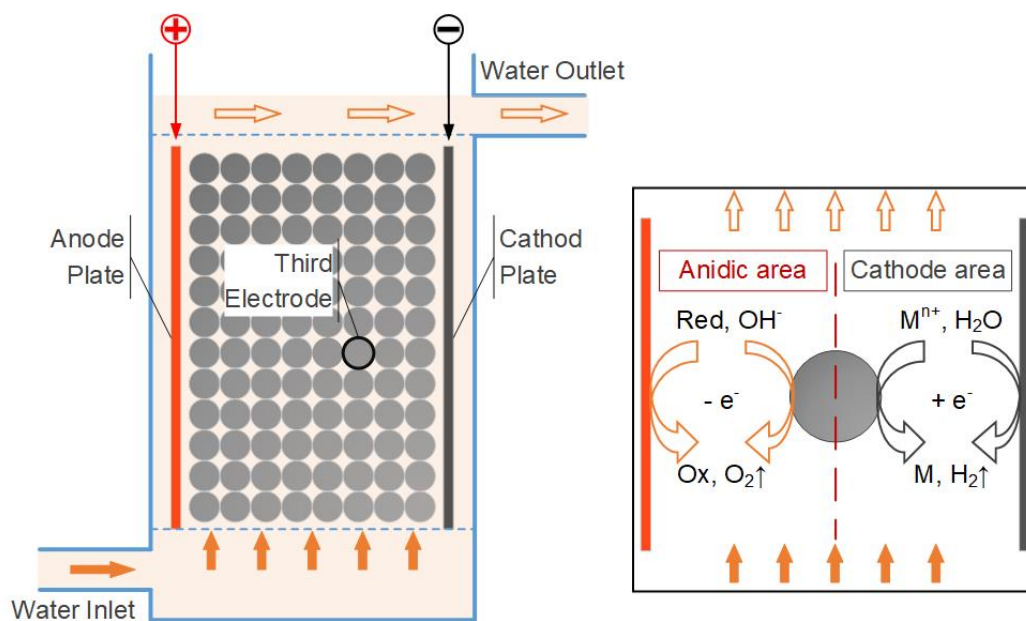


Figure 1. The schematic of Packed Bed Electrode Reactor.

9. Electrochemical Treatment Of Oil Sands Process Water Using Boron-Doped Diamond Electrode: Understanding The Radical Formation And Transformation Pathways

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Electro-oxidation (EO) using boron-doped diamond (BDD) electrode is an efficient and effective treatment process for the remediation of organic pollutant contaminated water and wastewater. This process involves the generation of radical and non-radical oxidants that concurrently participate in the degradation of the pollutants, depending on water chemistry (anion contents) and operation parameters (current/potential density). Oil sands process water (OSPW) which contains significant quantities of anions such as (hydrogen)carbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$), sulfate (SO_4^{2-}) and chloride (Cl^-) ions present such suitable conditions for the generation of different types of reactive species. In this study, the formation and transformation of different radical species during EO treatment of real OSPW using BDD were monitored by Electroparamagnetic Resonance Spectroscopy (EPR) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as probe molecule. The EPR spectra of treated OSPW showed three distinctive set of signals at all current density and electrolysis time studied. The signals at 3480, 3496, 3510 and 3525 G electric field with intensity ratio of 1:2:2:1 was assigned to the $\text{DMPO}^{\bullet}\text{-OH}$, indicating the formation of hydroxyl radicals ($^{\bullet}\text{OH}$) during the EO treatment. The $^{\bullet}\text{OH}$ was formed by water oxidation at the BDD electrode after the application of current. Sulfate radical ($\text{SO}_4^{\bullet-}$) formation was confirmed by the presence of it characteristic six signals with equal intensity (1:1:1:1:1:1) at 3485, 3490, 3500, 3508, 3515 and 3520 G electric field. The $\text{SO}_4^{\bullet-}$ is form from the oxidation of sulfate ions at the BDD electrode surface or by the electrogenerated $^{\bullet}\text{OH}$. The formation of $\text{SO}_4^{\bullet-}$ from direct oxidation of SO_4^{2-} was confirmed by performing electrolysis at very low voltage (0.5 and 1 V) and the EPR spectra showed the signals of $\text{DMPO}^{\bullet}\text{-OSO}_3$ along with $\text{DMPO}^{\bullet}\text{-OH}$. Since no $^{\bullet}\text{OH}$ is expected to form at such lower voltage, the $\text{DMPO}^{\bullet}\text{-OH}$ signals observed in these spectra was ascribed to the transformation of $\text{SO}_4^{\bullet-}$ to $^{\bullet}\text{OH}$ via the reaction of the former with water. The other three equidistance signals at 3476, 3503 and 3530 G electric field was suggested to be related to chlorine oxide radical (ClO_2^{\bullet}) which was generated from the oxidation of ClO_2^- (formed from oxidation of Cl^- ions). Comparative electrolytic studies were performed in synthetic water containing SO_4^{2-} , CO_3^{2-} or Cl^- and the EPR spectra showed the signals of $\text{SO}_4^{\bullet-}$ and ClO_2^{\bullet} along with $^{\bullet}\text{OH}$ in sulfate and chloride media, respectively. Interestingly, only $^{\bullet}\text{OH}$ signal was observed in EPR spectra of electrolyzed carbonate water which was due to instant transformation of generated carbonate radical ($\text{CO}_3^{\bullet-}$) to $^{\bullet}\text{OH}$, the later being the surrogate of the former. All the radical species actively participated in the degradation of organic compounds during the treatment of OSPW by EO. This study has shown that the anions in the OSPW can be beneficial during electrochemical treatment.

10. Understanding The Impact And Chemistry Of Treatment Of Naphthenic Acids Through By-Products Investigation

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Oil sand process water (OSPW) contains organic compounds that might be potentially harmful to the environment such as naphthenic acids (NAs). Therefore, treatment methods would be required to degrade or remove the organic compounds before discharging the OSPW into the environment. Oxidation treatment could effectively remove NAs from OSPW. However, by-products that are potentially more harmful than the parent compounds can be formed after oxidation treatment. The identification of by-products can therefore help to evaluate the potential toxicity after treatment and it also assist in the understanding of the chemistry of the treatment process, helping to optimize the treatment process.

Model NAs were first treated by selected treatment methods such as ozonation, photodegradation and sulfate radical-based oxidation. The treated samples were then analyzed for their by-products using ultra-high performance liquid chromatography coupled with time-of-flight mass spectrometry. After the identification of the by-products, possible reaction mechanisms were proposed and the toxicity was predicted using Quantitative Structure Toxicity Relationship.

Based on the by-products identified and from the proposed reaction pathways, the reaction mechanism of the oxidation of NAs involved first the H-abstraction by hydroxyl radical, followed by the reaction of oxygen, hydroxyl, nitro, chlorine etc. with the carbon radical to form the identified by-products. The identification of by-products from solar catalytic treatment of heteroatomic NAs indicated that OH addition that resulted in the bond cleavage of the compounds was the main mechanism for the formation of its by-products.

The acute toxicity (Fathead minnow LC₅₀ (mg L⁻¹), 96 hours), mutagenicity value and bioaccumulation factor of the by-products generated from the ozone/H₂O₂ or ozone/persulfate treatment of 1-Adamantanecarboxylic acid (ACA), a model NA, were predicted to be lower than the parent compound. While the development toxicity prediction of the by-products formed from the ozone/persulfate of ACA was lower than that of ACA, the predicted development toxicity from the by-products from ozone/H₂O₂ was slightly higher than ACA itself. Therefore, based on the predicted toxicity of the by-products generated, ozone/persulfate would be a better treatment option for NA removal. However, more detailed studies would be required to confirm the trend.

The identification of by-product facilitated the understanding of the reaction mechanism of the treatment, where H-abstraction was the main reaction pathway and thus by improving the rate of H-abstraction of the treatment process could improve the treatment efficiency. In addition, the toxicity prediction of the by-products also provided an inexpensive and faster method on the risk assessment of the treatment processes.

11. Development Of Microlens-Enhanced Photolysis Of Contaminants In Water

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In the field of water treatment, photoreactions are widely applied to decompose the contaminants due to the abundant light resource, relative lower cost, and less toxic residuals. The light energy, if it is used sufficiently, 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 were 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. There are some simple methods for basic water treatment, like solar water disinfection (SODIS), which can be applied in developing areas. Such methods are convenient and easily accessible but have restricted efficiency. A possible method for enhancing the photoreaction efficiency without adding processing cost is necessary.

Our project is aimed at exploring the application of surface microlenses (MLs), which are fabricated with solvent exchange, in the low-cost water treatment process. The surface microlenses have strong focus effect and are highly tunable due to the flexible conditions of solvent exchange. We chose methyl orange as the model compound to evaluate the performance of surface microlenses in the photodegradation. By changing the environmental factors that influencing the photodegradation, including the dissolved oxygen level, pH value, initial molybdenum (MO) concentration and light intensity, we found that the photodegradation efficiency of MO was obviously improved with applying MLs in the light treatment.

The kinetics and mechanism of the MO photodegradation process was further studied to see how the MLs influence the photodegradation process. The change of the MO concentration was monitored for 8 hours. It can be concluded that the kinetics of MO photodegradation was not changed after using MLs, but the process was only sped up. Furthermore, by analyzing the by-products and species formed in the photodegradation process without and with MLs, we found that the types of by-products remained same with applying MLs although the amount of the intermediates were different. This result indicated that the pathway of MO photodegradation kept same with MLs.

To optimize the performance of MLs in the photodegradation, we discussed the influence of the MLs properties on the degradation efficiency. The surface average, average size, number density and size distribution of MLs can be altered by changing the flow rate during the solvent exchange process. MLs with higher surface coverage and larger median size were proven to perform better. 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 because it will not change the mechanism and kinetics of the reactions.

12. Microbial Composition And Functional Diversity In Petroleum Coke-Based Biofilters Treating Oil Sands Processed Water: Bioaugmentation Improves System's Performance

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There is an increasing interest in developing biological systems that can be used as nature-based solutions for the environmental remediation of wastewater including oil sands process water (OSPW). To this end, potential of fixed-bed sand based biofilters, moving bed biofilm reactors, and integrated fixed-film activated sludge reactors have been investigated previously. It was suggested that fixed-bed bioreactors may be an effective choice for the remediation of OSPW compared to the suspended growth systems because they allow better colonization of microbial communities on the filtering media that help remediation in a short time. In this regard, choice of filtering media is crucial because it selects microbial communities specifically based on the nature of substrate as well as the wastewater. To this end, petroleum coke based biofilters may be a suitable option because it is readily available at the oil refining sites and is a byproduct of bitumen upgrading process. Hence, in this study, petroleum coke based biofilters were established and operated continuously following analyses on total and active bacterial communities in a metataxonomic fashion to elucidate underlying mechanisms of OSPW remediation. Results of total microbial community composition indicated the high abundance of aerobic bacterial communities within the biofilter among which hydrocarbon degraders were present ubiquitously. However, active bacterial fraction reflected that the expressed community was entirely anaerobic (>99 %) with metabolic activities related to scheme similar to beta-oxidation during anaerobic digestion of organics present in the OSPW. This process is generally documented in oil sands tailings ponds and lead to the production of acetate, CO₂, and H₂. The presence of hydrogenotrophic methanogens was also observed that could have facilitated CH₄ production in syntrophic mechanism. It is well-known that anaerobic digestion of naphthenic acids (NAs) is a slow process, hence, nine unique bacterial strains were immobilized on the petroleum coke to improve the existing remediation potential of the biofilters under modified redox conditions. These bacteria were isolated from the OSPW and oil sand tailings, and then screened for their successful growth on 15 different NAs as a sole carbon source. The removal of classical NAs was 19 % under natural conditions, which was enhanced to 32 % in the presence of inoculum. Synchronous fluorescence spectra indicated a higher degradation of single, two or more ring fluorophore (aromatic) compounds in the presence of bacterial augmentation. Likewise, improved reduction in chemical oxygen demand and toxicity was also observed in the bacterially augmented biofilters. The inoculated bacteria were able to colonize the petroleum coke effectively as observed through fluorescence microscopy and restriction fragment length polymorphism. These investigations suggest that bioaugmentation could be a useful strategy to improve the existing remediation potential of petroleum coke based biofilters.

13. Demonstration Pit Lake (DPL) Research And Monitoring Program

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The extraction of bitumen from the Athabasca oil sands produces large quantities of oil sands process water (OSPW) and fluid fine tailings (FFT) as waste products. These wastes contain high concentrations of dissolved organic acids, metals, hydrocarbons, and salts; and are therefore toxic to aquatic organisms. Management and reclamation of the huge volumes of FFT have been major challenges to oil sands mine operators. Recently, establishment of end pit lakes (EPLs) can be considered as one of the best methods for permanent reclamation of FFT. In pit lakes, FFT is capped with a mixture of OSPW and fresh water. Several studies have been carried out to understand the processes occurring in the pit lakes but more studies are required to monitor and model the (bio)geochemical properties of pit lakes using demonstration pit lakes (DPLs). Among the different conditions in these processes, the objective is to understand the essential effect of dissolved oxygen (DO) by establishing the DO profile as found in the lake. In addition, the rate of consolidation and lake water chemistry within the lake water are purposely being monitored.

The DPL process is being monitored in two big columns of height 2.4 m and diameter 0.2 m. The columns were filled with FFT and capped with lake water in the ratio 1:2. Diffusers were placed inside the lake water at the top and middle positions for aeration and the columns were then tightly closed. After complete filling of column, the consolidation was monitored daily for 24 days. Aeration and/or injection of pure oxygen gas through adjusted diffusers was used as alternative method for establishing the DO profile. For monitoring of lake water, samples were taken from different sampling ports within the water depth. To understand the stability of chemical properties when compared to the original lake water, column 2 was filled one week earlier.

Preliminary results indicate that consolidation is still improving after 24 days; however, the rate of consolidation has been slower after 2 days. The injection of pure oxygen is a better alternative as it provides stable DO profile of $8.1 \text{ mg L}^{-1} - 6.1 \text{ mg L}^{-1}$ (top – bottom) for one week in column 1. Column 2, on the other hand, had an uniform DO at the top and bottom. When nitrogen was added, a DO profile of less than 1 mg/l was observed at all depth but when oxygen was added, the DO profile became 8.5 mg L^{-1} at all depth. The stability of lake water property improved better for column 2 and water quality after two weeks of observation is close to the existing pit lake water quality.

The consolidation rate should still be monitored. The DO profile is improved and stable for one week with the injection of pure oxygen; however, more experiments are still on-going in order to extend DO profile monitoring. Subsequently, the adsorption and desorption effect of tailing as well as the biological processes involved in the experimental DPL system will be studied in detail using small columns.

Reclamation Success Session

14. Soil Invertebrate Indicators Of Land Reclamation Success

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Soil invertebrate communities are species-rich and functionally diverse, containing detritivores, microbivores, herbivores, predators, and ecosystem engineers. These soil invertebrate communities are shaped by the soil physical and chemical properties. They are also affected by past and present land use and management practices. Soil invertebrates are sensitive to anthropogenic activities including physical soil disturbances like mining and agricultural practices, pesticide and herbicide inputs, metal contamination etc. The type of response can vary among taxonomic groups. The composition of the soil biological community is directly linked to soil quality, ecosystem health, biodiversity, function, and influences ecosystem recovery. The importance of soil invertebrates in ecosystem recovery and health is well understood, however they are not currently included in reclamation monitoring because there are significant knowledge gaps that need to be addressed. Knowledge gaps include what soil invertebrate groups should be sampled, how we sample, when we sample, and does including soil invertebrates in reclamation monitoring improve the sensitivity of current practices. Current reclamation criteria mainly focus on soil physical and chemical properties and vegetation cover.

At the Genesee coal mine two forest reclamation sites were paired with a natural analog then assessed following reclamation criteria. Above and below ground soil invertebrates were collected using pitfall traps, litter collection, and soil cores monthly during the 2018 and 2019 growing season. Soil invertebrates were extracted from the litter and soil cores using the Tullgren funnel method and identified to order; we present preliminary results. Trends showed that the forest site had high soil invertebrate abundance regardless of the sampling month (Figure 1). The reclamation sites had similar trends but exhibited an increase in overall abundance beginning in August. The most abundant invertebrate groups were Oribatid mites, Prostigmatid mites, and Collembolans, however trends in their distribution and abundance differed by research site. Oribatid mites, which have low fecundity and dispersal rates, were more abundant in the forest site when compared to the reclamation sites. In most habitats they constitute the largest portion of the soil invertebrates, except in grasslands, where Prostigmatid mites dominate. The reclamation sites consistently had less than half the abundance of Oribatid mites when compared to the forest site. Prostigmatid mites, which are often soft bodied with short life cycles, were more abundant in the forest sites; this trend did switch starting in September. In August and September, we saw a large increase in Prostigmata mite abundance in both reclamation sites. Collembolans are omnivores and colonize new habitats quickly. General trends among our sites showed the forest site had higher Collembola abundance when compared to the reclamation sites. Collembolans in the reclamation sites were often smaller and soft bodied while larger surface dwellers were more common in the forest site. Initial results show clear differences between the forest and reclamation sites, but interestingly also differences between the two reclamation sites. Next steps include exploring the statistical significance of the results and incorporating soil and vegetation results. We will also be determining appropriate invertebrate groups to sample and ideal sampling times.

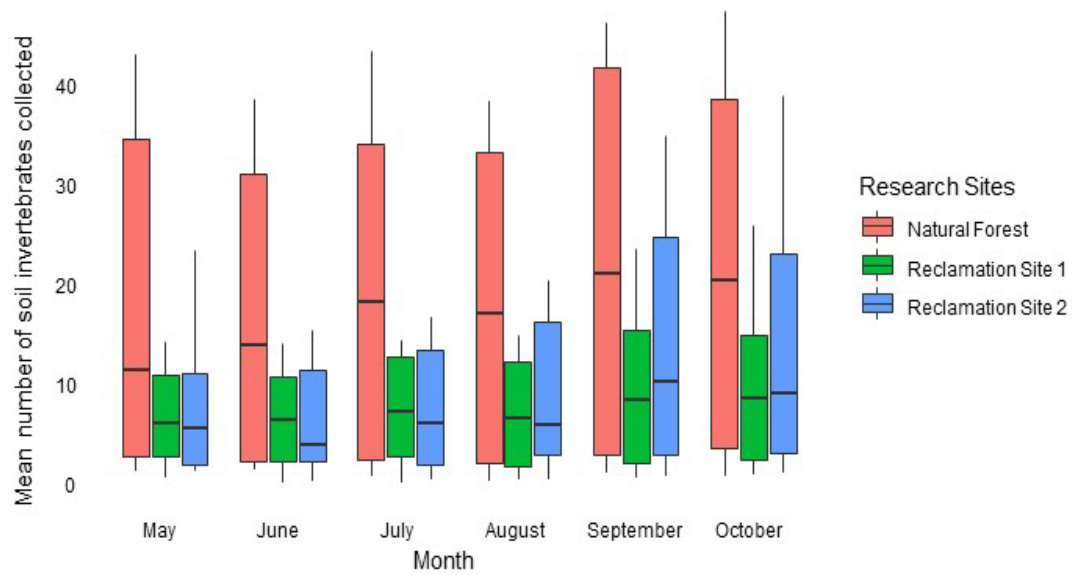


Figure 1. Mean number of soil invertebrates collected using litter and soil core samples from May to August 2018 and 2019 at Genesee Coal Mine, west of Edmonton, Alberta.

15. Salt Affected Well Sites: Quantifying Soil And Plant Community Indicators For Scientifically Based Reclamation Criteria

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Salt affected soils may occur with oil and gas production due to waste water spills and disposal of drilling fluids. Land reclamation on these sites follows regulatory requirements for electrical conductivity (EC) and sodium adsorption ratio (SAR) to measure success. However, EC and SAR are not always representative of soil quality and vegetation recovery. Current regulations require both soil EC and SAR to be below criteria even if a self sustaining, desired vegetation cover exists, resulting in the need for excavation and disposal of soil off site, and additional environmental damage. Other measures such as specific ion concentrations used in some provinces and jurisdictions, soil structural properties, and/or plant species abundances, may serve as appropriate indicators of detrimental salt contamination to better address the necessity for, and the methods to be used for, soil remediation and reclamation.

This research assessed 22 well sites in the dry mixed grass and central parkland regions of Alberta to determine whether EC and SAR are the most scientifically appropriate indicators for salt affected soil reclamation. Soil was sampled from 0 to 1.5 m depth and analyzed for EC, SAR, pH, and individual ions including sodium, chloride, sulfate, calcium, magnesium, and potassium. Vegetation assessments included ground and canopy cover and diversity. Relationships between soil parameters and those between soil parameters and vegetation variables were determined using correlations, non-metric dimensional scaling, linear mixed model, hierarchical partitioning, and redundancy analysis.

Soil salinity chemistry was highly dependent on ecoregion, soil depth and land use. EC and SAR were effective to identify soil salinity and sodicity, but were not sufficient measures to determine the magnitude of salt impacts or dynamics of individual salt ions which affect reclaimed plant communities. Sodium, chloride and sulfate, the most toxic salts for plants, were not always represented by EC and SAR, with the exception that SAR was a good indicator of sodium. Salts in the upper 0.45 m depth influenced plant community most. With depth soil salinity chemistry was more consistent among sample locations in both ecoregions, potentially due to fewer impacts of land management. Non native forage crested wheatgrass was common in dry mixed grass prairie and negatively impacted by salinity. Species richness and diversity were not directly impacted by soil salinity but were negatively associated with bare ground. Overall EC and SAR were not satisfactory measures to predict vegetation abundance or general condition. The majority of poor vegetation was explained by factors other than salinity and sodicity; although we can hypothesize what they may be, further research is needed if a predictive model is desired.

16. Poly(N-isopropylacrylamide)-Based Microgel Assemblies For Ion Sensing In Aqueous Systems

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Ionic species identities and their concentrations are important parameters in assessing water quality for a wide array of applications. Being routine quality assurance practices in city water supplies or testing lake waters to assess its susceptibility to eutrophication or to determine its safety for recreational swimming, ionic species are an important indicator of overall quality and health of an aqueous system. While routine drinking water quality testing for municipal authorities are done under controlled laboratory conditions, a niche exists for rapid, portable water quality testing systems that are user-friendly and economically feasible.

In this work, we used optical devices (etalons) developed by our group to study the concentration-dependant effects of several salts that are commonly found in natural aqueous systems on a series of poly (N-isopropylacrylamide)-based microgels. Microgels were synthesized by copolymerizing N-isopropylacrylamide (NIPAM) with 10 % acrylic acid (PNIPAM-co-10% AAc), 30 % acrylic acid (PNIPAM-co-30% AAc) and no acrylic acid (PNIPAM). Additionally, 10% vinyl acetic acid (PNIPAM-co-VAAc) and 5 % N-(3-Aminopropyl) methacrylamide (PNIPAM-co-APMAH)-containing microgels were also synthesized. In each case, 5 % N, N'-methylenebis(acrylamide) was added as a crosslinker. Etalon arrays assembled with each microgel type were exposed to concentrations ranging from 0 to 100 ppm of CaCl_2 , MgCl_2 , NaCl , NaHCO_3 and, Na_2SO_4 , 0 to 10 ppm of KCl and NaNO_3 and 0 to 0.25 ppm of Na_3PO_4 . In each case, an image of the etalon array was captured using a home-made camera setup built using a 3D-printed box, a Raspberry Pi camera system and an LED light source. Color changes of the etalons were characterized by transforming the sRGB values for the etalons to CIE xyY color space. Chromaticity coordinates (xy values of CIE xyY) for the etalons when exposed to deionized water were taken as the baseline and compared against those obtained when the same etalon arrays were exposed to mid-range concentration of a salt (i.e., 50 ppm for CaCl_2 , MgCl_2 , NaCl , NaHCO_3 and, Na_2SO_4 , 5 ppm for KCl and NaNO_3 and 0.05 ppm for Na_3PO_4). The chromaticity coordinates for PNIPAM microgels showed no response towards any concentration of any salt whereas PNIPAM-co-10% AAc showed a significant response only to CaCl_2 , MgCl_2 , NaCl , NaHCO_3 and, Na_2SO_4 . PNIPAM-co-30% AAc microgels exhibited a significant response to 5 ppm NaNO_3 in addition to responding to all the same salts as PNIPAM-co-10% AAc microgels. PNIPAM-co-VAAc responded in a similar manner to PNIPAM-co-10% AAc while PNIPAM-co-APMAH did not show a response to any salt at any of the concentrations studied. Furthermore, we compared the chromaticity coordinates for mid-range concentrations of all salts studied, thereby simulating a complex matrix containing more than one salt. While many salts showed overlapping responses, NaHCO_3 appeared to show a significantly different response to all other salts studied with PNIPAM-co-10% AAc microgels. These preliminary results indicate that etalon devices assembled with AAc and VAAc containing-PNIPAM-based microgels can be used as a Boolean detector for certain salts and that NaHCO_3 may be identified from a more complex aqueous matrix.

17. Community Engagement In Constructed Wetland Design: Current Results And Future Directions

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It is not only beneficial but imperative for firms to consider stakeholders who are impacted by firm operations. Our research focuses on consideration of a particular kind of stakeholder group: community. This project has three distinct stages. In this first stage of our study, we theorized and demonstrated the relative impacts of community engagement method on individual and group measures of the three elements of corporate social responsibility (CSR): environment, economics, and society. In this stage, we worked with the Resilient Reclaimed Land and Water Systems theme science team to identify constructed wetland designs that are being considered. Four were identified: Naturally Constructed, Free Surface Horizontal Flow, Sub-surface Horizontal Flow, and Sub-surface Vertical Flow. We then elicited feedback about those designs from community stakeholders via two methods: transactional, one-way town hall forums and collaborative, co-design engagement. Our findings show that we were able to reach better multimodal outcomes with the collaborative co-design engagement than the transactional, town hall forum.

In stage two, our current stage, we are looking at the effects of community expectations being violated by project proponents. To do this, we look at three social measures: perceived procedural justice, cohesion, and trust, at the individual and group level. These are measured before and after the violation. The violation treatment is that community members are told that the selected wetland design for the project was different than the one the group preferred. The violation is either high (very different from the wetland design selected by the group) or low (somewhat different from the group's selected design). We compare the impact on the social measures for groups engaged via the transactional town hall and the collaborative co-design forums. While we predicted that the stronger social-psychological contract built during collaborative co-design engagement would result more disengagement, so lower social measure scores, following a violation, our preliminary results indicate that social measures drop regardless of engagement type. Moreover, in our preliminary analysis, the scores for cohesion and trust were still significantly higher for those engaged via collaborative co-design than those engaged via a town hall forum. These finding will require further analysis to confirm and unpack.

Stage three of this research project is our future directions. Perhaps concurrently, we plan to further explore our preliminary findings from the first two stages by engaging stakeholders via an online stakeholder scenario study and to further explore community engagement and consequences by studying a real case of community engagement around a constructed wetland in Alberta's North.

18. Constructed Wetland Novel Materials Life Cycle Assessment Mapping

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Our overarching research objective is to address the problems created with our current energy system and create a cleaner, more efficient, and sustainable path moving forward. Specifically, we do this by analysing novel materials that are intended to be deployed as a treatment and remediation tool for oil sands process water in constructed wetlands. We do this by using a Life Cycle Assessment (LCA) tool called OpenLCA. Using this software, we can determine the material, chemical, water, and carbon inputs and outputs involved in manufacturing these novel materials. We worked with scientists and engineers in the Land and Water Reclamation Theme to build pilot process maps for two materials: biochar derived from agricultural waste, and keratin filaments sourced from chicken feathers. Using OpenLCA we are in the process of inputting our map of the manufacturing process, from acquiring the raw materials or feedstock from industry, to treating it chemically or mechanically within the laboratory, to running quality control and characterization experiments, to shipping and deploying this product in the field. Once this framework or map has been built, we will then pair each step with pertinent data collected about the material and steps in our map. This data helps us determine the energetic, carbon, heat and environmental costs at each step in the process and cumulatively, for the life cycle of the material. Using this information, we can determine and compare the net environmental benefit and costs of the manufacture and use of these novel materials as well as potential monetary costing down the road. The feedstock for most of these novel materials are waste products from other industries such as sawdust, sludge or chicken feathers. As such, if our LCA demonstrates a net positive effect on the environment after the amount of work and treatment that must occur to the product in the laboratory, it would be an absolute game-changer to the future of environmental remediation.

The implications of this research could be substantial, as it may be useful in clarifying the value of these novel materials, as well as helping get them to market. This information will be useful for the scientists who have produced these materials, as they can then make more informed decisions from an economic perspective about which novel materials to pursue for commercialization and environmental benefit. Information from the life cycle and cost analyses of these novel materials can be used to determine which novel material is the optimal candidate for commercialization. Outcomes from the LCA stage of this study will also be used in the future for stage two of our entrepreneurial pitch experiment, where we take the most economically viable materials and pitch their development to venture capitalists to see what makes them bite. These experiments will be designed to determine which information is best for acquiring the funding needed to support and develop these materials and get them to market.

19. Economic Analysis Of Oil Sands Process-Affected Water Treatment In Alberta

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An ongoing problem with the mining of bitumen in northern Alberta has been the accumulation of large volumes of oilsands process water (OSPW) in fluid tailings ponds. The OSPW is a complex mixture of suspended solids (sand, silt, clay) and residual bitumen with some toxic organic chemicals and elements that contributes to the emission of green house gases, could cause damage to underground water reservoirs, migrating birds, local fauna and affect the wellbeing of indigenous communities. One of the key problems in the treatment of the tailings is the long time it takes for the fine silt and clay portions of the suspension to settle (up to 30 years). This has led to a large accumulation of fluid tailings which currently occupy an area of 220 km² and a lengthy delay in reclamation of oil sands mines.

The present study main objective is to design and conduct an economic evaluation of a set of industrial scale options that use various plausible mixtures of active and passive treatments based on new technologies. Additionally, it will evaluate current policies in Alberta and examine how incorporating economic incentives might improve policy outcomes for the province on terms on reclamation. Furthermore, a set of policy frameworks that include status quo and alternative incentive-based systems will be constructed and incorporated in “economic valuation research” that will examine the acceptability of alternative approaches to policy and technology outcomes. This will allow to obtain the non use values of the land affected by the oilsands extraction activities.

To estimate the amount of OSPW by the end of each project, the study uses historical data and the water balances available for each project, as well as secondary sources. We observed that OSPW remained relatively stable for each project as approximately 91% of the water use in the production process comes from recycled water sources. By considering that the technology to extract water from the fine and mature fluid tailings will not suffer significant changes over the next 40 years, we obtain an approximation of the amount of OSPW that will need to be treated in each project (Figure 1). These values will be used to estimate the cost of applying different bundles of water treatment technologies (i.e., active, passive, or hybrid approaches) over time periods to each surface mine project in Alberta. The cost estimates will allow us to identify the most cost-efficient technologies for treatment, as well as different scenarios for land-water reclamation including pit-lakes, wetlands, and reforestation or combinations.

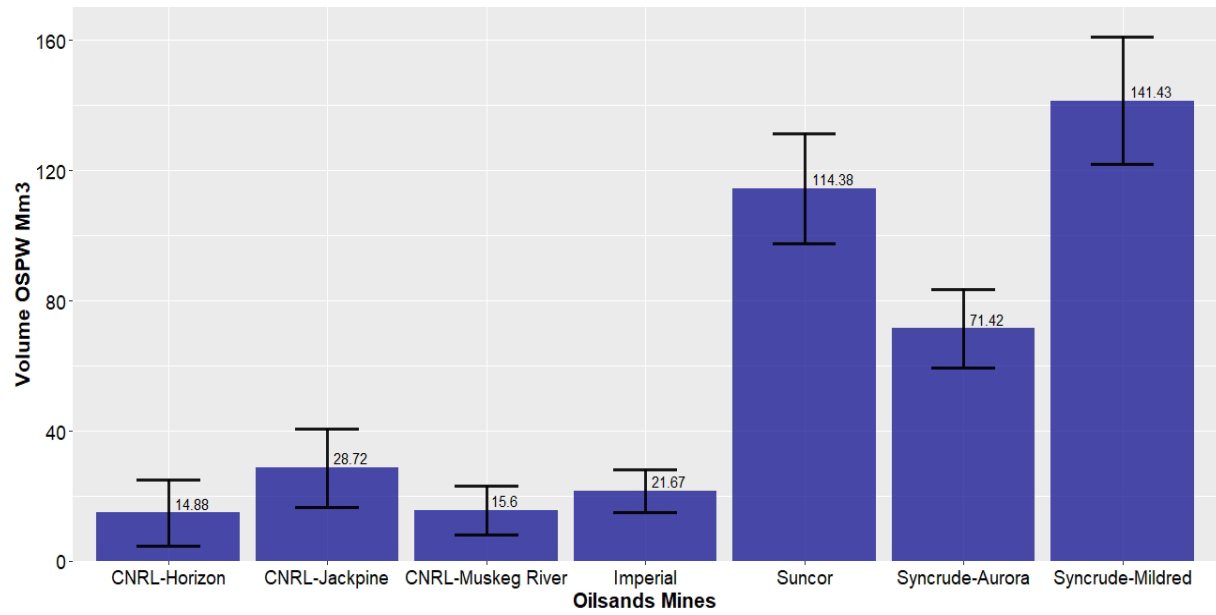


Figure 1. Estimated volume of oil sands process water (OSPW) requiring treatment (+/- 2 SD)