DEVELOPMENT OF TREATMENT TRAIN BASED ON GREEN TECHNOLOGIES FOR REMOVAL AND RECOVERY OF NAPHTHENIC ACIDS FROM OIL-SAND PROCESS AFFECTED WASTEWATER

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Each day large volumes of oil sands process-affected water (OSPW) are being produced during the extraction of bitumen in oil sands industry in northern Alberta. OSPW contains different polyaromatic hydrocarbons (PAHs), bitumen, as well as naphthenic acids (NAs), which not only are the major source of toxicity in OSPW, but also create operational problems such as corrosion of the equipment during bitumen recovery process. A recent figure indicates that about 720 billion liters of OSPW that were produced during the extraction of bitumen from Canadian oil sands industry have been stored in tailing ponds that cover approximately 170 km^2. Water treatment and management strategies are urgently needed for OSPW recycling in order to reduce the withdrawal of fresh water from the Athabasca River and to permit the safe release of treated OSPW to the receiving environment by removing these compounds. OSPW is highly saline water with myriad of organic and inorganic constituents, including metals, anions, organic compounds, and suspended particles.

Among all the different treatment methods, adsorption has gained significant attention due to its efficiency and fast removal rates. Recent studies on petroleum coke (PC), a relatively inexpensive and abundant feedstock, used as an adsorbent after activation, have brought renewed attention to the use of adsorption processes for OSPW treatment. The coagulation/flocculation (CF) process is widely used as a pre-treatment to other processes including adsorption. Besides adsorption, desorption of exhausted adsorbents is crucial to naphthenic acids recovery due to various industrial applications. The unique properties of the metallic soaps of naphthenic acids account for the major uses of the acid. The salts of naphthenic acids (alkali naphthenates) are applied as both emulsifying and demulsifying agents. The metallic naphthenates have also found industrial application in the fields of preservatives and driers. Copper and zinc naphthenates are effective insecticides and fungicides, and solutions of these salts in petroleum solvents are available commercially.

In this work, a treatment train of OSPW based on green processes is being developed and tested for pilot scale application. The train contains a pre-treatment process based on bio-coagulation, adsorption based on surface modified petroleum coke, regeneration of spent adsorbent and recovery of sorbed naphthenic acids, and toxicity analysis of the final effluent based on bioassay. Aluminum and iron salts and synthetic polymers are by far the most widely used coagulants in water and wastewater treatment. However, chemical cost and health hazards such as Alzheimer's disease (associated with residual aluminum in treated waters), large sludge volumes, and decrease in pH of water are some of the disadvantages of using a chemical coagulant. Although, trivalent aluminum coagulants, such as polyaluminum chloride (PAC) and polyaluminum silico sulphate (PASS) have improved the coagulation process considerably, they have not removed all the drawbacks mentioned earlier. Biocoagulants are natural polymer that can be a viable alternative for C/F pre-treatment of OSPW. Scientific understanding of the effectiveness and mechanism of natural coagulants of plant origin is crucial for large scale application of this process. Several indigenous biocoagulants are being tested for the removal of turbidity, dissolved organic matter and ions, and naphthenic acids.

Petroleum coke, or petcoke, is a byproduct of upgrading bitumen to crude, and a large amount of petcoke is being produced around the world. Petcoke is stable and non-toxic and can be used as feedstock for tires, batteries and steel, and adsorbents. However, raw petcoke has insignificant surface area and requires surface modification before it can be used as an adsorbent. In this work various surface modification methods are adopted and optimized to improve the surface hydrophobicity and polarity for removal of organics which can be adsorbed either due electrostatic or van Der Waal's interactions. Initially, temperature, KOH/Coke ratio, and the activation time were varied to maximize the surface area of petcoke. BET results show a significant increase of petroleum coke (PC) surface area from 12 to 1443 m^2/g during KOH activation, and mostly mesopores contributed to the increase in total surface area. Surface area modification method such as treatment with ammonia improved both the kinetics and equilibrium adsorption for both model naphthenic acids from synthetic wastewater and real OSPW. The effects of process variables such as initial concentration, pH, and presence of background ions are being evaluated in both batch and continuous adsorption. Kinetic and equilibrium models are being developed for modeling and scaling up of the process. The optimized adsorbents are pelletized for continuous treatment of real OSPW.

For the regeneration and recovery of naphthenic acids, various concentrations of solvents such as ethanol, methanol, and diethyl ether in presence of dilute concentration of NaOH were applied. 10% Methanol solution with NaOH was found to be the most green regeneration solution based on decision matrix with regeneration efficiency 60-80% for five regeneration cycles. The regenerate solution is concentrated using vacuum evaporation of the solvent and sodium salts of naphthenic acids are recovered and purity of the salt is being established.

Finally, the toxicity of the treated effluents are being evaluated using two freshwater algae species, chlorella vulgaris and chlamydomonas reinhardtii. Toxic effect was measured in terms of the growth rate (GR) of the algae species at their exponential phase. This work demonstrates several aspects of green processes such as: (i) use of inexpensive and indigenously available biocoagulant (ii) waste such as petcoke utilization in removal and recovery of another waste (naphthenic acids), (iii) optimization of process chemistry to obtain maximum surface area using least amount of inexpensive and harmless chemicals, and (iv) recovery of spent adsorbent using green solvent that can be easily reused.