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COMPARISON OF UV/HYDROGEN PEROXIDE, FERRATE(VI), AND OZONE IN OXIDIZING OIL SANDS PROCESS-AFFECTED WATER (OSPW)

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1 Introduction

Oil sands process-affected water (OSPW) is the water produced in the bitumen extraction and the following upgrading processes. Its composition is very complex, especially the organic fraction. The organic fraction of OSPW contains classical naphthenic acids (NAs), sulfur and nitrogen containing species, and aromatic compounds including trace amount of polyaromatic hydrocarbon (PAH) (Jones et al. 2013). NAs refers to a mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids, with a general formula $C_nH_{2n+z}O_x$, where n indicates the number of carbon atoms, z specifies the hydrogen deficiency arising from double bonds and/or rings, and x is the number of oxygen atoms (Mohamed et al. 2013). The high concentration and low biodegradability of the organic matters in OSPW prompted extensive chemical oxidation researches in OSPW treatment. However, a well-defined performance comparison among the different oxidation processes, especially between selective oxidation and unselective oxidation, is currently not available, mainly due to varying raw OSPW quality among different researches and different experimental designs. To fill this gap, this research compared the oxidation performance by UV/H₂O₂, potassium ferrate(VI), and ozone (with and without radical scavenger).

2 Objectives

The specific objectives of this study were as follows: (1) to compare the oxidation processes including UV/H₂O₂, potassium ferrate(VI), and ozone (with and without radical scavenger TBA) in transforming NAs and aromatics in OSPW; (2) to investigate the toxicity of the OSPW treated by different processes; and (3) to explore the oxidation mechanisms behind the performance differences.

3 Methodology

Batch reactors with rapid mixing were used in this study. All tests were conducted in duplicates. The dosage of potassium ferrate(VI), ozone, and H₂O₂ investigated in this study ranged from 0.1 mM to 4.0 mM.

4 Results

The findings of this research can be summarized as follows.

- Ozonation was the most effective process in treating OSPW, achieving almost complete removal of fluorescing aromatics, sulfur-containing NAs (NAs+S), and classical NAs (97.1%) at the dose of 2.0 mM O₃. Both pathways via direct ozone reaction and •OH reaction played important roles in transforming the organics, as supported by ozonation performance with and without TBA.
- UV/H₂O₂ oxidation was a combination of direct UV photolysis and •OH reaction. The efficiency of this process was compromised by the low molar extinction coefficient of hydrogen peroxide. 42.4% classical NAs were removed at a 2.0 mM H₂O₂ dose and 950 mJ/cm² UV dose.
- Ferrate(VI) oxidation showed high selectivity in removing two-ring and three-ring fluorescing aromatics, NAs+S, and NAs with high carbon number and high hydrogen deficiency. 46.7% classical NA removal was achieved at 2.0 mM Fe(VI).
- Acute toxicity towards *Vibrio fischeri* was reduced, with the order of efficiency as “O₃ > ferrate (VI) > UV/H₂O₂” at the same molar doses of the oxidants. In addition, toxicity on goldfish PKMs was also mitigated after all the treatments, with the order of efficiency as “O₃ > ferrate (VI) ≈ UV/H₂O₂”.
- The costs of treating 1 m³ of OSPW at chemical dose of 2.0 mM were estimated to be \$0.5, \$1.8, and \$0.4 for UV/H₂O₂ oxidation (UV dose: 950 mJ/cm²), ferrate(VI) oxidation, and ozonation, respectively. When NA removal is correlated to the chemical cost, it is apparent that ozonation is the most cost-efficient process in OSPW treatment.

5 Recommendations

Based on both the performance and the economic consideration, we recommend ozonation for OSPW oxidation. Based on the findings and unknowns regarding the mechanism study, we recommend the following for future studies. OSPW is a complex water matrix with various organic fractions. Understanding its composition is the precondition to explore the mechanisms behind its toxicity and to evaluate the performance of the water treatment technologies. Our NMR analyses indicated that the total concentration of aromatics in OSPW should be at the mg/L level, and very likely, these aromatics might be an important toxicity source in OSPW. It is advisable to work on exploring the concentrations, species, and the environmental impact of the aromatics in OSPW. Similarly, it is also essential for OSPW remediation to identify and quantify the sulfur and nitrogen containing species in OSPW with more analytical endeavors.

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