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Treating PAHs in Scrubber Washwater: an Investigation into Fenton-like Advanced Oxidation

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Abstract The maritime transport sector primarily uses fuel oil, leading to exhaust gas emissions that contain harmful substances like heavy metals and polycyclic aromatic hydrocarbons (PAHs), which pose risks to marine ecosystems. Exhaust Gas Cleaning Systems (scrubbers) are essential for complying with international emissions regulations, but the discharge of contaminated washwater presents a significant environmental challenge. This washwater, characterized by an acidic pH and the presence of metals and PAHs, contains naphthalene in high concentrations.

To address this issue, the evaluation and optimization of phenton-like advance oxidation processes that use two different approachs (with persulfate and hydrogen peroxide) to treat scrubber washwater are proposed. These technologies generate radicals with high oxidation potential, capable of eliminating hard-to-degrade compounds such as naphthalene. Activation will be carried out using UV light and transition metals, specifically iron and vanadium, which are already present in scrubber waters. Treatment effectiveness will be measured by analyzing naphthalene degradation at different metal concentrations, simulating conditions found in these systems.

Keywords: scrubber washwater, fenton-like, AOP, naphthalene, metals

1. Introduction

While Exhaust Gas Cleaning Systems (EGCS), or scrubbers, are indispensable for the maritime industry to comply with emissions regulations, the discharge of their contaminated washwater creates a serious environmental problem. EGCS washwater contains a complex range of pollutants—such as heavy metals, PAHs (polycyclic aromatic hydrocarbons), and inorganic compounds—that pose a risk to marine ecosystems (Picone et al., 2023). PAHs are particularly concerning due to their toxicity and persistence, with their concentration increasing in the effluents of closed-loop systems where water is recirculated (Teuchies et al., 2020). Despite the urgency, knowledge regarding the composition of this washwater and its environmental repercussions remains scarce (García-Gómez et al., 2023; Teuchies et al., 2020), which has led to a growing number of countries prohibiting its discharge in their ports.

To mitigate environmental impact and ensure regulatory compliance, developing efficient treatment technologies is crucial. Advanced Oxidation Processes (AOPs) show promise for removing PAHs (polycyclic aromatic hydrocarbons), given their ability to degrade persistent organic compounds (Chen et al., 2019). This study will focus on evaluating the effectiveness of Fenton-like AOPs for PAH removal in synthetic wastewater. The process leverages conditions already present in scrubber washwater (low pH, high temperature, and transition metals), combining them with UV light and H_2O_2. The results obtained will offer valuable insights into the potential of AOPs for treating PAH-contaminated scrubber effluents.

2. Material and methods

Synthetic scrubber water was used to study the degradation of single contaminants, with naphthalene (NPT) chosen as a representative PAH. Iron (Fe) and vanadium (V), commonly detected in washwaters, were selected as catalysts, and hydrogen peroxide and persulfate were used as oxidants. UV radiation was applied using a UV-LED reactor emitting at 265 nm with average irradiance of 0.765 mW/cm2 (Photolab LED 265-0.1-cb, APRIA Systems S.L). Experiments were conducted with varying concentrations of oxidants and catalyst, and NPT degradation (initial concentration: 0.1 mg/L) was monitored over time using Excitation-Emission Matrices (EEM), calibrated with GC-MS.

3. Results and discussion

Figure 1 presents results of NPT degradation experiments, comparing photo-driven processes with H_2O_2 as the oxidant and the effects of Fe and V as catalysts, both separately and together. NPT degradation by H_2O_2 photolysis showed a moderate rate (0.027 min-1). The addition of Fe significantly increased the rate to 0.152 min-1, while V alone slowed degradation. The combination of Fe and V accelerated the process to a rate similar to UV/H2O2/Fe (0.071 min-1), reducing NPT half-life to

below 10 minutes in photo-catalytic systems, compared to 25.21 minutes with UV/H_2O_2 alone.

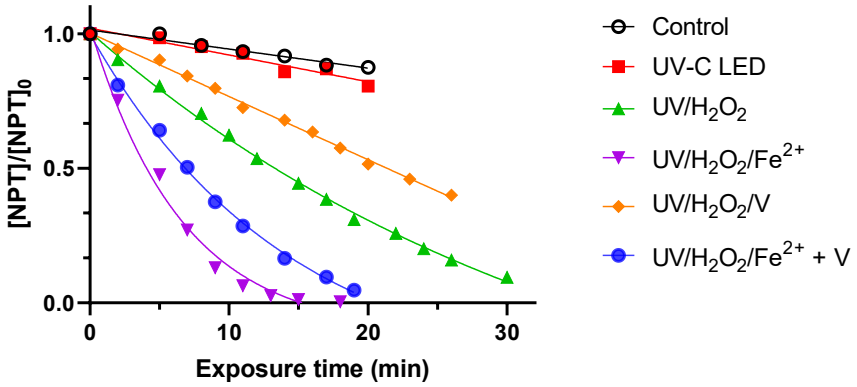

Figure 1. NPT degradation profile in synthetic EGCS washwater under different photo-driven processes: UV-C, UV-C/H2O2, UV-C/H2O2/Fe^{2+}, UV-C/H2O2/V, and UV-C/H2O2/ Fe^{2+}+V. Experimental conditions: [Fe2+] = 0.25 mg·L-1, [V] = 8 mg/L, [H2O2] = 10 mg/L, [NPT]0 = 0.1 mg/L, initial pH = 3.8.

On the other hand, preliminary results with persulfate showed that vanadium, in the presence of PDS (persulfate) and ultraviolet (UV) radiation, promotes faster and more efficient naphthalene degradation than iron. With vanadium, nearly complete degradation is achieved in a shorter exposure time.

4. Conclusions

The findings indicate that scrubber washwater's inherent properties, particularly its iron (Fe) content, make it well-suited for Fenton-like processes. While vanadium (V) has been suggested as an alternative catalyst (Cheng et al., 2023), its high concentrations in EGCS washwater appear to hinder degradation when using H_20_2 but enhance it when using PDS.

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