

Catalytic Peroxidation as a Feasible Approach to O-Phthalaldehyde (OPA) Oxidation in Wastewater

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Improper discharge of disinfectants to sewerage and wastewater treatment plants can cause acute intoxication and chronic low-dose exposure, which can promote the development of antibiotic resistance. Ortho-phthalaldehyde (OPA) is a commonly used high-level disinfectant for heat-sensitive, semi-critical medical devices in hospitals and clinical establishments, which is frequently discharged to the sewer network without a proper treatment.

The aim of this study was to evaluate for the first time the feasibility of treating OPA with catalytic peroxidation processes. The homogeneous Fenton oxidation, along with the heterogeneous Fenton-type process using a catalytic bed of Prussian Blue nanoparticles supported on alumina spheres (PBNP/ γ -Al₂O₃) were explored. Results demonstrated that, under appropriate operating conditions, a 180 min treatment could be effective to achieve a free OPA and non-toxic solution, with a low Dissolved Organic Carbon content, no residual H₂O₂, and no sludge.

Introduction

There is increasing concern regarding water quality due to emerging contaminants entering ecosystems through untreated effluent discharge. The extended disinfectant usage, especially in healthcare establishments to combat pathogens, poses risks of environmental contamination and disease dissemination. Improper disinfectant application can lead to sub-lethal concentrations, microbial resistance and decreased effectiveness of antimicrobial agents. To address the limitations of traditional biological treatments in the presence of toxins, innovative solutions are needed for the safe disposal of disinfection byproducts.

Among Advanced Oxidation Treatments, the Fenton process stands out for its simplicity, gentle or moderate operating conditions, cost-effectiveness, availability, and low toxicity of reagents [1]. However, its implementation often faces challenges such as potential formation of insoluble complexes between iron ions and organic matter, and the generation of sludge, which limit the treatment success [2, 3]. Alternatively, the use of heterogeneous catalysts can mitigate these issues by reducing sludge formation and allowing easier recovery and reuse. This study explores, for the first time, the feasibility of using catalytic peroxidation processes to oxidize commercial solutions of o-phthalaldehyde (OPA), a commonly used high-level disinfectant for heat-sensitive, semi-critical medical devices in hospitals and clinical establishments.

Material and Methods

The Homogeneous Fenton (HF) experiments were conducted in a thermostated agitated batch reactor. The reactor was filled with 150 mL of OPA solution at a known concentration and pH = 3. Once the desired temperature was reached, the reaction was initiated by adding ferrous sulfate and H₂O₂.

The Heterogeneous Fenton-type (HFT) oxidation

was investigated using a liquid batch-recycle reactor. The reactor consisted of an 11 mm ID glass column containing 5 g of randomly packed "insoluble" PBNP/ γ -Al₂O₃ catalyst, prepared as described in [4]. To start each test, 200 mL of OPA solution with a known concentration and pH = 3 were introduced into a reservoir. H₂O₂ was added and allowed to mix. The initial sample was collected, and the liquid flow through the reactor, set at 2.2 L/h, was initiated using a peristaltic pump. Temperature was maintained at 70°C by submerging the system in a thermostatic bath.

In both, HFT and HF processes, liquid samples were periodically taken out from the reservoir or the reactor and analyzed at once in terms of pH, UV-Vis spectrum, OPA, H₂O₂, total dissolved iron (TDI) and Dissolved Organic Carbon (DOC) concentrations.

Analytical techniques: H₂O₂ concentration was determined by a Glycemia enzymatic test (Wiener Lab.). OPA concentration was determined by gas chromatography in a Hewlett-Packard 5890 series II, equipped with a FID detector and a capillary column. TDI concentration was assessed by measuring the total iron content of filtered samples with the o-phenantroline method [5]. DOC was measured in a Shimadzu TOC-VCPN analyzer. Shimadzu UV-1800 spectrophotometer was used to obtain the UV-Vis spectrums between 190 and 800 nm. The carboxylic acids formed were quantified by ion-exclusion in an HPLC (Shimadzu LC-20AT) equipped with a Rezex ROA-Organic Acid H+ (8 %) 300 × 7.8 mm (Phenomenex) column. Toxicity was assessed by measuring the inhibition of respiratory activity (I_{SOUR}) of activated sludge system (ISO 8192 method).

Results and Discussion

Different homogeneous alternatives for treating OPA 1000 mg L⁻¹ (DOC = 700 mg_{DOC} L⁻¹) were evaluated.

The order of addition of Fenton reagents was crucial for the feasibility of HF treatment, with the oxidant needing to be added last. Using 80 mg L⁻¹ of Fe⁺² and the stoichiometric dose of H₂O₂ necessary to mineralize initial OPA, yielded excellent results (Figure 1).

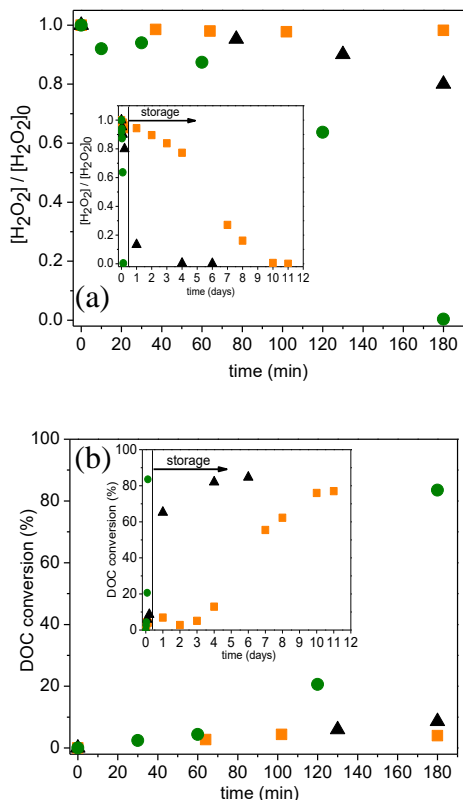


Figure 1. Temporal profiles of (a) normalized H₂O₂ concentration and (b) DOC conversion along the temperature-controlled process at T=(■) 30°C, (▲) 50°C and (●) 70°C for 180 min. Inset: Profiles during the storage stage at room temperature, without stirring and in darkness. Conditions: [OPA]₀ = 1000 mg L⁻¹, pH₀ = 3, [Fe⁺²]₀ = 80 mg L⁻¹, [H₂O₂]₀ = 135 mmol L⁻¹

Conclusions

This study demonstrated the feasibility of treating OPA solutions with highly oxidizing species generated in AOPs. Further work is being conducted to identify suitable operating conditions to effectively treat hospital disinfection wastewater to ensure its safe disposal into the sewer network.

Acknowledgments

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Complete H₂O₂ consumption, 100% OPA degradation, 77-85% mineralization and no toxicity ($I_{SOUR} \leq 0\%$) were achieved. Sludge formation was observed accompanied by a low oxidant consumption rate. The formation of carboxylic acids as intermediates, promoted a gradual increase in TDI concentration, favoring oxidant consumption and DOC conversion. The time required to attain these results depended on the operating temperature during the first 180 min (30°C, 50°C or 70°C). A storage stage (without stirring, dark and room temperature) was needed for reactions conducted at 30 and 50 °C, whereas a 180 min treatment was enough at 70°C.

These results indicate the potential for further investigation into HFT oxidation. The catalyst based in supported Prussian blue nanoparticles (PBNP/ γ -Al₂O₃) showed to be active in the HFT oxidation of OPA solutions (Figure 2). A solution of 1000 mg L⁻¹ could not be effectively treated with 5 g of catalyst, resulting in a solution with toxicity ($I_{SOUR} = 76\%$), despite 57% of mineralization was attained. In contrast, 95% of mineralization and a non-toxic solution ($I_{SOUR} = 0\%$) was achieved when treating a solution of 100 mg L⁻¹ in 180 min. These findings demonstrate that a non-toxic solution can be achieved under appropriate operating conditions.

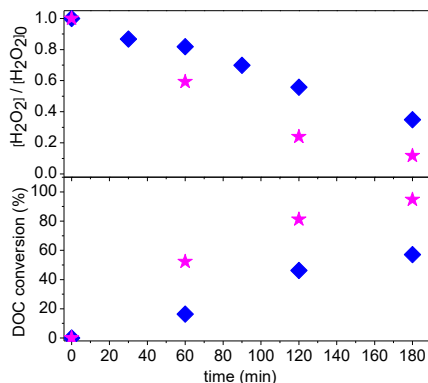


Figure 2. Evolution of normalized H₂O₂ concentration and DOC conversion in the HFT oxidation of solution with [OPA]₀ (◆) 1000 mg L⁻¹ and (★) 100 mg L⁻¹. [H₂O₂]₀ = 14 mmol L⁻¹.