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Coupling of Fenton and Biological Processes for Pulp Bleaching Wastewater Treatment

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Abstract - In this work, Fenton and biological aerobic processes were sequentially coupled for real pulp bleaching wastewater treatment. Biological treatment was conducted on raw pulp bleaching wastewater and on Fenton-treated wastewater, to search for a suitable treatment layout allowing for COD and recalcitrant pollution abatement. Biological treatment was conducted in 0.5 L glass flasks, under magnetic stirring and temperature of 20º C. A ratio of COD:N:P = 100:7:1 was used, with initial concentration of volatile suspended solids of 3 $g \cdot L^{-1}$. Different initial loads as soluble COD were tested. Fenton process experiments (0.5 L batch) were conducted under natural wastewater pH of 2.48 ± 0.20, 60 ºC, 6.0 mM of Fe^{2+} (as $FeSO_4.7H_2O$) and 139 mM of H_2O_2. The combination of processes successfully removed COD and AOX from both raw pulp bleaching wastewater and Fenton-treated wastewater, achieving the highest removals with the highest initial organic loads. Maximum removal of AOX of 94 % was achieved in the wastewater undergoing Fenton treatment followed by biological treatment, while the highest removal of COD was achieved in the wastewater submitted to biological treatment followed by the Fenton process, 84%, with a final concentration of 0.48 $g\ _sCOD \cdot L^{-1}$.

Keywords: Fenton, Biological treatment, AOX, COD, Pulp bleaching wastewater

1. Introduction

Biological aerobic treatment aims at the oxygen-assisted degradation of organic load by microorganisms, producing production of biomass, carbon dioxide and water [1]. The mechanism consists in three steps: adsorption by contact between the compounds present in the wastewater with the microorganisms; metabolism, which is the degradation of the contaminants through biochemical reactions; flocculation, consisting in the agglomeration of the biological material, yielding a settable sludge [2]. This process targets primarily the removal of COD and BOD_5 from the wastewater, however it does not present a high efficiency in the decomposition of recalcitrant compounds [2]. Fenton process is a widely studied method for wastewater treatment, recognized for its fast and effective abatement of recalcitrant pollution. It is based on the catalytic (Fe^{2+}) dissociation of H_2O_2 into hydroxyl radicals ($^{\bullet}OH$), which non-selectively oxidizes organic compounds [3]–[5].

Brink, Sheridan and Harding (2020) [6] used a combination of aerated biological treatment, in a moving bed biofilm reactor, followed by Fenton experiments run in batch reactors, for the treatment of pulp and paper industry wastewater. A 55 % removal of COD was achieved under hydraulic retention time (HRT) of 24 h, using and organic loading rate ranging 4.52 kg $COD \cdot m^{-3} \cdot d^{-1}$ to 9.04 kg $COD \cdot m^{-3} \cdot d^{-1}$, 3.1 $mg \cdot L^{-1}$ of dissolved oxygen, and pH ranging 8.0 to 8.5. The Fenton process was applied to the wastewater under 14.55 mM of H_2O_2, 17.91 mM of Fe^{2+} and pH = 3.33, with an additional 53.73 % degradation of COD after 60 min of treatment. Abedinzadeh et al. (2018) [7] used a sequential batch reactor followed by the Fenton treatment for the removal of COD from a pulp and paper wastewater. The SBR worked under 2 mg $O_2 \cdot L^{-1}$, VSS (volatile suspended solids) = 3 $g \cdot L^{-1}$, solids retention time of 20 days and HRT of 24 h. Removal of COD and colour of 74.8 % and 58.3 % was achieved, respectively. The combination of this treatment with the Fenton process (6.0 mM H_2O_2 and 3.0 mM Fe^{2+}) led to an overall COD and colour removal of 98 % and 94%, respectively.

This work aimed at tackling one major issue in this field of research: how to include in wastewater treatment plants a step that effectively removes recalcitrant compounds, without hindering biological reactor's activity. Biological treatment was conducted on raw pulp bleaching wastewater and on Fenton-treated pulp bleaching wastewater, to search for a suitable treatment layout allowing for COD and adsorbable organic halides (AOX) abatement.

2. Materials and Methods

The pulp bleaching wastewater – D_0 stream, after the first chlorine dioxide bleaching stage – was collected at a Portuguese pulp and paper industry that produces kraft pulp, mainly from *Eucalyptus globulus*. Biological sludge was collected at the wastewater treatment plant of the same industry. Biological aerobic treatment and Fenton process were coupled sequentially to remove COD and AOX from the collected pulp bleaching wastewater, according to the treatment layouts presented in Figure 1.

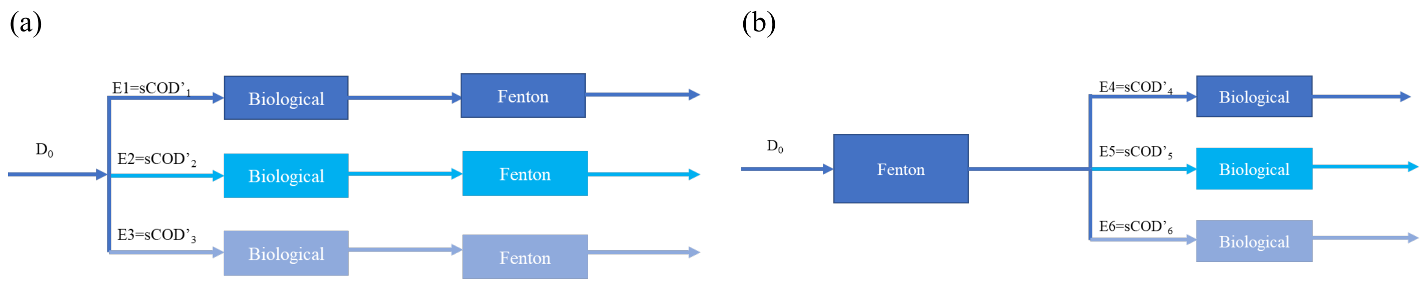

Figure 1. Schematic of the experimental planning for the combination of: (a) biological treatment followed by Fenton process and (b) combination of the Fenton process followed by biological treatment.

Biological treatment was conducted in 0.5 L glass flasks, under magnetic stirring, at 20º C, for five days. pH was adjusted to 6.5 – 7.5 at the beginning of the treatment, using 2.0 M NaOH and/or 32.5% HNO_3. Nutrients N and P were added to the flasks as 10 $g·L^{-1}$ NH_4Cl and 5 $g·L^{-1}$ KH_2PO_4, respectively, to ensure for COD:N:P of 100:7:1. Initial VV load of 3 g $VSS·L^{-1}$ was used. Wastewater was diluted to study the effect that initial organic load and/or the presence of inhibitory chemicals (for microbiological activity) could have on treatment efficiency. Dilution factors of 2.6 (E1 and E4), 1.7 (E2 and E5) and 1 (E3 and E6 – undiluted) were applied.

Fenton process experiments (0.5 L batch) were conducted under wastewater pH of 2.48 ± 0.20, which favours Fenton's effectiveness [5]. Regarding temperature, Fenton experiments were conducted at 60 ± 2 ºC, which is the natural temperature of this wastewater stream. When the wastewater reached the desired temperature, 6.0 mM of Fe^{2+} (as $FeSO_4.7H_2O$) and 139 mM of H_2O_2 (30 % w/v) were added. These operating conditions aimed at maximising AOX removal, as described elsewhere [8]. Magnetic stirring was maintained throughout the experiments at 200 rpm. Results previously published showed that AOX removal did not increase significantly with treatment time ranging 10 – 30 minutes [9], therefore Fenton experiments conducted in this work lasted for 10 minutes.

COD and AOX were measured according to Standard Methods 5220D and EN 16166:2012, ISO 9562:2004 and EPA Method 1650C [10]. Measurements were performed in the raw wastewater, and after each treatment step.

3. Results and Discussion

3.1. Biological Treatment Followed By Fenton Process

The dilution factors applied to raw pulp bleaching wastewater aimed at initial $_{s}COD·L^{-1}$ ranging 1.50 – 3.00. Experimental verification was performed, showing that initial COD loads for E1, E2 and E3 experiments were 1.59 g $_{s}COD·L^{-1}$, 2.07 g $_{s}COD·L^{-1}$ and 2.99 g $_{s}COD·L^{-1}$, respectively. After biological treatment, 0.74 g $_{s}COD·L^{-1}$, 0.96 g $_{s}COD·L^{-1}$ and 1.18 g $_{s}COD·L^{-1}$ were registered in those conditions, corresponding to removal of 54 %, 54 % and 61 %, respectively. These results show slightly higher removal rate with increasing initial organic load, proving the suitability of biological aerobic process to treat pulp bleaching wastewater. Additionally, AOX removal of 66 %, 64 % and 58 % were attained in conditions E1, E2 and E3, corresponding to final values of 5.33, 7.59 and 12.63 mg $AOX·L^{-1}$, respectively. As AOX acts as a co-substrate, with a higher increase in COD in the wastewater, leads to a decrease in its removal rates. The application of Fenton process to the biologically treated wastewater led to additional COD removal of 77 %, 64 % and 59 %, and AOX removal of 74 %, 81 % and 76 %, for the conditions E1, E2 and E3, respectively. Therefore, after the combined treatment, final concentrations of 0.17g $_{s}$COD·L^{-1} and 1.40 mg AOX·L^{-1}, 0.35 g $_{s}$COD·L^{-1} and ^{1} and 2.44 mg AOX·L^{-1}, 0.48 g $_{s}$COD·L^{-1} and 3.00 mg AOX·L^{-1}, were achieved for the conditions E1, E2 and E3, respectively. These results are depicted in Figure 2.

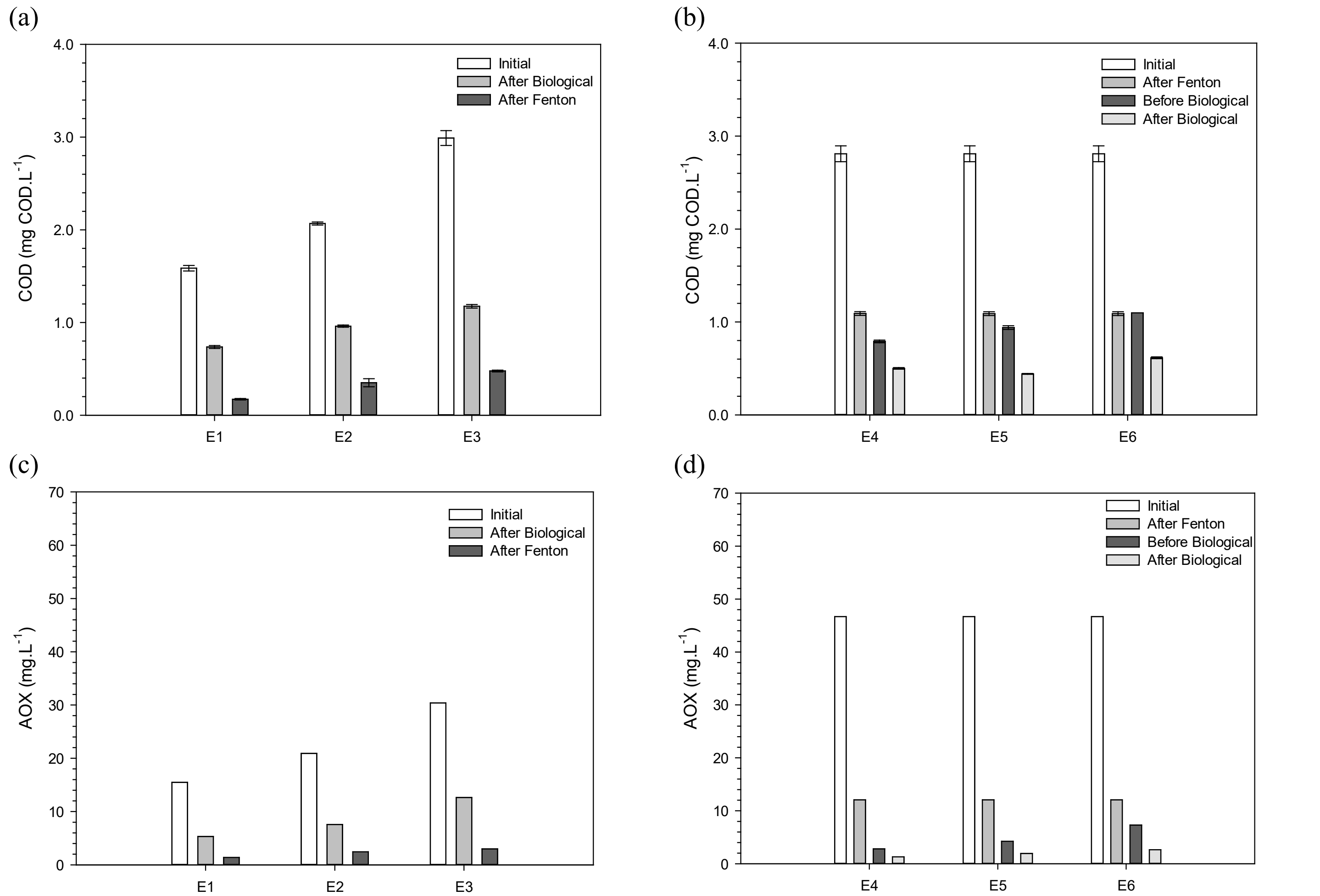

Figure 2. Concentration of: (a) COD at different stages of biological treatment followed by Fenton process; (b) COD at different stages of Fenton process followed by biological treatment; (c) AOX at different stages of biological treatment followed by Fenton process; (d) AOX at different stages of Fenton process followed by biological treatment.

3.2. Fenton process followed by biological treatment

Fenton process removed 66 % COD from the raw pulp bleaching wastewater, corresponding to final concentration of 1.09 g COD·L^{-1}. The subsequent dilution of the Fenton-treated wastewater was made to evaluate the presence of products resulting from the Fenton process that may act as inhibitors of microbiological activity. The same dilution factors were applied as before, leading to initial organic loads of 0.79 g $_{s}$COD·L^{-1}, 0.94 g $_{s}$COD·L^{-1} and 1.10 g $_{s}$COD·L^{-1}, for the experiments E4, E5 and E6, respectively.

Subsequent biological treatment achieved COD removal of 36 %, 53 % and 44 %, for experiments E4, E5 and E6, corresponding to final concentration of 0.50 g $_{s}$COD·L^{-1}, 0.44 g $_{s}$COD·L^{-1} and 0.61 g $_{s}$COD·L^{-1}, respectively. This treatment also removed 54 %, 54 % and 64 % of AOX, achieving final concentrations of 1.29 mg $AOX \cdot L^{-1}$, 1.95 mg $AOX \cdot L^{-1}$ and 2.66 mg $AOX \cdot L^{-1}$, in experiments E4, E5 and E6, respectively. These results are depicted in Figure 2.

4. Conclusions

Polluting load of the wastewater stream generated in the bleaching stage of the pulp production process was decreased by the combination of biological aerobic and Fenton processes.

The application of different initial organic loads allowed for the ascertainment of the biological sludge capacity to adapt and degrade both raw wastewater and chemically treated wastewater, with no apparent inhibition of microorganisms' activity. In fact, higher initial loads favoured the removal of COD and AOX, showing that the biological sludge was able to cope with high concentration of recalcitrant organic compounds and chemical products from Fenton reactions.

When comparing the two treatment layouts applied to undiluted wastewater (conditions E3 and E6), it was possible to conclude that the combined treatment yielded similar results, regardless of the adopted sequence: when Biological process was followed by Fenton process (E3), overall COD and AOX removal of 84 % and 90 % was achieved, corresponding to 0.48 g $_{s}COD \cdot L^{-1}$ and 3.00 mg $AOX \cdot L^{-1}$ in the treated wastewater; when Fenton process was followed by biological treatment (E6), overall COD and AOX removal of 78 % and 94 % was achieved, corresponding to 0.61 g $_{s}COD \cdot L^{-1}$ and 2.66 mg $AOX \cdot L^{-1}$ in the treated wastewater.

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