Low-Cost Fenton Catalyst For The Removal of Adsorbable Organic Halides From Industrial Wastewaters

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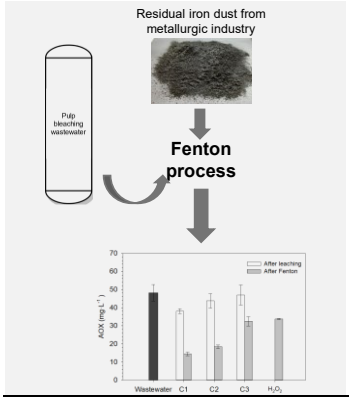

This work studied the removal of adsorbable organic halides (AOX) from pulp bleaching wastewater by Fenton process catalyzed by residual iron dust (RID) sourced from the metallurgic industry. The goal was to find a low-cost catalyst to increase the efficiency and competitiveness of the Fenton process. Reusability of RID was assessed under a simple collect-and-reuse methodology, without any modification between consecutive treatment cycles. The waste-derived catalyst allowed for similar AOX removal using less chemicals. Initial contact between RID and wastewater removed 11.4 – 13.2 % AOX; afterwards, Fenton process increased the overall AOX degradation to up to 66 %. Similar performance was observed over two consecutive treatment cycles.

Introduction

Fenton process is a well-studied advanced oxidation process, which main principles and advantages have been thoroughly discussed [1]. However, it is also subjected to some limitations: (i) high demand of chemicals, entailing high operating costs [2]; (ii) iron sludge formation [3]; (iii) catalytic activity limited by the Fe^{2+} – Fe^{3+} redox cycle [4]; and (iv) acidic condition (pH ranging 2.5 – 3.5) required to achieve maximum catalytic activity [5,6].

To overcome those drawbacks, recent research has focused on developing heterogeneous catalysts that could be easily separated from the treated wastewater and reused, whilst enabling operation under milder pH conditions and reducing the formation of iron sludge formation [7].

This work explored the innovative use of residual iron dust (RID) as Fenton catalyst. The waste material was applied without any pre-treatment, i.e., as a true low-cost waste-derived catalyst, under circular economy thinking. The focus was put on the removal of toxic and recalcitrant adsorbable organic halides (AOX) from real pulp bleaching wastewater.

Material and Methods

Pulp bleaching wastewater was sampled in a Portuguese pulp mill, immediately after the first pulp bleaching stage with chlorine dioxide since this stream typically exhibits the highest AOX concentration. RID was provided by a Portuguese metallurgical industry. Initially, RID was added to the wastewater, at previously defined optimal conditions (5 $g \cdot L^{-1}$, for 30 min) – the leaching step. Afterwards, H_2O_2 was added (100 mM in the reaction medium) to initiate Fenton reactions, which lasted for 10 minutes. Experiments were conducted under pH ≈ 2.5 and T = 60 °C, representing the conditions found in the pulp mill. At the end of treatment, supernatant samples were taken and immediately quenched with sodium sulphite to halt the reactions. RID was settled and collected after each experiment, dried, and reused in subsequent treatment cycles without further modification. Three consecutive treatment cycles were carried out. Additionally, a treatment assay was conducted with H_2O_2 alone, without catalyst. All treatment assays were performed in triplicate.

Results and Discussion

Figure 1 shows the concentration of AOX in the wastewater after heterogeneous Fenton process and after simple H_2O_2-oxidation over three consecutive treatment cycles.

The overall removal of AOX, encompassing both the leaching step and Fenton oxidation, was similar ($p < 0.05$) between the 1st and 2nd cycles: AOX concentration ≈ 15 $mg \cdot L^{-1}$, corresponding to 63.5 – 66.2 % removal. Those results show the successful reuse of RID without any intermediate regeneration step. In those cycles, the initial leaching step removed 11.4 % and 13.2 % of AOX from the wastewater, respectively. Downstream Fenton oxidation removed additional 62.1 % and 56.7 % AOX in the two respective cycles. Low removal by the RID may be explained not only by low affinity of the AOX molecules to this material, but also by the low surface area and porosity of RID particles.

In the 3rd cycle, overall AOX removal sharply decreased to 36.7 %, despite the AOX removed during the leaching step (8.4 %) did not differ

significantly from the previous cycles ($p > 0.05$). This reduction may result from catalyst surface deactivation owing to the occupation of the active sites by the organic intermediates from the wastewater, hindering the reaction between H_2O_2 and catalyst [8]. Another factor that may have possibly contributed to final AOX content was the desorption of organics from the RID surface to the wastewater and transport of organic compounds and fibers with the recovered RID particles between cycles. This increase in organics would compete with AOX for $^{\bullet}OH$ radicals, decreasing the treatment efficiency.

It must also be noted that RID-catalyzed Fenton process performed better than H_2O_2 alone (19.9 ± 1.1 % removal of AOX) in the 1st and 2nd cycles. In the 3rd cycle, the concentration of AOX in the treated wastewater was similar between heterogeneous Fenton and peroxidation. Additionally, control experiments were performed under conventional Fenton conditions, with iron being supplied as $FeSO_4.7H_2O$. AOX removal of those experiments did not differ statistically from the correspondent heterogeneous Fenton processes, showcasing the effectiveness of RID as substitute of conventional iron salts as source of Fenton catalyst.

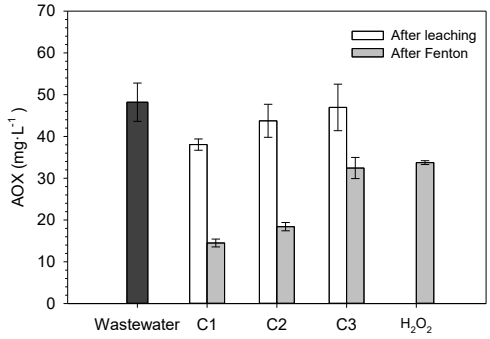

Figure 1. Concentration of AOX after Fenton treatment using RID as catalyst across three consecutive reuse cycles (C1 – C3), and after H_2O_2 treatment.

Conclusions

RID was successfully used as Fenton catalyst in the removal of AOX from real pulp bleaching wastewater. Catalyst dosage of 5 $g \cdot L^{-1}$ provided sufficient iron for the reaction to occur in the bulk solution, which was the main pathway of AOX removal. Global AOX removal of 63.5 – 66.2 % was observed over two consecutive treatment cycles, without any regeneration of the catalyst.

The solution presented in this work, aligned with circular economy principles, can contribute to reduce pollution, and increase industrial environmental performance and efficiency. Moreover, this work also shed some light on the potential of using wastes as true low-cost catalysts, without the need for high technology pre-treatment steps or synthesis processes. Further research should focus on increasing the reusability of this type of material and on its immobilization to facilitate post-use recovery and recycling.

Acknowledgments

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