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Waste printed circuit boards (PCBs) as catalysts in advanced water treatment by wet peroxide oxidation and ozonation

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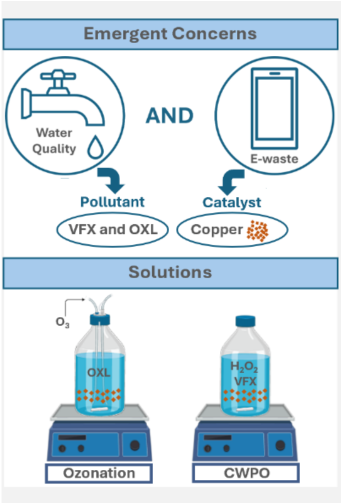

Recycled printed circuit boards (PCBs) were tested as catalysts for wet peroxide oxidation (CWPO - study A) and ozonation (study B) due to the high copper content of these materials (i.e., active phase). Study A targeted the removal of venlafaxine (VFX) at natural pH (~6.8) and at the pH known as optimal for the Fenton reaction (~2.8). Study B focused on the removal of oxalic acid (OXL) at natural solution pH (~3.5) and pH ~7.0. PCBs were submitted to thermal treatments under different temperatures (from 400 to 800 °C) and atmospheres (air or N_2) to remove impurities and improve the catalytic activity of these materials. The results of study A (CWPO) show that PCBs treated at 500 °C under N_2 achieved the fastest VFX removal at natural pH, with minimal copper leaching. Study B (ozonation) reveals that PCBs treated at 500 °C in air exhibited the quickest OXL removal at pH ~7.0. The thermal treatments effectively removed impurities from the original PCBs, these impurities causing secondary water contamination when leached to the liquid phase.

Introduction

Water contamination and scarcity are two relevant environmental issues affecting people worldwide, which has led to a growing demand for cost-effective water and wastewater treatment solutions. Ozonation and catalytic wet peroxide oxidation (CWPO) are among the advanced water treatment solutions with recognised effectiveness against several pollutants. Both processes benefit from the use of metal catalysts to improve their performance, although the use of metals needs to be avoided due to their environmental impact and growing scarcity in Earth's crust. The use of recycled e-waste appears as an opportunity to surpass such constraints. Printed circuit boards (PCBs) are e-waste that can be used as catalysts [1, 2], since these residues are rich in copper (Cu), among other metals that can be recycled for other purposes in line with sustainable management of resources. In this study, waste PCBs were tested as catalysts in CWPO to degrade venlafaxine (VFX) - an antidepressant detected in Portuguese surface waters [3], and in ozonation to degrade oxalic acid (OXL) - a persistent end-product typically formed by ozonation of other contaminants [4]. PCBs were tested as received and after being submitted to thermal treatment at various temperatures and atmospheres, as a strategy to enhance their catalytic activity. Their performance in CWPO and ozonation reactions was also evaluated at different pHs. In this context, this study aims to tackle multiple environmental issues, namely: managing e-waste, improving water quality through effective pollutant removal and promoting resource efficiency.

Material and Methods

PCBs used in this study were sourced from obsolete electronic devices collected from a local electronics store. They were mechanically separated, followed by organic swelling in a sealed reactor to separate their main constituents (fibreglass and copper laminates). Then, only the fractions richer in copper laminates were used in this study. These laminates were tested both in their original form or thermally treated under N_2 or air.

In study A, 1.1 g of original or treated PCBs were mixed in a 50 mL solution containing 250 μg.L^{-1} of VFX and 2.2 mmol.L^{-1} of H_2O_2. The solution's pH was adjusted to 2.8 with HCl when needed. The mixture was stirred constantly for 60 minutes, with 1 mL aliquots being taken over time. VFX concentration was monitored using ultra-high-performance liquid chromatography (UHPLC) with a fluorescence detector (FD).

In study B, 250 mg of original or treated PCBs were mixed in a 500 mL solution containing 10 mg.L^{-1} of OXL and bubbled with 50 g.Nm^{-3} of O_3 at

150 mL.min^{-1}. The pH was adjusted to 7 with NaOH when needed. The mixture was stirred for 180 minutes, with 1 mL aliquots taken over time. OXL concentration was monitored using high-performance liquid chromatography (HPLC) with an UV detector. Total organic carbon (TOC) was analysed using a Shimadzu TOC analyser, and leached metal content was determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Scientific iCAP 7000 Series).

Results and Discussion

For study A (CWPO), the thermal treatment substantially decreased the TOC leached from waste PCBs, possibly due to the removal of the organic solvent used in previous separation steps. Since all tested PCBs were able to remove VFX, the degradation rate constant (*k'*, min^{-1}) and Cu leaching were the parameters analysed to decide which material treatment performed better. The results showed that the PCB treated at 500 °C in N_2 resulted in the highest *k'*. No significant changes in treatment efficacy were observed at different pH (Figure 1), but Cu leaching was about twice as high at acidic pH compared to natural pH tests (with some exceptions). Therefore, using a natural pH is advantageous to minimise Cu release in CWPO, offering both economic and environmental benefits. In study B (ozonation), TOC and Cu leaching were consistently low (unquantifiable) regardless of the material and pH tested. For the experiments conducted at pH~3.5, none of the catalysts completely removed OXL. The highest removal achieved was 68% with PCBs treated at 500 °C under air and 800 °C under N_2. Given the negligible difference in *k'*, the PCB treated at 500 °C under air (Figure 1) was considered the most appropriate material since requires a lower temperature. PCBs were also tested at pH ~7.0, and it was confirmed that the PCB treated at 500 °C in air remained the most effective. Additionally, it was demonstrated that this pH is the most effective for all materials, with complete removal of the pollutant being achieved. This can be explained by the more prone ozone (O_3) conversion into hydroxyl radicals ($HO^{\bullet}$) in less acidic media. Overall, Figure 1 shows that materials revealed high catalytic activity in both processes at circumneutral pH, which is attractive for practical implementation.

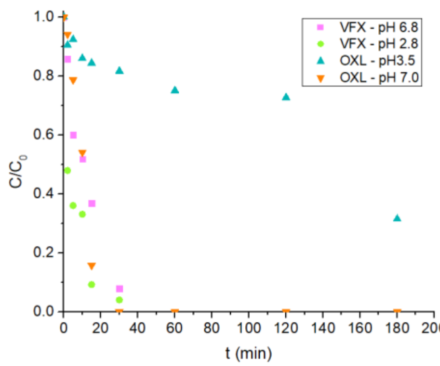

Figure 1. – VFX (study A) and OXL (study B) removal for PCB waste treated at 500 °C under N_2 (study A) and air (study B), respectively, at different pH values.

Conclusions

VFX and OXL were effectively degraded by the CWPO and ozonation processes, respectively, using PCB-derived catalysts. For both studies, performing the reactions at pH near neutral resulted in better performances with low Cu leaching, which increases the practical feasibility. The thermal treatment of PCBs proved to be beneficial, reducing TOC release (impurities) compared to that of the original PCBs. The best performances were achieved with PCBs treated at 500 °C in N_2 at natural pH for study A, and 500 °C in air at pH 7.0 for study B, as these comprise the best removal efficiencies and minimal TOC and Cu leaching.

Acknowledgments

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