Combined Oxidation Process For Antibiotic Degradation Using An Environmental Friendly Multi-Walled Carbon Nanotube.

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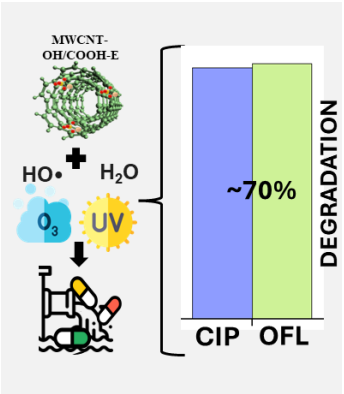

Antibiotics are contaminants that can cause toxicity to the environment and are already found in surface waters. For the degradation of these compounds, advanced oxidative processes are an efficient alternative that can be enhanced when combined. The choice of a green catalyst for this process involves a multi-walled carbon nanotube synthesized with plant biomass extract (MWCNT-OH/COOH-E), with the principle of making it an attractive residue and aiding in the degradation of the antibiotics ciprofloxacin (CIP) and ofloxacin (OFL). The stability and catalytic activity of MWCNT-OH/COOH-E was evident by FTIR. The results of the combined process (UV+O_3) with the catalyst had ~70% of CIP and OFL degradation, presenting good performance when compared to the individual processes.Improvements can still be explored to improve the degradation efficiency of these emerging contaminants.

Introduction

Antibiotics, such as, ciprofloxacin and ofloxacin, when present in the environment, are contaminants with the potential to cause adverse effects on the ecosystems and organisms. They are not subject to environmental regulation and difficult to be removed by conventional treatment [1]. In this way, more effective treatment methods need to be studied, like advanced oxidation processes (AOPs), for degrading these compounds.

AOPs including photocatalysis and catalytic ozonation, can decompose organic pollutants by generating reactive oxygen species, such as the hydroxyl radical. Catalysts bring advantages to the process, including higher efficiency and the possibility of recovery/reuse [2]. Nanomaterials such as carbon nanotubes (CNTs) are a promising material, and when functionalized, they improve efficiency and selectivity [3]. However, this process can involve harmful reagents. Therefore, the functionalization of CNT via green route, using iron nanoparticles and plant biomass, resultes in a more environmental friendly material, to be used as a catalyst. The aim of this study is to apply MWCNT-OH/COOH-E as a catalyst in a combined advanced oxidative process (UV+O_3) for degrading the antibiotics ciprofloxacin (CIP) and ofloxacin (OFL).

Material and Methods

Materials: Multiwalled carbon nanotubes functionalized with OH and COOH groups were purchase from NanoView (Brazil), which were refunctionalized by green synthesis with ($FeSO_4$•$7H_2O$) and eucalyptus leaves (E, *Corymbia citriodora*). Both antibiotics, CIP and OFL (99% purity), were donated by EMS pharmaceuticals.

Methods: Green Synthesis: MWCNTs were synthesized by impregnating them with metallic nanoparticles and plant extract, as reported in the literature [3,4]. The process involved biomass extraction and preparation of the metal solution. Subsequently, the NTC was mixed with the solutions and agitated for 24h. After agitation, the mixture was separated by centrifugation, and the solid material was dried in an oven and stored, resulting in MWCNT-OH/COOH-E.

Material characterization: MWCNT-OH/COOH-E was characterized before and after the process. Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted to detect and visualize potential alterations in vibrational behavior of functional groups present on its exterior.

Combined oxidation process: In all experiments, antibiotic solutions were used at an initial concentration of 0.1 mmol/L with a volume of 100 mL, and MWCNT-OH/COOH-E was used at a dosage of 1.5 g/L. The combined process resulted from the methods of photocatalysis and catalytic ozonation mentioned subsequently, occurring simultaneously. Samples were collected every five minutes and remained antibiotic solution was measured in UV-Vis at 276 nm for CIP and 290 nm for OFL. The degradation percentage (%) was calculated using Equation 1.

$$\%Degradation = \left(\frac{C_0 - C_f}{C_0}\right) 100 \quad (1)$$

Photocatalysis:The system used has a fluorescent UV-A lamp, model G8T5E (8 W). 100 mL of antibiotic solution was placed within a dark chamber, from the lamp placed on the top section. CNT was added to

the system and the UV lamp was switched on right away and kept under agitation for 30 min.

Catalyst ozonation:The reactions were conducted in a benchtop ozone generator (600 mg/h of O_3, RoHS, model GL-3189A, 1 atm). The CIP/OFL was added with the CNT and the ozone generator, bubbling through a porous stone diffuser for 30 min.

Results and Discussion

Material characterization: The observed vibrational spectra (Figure 1), demonstrate that there was a slightly change in the material after the process. The spectra of the material prior the process can be seen in a previous study [5]. When analyzing the material before the process, bands commonly found in multi-walled carbon nanotubes are observed at 3500 to 3400 cm^{-1}. The bands in the range of 1200 to 1000 cm^{-1} represent C-O bonds, and those at 3000 and 2800 cm^{-1} represent C-H bonds, typical of covalent bonds. Upon analyzing the post-processed material in the presence of both antibiotics, a typical band of this family of drugs is noted at 1050 to 1000 cm^{-1}, along with bands at 3600 to 3400 cm^{-1} corresponding to OH bonds [5]. Due to the bands observed in the spectra and the minimal modification found, the stability of the produced material can be confirmed.

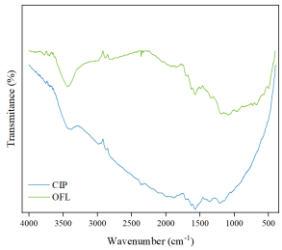

Figure 1. FTIR spectra, MWCNT-OH/COOH-E post combined process, contaminated with CIP and OFL.

Combined oxidation processes: The combined treatment methods (UV+O_3) can be seen in Figure 2, where a degradation percentage of 70% was achieved for CIP and 71% for OFL.

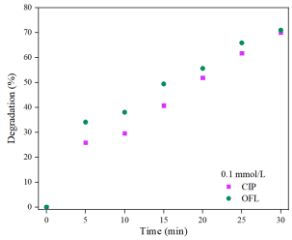

Figure 2. UV+O_3 for the degradation of CIP and OFL.

The study of individual processes was also conducted to compare their efficiency (Figure 3). In catalyst ozonation, the percentage achieved was 70% for CIP and 63% for OFL, in photocatalysis, it was 67% and 65%, respectvely. It is clear that for ofloxacin, the combination of methods was more effective for degradation in water, when compared to the individual process. The difference was not significant enough to justify the use of combined treatments, but it shows that it is a promising method that may be improved. Other studies reported in the literature shows that combined oxidation process for degradation of antibiotics was favorable and should be more investigated [6][7].

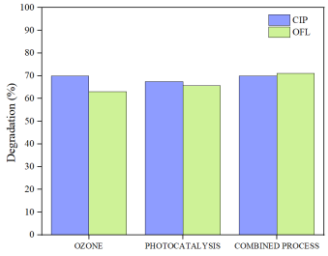

Figure 3. Individual and combined oxidation process for degradation of CIP and OFL.

Conclusions

This study investigated the use of carbon nanotubes as a catalyst for the degradation of CIP and OFL in an aqueous matrix. Analysis of the material after AOP indicated that the material structure remained similar, showing that stable connections between the material and the antibiotics was formed and the catalyst stabylity. The results of the combined process has showed to be satisfactory, however, when compared to individual processes there is no bigger improvements. The MWCNT-OH/COOH-E was considered a good catalyst to be used in antibiotic oxidation processes, further comprehensive investigations are still needed to refine the operational parameters for more expressive degradation percentages.

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