Intensified filtration process with wet peroxide oxidation for the treatment of sulfamethoxazole-polluted water using carbon nanotube composite polymeric membranes

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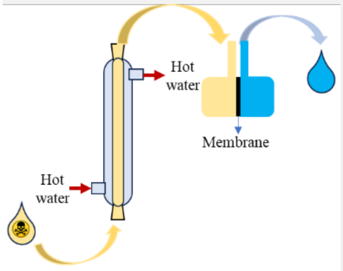

Hospital wastewaters are amongst the most complex streams to be treated. The pharmaceutical compounds present in this effluent are resistant to many technologies used in conwastewater treatment plants. For this reason, solutions are required to equip local treatment plants in hospitals with feasible tertiary treatments. This study investigated the degradation of sulfamethoxazole (SMX), a common antibiotic in hospital wastewater, assessing the intensification of filtration systems using carbon nanotubes (CNTs) composite polymeric membranes with catalytic wet peroxide oxidation (CWPO) . The antibiotic was chosen to represent organic pollutants commonly found in hospital wastewater. Results demonstrated that CNT composite membranes are active in the degradation of SMX, opening a wide perspective for application of the developed system to the removal of other pollutants of interest.

Introduction

Water contamination with contaminants of emerging concern (CECs) has been recognized as a threat to the water ecosystem and human health. The lack of proper wastewater treatment plant (WWTP) technologies to remove such pollutants leads to their constant discharge into river waters. Several works reported severe environmental consequences due to living beings exposed to CECs, such as endocrine disruption, reproduction cycle damage, and others [1]. One source of great pollution is hospital wastewater, containing antibiotics of controlled usage and other pharmaceutical compounds resistant to WWTP. In most cases, the hospital wastewater is directly sent to urban wastewater.

The pharmaceutical pollutants in hospital wastewater have complex structures that are difficult to degrade via biochemical processes and are highly toxic to living beings. One possible solution to avoid discharging these contaminants into the environment is treating hospital wastewater before sending it to the urban wastewater system. Advanced oxidation processes (AOPs) have demonstrated potential applicability in this scenario. These technologies are characterized by generating reactive oxygen species with a strong oxidation capacity to oxidize the pollutants [2]. Current literature on this topic mainly focuses on electrocatalysis, photocatalysis and ozonation processes. However, catalytic wet peroxide oxidation (CWPO) could also represent one interesting alternative due to its efficiency and low operational cost. On the other hand, carbon materials, such as carbon nanotubes (CNTs), have been explored in recent years due to their good electron donor-acceptor properties [3]. Studies majorly report the use of catalysts in batch experimental setups, which needs to be improved to increase the closeness to real scenarios.

Another process used to treat contaminated waters is filtration with polymeric membranes. However, the removal process is a mere transference from one phase to another. Several studies have evaluated combining membrane filtration technology with AOPs, to increase the efficiency of the process. On the other hand, the oxidation processes evaluated so far employ UV light and ozone, which can increase the operational cost.

This work proposes the incorporation of CNTs in composite polymeric membranes, synthesized dispersing CNTs prepared from plastic solid wastes in polyvinylidene fluoride (PVDF) and polyvinylpyrrolidone (PVP). The membranes were further applied for the treatment of CECs (simulated water containing sulfamethoxazole) by CWPOassisted polymer-mixed matrix membrane process. Hydrogen peroxide was added to the contaminated water, to generate hydroxyl radicals upon interaction with the membrane.

Material and Methods

CNTs were synthesized following the methodology well-described in a previous work [3], via CCVD (Chemical Vapor Deposition) over a metal phase catalyst supported on alumina. The metal catalyst was prepared through a sol-gel method, which entailed synthesizing a mixture of iron oxide (20 *wt.*%) on alumina. The sol-gel procedure involved rapidly hydrolyzing mixed iron (II) and iron (III) salts in ethanol and ethanediol, respectively. Following heating and amalgamation with alumina, the resultant gel was subjected to drying and calcination. CCVD was executed in a single-chamber reactor at 850°C under a nitrogen flow for 1.5 h, preceded by a 2 h purge. The recovered CNTs were stored and used without purification.

To produce the membranes, a mixture of 0.07 g of PVP and 0.234 g of CNTs was added to a beaker, followed by 6 mL of 1-methyl-2-pyrrolidone (NMP), and then subjected to ultrasonication for 3 h to achieve a homogeneous mixture. Subsequently, 1.070 g of PVDF was added to form the gel, which was then placed in an agitated bath at 40 °C, 200 rpm, for 48 h. The material was then left to rest for at least 12 h. After this resting period, the material was spread using a knife film applicator equipment at thicknesses of 150 µm. Following the material spreading, the gel was immersed in a coagulation bath of distilled water [4]. Filtration experiments intensified with CWPO were performed in continuous mode (dead-end) at 80 °C, pH 3.5 adjusted using H_2SO_4 (0.5 M) addition, and flow rate of 1 mL min^{-1}. The solution fed to the reactor contained the pollutant SMX (10 µg mL^{-1}) and the stoichiometric concentration of the oxidant source (44.3 µg mL^{-1}). Samples were collected at 60, 120, 240, 360, and 480 minutes upstream and downstream. The non-catalytic experiment was carried out without the composite membrane, and filtration experiments were performed in the absence of H_2O_2.

Results and Discussion

Figure 1 shows the results obtained for SMX and H_2O_2 concentrations evolution over the experiment. The non-catalytic run revealed no significant difference between the upstream and downstream concentrations of pollutant and oxidant source (not shown).

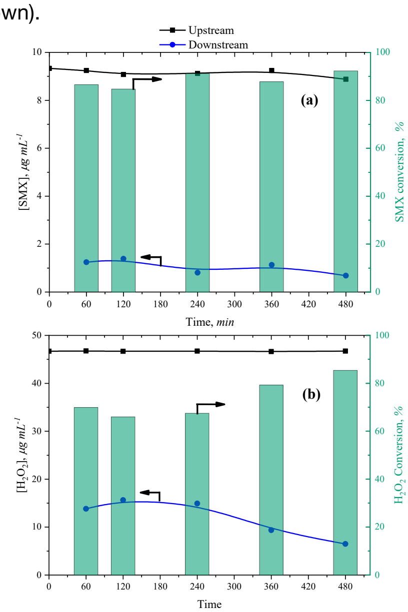

Figure 1. (a) SMX and (b) H_2O_2 concentrations evolution upstream and downstream during the experiment.

The results demonstrate that the composite membrane can keep the pollutant removal up to 80% during the experiment. In addition, SMX removal reached more than 80% in only 60 min of reaction. The same behavior was observed for H_2O_2 decomposition, reinforcing the membrane's ability to convert H_2O_2 into hydroxyl radicals. Filtration results revealed a maximum removal of 9% during all times, confirming oxidation intensifies pollutant removal.

Conclusions

This work demonstrated the applicability of CNT composite membranes for the degradation of SMX in a continuous system. The results showed that the membrane can decompose H_2O_2 into hydroxyl radicals, keeping the pollutant removal up to 80% in all reaction times.

Acknowledgments

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