From Waste to Value: Enhancing Catalytic Activity of Plastic-derived Carbon Nanotubes for Microplastic Remediation

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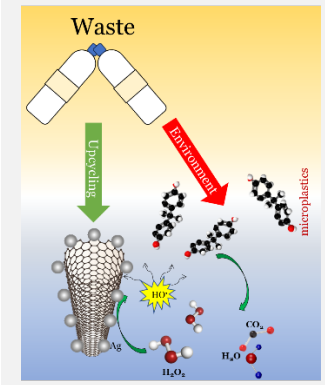

Plastic solid waste and microplastics are currently acute environmental problems. In this work is presented one approach for upcycling plastic solid waste via synthesis of carbon nanotubes (CNTs). In addition, is evaluated the environmental catalytic activity of the CNTs for the removal of bisphenol-A, chosen as model microplastic pollutant. For this purpose, CNTs were doped with 5 and 10% of silver to evaluate catalytic activity improvement. The results demonstrated that Ag-doping significantly increased hydrogen peroxide decomposition and pollutant degradation. In addition to the improved catalytic performance, Ag-doped CNTs opens a broad perspective for evaluating antimicrobial activity during CWPO reactions, considering the well known antimicrobial activity of Ag.

Introduction

Plastics have been used for several years in various applications, such as packaging, electronics, and automotive industries. However, up to 79% of plastic products are discarded after the first use. Some fraction of the discarded plastic, those with a diameter smaller than 5 mm, are defined as microplastics (MPs). Due to their small size, these materials can migrate between water bodies and terrestrial environments. In fact, microplastics have already been detected at trace levels in drinking water. The spread of contamination of water reservoirs with microplastics is particularly concerning considering the adverse effects on human health and the ecosystem. For this reason, several technologies have been studied to remove MPs from contaminated waters. Despite the advances, most methods lack efficiency in removing MPs smaller than 10 micrometers [1].

In this scenario, advanced oxidation processes emerge as suitable technologies capable to degrade microplastics. These technologies are based on the generation of reactive oxygen species, such as hydroxyl radicals, to break down the contaminants. Among those technologies, catalytic wet peroxide oxidation (CWPO) has demonstrated potential applicability to degrade several organic pollutants. However, most catalysts studied for this technology are metal-based, which implies further problems with loss of activity and water contamination with metals due to leaching. One possible solution to overcome this drawback is the use of carbon-based materials.

Therefore, in this work, one alternative was explored, considering the chemical recycling of plastics via the synthesis of carbon nanotubes. The materials were doped with silver and applied in the degradation of bisphenol-A (BPA), chosen as a model microplastic pollutant. The presented solution allows increasing the plastic recyclability and also the use of an upcycled advanced material for removing microplastics from contaminated waters. The results demonstrate that silver doping improves hydroxyl radicals formation and BPA removal.

Material and Methods

CNTs were synthesized using a modification of the method presented in a previous work [2]. The carbonaceous materials were initially produced through catalytic chemical vapour deposition (CCVD), considering a metal phase catalyst supported on alumina. The metal catalytic substrate was prepared via a sol-gel process, involving the synthesis of a mix of cobalt and nickel ferrites (15 wt.%) on alumina, with a defined molar ratio of nickel to cobalt of 3:7, as previously optimized. The sol-gel process included rapidly hydrolyzing mixed Ni and/or Co salts in ethanol and an Fe salt in ethanediol. After heating and combining with alumina, the resulting gel was dried and calcined. CCVD was carried out in a one-chamber reactor at

850°C under nitrogen flow for 1.5 hours, preceded by a 2-hours purge.

CNTs were then carboxylated using a 15 M HNO_3 solution for 48 hours, followed by rinsing with water and drying. Carboxylated CNTs were doped with 5 and 10% Ag using a methodology reported in another work [3]. In short, carboxylated CNTs were dispersed and sonicated in ethanol for 30 minutes. Then, a stoichiometric amount of $AgNO_3$ solution in ethanol was added dropwise. After another 30 minutes of sonication and overnight drying at 70°C, the material was thermally treated in a N_2 atmosphere at 450°C for 3 h. The resulting materials were named CNT-COOH/Ag-5% and CNT-COOH/Ag-10% for CNTs doped with 5 and 10% Ag, respectively.

CWPO reactions were conducted in a two-necked round bottom flask with 100 mL of the model pollutant solution adjusted to pH 3.5 using H_2SO_4. The initial pollutant concentration was 100 µg mL^{-1} (BPA), and the stoichiometric amount of H_2O_2 (562 µg mL^{-1}) for complete oxidation was added. The flask, placed in an oil bath at 80°C, was stirred for 5 minutes for uniform heating and dispersion. Samples were taken to measure initial pollutant and oxidant concentrations before adding the catalyst to start the reaction. Subsequent samples were collected at 15, 30, 60, 120, 240, 360, and 480 minutes to monitor pollutant and H_2O_2 concentrations.

Results and Discussion

Figure 1 presents the results obtained for BPA and H_2O_2 concentrations evolution over time. The noncatalytic run achieved 18% H_2O_2 decomposition and 16% BPA removal. All CNTs could completely remove the pollutant within 480 min of the reaction. The CNTs doped with Ag presented an increased activity compared to the carboxylated CNT sample. The fastest pollutant removal with doped CNT is further supported by the fastest H_2O_2 decomposition profile obtained using Ag-doped CNTs. The improved catalytic activity of Ag-doped CNTs compared with the bare samples can be related to silver's high electron transfer efficiency, which is fundamental to generating hydroxyl radicals.

Comparision between the 10 and 5% Ag-doped CNT revealed that 5% doping performed better. This could be related to the possible aggregation of Ag nanoparticles during the doping procedure due to the increased amount of silver in 10% doping. Other studies have already discussed the catalytic activity of Ag-doped catalysts and concluded that well-dispersed Ag nanoparticles are the key to improve catalytic activity [4].

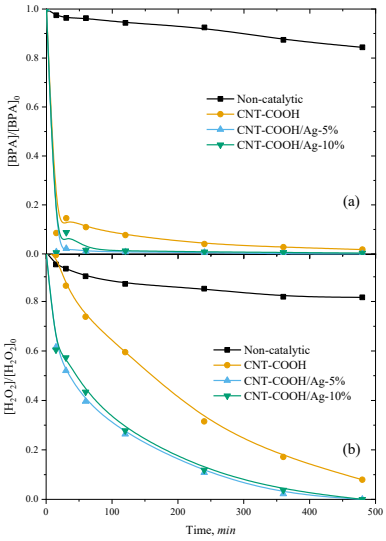

Figure 1. (a) BPA and (b) H_2O_2 relative concentrations evolution during CWPO.

Conclusions

In this work, it was demonstrated that silver doping can significantly increase the catalytic activity of CNTs in CWPO reactions. The increased catalytic activity of the CNTs upon doping opens the horizon for evaluating the combined organic pollutant degradation and antimicrobial activity of carbon-based materials doped with Ag. Furthermore, the results also demonstrated that higher amounts of silver could hinder the catalytic activity, due to aggregation.

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