Application of Polyaniline as an Adsorbent and a Photocatalyst for the Removal of Parabens from Wastewaters

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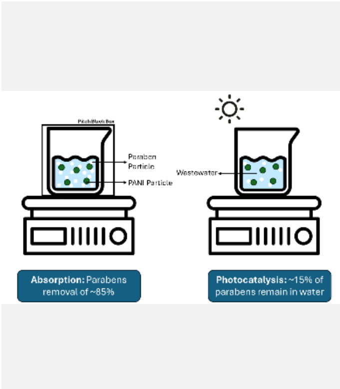

Parabens are an environmental concern due to their endocrine disruption activity and the inefficiency of wastewater treatment plants on their degradation. Thus, advanced oxidation processes like photocatalysis are being considered as an alternative. The most efficient photocatalyst reacts in the presence of UV irradiation and requires time-consuming and costly downstream processes for its removal from treated water. Thus, in this work, polyaniline (a conductive polymer that absorbs visible radiation) was applied as an absorbent and a photocatalyst for the abatement of parabens. It was concluded that ~65% of parabens were removed by absorption in less than 15 min and that after solar photocatalysis (60 min) only ~15% of the initial pollutants remain in the water. Moreover, despite the presence of leachable compounds in the treated water (byproducts of polyaniline synthesis), the germination of *L. sativum* was not inhibited.

Introduction

The presence of contaminants of emerging concern (CEC), such as parabens, in wastewater and natural water resources has become a major concern and focus of scientific research, due to their environmental impact [1]. Parabens are classified as ubiquitous in the aquatic environment, can cause endocrine disruption and can bioaccumulate [1-4]. Due to the inefficiency of conventional wastewater treatment plants (WWTPs), advanced oxidation processes, like photocatalysis, may be applied as a solution [4]. Photocatalysis is a simple, cost-effective and environmentally friendly process that can be easily scaled up [3,5,6]. Yet, the most used photocatalyst (TiO_2), reacts only in the presence of UVA radiation (a small fraction of natural sunlight) and must be removed from treated waters, which involves time-consuming and costly downstream processes [5,6]. Thus, supported photocatalysts have become a focus of interest. Polyaniline (PANI) is a promising option, since it can act as an absorbent, a photocatalyst/composite under visible radiation, a hole trap and an activator in sulfate radical-based advanced oxidation processes [6-9].
Thus, in this work, the role of PANI as an absorbent and photocatalyst for the removal of more complex pollutants, than those reported in the literature, was evaluated. The toxicity of the oligomers produced during PANI synthesis and lixiviated to the water was also determined, which to the best of the authors knowledge has not been reported in the literature.

Material and Methods

The synthesis of PANI was adapted from Pawar et al. [10]. Briefly, 2 mL of aniline were added to 50 mL of HCl (1 M) and agitated for 15 min in a cold bath (0-5 ºC), while 5 g of ammonium persulfate (APS) were dissolved in 50 mL of ultrapure (UP) water for 15 min. Afterwards, the APS solution was transfer to the aniline mixture at a rate of 1 mL/min, at controlled temperature (0-5 ºC). Then, the mixture was left without agitation for 24 h at 25 ºC to precipitate the PANI particles. Later, the mixture was filtered and washed with different solutions and dried for 48 h at ambient conditions.
The synthetic wastewater contained 1 mg/L of each paraben (methylparaben-MP-, ethylparaben-EP- and propylparaben-PP) dissolved in UP water. A total volume of 100 mL was used and stirred at 700 rpm in a glass reactor to which PANI particles were added. The adsorption experiments were performed in dark conditions during 2 h and the photocatalysis experiments were performed for 2 h, under a solar natural irradiation (UV index = 8.4 ± 0.9; irradiance = 842.2 ± 37.7 W/m^2). All experiments were performed in duplicate.
The parabens concentration was followed through high-performance liquid chromatography (HPLC). The injection volume was 100 µL and the mobile phase (1 mL/min) consisted in 50:50 (v/v) mixture of methanol and 0.1 w/w% H_3PO_4 aqueous solution. A C18 column was used at 40 °C, and the compounds detection was performed at 255 nm.
To evaluate the toxicity of the oligomers, PANI

particles washed with different solutions during filtration were placed in UP water for 2 h under agitation. Samples were collected and the toxicity over *Lepidium sativum* was assessed according to norm ISO 18763:2016.

Results and Discussion

PANI has been successfully applied in the removal of dyes and CEC through absorption [6-8] and PANI composites with conventional photocatalyst have been successfully applied for the degradation of dyes [9]. Given the promising performance of PANI, in this study, it was applied as an absorbent and photocatalyst for the removal of more complex target pollutants and the results are presented in Figure 1. From Figure 1, it can be perceived that PANI can remove ~65% of parabens by absorption in less than 15 min and that after solar photocatalysis only ~15% of the initial pollutants remain in the water. From the study it was also concluded that increasing the PANI concentration did not increase its performance (results not shown).

Despite PANI good performance, throught HPLC analysis, byproducts (oligomers) from PANI synthesis were detected in water samples. As these byproducts are unidentified and unknown, toxicity tests were conducted, and the results are presented in Table 1. Moreover, to minimize their presence different wash solutions were applied. From Table 1, it can be observed that the oligomers did not inhibited plant grow. It was also concluded that the different washing solutions do not influence neither the concentration of leachable compounds in the water, nor the materials performance, band gap and chemical composition (results not shown).

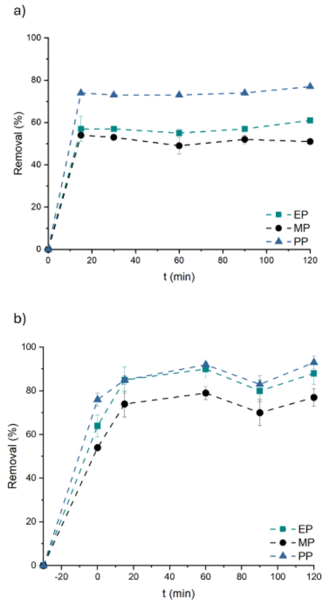

Figure 1. PANI performance on the removal of parabens by (a) adsorption and (b) solar photocatalysis ([PANI] = 70 mg/L).

Table 1. Influence on the germination index (GI) of *L. Sativum* of the wash solution used during PANI synthesis (filtration step).

Wash Solution	Ultrapure Water	0.5 M HCl	1 M HCl	Ultrapure Water + 0.5 M HCl + 1 M HCl
GI (%)	112.4 ± 13.5	102.8 ± 11.1	111.6 ± 6.5	90.3 ± 16.2

Conclusions

This study shows that PANI is a material of interest for removing CEC due to its remarkable performance in adsorption and solar photocatalytic processes, as it removed around 85% of parabens from the waters after the process's integration. It was also concluded that although the presence of leachable compounds has not been avoided or eliminated, they do not inhibit the germination of *L. Sativum*. However, the performance of PANI is dependent on its synthesis conditions which will be further optimized.

Acknowledgments

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