

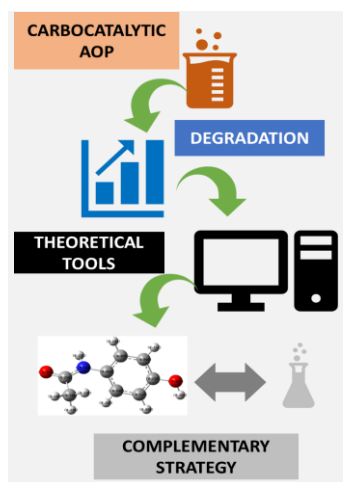
Theoretical tools as a complement to explain the experimental results of the paracetamol degradation in water by carbocatalysis

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Carbocatalytic advanced oxidation processes have been successful in degrading pharmaceuticals in water. Herein, the paracetamol treatment by carbocatalysis was considered. The degradation routes, primary transformations, and phytotoxicity were determined experimentally. At the same time, theoretical tools were applied to understand better/support the action of the process. An atomic charge calculator (ACC), the natural bonding orbitals (NBO) approach and a predictor of biological activity were used to complement the experimental analyses, providing a better comprehension of the paracetamol interaction with the degrading species and the toxicity evolution. ACC and NBO revealed the electron-rich moieties susceptible to the attacks of the oxidizing species formed carbocatalytically. Additionally, ACC (free and fast) led to similar results to NBO (requiring specialized software). Finally, the predictor of biological allowed us to explain the phytotoxicity decrease observed experimentally.

Introduction

The treatment of contaminants of emerging concern (CECs), such as pharmaceuticals, by carbocatalytic advanced oxidation processes (CAOPs) is gaining the scientific community's attention. In the carbocatalytic systems, a carbonaceous material is used to activate peroxymonosulfate toward reactive species (e.g., HO^{\bullet} , $\text{SO}_4^{\bullet-}$, or $^1\text{O}_2$) for degrading organic pollutants in water [1]. During the treatment by carbocatalysis, the pharmaceuticals are transformed into other compounds. Then, the changes in the chemical structure and properties (e.g., toxicity) of the pollutants can be determined experimentally. At the same time, theoretical tools can be utilized to understand better/support the action of the CAOPs on the pharmaceuticals. For instance, quantum chemistry calculations help identify the moieties of pollutants susceptible to attacks by degrading species, which helps explain the primary transformations [2].

This work considered the degradation of paracetamol by peroxymonosulfate (PMS) activated with a pyrogenic carbonaceous material. Herein, we present the use of an atomic charge calculator, NBO approach, and a predictor of biological activity to complement the experimental results and better comprehend the interaction of paracetamol with the degrading species and the toxicity evolution.

Material and Methods

A pyrogenic carbonaceous material obtained from rice husk wastes was used. OXONE was employed as the PMS source. Paracetamol (PCT, also named acetaminophen) was selected as a representative pharmaceutical due to its high consumption and occurrence in municipal wastewater. The evolution of PCT was followed by HPLC. The reactive species responsible for the PCT degradation were determined using EPR. The primary transformations of PCT were determined by the LC-MS technique. Phytotoxicity tests against mung bean were performed by measuring the germination index [3]. Regarding the theoretical analyses, we should mention that the atomic charge calculations (ACC) were carried out in the free online ACCII software. The atomic natural charge was analyzed using the Natural Bond Orbital (NBO 3.1) by using the Gaussian09 software package. In turn, the predictions on biological activity were obtained using the free online PASS software.

Results and Discussion

Firstly, the ability of the carbocatalytic system to degrade the target pharmaceutical in water was assessed. Fig. 1A shows that in the PCT removal under the optimized process, at 3 min, the carbonaceous material alone adsorbed ~37% of the pharmaceutical, and PMS induced a low direct oxidation (<5%); whereas the carbocatalytic

process degraded 90% of PCT; evidencing the high efficiency and synergy in such a process. Besides, EPR analyses were performed to determine the main species responsible for PCT degradation in the carbocatalytic process. This evidenced the participation of singlet oxygen formation in the carbocatalysis.

The action of the produced singlet oxygen on PCT formed an intermediate with a hydroxylation on the aromatic ring. The formation of P₁ in our system can be explained by considering an initial attack of the singlet oxygen on the nitrogen atom on ACE (which is the moiety richest in electron density, as supported by atomic charge analysis and NBO (Fig. 1B)). Besides, ACC (which is free and fast) led to similar results to NBO (it requires specialized software). Table 1 shows a comparison of these two theoretical tools.

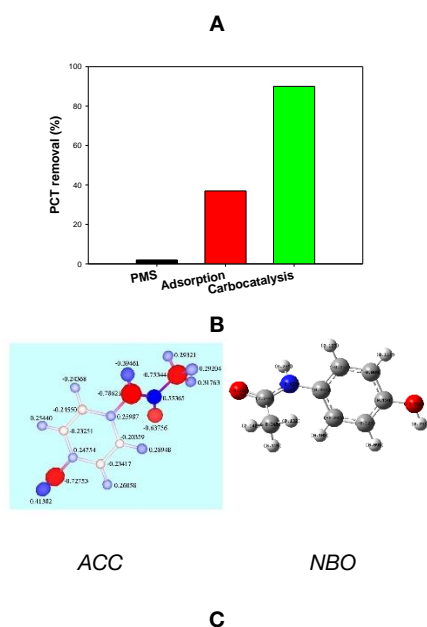


Figure 1. Treatment of PCT by the carbocatalytic system. **A.** Removal by PMS, adsorption and carbocatalysis. **B.** Identification of electron-rich regions using ACC and NBO. **C.** the predictions on biological activity.

Table 1. Comparison between ACCII and Gaussian tools.

Software	Cost	Time for calculations	Trained personnel
ACCII	Free	Seconds to minutes	No
Gaussian	License	Seconds to minutes	Yes

On the other hand, as the treated water has the potential to be reused for crop irrigation, the phytotoxicity of the resultant solution (which contains the transformation product, TP) was analyzed. The germination index was obtained, showing that the carbocatalytic process decreased the phytotoxicity regarding the non-treated pollutant. To better support the experimental results, the biological activity of PCT and its intermediate was studied. Fig. 1C Shows the probabilities of being active (Pa). Interestingly, TP exhibited Pa values lower than the PCT for each of the considered activities, suggesting that the carbocatalytic treatment of PCT produced a substance with lower biological effects than the parent pharmaceutical, which explains the observed reduction of the phytotoxicity.

Conclusions

PCT was removed by the carbocatalytic system through a combination of adsorption and degradation by ¹O₂. The ACC and NBO tools allowed recognition of the electron-rich moieties on PCT susceptible to the attacks and transformations carbocatalytically. Furthermore, the theoretical analyses of biological activity provided explanatory support for the experimental phytotoxicity reduction.

Acknowledgments

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