KINETICS OF ENVIRONMENTAL BIOCOMPLEXITY: EXPERIMENTS, QUANTUM CHEMISTRY AND MACHINE LEARNING

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INTRODUCTION

Micro-pollutants of emerging concern have imposed a major technological challenge: pesticides, drugs, and other anthropogenic substances are increasingly found in aquatic and atmospheric environments and even in water supplies, being related to adverse effects on biota and human health [1-2]. Overcoming this challenge requires understanding the behavior of these species in the environment and developing technologies that minimize their dissemination.
Theoretical chemical kinetics, combined with machine learning, can be useful for understanding and predicting the behavior of emerging micro-pollutants in the environment [3-5]. This can help develop more effective technologies to minimize their dissemination and negative impacts. With this knowledge, it is possible to optimize processes for the degradation of organic pollutants, making them more efficient and economical.

METHODS

Viable alternatives applied in this thesis include the use of radical-based oxidation processes using both experimental – via the competition kinetics method – and theoretical protocols – blend of kinetic, quantum chemistry, and machine learning calculations.
In this study, the *deformed*-Transition State Theory was used to compute the values of the reaction rate constant. Gaussian 16 software was employed to perform quantum chemistry calculations. Machine learning models were used to train the data, including XGBoost, Random Forest, and MLP.

RESULTS

In a first study, the mechanisms, kinetics, and an evaluation of the toxicity of picloram degradation – a pesticide widely used in the world - initiated by OH radicals indicate that: i) two favorable pathways occur by addition to the pyridine ring, ii) picloram and the majority of degradation products are estimated as harmful; however, ii) these compounds can suffer photolysis by sunlight. However, the competition kinetic method and the quantum chemistry description make the degradation analyses a formidable enterprise, considering the costs of ad hoc instrumental equipments and dedicated computational efforts. To overcome the demanding conventional procedures, we developed a free and user-friendly web application (www.pysirc.com.br) based on holistic machine learning combined with molecular fingerprints models that permits the compilation of kinetic parameters and mechanistic interpretation of radical-based oxidation attacks according to the OECD principles. Machine learning algorithms were implemented, and all models provided high goodness-of-fit for radical-based degradation in aquatic and atmospheric environments. The models were interpreted using the SHAP (SHapley Additive exPlanations) method: the results showed that the model developed made the prediction based on a reasonable understanding of how electron-withdrawing/donating groups interfere in the reactivity of the radicals.

CONCLUSIONS

We argue that our models and web interface can stimulate and expand the application and interpretation of kinetic research on contaminants in water and air treatment units based on advanced oxidative technologies. By providing an accessible and user-friendly platform, researchers and practitioners can easily apply our models to their own data, facilitating the development of more effective and efficient treatment strategies for emerging micro-pollutants.

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