Enhancing Imidacloprid Degradation: A Synergistic Approach Using Ozonation and MBBR

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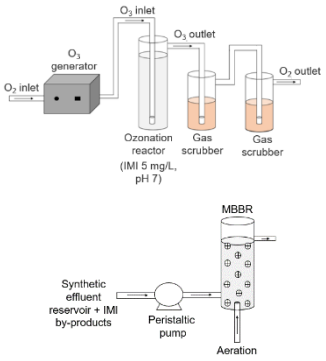

Imidacloprid is an insecticide frequently found in water bodies that has potential acute and chronic toxicity, representing a threat to the environment and the health of living beings. In this work, ozonation and moving bed biofilm reactor (MBBR) were associated for the degradation of imidacloprid and its by-products. Ozonation was carried out in batch with 5 mg/L imidacloprid, 20 mg/L ozone and at pH 7. The degradation of the imidacloprid ozonation products was carried out in continuous mode in an MBBR. Degradation of imidacloprid occurred after 10 minutes of ozonation. The impact of the formed intermediaries was evaluated in the MBBR. A negative impact was observed on the removal of COD and ammoniacal nitrogen. Even with a negative impact, the average removal of COD and ammonia nitrogen was 81.7 ± 11.5 and 93.6 ± 4.6%, respectively.

Introduction

Imidacloprid (IMI) is an insecticide widely used in the treatment of seeds against various types of insects. It has been detected in surface waters, agricultural areas and municipal wastewaters at trace levels (ng/L to µg/L), posing toxicity risk over human beings and fauna overall. In this sense, robust strategies for degrading this and other pesticide residues are needed, protecting the environment and maintaining sustainability [1].

Advanced oxidative processes (AOP) are based on hydroxyl radicals generation to degrade emerging contaminants. Ozonation stands out for being used in several areas and for its advantages, such as high selectivity in the degradation of unsaturated organic compounds and minimal risk to health and the environment [2].

In parallel, the moving bed biofilm reactor (MBBR) is a consolidated, high value for money, process, capable of mitigating a variety of emerging pollutants in addition to bulk organic and nitrogenated matter [3].

Therefore, this work proposes the use of the ozonation process to degrade imidacloprid and evaluate the impact of its intermediates formed in a MBBR.

Material and Methods

The degradation of 5 mg/L of IMI was tested using the ozonation process (20 mgO_3/L at pH 7) for durations from 1 to 30 minutes. Initially, the MBBR was being used as a control experiment for another work and had an operating period of 760 days, where the reactor was fed only with synthetic medium (200 mg/L soluble chemical oxygen demand (sCOD) and 30 mgNH_4^+-N/L) devoid of the ozonized solution. After assessing the optimal duration, the ozonized solution containing the by-products was mixed with the synthetic medium and subjected to post-treatment in a MBBR. The latter was under monitored operation with the synthetic matrix before the IMI addition, so the impact over the MBBR performance could be studied.

Results and Discussion

It was considered that 10 min ozonation is enough to obtain the opening of the pyridine ring of imidacloprid (Figure 1). The absorption peak at 269 nm refers to the conjugated double bonds of the ring. Therefore, as this absorption decreases, it can be said that it is being oxidized and the IMI is being degraded.

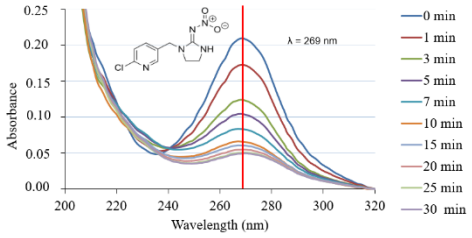

Figure 1. Absorption spectrum of 5 mg/L IMI (0 min) and after different ozonation times, with 20 mgO_3/L.

Before the addition of ozonated IMI, the COD removal (Figure 2) averaged 87%. In the first 30 hours after adding the ozonized effluent, the average COD removal was 54.7%. Between days 764 and 778 (adaptation period of the reactor to the ozonized solution), the mean removal was 76%, indicating that the presence of ozonation by-products negatively affected COD removal. After

this period, COD removal increased again, which may indicate the acclimatization of the biofilm to the presence of intermediate compounds. Regarding ammoniacal nitrogen, the average removal before the addition of ozonated IMI was higher than 90%. In the first 30 hours after adding the ozonized effluent, the average removal was 94.6%. It was noticed that the intermediate compounds contained in the effluent did not affect the removal of ammonia nitrogen in the reactor at this first moment. After IMI addition, the overall average removal was 94%. Initially, until day 776, the removal remained stable at around 96%; however, from that day on the removal declined down to 85%, indicating that the biomass was possibly losing its nitrification capacity.

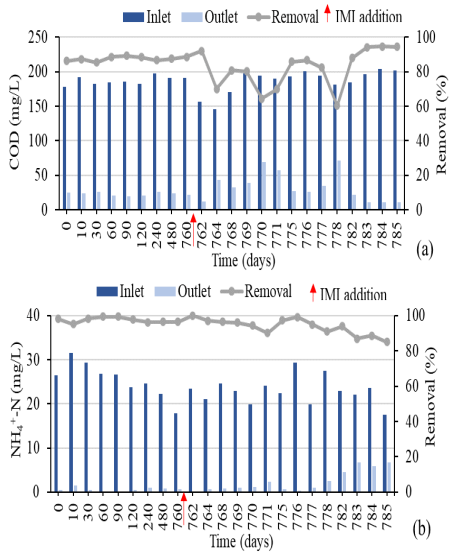

Figure 2. Removal of (a) soluble COD and (b) ammoniacal nitrogen during the MBBR operation.

Conclusions

This work shows that a longer MBBR monitoring time is needed to validate this performance loss and verify whether over time the IMI byproducts have a greater impact on ammoniacal nitrogen removal, or the microbial consortium adapts. However, despite the intermediate ozonation negative impact on the MBBR, high COD and ammoniacal nitrogen average removals were still attained, 82 ± 12% and 94 ± 5%, respectively.

Acknowledgments

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