High resolution mass spectrometry to investigate the fate of pesticides during microalgae-based bioremediation treatment of water

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1. Introduction

Pesticides are substances highly used for many purposes worldwide. After their use, they may end up in the aquatic environment, representing a risk to exposed organisms. To reduce their environmental impact, it is necessary to develop technologies capable of removing them before their release into the environment or from pesticide-containing waters.

Some non-biological processes have been proposed for this purpose, such as adsorption on granular activated carbon [1] or advanced oxidation processes (AOPs) [2]. However, these methods are very expensive or their efficiency depends on the selected AOP and the chemical characteristics of the matrix.The use of biological treatments, using fungi or other types of microorganisms, such as microalgae, could be an alternative to these processes. It has already been shown that some pesticides, such as DDT [3] could be degraded using fungi. Meanwhile, microalgae-based treatments have been succesfully used for the elimination of persistent and emerging organic pollutants [4].

In this context, the objective of this work was to study the capability of microalgae to treat pesticide-containning waters. In addition, degradation achieved by microalgae in comparison to photodegradation and adsorption was studied. Identification of transformation products (TPs) potentially formed during the process was also the focus of the investigation.

2. Materials and methods

The pesticides investigated included the insecticide acetamiprid, and the herbicides propanil and bentazone (see Figure 1). These pesticides were selected because they have been found frequently and at high concentrations in different monitoring studies conducted by the authors, and in particular in the aquatic environment of the Ebro River Delta (northeast of Spain), where both intensive rice cultivation and seafood production take place.

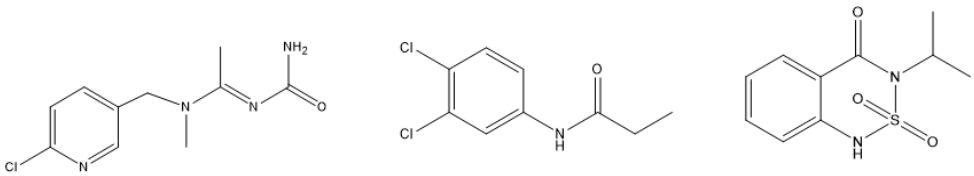

Figure 1: Chemical structure of the pesticides investigated.

The degradation studies were carried out at lab-scale in 250 mL Erlenmeyer flasks. 100 mL of microalgae biomass from a pilot-plant tubular photobioreactor [5], and the pesticide at a concentration of 1 mg/L were added. Erlenmeyers were placed in a thermostaticed chamber at 25ºC, with continuous light, under orbital shaking at 100 rpm. For each pesticide four different cultures, in triplicate, were carried out (see Table 1).

Experimental	Abiotic	Control	Killed
Microalgae	Mili-Q Water	Microalgae	Autoclaved microalgae
Pesticide	Pesticide	-	Pesticide
Light	Light	Light	Light

Table 1: Experimental conditions of each culture

Samples (i.e., a five-mililiter aliquot) were collected from each culture at time zero, 2 days and 7 days of the experiment. All samples were centrifuged at 10,000 rpm for two minutes at 25 ºC and then 1.5 mL of the supernatant was transferred to a vial containing 75 µL of the internal standard at a concentration of 10 µg/mL. Finally, the samples were stored at – 20 ºC until their analysis.

The analysis of the samples was performed on a Waters Acquity ultra-high performance liquid chromatgraphy (UHPLC) system coupled to a hybrid quadrupole-Orbitrap (Q-Exactive) tandem mass spectrometer equipped with a heated-electrospray ionization source HESI II. The HESI interface was operated in both the positive and the negative ionization modes. First, a full scan MS spectra was acquired in the rangre from 70 to 1,000 at a full width at half maximum (FWHM) resolution of 70,000 (at m/z 200). Once retention times and accurate masses of the pesticides were obtained, a subsequent data-dependant MS/MS scan event was conducted at a FWHM resolution of 17,500 (at m/z 200). Pesticide quantification was done with the isotope dilution method using the corresponding deuterated compound. Identification of TPs was based on the accurate mass of the molecular ion and associated MS/MS fragments and the presence of isotopic patterns.

3. Results and discussion

The results obtained showed that propanil and acetamiprid were degraded in the presence of the microalgae. In the case of propanil, the herbicide was fully degraded after 2 days of treatment. In the case of acetamiprid, degradation was slower than that observed for propanil. About 50% of the herbicide still remained in solution after 2 days of treatment, whereas it completely desappeared after 7 days. On the contrary, microalgae were not capable of degrading bentazone, as its concentration in solution remained stable after 7 days of treatment.

In the different control cultures (abiotic, control, and killed) pesticide concentrations were observed to be constant throughout the experiments. This indicates that the pesticides were not absorbed onto the biomass and, thus, analysis of the biomass was not required.

Analysis of full scan MS data obtained at t=0, 2 and 7 days of treatment using the Sieve software (Thermo Scientific) showed the formation of TPs, e.g., what appears a hydroxylation product of acetamiprid.

4. Conclusions

This work demonstrates the potential of microalgae to bioremediate pesticide-containing waters. The use of high resolution mass spectrometry-based analytical methods not only allowed evaluating the degradation potential of this treatment but also the fate of the pesticides during the treatment, including the potential formation of TPs.

5. References

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