



# Propionate addition enhances the biodegradation of the xenobiotic herbicide propanil and its metabolite

A. Oehmen<sup>a,\*</sup>, R. Marques<sup>a,b</sup>, J.P. Noronha<sup>a</sup>, G. Carvalho<sup>a,b</sup>, M.A.M. Reis<sup>a</sup>

<sup>a</sup> REQUIMTE/CQFB, Department of Chemistry, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

<sup>b</sup> Instituto de Biologia Experimental e Tecnológica (IBET), Av. da República, 2780-157 Oeiras, Portugal

## HIGHLIGHTS

- Enhanced degradation rates of propanil and DCA achieved with propionate addition.
- Co-metabolism of the xenobiotics with propionate was not a significant mechanism.
- Metabolic model was developed for biodegradation of the herbicide and its metabolite.
- Higher metabolic efficiency of the culture led to the stimulated degradation rates.

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## ABSTRACT

This study investigated ways of stimulating the biodegradation rates of the commonly applied herbicide, 3,4-dichloropropionanilide (propanil), and its metabolite, 3,4-dichloroaniline (DCA), as well as the growth rate of propanil- and DCA-degrading organisms in a mixed culture. Propionate, the other metabolite of propanil, stimulated the specific degradation rates of both propanil and DCA after a brief acclimation period. A metabolic model developed to characterise the metabolism of propanil and DCA biodegradation showed that the efficiency of oxidative phosphorylation (i.e. P/O ratio), which measures the metabolic efficiency, increased over time by 6- to 10-fold. This increase was accompanied by a 5- to 10-fold increase in the propanil and DCA biodegradation degradation rates. The biodegradation rates of the culture were unaffected when using an irrigation water matrix (Tejo river, Portugal), highlighting the utility of the culture for bioaugmentation purposes.

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## 1. Introduction

3,4-Dichloropropionanilide (propanil) is a herbicide that is applied worldwide in rice paddies. Propanil is primarily transformed in nature into propionate (readily biodegradable), and 3,4-dichloroaniline (DCA), which is very difficult to biodegrade. Both propanil and DCA can attack the nervous and immune systems and cause methemoglobinemia (Salazar et al., 2008). Therefore, these compounds should be removed from irrigation waters to avoid contaminating aquatic systems, soils and drinking water supplies. Propanil and DCA have been found in irrigation waters at levels that were several orders of magnitude above the maximum allowable discharge limit for pesticides of 0.1 µg L<sup>-1</sup> (Primel et al., 2007; Pesticides Framework Directive, 2009/128/EC).

In an earlier study, a suitable mixed culture for the degradation of both propanil and DCA in a sequencing batch reactor (SBR) was established for the purpose of treating irrigation waters through bioaugmentation (Carvalho et al., 2010). When a single feed at high initial propanil concentrations was replaced by step-feeding at lower initial propanil concentrations, the rate of propanil and DCA biodegradation increased after an acclimatisation period and DCA inhibition was not observed.

Despite the faster kinetics achieved with step-feeding, the overall removal of propanil and DCA by the culture was still limited by a very low biomass growth rate. This implies that a very long enrichment phase would be needed in order to cultivate the biomass and use it for bioaugmentation if propanil was used as the only carbon source. For this reason, in the present study, supplementary propionate was added, since the culture had already been demonstrated to degrade this readily biodegradable substrate generated through the primary degradation of propanil (Carvalho et al., 2010). Furthermore, the effect of propionate on the metabolism of the enriched

\* Corresponding author. Tel.: +351 212948571; fax: +351 212948550.

E-mail address: [a.oehmen@fct.unl.pt](mailto:a.oehmen@fct.unl.pt) (A. Oehmen).