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Batch *vs* continuous-feeding operational mode for the removal of pesticides from agricultural run-off by microalgae systems: A laboratory scale study

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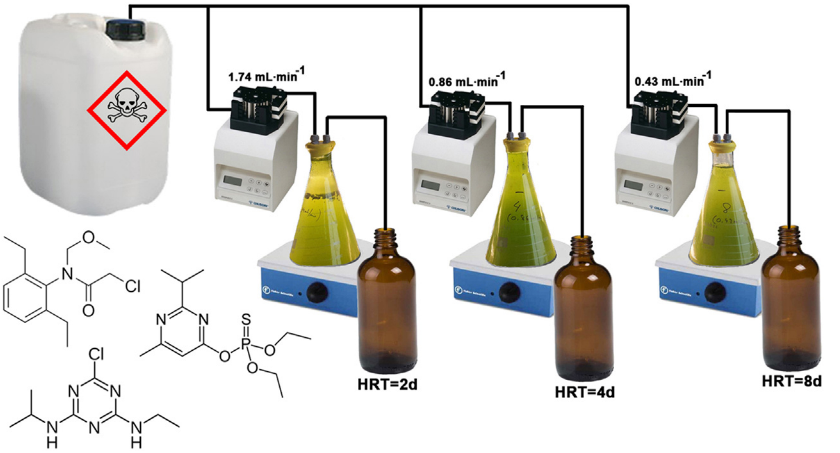
HIGHLIGHTS

- The effect of microalgae on the removal of pesticides has been evaluated.
- Continuous feeding operational mode is more efficient for removing pesticides.
- Microalgae increased the removal of some pesticides.
- Pesticide TPs confirmed that biodegradation was relevant.

GRAPHICAL ABSTRACT



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ABSTRACT

Microalgae-based water treatment technologies have been used in recent years to treat different water effluents, but their effectiveness for removing pesticides from agricultural run-off has not yet been addressed. This paper assesses the effect of microalgae in pesticide removal, as well as the influence of different operation strategies (continuous *vs* batch feeding). The following pesticides were studied: mecoprop, atrazine, simazine, diazinone, alachlor, chlorfenvinphos, lindane, malathion, pentachlorobenzene, chlorpyrifos, endosulfan and clofibric acid (tracer). 2 L batch reactors and 5 L continuous reactors were spiked to 10 μg L^{-1} of each pesticide. Additionally, three different hydraulic retention times (HRTs) were assessed (2, 4 and 8 days) in the continuous feeding reactors. The batch-feeding experiments demonstrated that the presence of microalgae increased the efficiency of lindane, alachlor and chlorpyrifos by 50%. The continuous feeding reactors had higher removal efficiencies than the batch reactors for pentachlorobenzene, chlorpyrifos and lindane. Whilst longer HRTs increased the technology's effectiveness, a low HRT of 2 days was capable of removing malathion, pentachlorobenzene, chlorpyrifos, and endosulfan by up to 70%. This study suggests that microalgae-based treatment technologies can be an effective alternative for removing pesticides from agricultural run-off.

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1. Introduction

Due to population growth and the resulting requirement to improve crop yields, pesticide use has risen considerably in recent years. The global market value for pesticides stood at US$54.8 billion in 2014 and is projected to reach US$81.8 billion by 2020 [1]. Agricultural run-off of these compounds from crops after a rainfall event is reported to be the main source of their presence in the aquatic environment. Consequently, it has been reported that macroinvertebrate community structures and ecosystem functions may be impaired by the presence of pesticides in agricultural streams [2]. For instance, chemicals such as atrazine and alachlor, to name just two, have been banned by several governments, whilst others, such as malathion or diazinone, remain under constant review and may be either gradually phased out or banned.

Several phytoremediation technologies, such as buffer wetlands or microalgae-based ponds, can be used to overcome this issue [3]. Although most of the systems used for pesticide attenuation in agricultural run-off are wetlands, microalgae acceptation is on the rise for many reasons, such as the resource recovery of algal biomass, for use as a fertilizer, a source of products or biofuel. It also has the advantage of providing a high-quality treated effluent [4]. Although the capability of microalgae treatment systems to remove organic matter and nutrients from polluted water has already been studied, few studies have focused on the removal of organic microcontaminants. Existing laboratory-scale studies dealing with microalgae's capacity to remove organic microcontaminants such as phenolic compounds, surfactants, biocides and polycyclic aromatic hydrocarbons suggest that microalgae-based wastewater treatment systems may remove them by evaporation, photodegradation, biodegradation, or microalgae uptake [5–7]. Nevertheless, little attention has been paid to the processes involved in pesticide removal or the effect of microalgae on them.

The performance of microalgae-based systems depends on the cultivation strategies followed. Ho and Ye [8] showed that the fed-batch and continuous-culture systems have certain advantages, including high biomass productivity and low operational cost. However, reported studies on the attenuation of pesticides by microalgae systems have been performed only in shake flasks (batch mode) under controlled sterile conditions [5,9]. Therefore, it is difficult to scale up the results to pilot-scale plant systems, which normally operate in continuous mode and are fed with real water effluents containing bacteria and other complex components. Another key factor in designing an operation strategy is hydraulic retention time (HRT). It is widely accepted that the longer the HRT, the more likely the biodegradation, photodegradation and sorption processes are to occur in biologically-based treatment technologies [10]. Nevertheless, there are gaps in the knowledge regarding the capability of microalgae to remove pesticides from agricultural run-off and how the different operation strategies (batch *vs* continuous feeding and HRT) affect it. The results of this study can thus be applied to different agricultural run-off scenarios, such as those from intensive agriculture (*e.g.,* greenhouse industry).

This study aimed to evaluate the effect of the presence of microalgae, HRT and the feeding operational mode on the removal efficiency of 11 pesticides by microalgae-based treatment system. The pesticides were selected on the basis of their concentration, their high frequency of detection in surface water bodies and, above all, their inclusion on the EU priority list.

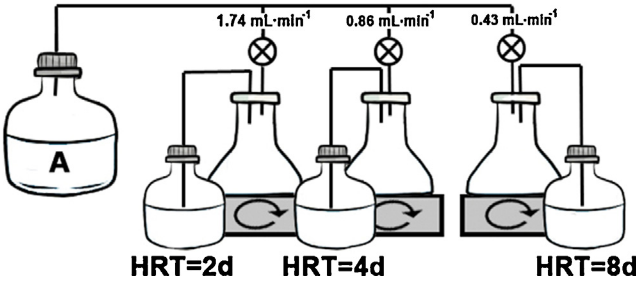

Fig. 1. Continuous feeding reactors (5 L). A shows the reservoir tank (10 L).

2. Material and methods

2.1. Experimental design

2.1.1. Batch reactors

In order to study the effect of microalgae on the removal of microcontaminants, 2 different types of reactors were studied (presence *vs* absence of microalgae), with 3 replicates per type (6 reactors in total). All reactor systems consisted of 2.5 L glass containers. Standard solution containing the 11 microcontaminants and a tracer compound in methanol solution was added to each reactor (final water volume of 2 L) to obtain a final concentration of 10 $\mu g\,L^{-1}$. This concentration was in keeping with the high concentration levels detected for pesticides in agricultural surface water following a runoff or spray drift events [11,12]. The tracer compound clofibric acid was used to follow the attenuation process as reported elsewhere [13]. The setup included magnetic stirred reactors with and without microalgae. Microalgae reactors were inoculated with a microalgae consortium obtained from an experimental high-rate algal pond treating urban wastewater [14] and were acclimatised with agricultural drainage water for more than 1 month. The microalgae were inoculated to a concentration of approximately 500 $mg\,L^{-1}$ dry weight biomass per reactor to simulate the average biomass concentration observed in the continuous feeding reactors after 1 month of acclimatisation (see Section 3.1). The experiments were run simultaneously for 10 days.

2.1.2. Continuous reactors

Each experimental setup consisted of one 10 L glass tank (reservoir tank) and three 5 L glass reactors (Fig. 1). Each reactor was fed with agricultural drainage water from the reservoir tank by means of a Minipuls 2 peristaltic pump (Gilson, Villiers le Bel, France) at water flows of 0.43, 0.86 and 1.74 $mL\,min^{-1}$. Finally, the water from the reactors was collected in 2.5 L amber glass tanks. The reactors were inoculated with microalgae to a concentration of approximately 100 $mg\,L^{-1}$ dry weight biomass. They were then operated for three different HRTs each (2, 4 and 8 days) for a month. Following that acclimatisation time, the reactors were spiked with pesticides to obtain a final concentration of 10 $\mu g\,L^{-1}$.

2.1.3. Microalgae and water composition

The microalgae consortium was pre-acclimatised to the growth conditions for more than 1 month before the reactors were stocked with it. The main populations were made up of *Chlorella* sp. and *Scenedesmus* sp. Note that this inoculum also contained bacteria; however, microalgae accounted for over 90% of the biomass, as is usually the case in high rate algal ponds (HRAPs) [15]. The agricultural run-off water used for the experiments was collected from agricultural drainage channels (41°17′22.4″N 2°02′39.4″) and had the following average composition: total suspended solids (TSS), 50 ± 8 $mg\,L^{-1}$; total chemical demand of oxygen (COD), 30 ± 5 $mg\,L^{-1}$; NH_4-N, 4 ± 1 $mg\,L^{-1}$. The reactors were set up in a temperature-controlled growth room at 23 ± 5 °C