Journal of Hazardous Materials 288 (2015) 34–42

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Capability of microalgae-based wastewater treatment systems to remove emerging organic contaminants: A pilot-scale study

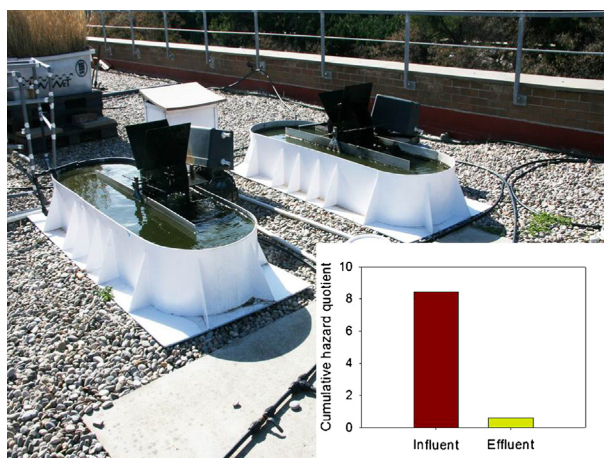
Víctor Matamoros [a,*], Raquel Gutiérrez [b], Ivet Ferrer [b], Joan García [b], Josep M Bayona [a]

[a] Department of Environmental Chemistry, IDAEA-CSIC, c/Jordi Girona, 18-26, E-08034, Barcelona, Spain
[b] GEMMA-Group of Environmental Engineering and Microbiology, Department of Hydraulic, Maritime and Environmental Engineering, Universitat Politècnica de Catalunya BarcelonaTech, c/Jordi Girona, 1-3, Building D1, E-08034, Barcelona, Spain

HIGHLIGHTS

- The effect of hydraulic retention time and seasonality has been evaluated.
- Removal efficiency ranged from undetectable removal to more than 90%.
- Biodegradation and photodegradation were the most important removal pathways.
- We suggested that microalgae enhance the biodegradation of emerging contaminants.
- Up to 90% of the contaminant toxicity risk was removed by microalgae treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 July 2014
Received in revised form 12 January 2015
Accepted 1 February 2015
Available online 3 February 2015

Keywords:
Emerging organic contaminants
Microalgae
High-rate algal pond
Photodegradation
Biodegradation
Volatilization

ABSTRACT

The effect of hydraulic retention time (HRT) and seasonality on the removal efficiency of 26 organic microcontaminants from urban wastewater was studied in two pilot high-rate algal ponds (HRAPs). The targeted compounds included pharmaceuticals and personal care products, fire retardants, surfactants, anticorrosive agents, pesticides and plasticizers, among others. The pilot plant, which was fed at a surface loading rate of 7–29 g of COD m^{-2} d^{-1}, consisted of a homogenisation tank and two parallel lines, each one with a primary settler and an HRAP with a surface area of 1.5 m^2 and a volume of 0.5 m^3. The two HRAPs were operated with different HRTs (4 and 8 d). The removal efficiency ranged from negligible removal to more than 90% depending on the compound. Microcontaminant removal efficiencies were enhanced during the warm season, while the HRT effect on microcontaminant removal was only noticeable in the cold season. Our results suggest that biodegradation and photodegradation are the most important removal pathways, whereas volatilization and sorption were solely achieved for hydrophobic compounds (log Kow > 4) with a moderately high Henry's law constant values (11–12 Pa m^{-3} mol^{-1}) such as musk fragrances. Whereas acetaminophen, ibuprofen and oxybenzone presented ecotoxicological hazard quotients (HQs) higher than 1 in the influent wastewater samples, the HQs for the effluent water samples were always below 1.

* Corresponding author. Tel.: +34 934006100.
E-mail address: victor.matamoros@idaea.csic.es (V. Matamoros).

http://dx.doi.org/10.1016/j.jhazmat.2015.02.002
0304-3894/

1. Introduction

Emerging organic contaminants (EOCs) include a wide range of compounds belonging to different chemical classes, such as pharmaceuticals, personal care products, plasticizers, flame retardants, surfactants, and certain pesticides, among others, the ecotoxicological effects of which are relatively unknown [1]. Since conventional wastewater treatment plants (WWTPs) are not designed to remove emerging and related contaminants, many of these compounds occur at different concentrations in natural water bodies [2], where they may exert ecotoxicological effects at relatively low concentrations [3,4]. Although some of the compounds have been proposed for inclusion on regulatory lists of contaminants (European Commission, 2006), there is relatively little information on the ecotoxicological effects of complex mixtures at environmental levels, and, to date, they have not been regulated [1]. Known environmental effects of some EOCs include the reduction of macroinvertebrate diversity in rivers [3], behavioural changes in mosquito fish [4] and reproductive disruption in fish [5], among others. Due to the difficulty of assessing the effects of EOCs on ecosystems, the use of hazard quotients (HQs) based on the chemical composition of water samples and tabulated predicted non-effect concentrations (PNECs) for different aquatic organisms has been postulated as a good screening strategy [6].

Microalgae-based wastewater treatment technologies such as high-rate algal ponds (HRAPs) have received considerable attention in recent years due to the resource recovery of algal biomass, for use as fertilizer, protein-rich feed or biofuel, and a high-quality effluent (treated wastewater) [7]. HRAPs are shallow raceway reactors in which microalgae and bacteria grow in symbiosis. In such systems, organic matter is degraded by heterotrophic bacteria, which consume oxygen provided by microalgal photosynthesis; therefore, no aeration is needed [8]. Although the capability of microalgae wastewater treatment systems to remove nutrients, heavy metals, bacteria, and helminthic eggs has been studied since the 1950s, few studies have focused on the removal of organic contaminants [9–12]. Indeed, no attention has been paid to the effectiveness of HRAPs for removing EOCs of environmental concern.

The removal of EOCs by conventional activated sludge WWTPs has been widely studied, but the effectiveness of HRAPs for removing EOCs from wastewater has not yet been addressed. There is only one study dealing with HRAPs' capacity to remove tetracyclines, and it was performed at laboratory-scale with synthetic wastewater [13]. Other studies dealing with microalgae's capacity to remove organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), biocides (e.g. organotin compounds), surfactants and phenolic compounds, suggest that microalgae-based wastewater technologies may remove microcontaminants by both abiotic (sorption, volatilization or photodegradation) and biotic (biodegradation, microalgae uptake or metabolization) processes [14–16].

The aim of this study was to evaluate for the first time, the effect of hydraulic retention time (HRT) and ambient temperature/sunlight irradiation (seasonality) on the removal efficiency of 26 EOCs in two HRAP pilot plants fed with real urban wastewater. The selected compounds were high production volume chemicals (e.g. fire retardants, surfactants, anticorrosive agents, pesticides, plasticizers, pharmaceuticals and personal care products, among others). Finally, aquatic risk assessment was performed based on the concentrations of the detected EOCs in the influent and effluent water samples, and the listed EC50 values for *Daphnia magna.*

2. Material and methods

2.1. Chemicals and reagents

Gas chromatography (GC) grade (Suprasolv) hexane, methanol, and ethyl acetate were obtained from Merck (Darmstadt, Germany). Analytical-grade hydrogen chloride was obtained from Panreac (Barcelona, Spain). Caffeine, acetaminophen, ibuprofen, methyl dihydrojasmonate, oxybenzone, ketoprofen, hydrocinnamic acid, 5-methylbenzotriazole, naproxen, carbamazepine, galaxolide, benzothiazole, diclofenac, methylparaben, benzotriazole, tonalide, OH-benzothiazole, tributyl phosphate, tris(2-chloroethyl) phosphate, triphenyl phosphate, triclosan, cashmeran, octylphenol, diazinon, celestolide, atrazine, bisphenol A, 2,4-D, atrazine D5, mecoprop D3, tonalide D3 and dihydrocarbamazepine were purchased from Sigma–Aldrich (Steinheim, Germany). Trimethylsulfonium hydroxide (TMSH) was obtained from Fluka (Buchs, Switzerland). Strata-X polymeric SPE cartridges (200 mg) were purchased from Phenomenex (Torrance, CA, USA) and the 0.7 μm glass fibre filters (Ø 47 mm) were obtained from Whatman (Maidstone, UK).

2.2. Description of the HRAP pilot plant

The experimental set-up was located outdoors at the laboratory of the GEMMA research group (Universitat Politècnica de Catalunya–BarcelonaTech, Spain). The system has been operated since March 2010. The microalgae production system was composed of a screening pre-treatment and two identical parallel lines, each one equipped with a primary settler, a pilot high-rate algal pond and a final settler for biomass separation (Fig. 1). Paddle wheel was set at 5 rpm giving mixed liquor with a linear velocity of recirculation of 11 cm s^{-1}, enough to ensure complete mixing. Urban wastewater was pumped from a municipal sewer to a homogenisation tank (1.2 m^3), which was continuously stirred to avoid solids sedimentation. From there, the wastewater was pre-treated and conveyed to each line. The primary treatment included a settler with an internal diameter of 0.3 m, a total height of 0.4 m and an effective volume of 7 L that was operated at an HRT of 0.9 h. Primary effluent from the settlers was pumped to the HRAPs by means of peristaltic pumps. The experimental HRAPs were PVC raceway ponds equipped with a paddle wheel for stirring the mixed liquor (Fig. 1). The two HRAPs had a nominal volume of 0.47 m^3, a surface area of 1.54 m^2 and a water depth of 0.3 m, and they were operated simultaneously with different HRTs (4 and 8 days corresponding to 117.5 and 58.8 L d^{-1}, respectively). The final settlers for biomass separation had an internal diameter of 0.15 m, a total height of 0.3 m and an effective volume of 3.5 L that were operated at an HRT of 0.7 and 1.4 h for the HRAP set at 4 days HRT and 8 days, respectively. Note that these settlers were only used for biomass separation, which was not recycled back to the HRAPs.

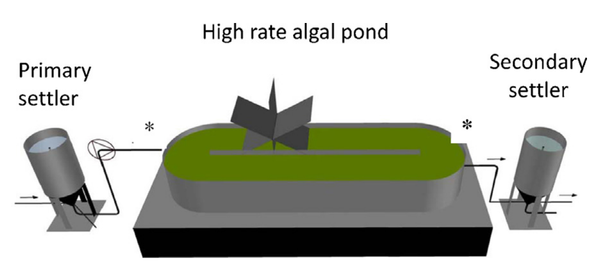


Fig. 1. 3D view of treatment units of one line. Primary settler is fed with screened wastewater. Secondary settler allows separation of the biomass produced in the HRAP. Sampling points are indicated (*).