Water Research 119 (2017) 136–149

Contents lists available at ScienceDirect

Water Research

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

# Environmental risk assessment of effluents as a whole emerging contaminant: Efficiency of alternative tertiary treatments for wastewater depuration

B. Díaz-Garduño [a, *], M.G. Pintado-Herrera [a], M. Biel-Maeso [a], J.J. Rueda-Márquez [b], P.A. Lara-Martín [a], J.A. Perales [b], M.A. Manzano [b], C. Garrido-Pérez [b], M.L. Martín-Díaz [a]

[a] Physical Chemical Department, Centro Andaluz de Ciencia y Tecnologías Marinas (CACYTMAR), Instituto Universitario de Investigaciones Marinas (INMAR), Campus de Excelencia Internacional del Mar (CEI•MAR), Universidad de Cádiz, Campus Universitario de Puerto Real, 11510, Puerto Real, Cádiz, Spain

[b] Environmental Technologies Department, Centro Andaluz de Ciencia y Tecnologías Marinas (CACYTMAR), Instituto Universitario de Investigaciones Marinas (INMAR), Campus de Excelencia Internacional del Mar (CEI•MAR), Universidad de Cádiz, Campus Universitario de Puerto Real, 11510, Puerto Real, Cádiz, Spain

A R T I C L E I N F O

*Article history:*
Received 17 November 2016
Received in revised form
3 April 2017
Accepted 8 April 2017
Available online 10 April 2017

*Keywords:*
Microalgae-culture
Aquatic ecosystem
Removal efficiency
Advance oxidation processes
Pharmaceutical and personal care products
Regulated compounds

A B S T R A C T

Emerging contaminants (ECs) and regulated compounds (RCs) from three different WWTP effluents were measured in the current study. The efficiency of two tertiary treatments, Photobiotreatment (PhtBio) and Multi-Barrier Treatment (MBT), for removing contaminants was determined. Results indicated different percentages of removal depending on the treatment and the origin of the effluent. Risk Quotients (RQs) were determined for different species of algae, *Daphnia*, and fish. RQ results revealed diverse risk values depending on the bioindicator species. Tonalide, galaxolide (fragrances), and ofloxacin (antibiotic) were the most persistent and harmful substances in tested effluents. "Negligible risk" category was reached since a wide diversity of ECs were removed by MBT with high removal percentages. Contrarily, PhtBio was effective only in the depuration of certain chemical compounds, and its efficiency depended on the composition of the raw effluent.



## 1. Introduction

Currently, detection of emerging contaminants (ECs) at very low concentrations due to the advances in analytical techniques, has revealed a worldwide issue (Stuart et al., 2012). During the last decade, research studies regarding the environmental impact of chemical pollution have switched from conventional priority contaminants to compounds that are present at lower concentrations as ECs (Papa et al., 2013). Municipal effluents have been recognized as a major source of many environmental contaminants such as regulated compounds (RCs) including: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides (Pintado-Herrera et al., 2014); or heavy metals (Fu and Wang, 2011).

Recently, pharmaceutically active compounds (PhACs) and personal care products (PCPs), among other ECs, have been identified in municipal effluents (Lara-Martín et al., 2014; Maranho et al., 2015; Pintado-Herrera et al., 2014). Adverse effects have been reported in previous publications for aquatic environments such as neuroendocrine, mutagenic, or health effects due to the exposition of ECs (e.g. François et al., 2015; Quinn et al., 2011). Additionally, several ECs (e.g. synthetic musks) are persistent and bio-accumulative due to their hydrophobicity, even though it occurs at very low concentrations (μg–ng/L) (Deblonde and Hartemann, 2013). Hydrophobic compounds come into the aquatic organisms through different pathways like gills or cellular walls to their circulatory fluid (Lee et al., 2015). Presence of these xenobiotics activates the defensive mechanism of the organisms and provokes metabolic responses, and consequently adverse effects in their bodies. Likewise, recent studies of PCPs have documented adverse effects in aquatic biota exposed to wastewaters

* Corresponding author. Present address: Andalusian Centre for Marine Science and Technology (CACYTMAR), Instituto Universitario de Investigaciones Marinas (INMAR), Universidad de Cádiz, Campus Universitario de Puerto Real, 11510, Puerto Real, Cádiz, Spain.
*E-mail address:* beatriz.diaz@uca.es (B. Díaz-Garduño).

http://dx.doi.org/10.1016/j.watres.2017.04.021
0043-1354/

**Acronyms**

| | |
|---|---|
| AHTN | Tonalide |
| ALBU | Albuterol |
| ALOL | Atenolol |
| AMT | Amitriptyline |
| AOP | Advance oxidation process |
| AZMYC | Azithromycin |
| BFIF | Benzafibrate |
| BOD | Biological oxygen demand |
| BP3 | Benzophenone |
| BpA | Bisphenol A |
| CAFF | Caffeine |
| CBZ | Carbamazepine |
| CELE | Celestolide |
| CHLO | Chlorpyrifos |
| CLIND | Clindamycin |
| COD | Chemical oxygen demand |
| CWPO | Catalytic wet peroxide oxidation |
| DDT | Dichloro diphenyl trichloroethane |
| DEET | N,N-Dietil-meta-toluamida |
| DIC | Diclofenaco |
| $EC_{50}$ | Half maximal effective concentration |
| ECs | Emerging Contaminants |
| EMYC | Erythromycin |
| EST | Estrone |
| FAMO | Famotidine |
| FENO | Fenofibrate |
| FLUX | Fluoxetine |
| FURO | Furosemide |
| GAC | granular activated carbon |
| GEMF | Gemfibrozil |
| GLYB | Glyburide |
| HCTZ | Hydrochlorothiazide |
| HHCB | Galaxolide |
| RQ | Risk Quotient |
| HRAP | High rate algal ponds |
| IBU | Ibuprofen |
| KPF | Ketoprofen |
| LINCO | Lincomycin |
| MBT | Multibarrier treatment |
| MEC | Measured environmental concentration |
| MK | Musk ketone |
| MLOL | Metoprolol |
| MNS | Monensin |
| MNZ | Metronidazole |
| MS | Mass Spectrometry |
| MTCS | Methyl-Triclosan |
| MX | Musk xylene |
| NANO | Nadolol |
| NCIN | Norfloxacin |
| NPX | Naproxen |
| O&M | Operational and Maintenance |
| OCIN | Ofloxacin |
| OTNE | 1-(1,2,3,4,5,6,7,8 Octahydro-2,3,8,8-tetramethyl-2-naphthalenyl) ethanone |
| PAHs | Polycyclic aromatic hydrocarbons |
| PCBs | polychlorinated biphenyls |
| PCPs | Personal care products |
| PhACs | Pharmaceutically active compounds |
| PHE | Phenazone |
| PHEN | Phenantreno |
| PhtBio | Photobiotreatment |
| PNEC | Predicted no-effect concentration |
| PRLOL | Propranolol |
| RANI | Ranitidine |
| RCs | Regulated Compounds |
| RMYC | Roxithromycin |
| SBSE | Stir bar sorptive extraction |
| SMZ | Sulfamethoxazole |
| SMZO | Sulfamethizole |
| SPE | Solid phase extraction |
| SS | Suspended solids |
| STZ | Sulfathiazole |
| TCS | Triclosan |
| TLOL | Timolol |
| TMT | Trimethoprim |
| TPP | Triphenylphosphate |
| UV | Ultraviolet |
| WET | Whole effluent toxicity |
| WWTPs | Wastewater treatment plants |

(e.g. Vallecillos et al., 2015).

Worldwide consumption of substances containing ECs has increased along with their detection in wastewater and receiving aquatic ecosystems (Lara-Martin et al., 2015; Maranho et al., 2015). Following the legislation requirements, WWTPs are designed to eliminate suspended solids, organic matter, and nutrients. Nevertheless, several studies have pointed out that conventional methodologies used to depurate municipal wastewater treatment plant (WWTPs) effluents are generally unable to effectively remove ECs (Gracia-Lor et al., 2012; Verlicchi et al., 2012b).

In recent years, many international research groups and governmental institutions have directed their efforts on assessing together the environmental quality of wastewater discharges and the potential adverse effects on the receiving ecosystems. Moreover, researchers have also focused on the incorporation of an additional tertiary treatment to the traditional ones in order to achieve a higher level of depuration aiming to remove specific groups of chemicals, pathogens, etc. that are not removed with traditional technologies (Gupta and Thakur, 2015).

Together with the sequestration of heavy metals (Suresh Kumar et al., 2015), organic pollutants (Hemalatha and Venkata Mohan, 2016) and pathogen organisms (García et al., 2008), the use of microalgae biotechnology for wastewater treatment is particularly attractive because of its photosynthetic capabilities, producing useful biomass using solar energy and incorporating nutrients (nitrogen and phosphorus) causing eutrophication (Mennaa et al., 2015).

Using microalgae for wastewater treatment was first published sixty years ago by Oswald and Gotaas (1957). Since then, it has been intensively tested and nowadays there are some examples of full-scale application of microalgae processes in WWTP (e.g. EU FP7 ALL-GAS project, n° ENER/FP7/268208) (All-Gas, 2016). The main disadvantages of the traditional advanced Biological Nutrient Removal technologies (BNR) for nutrients removal are high costs, complex operation and great volume of waste sludge production (Lugowski et al., 2007). In the case of tertiary treatments for