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Effect of advanced oxidation processes on the micropollutants and the effluent organic matter contained in municipal wastewater previously treated by three different secondary methods

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ABSTRACT

In this study, wastewater from the output of three different secondary treatment facilities (Activated Sludge, Moving Bed Bioreactor and Coagulation-Flocculation) present in the municipal wastewater treatment plant of Vidy, Lausanne (Switzerland), was further treated with various oxidation processes (UV, UV/H_2O_2, solar irradiation, Fenton, solar photo-Fenton), at laboratory scale. For this assessment, 6 organic micropollutants in agreement with the new environmental legislation requirements in Switzerland were selected (Carbamazepine, Clarithromycin, Diclofenac, Metoprolol, Benzotriazole, Mecoprop) and monitored throughout the treatment. Also, the overall removal of the organic load was assessed. After each secondary treatment, the efficiency of the AOPs increased in the following order: Coagulation-Flocculation < Activated Sludge < Moving Bed Bioreactor, in almost all cases. From the different combinations tested, municipal wastewater subjected to biological treatment followed by UV/H_2O_2 resulted in the highest elimination levels. Wastewater previously treated by physicochemical treatment demonstrated considerably inhibited micropollutant degradation rates. The degradation kinetics were determined, yielding: $k_{(UV)} < k_{(UV/H2O2)}$ and $k_{(Fenton)} < k_{(solar\ irradiation)} < k_{(photo\text{-}Fenton)}$. Finally, the evolution of global pollution parameters (COD & TOC elimination) was followed and the degradation pathways for the effluent organic matter are discussed.

1. Introduction

Currently, one of the environmental concerns in global scale is the presence and accumulation of micropollutants (MPs) in the natural environment. These substances are comprising an increasing list of anthropogenic contaminants, which include among others, pharmaceuticals, personal care products, steroid hormones, industrial chemicals, pesticides and many other emerging compounds (Luo et al., 2014). The majority of these substances are designed to be biologically active, and therefore, their occurrence can affect the receiving environment. Some of the associated problems to MPs' presence are the ecotoxicity of their mixture (Gregorio and Chèvre, 2014), the enhancement of antibiotic resistance by the presence of antibiotics and their metabolites in the environment (Rizzo et al., 2013), or the problematic identification of the transformed metabolites of drugs in the nature (Fatta-Kassinos et al., 2011).

Wastewater treatment plants have been built, transformed and updated through the years to effectively remove -among others-solids, organic and inorganic compounds (carbon, nitrogen,

Abbreviations: AOP, Advanced Oxidation Process; AOS, Average Oxidation State; AS, Activated Sludge; CDOM, Chromophoric Dissolved Organic Matter; CF, Coagulation-Flocculation; COD, Chemical Oxygen Demand; DOC, Dissolved Organic Carbon; DOM, Dissolved Organic Matter; EfOM, Effluent Organic Matter; EPS, Extracellular Polymeric Substances; FOEN, Federal Office for the Environment; MBBR, Moving Bed Bioreactor; MP, Micropollutant; NOM, Natural Organic Matter; OxOM, Oxidizable Organic Matter; PhOM, Photo-sensitizable Organic Matter; SMP, Soluble Microbial Products; SPE, Solid Phase Extraction; SRT, Sludge Retention Time; SUVA, Specific UV Absorbance; TOC, Total Organic Carbon; TSS, Total Suspended Solids; WW, Wastewater; WWTP, Wastewater Treatment Plant.

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phosphorus etc.), which were previously disposed in the environment. However, the challenge posed by the hydrophilic MPs, is an obstacle the majority of the WWTPs are not equipped to handle. Margot et al. (2013) have reported that from the 70 dissolved organic MPs detected in raw effluents, many of them were removed at less than 30% in the conventional activated sludge process.

However, micropollutant degradation has been achieved by the use of ozonation or Advanced Oxidation Processes (AOPs). These processes have successfully mineralized or converted the persistent MPs to less harmful forms (Ikehata et al., 2006). Although the hydroxyl radical (HO•) is the main oxidizing agent in these processes (oxidative power: 2.80 eV), their application often induces the production and participation of other reactive oxygen species (ROS), such as superoxide radical anions, hydroperoxyl radicals, singlet and triplet oxygen etc. (Ikehata et al., 2006). The main advantage of the AOPs application is the characteristic versatility with which the method can be achieved. For instance, photolysis acts directly or indirectly, by absorption of energy and excitation or photosensitizing agents, typically dissolved organic matter (DOM) (de la Cruz et al., 2012).

In Switzerland, actions against the issue of MPs were systematically taken since 2006, when the Micropoll Strategy was implemented, by the Federal Office for the Environment (FOEN, 2014). The outcome of the project was an adaptation of the Water Protection Ordinance (GSchV) and 80% of the total MPs was decided to be eliminated, with 5 substances playing the role of indicator (Table 1). The adaptation was finally voted in 2014 and will be effective starting January 2016. WWTPs will have to eliminate at least 80% amount of 6 pollutants (from a list of 12), divided in "very well eliminated" and "well eliminated", as presented in Table 1. Oxidation (for instance by ozone or AOPs) or adsorption (activated carbon) are suggested to tackle the issue.

In this work, the ability of AOPs to degrade MPs at lab scale, after 3 different secondary treatment methods is tested. UV/H_2O_2 and solar photo-Fenton, as well as their three composing sub-processes (UV-C at 254 nm, solar light and Fenton reaction), are considered as a final treatment step after Activated Sludge (AS), Moving Bed Bioreactor (MBBR) or Coagulation-Flocculation (CF) treatment. 6 pollutants were selected from the list of 12 indicators provided by FOEN, also contained in the WW from Vidy WWTP (Lausanne, Switzerland). The degradation kinetics, the oxidation levels and the effect of the preceding secondary treatment are given and the dependence of success as a function of the previous treatment steps. Finally, considerations on the role of effluent organic matter (EfOM) are given.

2. Materials and methods

2.1. Sampling campaign

In total, 4 sampling campaigns took place. The strategy was as follows: for two consecutive days, 2-L samples were taken at 9am, 12pm and 15pm. The composite sample (12 L) was then mixed and analyzed/treated. The physicochemical analysis was immediately performed, while the MPs were analyzed the day after the creation of the composite (preservation at 4 °C). The samples were collected from the primary effluents (point 1, Fig. 1) and at the output of the different secondary treatment facilities in the WWTP of Vidy: Activated Sludge (AS), Moving Bed Bioreactor (MBBR) and Coagulation-Flocculation (CF) (points 2, 3 and 4, Fig. 1).

2.2. Chemicals and reagents

All the chemicals for the experiments were used as received. Hydrogen Peroxide 30%, Iron Sulfate Heptahydrate and Titanium Oxysulfate (1.9–2.1%) were acquired from Sigma–Aldrich (Switzerland) and Sodium Bisulfite from Acros Organics (Switzerland).

2.3. Employed reactors

For the UV-C irradiation and UV/H_2O_2 treatment methods, two 300 mL double-wall, water-jacketed glass batch stirred reactors were used in parallel. Each of them contained a 36-W, low-pressure

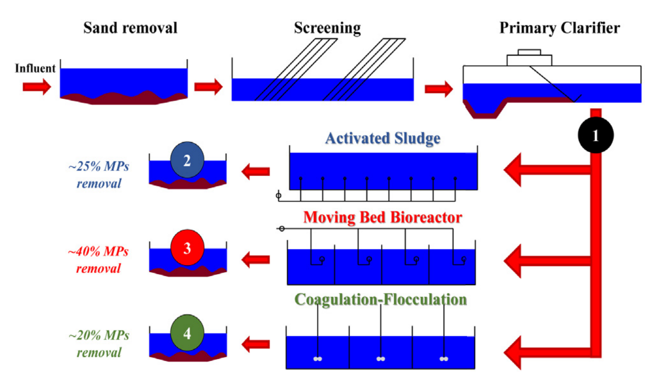

Fig. 1. Simplified overview of the Vidy WWTP and the sampling points used in the study.

Table 1
Evolution of indicator pollutants in the Swiss legislation.

5 Indicators (2009 list)	List of 12 indicators (2016 enforcement)	Pollutant type
	Very Well Eliminated	
Benzotriazole	Amisulpride	*Antidepressant*
Carbamazepine	Carbamazepine	*Antiepileptic*
Diclofenac	Citalopram	*Antidepressant*
Mecoprop	Clarithromycin	*Antibiotic*
Sulfamethoxazole	Diclofenac	*Analgesic*
	Hydrochlorothiazide	*Diuretic*
	Metoprolol	*Beta blocker*
	Venlafaxine	*Antidepressant*
	Well Eliminated	
	Benzotriazole	*Anticorrosive*
	Candesartan	*Angiotensin II antagonist*
	Irbesartan	*Angiotensin II antagonist*
	Mecoprop	*Herbicide*