Application of (V)UV/O₃ technology for post-treatment of biologically treated wastewater: A pilot-scale study

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HIGHLIGHTS

- (V)UV irradiation involving *in situ* generated O₃ was applied to treat wastewater.
- Removal efficiencies of the selected drugs were >95% in the pilot plant.
- High disinfection capacity (>log-5) was achieved.
- Wastewater after post-treatment showed no genotoxicity nor acute toxicity.

ARTICLE INFO

ABSTRACT

For the first time, high energy VUV photons and generation of O₃ by (V)UV lamps were applied together for removal of active pharmaceutical ingredients (APIs) from biologically treated wastewater (BTWW) in pilot-scale. The core of the pilot container unit was a photoreactor assembly consisting of six photoreactors, each containing a low-pressure Hg lamp (UV dose of 1.2 J/cm² and 6.6 J/cm² at 185 nm and 254 nm, respectively). BTWW was irradiated (4.75 min residence time) by (V)UV light in presence of *in situ* photochemically generated O₃ from coolant air of the lamps. Experiments were conducted at the site of two wastewater treatment plants. Out of seven target APIs (namely carbamazepine, ciprofloxacin, clarithromycin, diclofenac, metoprolol, sitagliptin, and sulfamethoxazole), 80−100% removal was accomplished for five and 40−80% for two compounds. Two degradation products of carbamazepine were detected. Degradation products of other target compounds were not found. The applied O₃ dose was 30−45 μg O₃/mg dissolved organic carbon. Inactivation of up to log-4.8, log-4.5 and log-3.8 could be achieved for total coliform, *Escherichia coli* and *Enterococcus faecalis*, respectively. SOS Chromotest indicated no genotoxicity nor acute toxicity. Generation of neither NH_4^+, NO_2^- nor NO_3^- was observed during post-treatment. Electric energy per order values were calculated for the first time for (V)UV/O₃ treatment in BTWW with a median value of 1.5 kWh/m³. This technology can be proposed for post-treatment of BTWWs of small settlements or livestock farms to degrade micropollutants before water discharge or for production of irrigation water. Further studies are essential in pilot-scale for other applications.

1. Introduction

High (over)consumption of drugs is a worldwide phenomenon. Pharmaceuticals are consumed in growing quantities, partly driven

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by the increasing demand for drugs to treat chronic diseases or aging-related problems. In general, active pharmaceutical ingredients (APIs) administered to humans are not completely metabolized in the body, thus they are excreted partially in unchanged form together with various metabolites and conjugates through urine or feces (Salimi et al., 2017). Moreover, direct disposal of unused or expired drugs into communal sewage systems also plays a key role in their presence in communal wastewater. Traditional procedures implemented in wastewater treatment are unable to remove a wide range of APIs (Gomes et al., 2017; Guillossou et al., 2019). As a consequence, APIs together with other emerging contaminants (ECs) such as personal care products, pesticides, industrial additives etc., have been detected in raw and treated wastewater, surface and groundwater up to μg/L concentrations, some of them are even present in drinking water, usually in ultra-low traces (ng/L) (Gros et al., 2012; Wilkinson et al., 2017). Some of these compounds are highly persistent in the aquatic environment and are hardly degraded. Moreover, even compounds with shorter environmental half-lives become persistent in surface waters because their discharge into rivers and lakes is continuous, hence they are also referred to as pseudo-persistent organic pollutants (Licul-Kucera et al., 2019). Furthermore, possible cocktail effects from the combined presence of many ECs in the environment are not well understood (European Commission, 2019).

As a direct consequence of the abovementioned issues, development of antibiotic-resistance in freshwater ecosystems is of particularly high concern (Russell and Yost, 2021). According to a 2019 report of the Centers for Disease Control and Prevention, each year more than 35 000 people die in the United States as a result of antibiotic-resistant infections (CDC, 2019). In their report, 18 antibiotic-resistant bacteria and fungi of high threat were listed including several multidrug-resistant ones.

In recent years, several advanced oxidation processes (AOPs) have been investigated in pilot- or full-scale for the removal of APIs as an additional step for conventional wastewater treatment. One of the most commonly implemented AOP is ozonation. Full-scale ozonation was efficiently applied in several wastewater treatment plants (WWTPs) and is being implemented in >100 WWTPs within the frames of the Swiss Government's national policy for reducing micropollutants (Logar et al., 2014). Bourgin et al. investigated full-scale ozonation in a WWTP followed by different additional post-treatments (i.e., sand filtration, moving bed, fixed bed and granular activated carbon (GAC) filtration) (Bourgin et al., 2018). Based on their results, a specific dose of 0.55 g O_3/g dissolved organic carbon (DOC) was recommended. About 200 micropollutants could be detected in the influent and an abatement of >79% was observed on average (Bourgin et al., 2018). Hollender et al. investigated 24 pharmaceuticals in municipal wastewater after full-scale ozonation and sand filtration (Hollender et al., 2009). Compounds such as carbamazepine, diclofenac and sulfamethoxazole could be eliminated to concentrations below detection limits with a dose of 0.47 g O_3/g DOC. For other compounds such as metoprolol and atenolol, a removal efficiency of >85% by ~0.6 g O_3/g DOC was achieved (Hollender et al., 2009). Blackbeard et al. carried out pre- and post-ozonation experiments at full-scale followed by UV and chlorine treatments (Blackbeard et al., 2016). In their study, 387 substances were monitored and the final effluent contained micropollutants below levels of relevance based on Australian guidelines for reuse and irrigation (Blackbeard et al., 2016).

Additional AOPs have also been tested in pilot-scale. A UV/H_2O_2 system was investigated by James et al. in secondary effluent preceded by microfiltration and/or reverse osmosis (James et al., 2014). Removal efficiencies were >85% for the investigated endocrine disrupting compounds, herbicides and pesticides except for met-aldehyde with removal efficiency of 45%. In another study, solar

photo-Fenton process was compared to ozonation in pilot-scale (Arzate et al., 2019). It was concluded that although both tertiary treatments reduced water stress locally, ozonation had better overall environmental performance due to three main factors: i) lack of reactants needed, ii) continuous operation day and night, iii) no drawbacks originating from the need of pH adjustment as for solar photo-Fenton process. In recent years, application of O_3/UV was also studied with different wastewater samples. A few studies dealt with the combined effect of ozonation and UV irradiation for wastewater purification (Lafi et al., 2009; Lucas et al., 2010). Lafi et al. aimed to reduce the chemical oxygen demand (COD) of olive mill wastewater in lab-scale experiments and found that high COD removal (up to 91%) could be achieved by UV/O_3 treatment followed by aerobic biodegradation. In a pilot-scale study, O_3/UV and O_3/UV/H_2O_2 were found to be feasible for the treatment of winery wastewater. The very high total organic carbon (TOC) content (>1000 mg/L) was most effectively reduced by O_3/UV/H_2O_2 at pH 4. Removal efficiency was >80% by 300 min treatment time.

Most of AOPs involve *in situ* generation of hydroxyl radicals that are highly reactive and capable of oxidizing, thus degrading or, to some extent, mineralizing organic pollutants (Zoschke et al., 2014). UV-based AOPs are widely studied and new techniques are being invented, and usually Hg- or, less frequently, excimer lamps are used as light sources. When low-pressure Hg lamps are applied, photons at two main resonance lines of Hg should be considered: 185 nm and 254 nm (nominal values) (Zoschke et al., 2014). Conventional low-pressure Hg lamps mainly emit photons at 254 nm. These photons have lower energy than photons with wavelength of 185 nm but they can also contribute to the direct photolysis of micropollutants. Several publications have also dealt with irradiation by VUV lamps in bench-scale (Arany et al., 2014; Bagheri and Mohseni, 2017; Moradi and Moussavi, 2018). VUV photons have very small penetration depth into water, e.g. 90% of photons with wavelength of 185 nm are absorbed in a water layer of 5.5 mm (Han et al., 2004; Zoschke et al., 2014). Therefore, high heterogeneity exists between the irradiated volume near the lamp surface and the non-irradiated volume of the aqueous solution in the photoreactor, which can be attenuated by applying high turbulence i.e. efficient gas purging (Zoschke et al., 2014). The prime advantage of VUV irradiation is that VUV photons have enough energy to induce direct photodissociation of water molecules with a substantial quantum yield of $\Phi_{OH} = 0.33$ at 185 nm wavelength, producing hydroxyl radicals and hydrogen atoms (Eq. (1)) (Huang et al., 2016).

$$H_2O + h\nu \ (185 \ nm) \rightarrow \ ^\bullet OH + \ ^\bullet H \tag{1}$$

Moreover, in the presence of O_2, O_3 is formed as a result of the primary and secondary photochemical reactions of Eq. (2) and Eq. (3).

$$O_2 + h\nu \ (185 \ nm) \rightarrow O(^3P) + O(^3P) \tag{2}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{3}$$
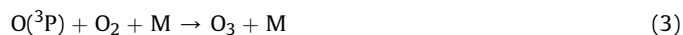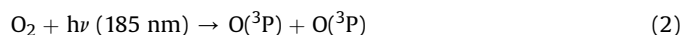
Ozone in pure water has absorption maximum at 261 nm (Levanov et al., 2016), thus it can effectively absorb the dominant emission of the low-pressure Hg lamp. This results in the production of hydroxyl radicals and hydrogen peroxide through the generation of nascent oxygen atom (^1D) and its subsequent reactions (Huang et al., 2016). Moreover, O_2 can react with $^\bullet$H generated in Eq. (1) forming $HO_2^\bullet$ which is another oxidation agent. In this way, O_2 also reduces the significance of recombination reaction of $^\bullet$OH with $^\bullet$H (Huang et al., 2016).

In our previous laboratory-scale studies, the photodegradation of three APIs, namely diclofenac, naproxen and carbamazepine was

studied by conventional UV and (V)UV irradiation in the presence and absence of O_2 (Krakkó et al., 2019a). It was found that (V)UV photooxidation was efficient in removing the target analytes even in wastewater samples spiked to 5×10^{-6} M which is several orders of magnitude larger than the average concentration of these compounds in effluent wastewater. Removal of the abovementioned three APIs under batch and flow conditions in model solutions and in spiked wastewater by GAC was also investigated (ELAbadsa et al., 2019; Varga et al., 2019). Furthermore, a high resolution mass spectrometric method was developed for the quantitative analysis of 10 APIs in drinking water, surface water and wastewater that was applied for monitoring the results in the current study (Krakkó et al., 2019b).

Publications dealing with removal of APIs from different water matrixes by (V)UV irradiation are limited to laboratory-scale experiments only. To the best of our knowledge, on-site pilot-scale experiments for the (post-)treatment of industrial or municipal wastewater by applying (V)UV or (V)UV/O_3 have not been published yet. In the present study, a pilot-scale container unit applying (V)UV/O_3 treatment is discussed. This container unit combines (V) UV irradiation and additional O_3 treatment in one step aiming at the post-treatment of biologically treated wastewater (BTWW) removal of APIs. Efficiency of this method was characterized by monitoring the concentration of seven APIs, namely carbamazepine (CARB), ciprofloxacin (CIPR), clarithromycin (CLAR), diclofenac (DICL), metoprolol (METO), sitagliptin (SITA) and sulfamethoxazole (SULF). Granular activated carbon was tested for the removal of degradation products after irradiation. Furthermore, bacteria inactivation and testing of acute and chronic toxicity were also studied. Pilot-scale experiments were conducted on-site with the BTWW of two medium-sized WWTPs located in Hungary.

2. Materials and methods

2.1. Chemicals and reagents

Detailed information on analytical standards and isotopically labeled internal standards as well as stock solutions for the determination of APIs can be found elsewhere (Krakkó et al., 2019b). An ELGA Purelab Option-R7 unit (ELGA LabWater/VWS Ltd., High Wycombe, UK) was used for ultra-pure water generation (resistivity of 18.2 MΩ cm). Acetonitrile, methanol and formic acid (99%) of LC-MS grade were purchased together with 2 M hydrochloric acid and ethylenediaminetetraacetic acid disodium salt dihydrate ($Na_2EDTA \cdot 2H_2O$) (99.6% purity) from VWR International Ltd. (Debrecen, Hungary). For ion chromatographic measurements, ammonium chloride, calcium chloride, magnesium chloride hexahydrate, potassium chloride, sodium nitrate and sodium sulphate were purchased from Sigma-Aldrich Ltd. (Budapest, Hungary). Granulated activated carbon Organosorb10 AA of particle size ranging between 0.42 and 1.70 mm was purchased from Desotec HQ (Roeselare, Belgium). The physico-chemical characterization of the GAC applied in the present study has been evaluated elsewhere (Varga et al., 2019).

2.2. Location of the wastewater treatment plants

Pilot-scale experiments were conducted at two medium-sized WWTPs. Besides primary treatment, these WWTPs apply secondary wastewater treatment by conventional activated sludge process. WWTP-1 is located at Kiskunlacháza, Central Hungary (GPS coordinates: 47°10′38.3″N,19°01′30.3″E), WWTP-2 is situated at Siófok, Hungary (GPS coordinates: 46°53′46.9″N, 18°05′04.4″E). Typical characteristics of the wastewater effluents can be found in Table S1.

2.3. Set-up of the pilot-scale container unit

For the pilot-scale experiments conducted in this study, an approx. $6.1 \times 2.4 \times 2.6$ m (length × width × height) container unit was constructed and operated on-site at the two WWTPs. The inlet water for the pilot-scale container unit was sampled directly from the effluent wastewater stream of the WWTPs. During the experiments, BTWW was further treated in three steps: *i)* filtration using process filters *ii)* (V)UV photooxidation in the presence of *in situ* generated O_3 and *iii)* GAC adsorption. A schematic representation of the (V)UV/O_3 pilot-scale set-up is presented in Fig. S1.

The BTWW was pooled into a stainless-steel inlet tank of 1.2 m³ with the help of a submersible water pump (Pedrollo, UPm 8/4 GE). The water was carried to the photoreactors by a progressive cavity pump (Seepex, MD 025-6L) through the process filter with pore size of 0.45 μm (Graver Technologies LLC, Glasgow, Scotland). Altogether, six cylindrical photoreactor units positioned vertically were installed and operated in serial connections. Each reactor contained a newly developed low-pressure Hg lamp constructed by LightTech Ltd. having UV output of 3 W and 16 W at 185 nm and 254 nm, respectively. The lamps were surrounded by quartz sleeves and operated at optimal electrical parameters. Coolant air was continuously pumped through the sleeves by means of a portable industrial air compressor (FIAC, AB 50−268 M). From the O_2 content of air, O_3 was *in situ* photochemically generated. The O_3-rich air flows leaving the sleeve jackets of the lamps were continuously fed into the reactors from the bottom through stainless steel nozzles. These nozzles dispersed the entering gas flows, providing powerful stirring needed due to the very short penetration depth of the VUV radiation. Similar batch-scale technique was applied in other studies in recirculation mode with model solutions using a Xe excimer lamp or different low-pressure Hg lamps (Hashem et al., 1997; Zoschke et al., 2012). Temperature of the reaction mixture was measured downstream after the reactors using an industrial thermometer (Pt100). Reaction temperatures were in good agreement for each reactor block, typical values were 25.5 ± 1 °C and 18 ± 2 °C at WWTP-1 and WWTP-2, respectively. A stainless-steel buffer tank of 0.3 m³ pooled the effluent from the reactor blocks where the separation of O_3 and treated water was achieved by venting. Finally, two fixed bed adsorption columns and an outlet tank of 0.8 m³ were placed after the buffer tank. The columns (each of 57 cm height) were packed with 5 kg GAC, with empty bed contact time of 4.4 min. In case of plugging, process filters and GAC columns could be switched from one unit to another. Treated water was transferred from the buffer tank to GAC columns and from the outlet tank to the sewer by progressive cavity pumps (Seepex, MD 025-6L). Four water sampling points were positioned along the purification line (Fig. S1). The container unit was operated by custom-made software, enabling automated operation with online monitoring as well as complete manual controlling.

2.4. Analytical techniques

2.4.1. Sample preparation and quantitative analysis of pharmaceuticals

Samples taken for LC-MS analysis were filtered through 0.45 and 0.2 μm Whatman™ nylon membrane filters (GE Healthcare, Little Chalfont, UK) in decreasing pore size order. Then, $Na_2EDTA \cdot 2H_2O$ was added in 1 g/L concentration and sample pH was set to 4 with formic acid. The detailed description of the solid phase extraction method applied for purification and preconcentration of the samples can be found elsewhere (Krakkó et al., 2019b).

Determination of target compounds was carried out on a Bruker Elute ultra-high performance liquid chromatograph coupled to a Bruker Compact quadrupole time-of-flight mass spectrometer,

purchased from Bruker Daltonik GmbH (Bremen, Germany). Detailed description of the liquid chromatograph, chromatographic separation and mass spectrometric conditions are discussed elsewhere (Krakkó et al., 2019b).

2.4.2. Characterization of water matrix

The concentration of TOC and DOC were determined by using a Multi N/C 3100 TC-TN analyzer (Analytik Jena, Jena, Germany). The concentrations of several inorganic cations (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (Cl^-, SO_4^{2-} and NO_3^-) were determined by using a dual channel ion chromatograph (Dionex ICS 5000+, Thermo Fischer Scientific, USA). Operating parameters of both instruments can be found in Supplementary Materials Text S1. COD was determined by standard method (Eaton et al., 2005). Nephelometric turbidity of BTWW samples was determined on site with a Lovibond TB 210 IR device (The Tintometer Ltd., Amesbury, UK) and was indicated in nephelometric turbidity units (NTU).

2.4.3. Measurement of ozone

Concentration of O_3 in the air stream entering the photoreactors was measured using the Model 202 Ozone Analyzer (2B Technologies, Boulder, Colorado, USA).

2.5. Microbiological analysis and toxicity tests

Spiked drinking water as well as spiked and unspiked BTWW was used for testing of bacteria inactivation. Spiking was done with *Escherichia coli* (*E. coli*) culture grown in laboratory on nutrient agar slants (pH = 7) in fixed water volumes. Drinking water was purged by air before spiking to remove chlorine. To determine genotoxicity and acute toxicity, SOS Chromotest kits were used (Environmental Bio-Detection Products Inc., Ontario, Canada). Microbiological analysis and toxicity tests are further detailed in Text S2.

3. Results and discussion

3.1. Study design

The pilot-scale container unit was developed based on laboratory studies which are partly discussed elsewhere (ELAbadsa et al., 2019; Krakkó et al., 2019a; Varga et al., 2019). During pilot-scale experiments, filtration of the BTWW was used to eliminate suspended solids that can adversely affect the efficiency of the (V)UV irradiation by photon absorption and by acting as free radical scavengers. In our previous study, ten target APIs have been selected based on compliance with regional trends within the European Union in terms of drug sales and consumption (Krakkó et al., 2019b). Seven out of the ten compounds, namely, CARB, CIPR, CLAR, DICL, METO, SITA and SULF could be detected in both WWTP effluent and in Danube River samples. Thus, based on their persistency during wastewater treatment, they were selected as the target compounds of this study. In addition to our findings, several studies reported very poor removal efficiencies for CARB and DICL (<30%) and moderate removal efficiencies for the other five compounds (42%−85%) (Ben et al., 2018; Liu et al., 2017; Thiebault et al., 2017). To evaluate the effectiveness of the developed AOP method, the concentration of the seven APIs were monitored in each step of the purification procedure, namely filtration through 0.45 μm process filters, (V)UV/O_3 treatment and consequent GAC adsorption. In addition to APIs, degradation products previously identified in laboratory experiments by our research group for CARB and DICL (Krakkó et al., 2019a), as well as for CIPR and SITA were also monitored. Application of GAC columns was designed to adsorb potentially harmful degradation products after irradiation. Other monitored parameters included TOC content, concentration of

inorganic ions and that of the *in situ* generated O_3. Post-treatment was further assessed by investigating disinfection capacity and change in general and acute toxicity.

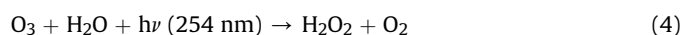### 3.2. Optimization of operational conditions

In the first step, the flow rate of the wastewater in the container unit was optimized. Experiments were conducted with the lowest and fastest flow rate settings of 2 and 4 L/min, respectively, available by the cavity pumps. The removal efficiency values of the target APIs were compared. Slightly better results (approx. 10−15%) for the less easily degradable compounds were achieved e.g. CARB from 88% to 100%, METO from 66% to 80% and SITA from 43% to 57% when the lower flow rate was used. In order to increase the daily load of the container unit, 4 L/min was chosen for further experiments. Thus, a total residence time of 4.75 min was achieved in the six reactors. According to our batch-scale experiments with a shorter version of the (V)UV lamp, this residence time was sufficient to degrade at least 50% of the target compounds in BTWW (Krakkó et al., 2019a).

Flow rate of the lamp coolant air was tested at 0.8, 1.6 and 3.2 L/min/reactor. The concentration of O_3 generated by the (V)UV lamps was measured and found constant within 10% for all six reactors. With increasing flow rates, the applied O_3 dose was 0.27, 0.52 and 0.68 mg O_3/L water at 0.8, 1.6 and 3.2 L/min/reactor air flow, respectively. In conclusion, air flow rate of 1.6 L/min/reactor was selected for further experiments which provided similar API removal efficiencies compared to the highest settings.

It is to be noted that replacement of coolant air with high purity O_2 resulted in >96% removal of all target analytes (see Section 3.3 for comparison) with the chosen flow rate of 1.6 L/min. Thus, the implementation of swing absorber technology for preconcentration of O_2 from air to use it as lamp coolant instead of air could also be recommended. However, the main focus of our study was to investigate removal of APIs using air as lamp coolant.

3.3. Removal of active pharmaceutical ingredients

More than 80% of removal efficiency was achieved for five out of seven target APIs (namely, CARB, CIPR, CLAR, DICL and SULF) by (V) UV/O_3 treatment at both WWTP-1 and WWTP-2 (Fig. 1). Least degradable compounds were METO and SITA with removal efficiencies of 66% and 71% as well as 43% and 46% for both WWTP-1 and WWTP-2, respectively (Fig. 1a–b). In case of combined (V) UV/O_3 treatment and GAC adsorption, removal efficiencies were ≥95% for all APIs (Fig. 1). The applied O_3 doses were 0.045 and 0.030 g O_3/g DOC at WWTP-1 and WWTP-2, respectively. This is several orders of magnitude less than what is usually applied at full-scale ozonation (Blackbeard et al., 2016; Bourgin et al., 2018; Hollender et al., 2009). However, high removal efficiencies within short residence time were achieved due to synergy of 254 nm UV photons and O_3 according to Eqs. 4-6 (Fu et al., 2020).

$$O_3 + H_2O + h\nu \ (254 \ nm) \rightarrow H_2O_2 + O_2 \tag{4}$$

$$H_2O_2 + 2O_3 \rightarrow 2\text{•OH} + 3O_2 \tag{5}$$

$$H_2O_2 + h\nu \ (254 \ nm) \rightarrow 2\text{•OH} \tag{6}$$

Due to the low penetration depths of VUV photons, the short contact time and low dose of O_3, degradation of the micropollutants was considered to be driven mainly by hydroxyl radicals. In laboratory-scale studies, diclofenac was readily degradable even by conventional UV irradiation at 254 nm. In this case, degradation was initialized by photolytic cleavage of the bond between carbon
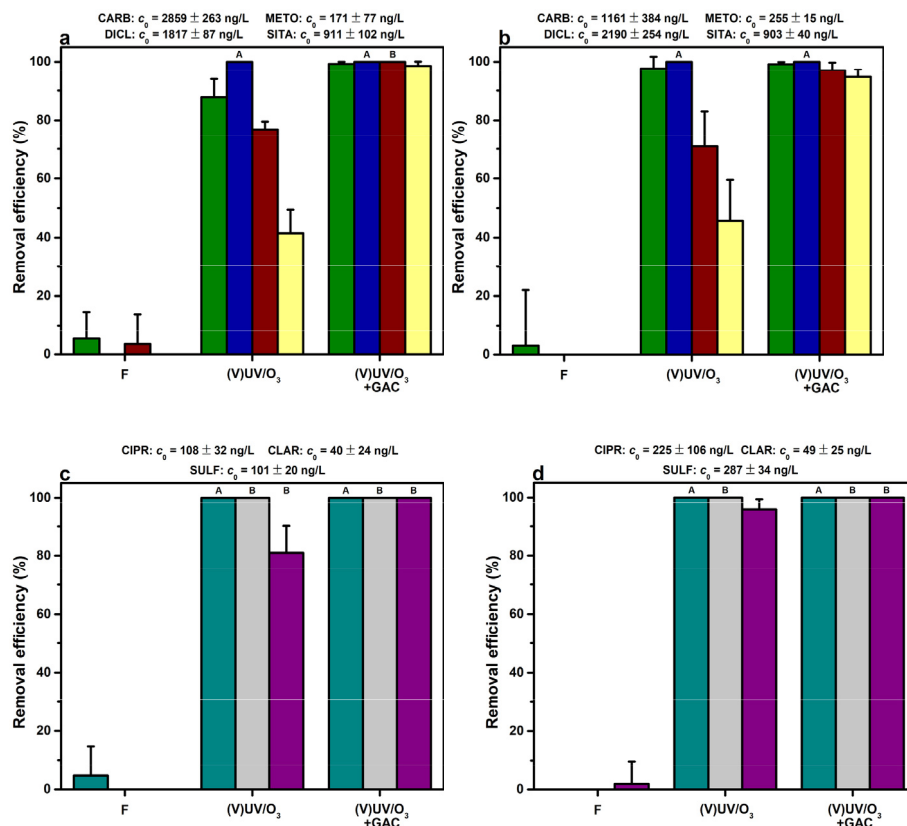
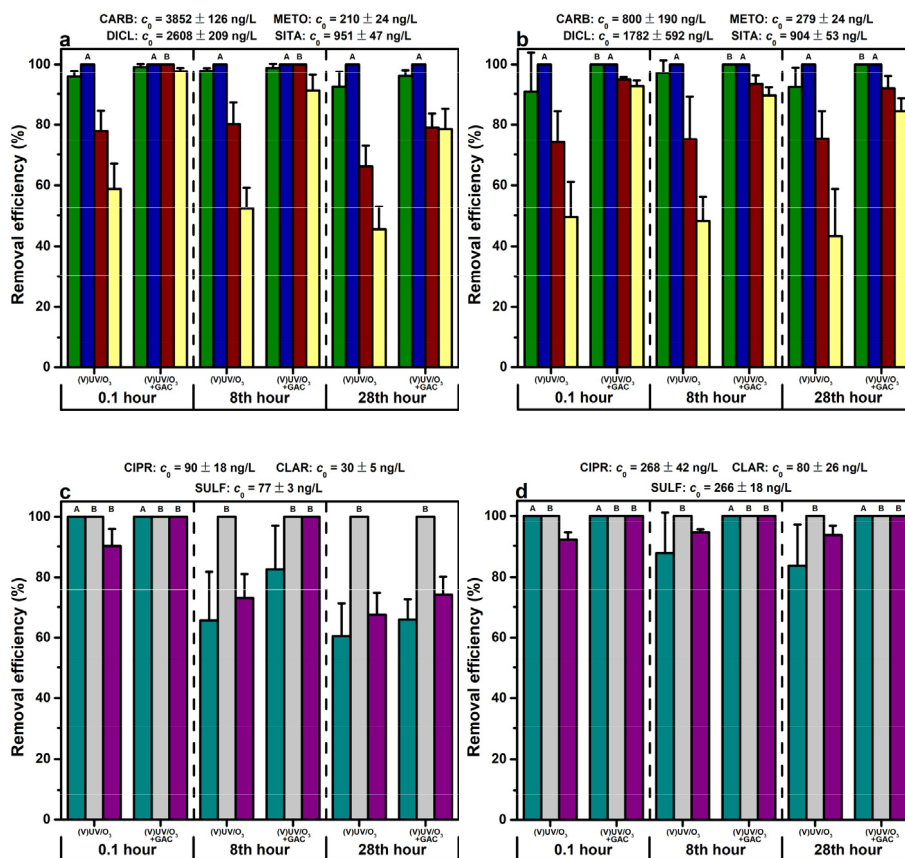**Fig. 1.** Concentration changes of target active pharmaceutical ingredients used for the treatment of chronic diseases (a, b) and acute symptoms (c, d) during post-treatment of biologically treated wastewater of WWTP-1 (a, c) and WWTP-2 (b, d). Colors: blue = diclofenac; cyan = ciprofloxacin; grey = clarithromycin; green = carbamazepine; purple = sulfamethoxazole; red = metoprolol; yellow = sitagliptin. Abbreviations: F = filtration through process filters with pore size of 0.45 μm; (V)UV/O_3 = VUV (185 nm) + UV (254 nm) irradiation in the presence of *in situ* generated O_3 after filtration; (V)UV/O_3+GAC = combined (V)UV/O_3 treatment and granulated activated carbon adsorption after filtration. Limit of detections were A = 25 ng/L, B = 10 ng/L. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

and chlorine atoms (Krakkó et al., 2019a). Fast degradation by (V) UV irradiation was reported for CARB, CIPR, DICL and SULF (Hu et al., 2019; Krakkó et al., 2019a; Šojić et al., 2012). There is no information about the (V)UV irradiation of CLAR, METO or SITA in the literature. Lower removal efficiencies for METO and SITA are not completely understood. More studies are needed in this field in wastewater matrix, taking into consideration several possible scavenging agents such as inorganic ions, their concentrations, and rate coefficients (Liao et al., 2001).

For CIPR, DICL and SITA, none of the degradation products previously identified in laboratory experiments could be observed after post-treatment. Thirteen degradation products were identified for CARB in our previous study by UV and (V)UV irradiation in a batch reactor with an initial CARB concentration of 5 × 10⁻⁶ M (Krakkó et al., 2019a). In this study, two out of the 13 degradation products of CARB could be detected at both WWTP-1 and WWTP-2 (Fig. S2). The first one, labeled as DP1, is the product of the reaction of CARB with a hydroxyl radical resulting in ring shrinkage. Subsequent loss of the carbamoyl functional group and reaction with yet another hydroxyl radical gives DP2 (Krakkó et al., 2019a). DP1 and DP2 were identified based on retention time, accurate mass and fragment ions (Fig. S2). In lack of appropriate analytical standards, concentrations of DP1 and DP2 could not be determined. However, based on their chromatographic peak areas, estimated concentrations were 100 ng/L and 20 ng/L for DP1 and DP2, respectively. After GAC adsorption, chromatographic area of DP1
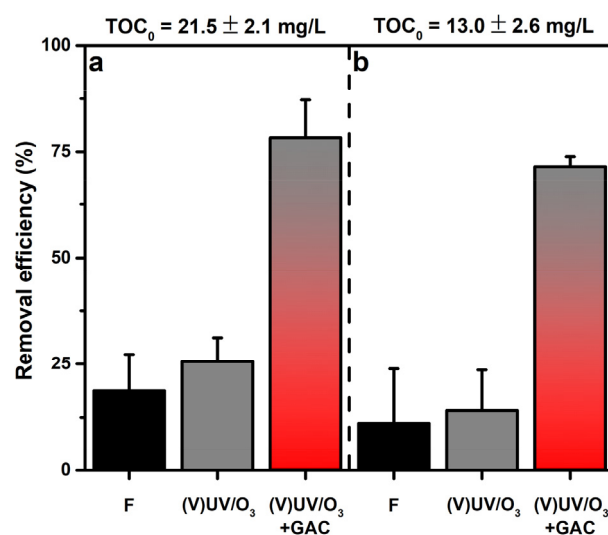
Fig. 2. Changes of total organic carbon content during post-treatment of biologically treated wastewater from WWTP-1 (a) and WWTP-2 (b). Abbreviations: F = filtration through process filters with pore size of 0.45 μm (black); (V)UV/O_3 = VUV (185 nm) + UV (254 nm) irradiation in the presence of *in situ* generated O_3 after filtration (grey); (V)UV/O_3+GAC = combined (V)UV/O_3 treatment and granulated activated carbon adsorption after filtration (grey-red). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3. Concentration changes of target active pharmaceutical ingredients used for the treatment of chronic diseases (a, b) and acute symptoms (c, d) during post-treatment of biologically treated wastewater from WWTP-1 (a, c) and WWTP-2 (b, d) conducted for 28 h. Colors: blue = diclofenac; cyan = ciprofloxacin; grey = clarithromycin; green = carbamazepine; purple = sulfamethoxazole; red = metoprolol; yellow = sitagliptin. Abbreviations: $(V)UV/O_3$ = VUV (185 nm) + UV (254 nm) irradiation in the presence of *in situ* generated O_3 after filtration; $(V)UV/O_3+GAC$ = combined $(V)UV/O_3$ treatment and granulated activated carbon adsorption after filtration. Limit of detections were A = 25 ng/L, B = 10 ng/L. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

decreased by 90% and DP2 could no longer be detected in any of the samples.

3.4. Change of total organic carbon content

Although the primary objective of the post-treatment experiments was to study the removal efficiencies of target APIs, it was useful to monitor how TOC and DOC contents changed during the treatment. Filtration was able to reduce TOC content of the BTWW by about 20% and 10% for WWTP-1 and WWTP-2, respectively (Fig. 2). The nearly 10% difference can be attributed to the higher amount of suspended solids characterized by higher turbidity of the BTWW in WWTP-1. Turbidity values ranged between 2.5 and 6.8 NTU and 0.8−2.9 NTU for WWTP-1 and WWTP-2, respectively. The large difference in suspended solid content in the effluent of the two WWTPs could be explained by better secondary sludge separation at WWTP-2. In another study, high TOC removal by applying UV/O_3 was achieved by long treatment time of 300 min and high O_3 dose of >100 mg O_3/min in a 9-L reactor (Lucas et al., 2010). The O_3 dose in this study was 0.52 mg O_3/L/min which is several orders lower than the applied dose by Lucas et al. A relatively small TOC decrease of <6% could be achieved by the $(V)UV/O_3$ treatment. Although generally high mineralization can be reached by (V)UV irradiation in pure water spiked by pharmaceuticals (Illés et al., 2014; Imoberdorf and Mohseni, 2012; Krakkó et al., 2019a; Moradi and Moussavi, 2018), low mineralization in wastewater was achieved in laboratory experiments for 30 min irradiation (Krakkó

et al., 2019a). This is because these micropollutants constitute a negligible fraction of the TOC content of the wastewater and the main components (containing e.g., humic, fulvic and other aliphatic acids) generally have a higher degree of oxidation and are less prone to photooxydation. As previously described, most of the target compounds were oxidized to a high extent as their aromatic degradation products could not be detected except for CARB. To assess the change in degree of oxidation of the wastewater by the $(V)UV/O_3$ treatment, COD/DOC ratios were measured before and after treatment. The COD/DOC ratio showed no decrease, indicating that the main constituents of the wastewater were not affected by this treatment.

A large decrease of TOC was observed after GAC adsorption with an average of ≥72% TOC reduction in both WWTPs (Fig. 2). Larger TOC removals in WWTP-1 can be explained by the larger amount of suspended solids.

3.5. Effect of operational time

Continuous operation up to 28 h was tested at both WWTPs (Fig. 3). During these tests, filters had to be replaced frequently in order to prevent clogging and overpressure in the system. Moreover, gradual exhaustion of the GAC columns was also observed. Due to the large amount of suspended solid in the effluent of WWTP-1, the filtration step showed a decrease in efficiency after several hours. This could have contributed to the notable decline in removal for CIPR and SULF. In conclusion, $(V)UV/O_3$ subunits

Table 1
Electric energy per order (EEO) calculated for the seven investigated active pharmaceutical compounds at both wastewater treatment plants (WWTPs). Abbreviations: CARB = carbamazepine; CIPR = ciprofloxacin; CLAR = clarithromycin; DICL = diclofenac; METO = metoprolol; SITA = sitagliptin; SULF = sulfamethoxazole.

	EEO (kWh/m^3)						
	CARB	DICL	METO	SITA	CIPR	CLAR	SULF
WWTP-1	1.3 ± 0.3	0.8 ± 0.2	3.1 ± 0.9	5.3 ± 1.4	1.6 ± 0.2	2.4 ± 0.8	1.7 ± 0.2
WWTP-2	0.8 ± 0.3	0.6 ± 0.1	2.3 ± 0.7	4.9 ± 1.8	1.1 ± 0.1	1.5 ± 0.2	0.9 ± 0.1

showed operational stability with respect to micropollutant degradation. Generally, removal efficiencies after 28 h by (V)UV/O₃ treatment were 45–100% and 43–100% for APIs used for the treatment of chronic diseases at WWTP-1 and WWTP-2, respectively. For antibiotics, these values ranged between 66-100% and 83–100% at WWTP-1 and WWTP-2, respectively.

3.6. Disinfection efficiency

Water disinfection by UV light is one of the most widely used methods. The best germicidal effects can be reached by photons in the UV range of 200–300 nm due to the relatively high absorbance of DNA molecules. However, some microbes and viruses can overcome DNA damage through photoreactivation or by host cell machinery during viral replication (Gomes et al., 2019). Depending on the dose, UV irradiation is able to reduce vegetative bacteria by 4–8 logs (Guo et al., 2009). It was found that UV dose of 15 mJ/cm² is needed with either low-pressure or medium-pressure UV lamps for effective inactivation of *E. coli* in pure water samples with no further photoreactivation detected (Guo et al., 2009). After the application of UV dose of 40 mJ/cm² by either of these two types of lamps in wastewater samples, the percentage photoreactivation was less than 1% for microorganisms present in the wastewater (Guo et al., 2009). As an alternative to UV irradiation, ozonation can also be used to disinfect water. Ozonation with a 0.09 g/L·h production of O₃ in synthetic fresh-cut wastewater resulted in >log-5 inactivation in 2 and 4 min for *E. coli O157:H7* and *Salmonella enteritidis*, respectively (Nahim-Granados et al., 2019). In another pilot-scale study, log-5.72 inactivation of *Enterococci* as well as up to log-4.59 of antibiotic resistance genes could be achieved by combined biological treatment with O₃ disinfection in wastewater from high-speed railway trains (Wei et al., 2020).

The applied UV dose in our study was estimated at 1.2 J/cm² and 6.6 J/cm² at wavelengths of 185 nm and 254 nm, respectively. Experiments in drinking water spiked with *E. coli* suspension resulted in inactivation of up to log-6.7 by (V)UV/O₃ treatment. In unspiked BTWW, inactivation rates for total coliform, *E. coli* and *E. faecalis* were, in best case scenario, log-4.8, log-4.5 and log-3.8, respectively. Bacteria inactivation was constantly achieved during the 28 h operation experiments sampled at 0.1, 8 and 28 h. It was beyond the scope of this paper to study bacterial photoreactivation, however, it is considered to be relevant for future applications.

3.7. Acute and chronic toxicity

In this study, SOS Chromotest kits were applied to determine genotoxicity and acute toxicity of the treated wastewater. Based on studies applying SOS Chromotest kits, untreated wastewater from urban or hospital origin can potentially be genotoxic but conventional wastewater treatment can effectively reduce their toxicity (Laquaz et al., 2017; Sharma et al., 2015; Völker et al., 2019). However, residual toxic effects may still be present in the effluent (Völker et al., 2019). Discharge into surface water will generally reduce toxic effects because of dilution (Iqbal et al., 2020). AOPs can increase the toxicity of wastewater. For example, increased

genotoxicity of paracetamol wastewater was observed by SOS Chromotest after applying Fenton process (Kocak, 2015). Ozonation was also found to increase toxicity of wastewater because of the formation of organic byproducts such as aldehydes, organic acids, N-nitrosamines, perfluoroalkyl acids etc (Bourgin et al., 2018; Pisarenko et al., 2015; Schindler Wildhaber et al., 2015). However, toxicity after ozonation can be decreased after a second biological treatment because of the higher biodegradability of the byproducts (Bourgin et al., 2018). According to our results, none of the samples indicated genotoxicity (Fig. S3). The (V)UV/O₃ treatment did not increase the induction factor value of the BTWW. On the contrary, a slight decrease in induction factors was observed in the order of BTWW > (V)UV/O₃ irradiation > combined (V)UV/O₃ irradiation followed by GAC adsorption (Fig. S3). Samples showed no acute toxicity either as cell viability was >90% in each case.

3.8. Other monitored parameters

Ozonation can generate nitrogenous oxidation by-products as well as NO_2^-, NO_3^- and NH_4^+ from dissolved organic matter (de Vera et al., 2017; Song et al., 2017; Völker et al., 2019). Generation of NO_3^- is also crucial for irrigation purposes as its maximum allowed concentration is 50 mg/L under European Union legislation (European Comission, 1991). According to our results, NO_3^- was present in <50 mg/L while NO_2^- and NH_4^+ was only detected in some cases in concentrations of <2 mg/L and <3 mg/L, respectively. Initial concentration of inorganic ions did not increase after post-treatment, generation of additional NO_2^-, NO_3^- or NH_4^+ was not observed probably because of the relatively low O₃ dose applied compared to other ozonation studies mentioned above. Moreover, the concentration of other inorganic anions and cations did not considerably change during post-treatment (Table S2).

Finally, the color of the BTWW improved with the pilot-plant treatment and became cleaner. The best results were obtained when all three treatment steps were applied. Absorbance of samples decreased in the 245–400 nm region on average by a factor of 30 (Figs. S4-6).

3.9. Estimation of electrical energy per order

Energy efficiency of UV based AOPs is usually quoted in terms of electrical energy per order (E_{EO}), which is the number of kW hours of electrical energy required to reduce the concentration of a contaminant by one order of magnitude (90%) in 1 m³ of contaminated water (Bolton et al., 2001).

Higher EEO values obtained for WWTP-1 can be explained by higher TOC content and turbidity of the BTWW. When TOC is higher, smaller fraction of the generated radicals reacts with the target compounds as more free radical scavengers as well as O₃ scavengers are present in the water. Moreover, higher turbidity hinders the efficiency of direct photolysis of target compounds and the photodissociation yield of water (Eq. (1)) that results in the generation of less •OH.

The median of the EEO values presented in Table 1 is 1.5 kWh/m³. According to Miklos et al., AOPs with median EEO

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