Decreased UV absorbance as an indicator of micropollutant removal efficiency in wastewater treated with ozone

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ABSTRACT

Ozone transforms various organic compounds that absorb light within the UV and visible spectra. UV absorbance can therefore be used to detect the transformation of chemicals during ozonation. In wastewater, decolourisation can be observed after ozonation. This study investigates the correlation of the UV absorbance difference between the ozonation inlet and outlet and the removal efficiency of micropollutants in wastewater. The absorbance at 254 and 366 nm was measured at the ozonation inlet and outlet, as was the concentration of 24 representative micropollutants and the dissolved organic carbon (DOC). The results clearly showed that the relative decrease of absorbance (ΔAbs) is positively correlated with the relative removal efficiency of micropollutants. We therefore suggest that UV absorbance can be used as a feedback control parameter to achieve optimal ozone dosage in wastewater treatment plants and to gain a fast insight into the process efficiency and stability of the ozonation.

Key words | control strategy for ozone dosage, feedback control, micropollutants, optimized ozone dosage, wastewater treatment plant

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INTRODUCTION

The use of various pharmaceuticals, cleaning agents, pesticides and cosmetics has increased in recent years. These substances, henceforth called micropollutants, reach surface water bodies in large amounts, as not all of them are completely biologically degradable in today's municipal wastewater treatment plants (WWTPs). Micropollutants can have negative effects on the ecosystem, such as hormone-active substances that disturb fish reproduction (Routledge *et al.* 1998; Kidd *et al.* 2007). In 2014, the Swiss Parliament agreed to upgrade selected WWTPs with an additional step to remove micropollutants; the Swiss water protection law was changed accordingly and will become effective in 2016. Following this change, about one-hundred Swiss WWTPs will have to add a further treatment step, such as ozonation or powdered-activated carbon (PAC), to remove micropollutants. The efficiency of this step will be supervised by selected indicator substances, which have to be eliminated by 80% over the whole wastewater treatment process (mechanical, biological and post-treatment). Potential indicator substances selected are carbamazepine, diclofenac, sulfamethoxazole, benzotriazole and mecoprop.

Many studies have been conducted to identify the elimination potential of ozonation and PAC (Hollender *et al.* 2009; Flyborg *et al.* 2010; Boehler *et al.* 2012; Löwenberg *et al.* 2014; Kovalova *et al.* 2013); however, questions remain concerning their full-scale operation in WWTPs. One big issue is the need for an optimal control strategy for ozone dosage requiring minimum maintenance, which gives parallel in-time insights into process behaviour and micropollutant elimination.

The analytical analysis of micropollutants, such as the above-mentioned indicator substances, is time-consuming and cost-intensive. Consequently, regular control of ozone dosage based on such results is not realistic. Cantonal authorities will need to use the analytical analysis of several samples over the year to check the compliance of treatment plants with the future water protection law. However, as discussed above, continuous monitoring of the removal efficiency and control of the ozone dosage requires online measurement. Ozone reacts with various light-absorbing unsaturated organic substances (within the UV and visible spectra), which leads to a decrease of absorbance (ΔAbs). Establishing a correlation between ΔAbs and

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micropollutant removal efficiency would therefore allow online identification of the relevant process behaviour in an ozone reactor. However, different micropollutants react differently with ozone and thus show a different correlation to ΔAbs. We therefore examined the removal efficiency of 24 substances with various ozone reactivities.

UV absorbance is a relatively simple and stable measurement and is a promising parameter for identifying the efficiency and behaviour of ozone (Nanoboina & Korshin, 2010; Gerity *et al.* 2012) and PAC addition (Bahr *et al.* 2007; Zietzschmann *et al.* 2014) to biologically treated wastewater and gives a good insight into the correlation between the decrease of UV absorbance, the ozone and PAC dosage as well as the elimination of micropollutants. Nanoboina & Korshin (2010) used wastewater from Seattle and carried out laboratory experiments, and Gerity *et al.* (2012) did likewise with wastewater samples from all over the world; however, they added micropollutants to the wastewater they studied, which could have modified the wastewater matrix. To identify the influence of the wastewater matrix and the removal efficiencies of realistic micropollutant mixtures, we used different Swiss wastewater samples without spiking micropollutants in batch experiments. Additionally, we carried out long-term tests with effluent wastewater from the Eawag nutrient removal plant, treating continuous raw wastewater from a big sewer passing the Eawag experimental site, using a semi-technical pilot plant with online UV sensors to identify the potential of UV control for full-scale plants. Nitrite reacts very fast with ozone, consumes 3.5 gO_3/gN and therefore reduces the ozone reacting with micropollutants and dissolved organic carbon (DOC). Because there is less ozone reacting with DOC, nitrite also decreases the corresponding delta UV absorbance. Control of ozone dosage with delta UV absorbance includes, therefore, the effect of nitrite without measuring the inlet nitrite concentration.

METHODS

Laboratory batch experiments

Typical dry weather 24-h composite samples (one per plant) of effluent wastewater from three different WWTPs were used for the laboratory batch experiments. The characteristics of the three analysed wastewater samples are shown in Table 1.

To optimize the UV–VIS spectra measurement, the samples were filtered using filters with a pore size of 0.45 μm (Whatman GF/G, Sigma-Aldrich, Buchs, Switzerland). The three samples were treated with different ozone dosages at approximately 0.3, 0.6, 0.9 and 1.2 g O_3/g DOC by adding cold ozone-saturated deionized water. After the ozone had been applied, the samples were stirred for 30 minutes. The UV–VIS spectra before and after treatment were measured with a Carry 100 scan spectrometer (Varian, Agilent Technologies, Santa Clara, CA, USA).

Table 1 | Characteristics of three different dry weather wastewater samples used for the batch experiments

		DOC [mg/L]	Nitrite (mg NO_2^- N/L)	pH (–)	Sampling point
A	WWTP Eawag	7.3	<0.6	8.3	After SC[a]
B	WWTP Werdhölzli	9.2	<0.6	8.1	After SC[a] and SF[b]
C	WWTP Uster	4.3	<0.6	8.0	After SC[a]

[a]SC, secondary clarifier.
[b]SF, sand filter.
The different UV absorbance profiles are given in Figure 2.

Semi-technical pilot plant experiments

An ozonation pilot plant was installed directly after the secondary clarifier (SC) of the WWTP Eawag (A). Figure 1 shows a schematic of the installed pilot plant. Ozone was produced on-site with an ozone generator (Sander; Ozonisator S1000, Sander GmbH, Wuppertal, Germany). Pressurized air was enriched with ozone and then injected into a first reactor column in counter-current flow, with the treated wastewater as the influent. A second column was attached to achieve a hydraulic residence time sufficient for the ozone to react completely before the treated wastewater left the system. The transferred ozone dose was calculated from the difference between the applied dose and the ozone in the off-gas (ozone

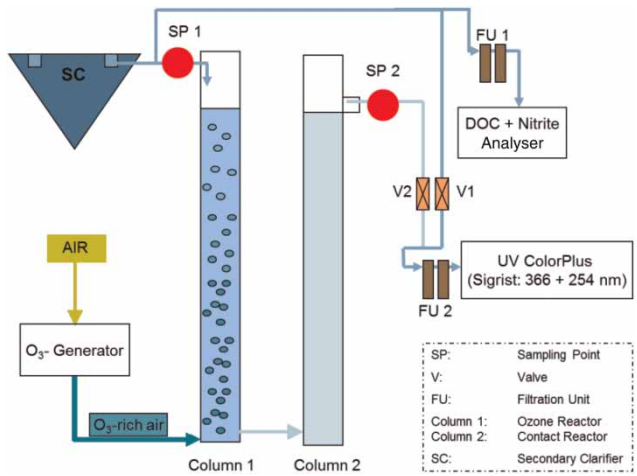

Figure 1 | Flow scheme of the ozonation pilot plant at WWTP Eawag (A).

transfer efficiency 66–78%). The absorbance, at wavelengths of 254 and 366 nm, was measured in the influent at the first column (SP1) and the effluent of the second column (SP2), where, from our experience with batch experiments, all ozone is depleted (Sigrist Photometer ColorPlus, Emmetten, Switzerland, regularly calibrated with an internal standard).

A 0.5 μm filter (Unifil AG; GF9-3/4-PP-0.5, Niederlenz, Switzerland) was mounted in front of the UV measurement device. After a certain ozone dosage had been set by adjusting the capacity of the ozone generator (0.1, 0.3, 0.6, 0.9 g O_3/g DOC), the pilot plant ran for 3.5 h to achieve a steady state. The hydraulic retention time in the two columns was 30 minutes at a water flow of 30 L/h. Grab samples were taken at SP1 and SP2 after 3.5 and 4 h of the experiment runtime, respectively.

To test the maintenance and measurement stability of the online UV measurement, different filters (pore size 0.5, 1, 5, 10, 20 and 50 μm) were used. The main focus was on the evaluation of filter blockages and on the cleaning interval of the measurement cell.

Sample preparation and chemical analysis of micropollutants

The samples were stored at −20 °C in the dark. Filtered (0.7 μm, Whatman GF/F) samples were spiked with internal standards before measurement. The analysis was conducted with an online SPE-LC/MS/MS method described by Kovalova *et al.* (2012). Isolute ENV+ (Biotage, Uppsala, Sweden) and Oasis HLB sorbent (Waters, Baden, Switzerland) were used for online enrichment. The samples from the online SPE were eluted with methanol. The methanolic extract was mixed with formic acid 0.1% (v/v) to form the chromatographic gradient. Separation was carried out with an HPLC column (Atlantis T3, 150 × 3 mm, 3 μm, Waters, Baden, Switzerland). A triple quadrupole mass spectrometer (TSQ Quantum Ultra, Thermo Fisher Scientific, Reinach, Switzerland) was used for the measurements. The quantification limits and relative recoveries were determined by spiking samples (see Tables S1 and S2 in the Supplementary Information, available online at http://www.iwaponline.com/wst/071/053.pdf). The uncertainty range of most of the substances was ±20%.

RESULTS AND DISCUSSION

UV absorbance

In Figure 2, the UV–VIS spectra of the biologically treated wastewater from the three different WWTPs are shown. The absolute absorbance of wastewater differed between the WWTPs. Among the unfiltered samples, that from WWTP Werdhölzli showed the lowest absorbance. This sample was taken after the SC including a sand filtration, whereas at the other two WWTPs, the samples were taken directly after the SC. The wastewater matrix from different WWTPs may also differ depending on their composition. A clear decrease of absorbance due to filtration could be observed. The smallest decrease occurred at WWTP Werdhölzli.

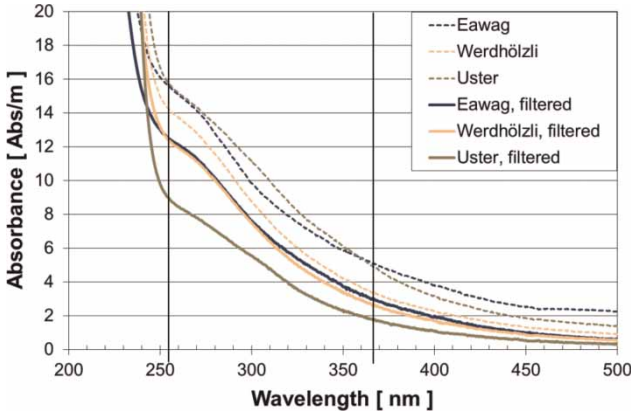

Figure 2 | UV–VIS spectra of wastewater effluents (unfiltered and filtered) from three different WWTPs.

The online UV absorbance measurements in the pilot plant were relatively easy to implement. The device used during the pilot tests (UV-ColorPlus from Sigrist AG) was simple to handle and pre-filtration of the wastewater achieved optimal signal and maintenance performance. The main challenges for maintenance arose from the filtration, the cleaning of the measurement cell, and the calibration. The photometric measurement is sensitive to disturbances such as those from small particles remaining in the wastewater after SC. The water must consequently be filtered before entering the measurement device. The larger the filter pore size, the more frequently the cell must be cleaned, but the filter can be used for longer before being replaced. From the tests with the pilot plant, a filter with 50 μm pores shows very good filtering behaviour and did not block within 2 months. However, the cell had to be cleaned every week, and cleaning is expected to be even more frequent for the measurement device in the ozonation outlet, as faster biofilm growth was observed. An automatic filter with backwash possibilities could offer a solution here, and a second pre-filter step (20 μm) could be included.

Decrease of UV absorbance vs. ozone dosage

The results for the absorbance differences between the influent and effluent of the ozonation (ΔAbs) at 254 and 366 nm

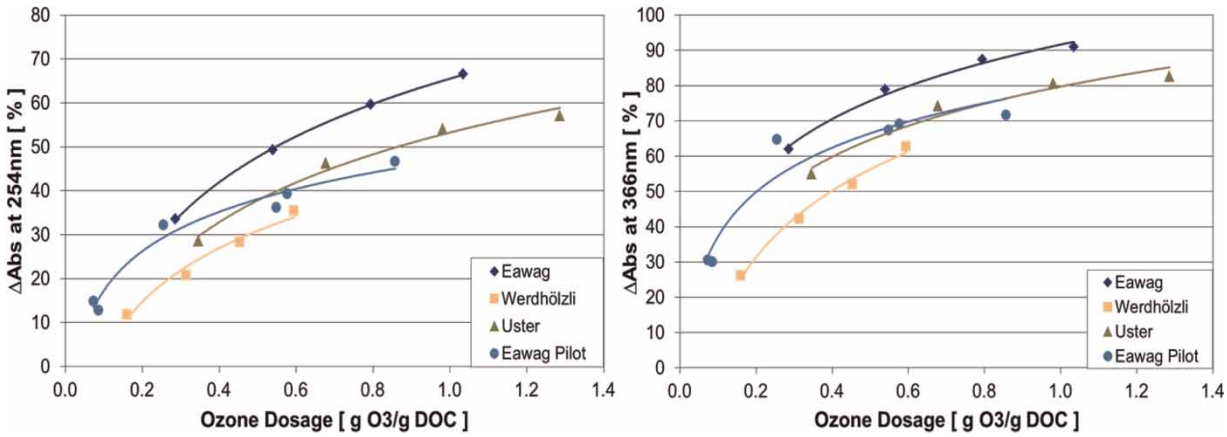

Figure 3 | Correlation of ΔAbs with ozone dosage for the three different wastewaters (Table 1 and Figure 2) and dry weather values from the online UV sensors of the Eawag pilot plant. The different profiles for Eawag laboratory and Eawag pilot experiments may be due to the varying wastewater matrix due to seasonal and industrial effects. ΔAbs has to be regularly adapted if used as a control signal for ozone dosing.

for different ozone dosages are shown in Figure 3. The higher the ozone dosage, the greater the ΔAbs; 366 nm was selected because of the low residual absorbance at high-ozone dosages, whereas at 254 nm the absolute decrease of absorbance is significantly higher. The recommended ozone dosage for a full-scale WWTP is in the range from 0.6 to 1 gO_3/g DOC. In this range, measurements at 254 nm are more sensitive than at 366 nm, as the ΔAbs slope is steeper. Similar correlations between ΔAbs and ozone dosage were observed for all the wastewater samples tested.

Decrease of UV absorbance vs. removal of micropollutants

The elimination rates of micropollutants at different ozone dosages are presented in the Supplementary Information in Section 3 (available online at http://www.iwaponline.com/wst/071/053.pdf). Figure 4 shows the relationship between the elimination of benzotriazole and ΔAbs at different ozone dosages. Most tested substances showed similar behaviour, with a steep increase of the elimination rate within a certain range of absorbance; ΔAbs was determined graphically at 50 and 80% elimination for benzotriazole and the other compounds from these curves as shown in Figure 4. The corresponding values are given in Table 2 (the values for 366 nm are given in Supplementary Information Table S5, online at http://www.iwaponline.com/wst/071/053.pdf).

The results showed that the absorbance characteristics vary greatly for different wastewaters and compounds. Quite a few compounds (e.g., atenolol, metoprolol and venlafaxin) need ΔAbs to be up to twice as high for a removal efficiency of 50% in the wastewater of WWTP C. The correlation between

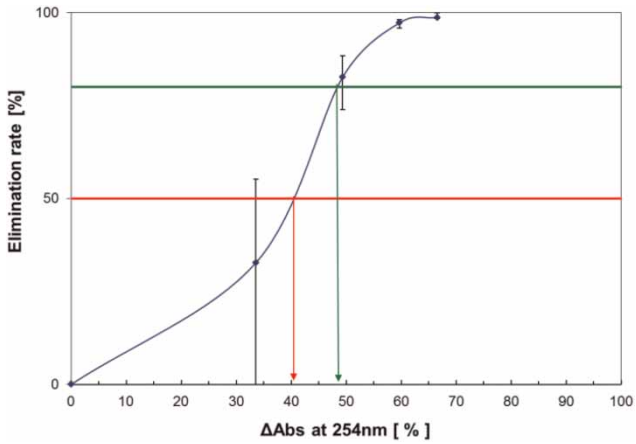

Figure 4 | Correlation between the elimination rate of benzotriazole and ΔAbs at 254 nm observed during laboratory experiments with wastewater from WWTP Eawag at different ozone dosages (0.3, 0.55, 0.8 and 1.05 g O3/g DOC; see also Appendix 3 in the Supplementary Information, available online at http://www.iwaponline.com/wst/071/053.pdf).

ΔAbs and the removal of selected substances at different ozone dosages must therefore be identified for each wastewater sample separately in order to define the specific range of ΔAbs in which the ozonation process should be conducted.

Control strategies

Benzotriazole is one of the current indicator substances showing the lowest elimination rates during ozonation. Depending on the elimination occurring during mechanical and biological treatment, which can be up to 40% for benzotriazole, the elimination by ozonation should be defined to achieve a quality goal of 80%. In WWTP A, where 40% elimination without ozonation is achieved, a required additional

Table 2 | Relative decrease of absorbance at 254 nm for 50 and 80% elimination of selected micropollutants in different wastewaters (A: Eawag, B: Werdhölzli, C: Uster)

	ΔAbs at 254 nm for 50% MP elimination						ΔAbs at 254 nm for 80% MP elimination				
	Lab-exp			Pilot-exp	Literature		Lab-exp			Pilot-exp	Literature
	A	B	C	A	Gerity[a]	Nanoboina & Korshin[b]	A	B	C	Eawag	Gerity[a]
	ΔAbs (%)						ΔAbs (%)				
Atenolol	24	–	42	25	20	25	39	–	52	34	38
Atenolol acid	26	–	47	24	x	x	40	–	55	35	x
Benzotriazole	41	–	–	41	x	x	49	–	–	45	x
Bezafibrate	37	–	–	x	x	x	60	–	–	x	x
Carbamazepine	17	17	16	20	12	13	27	33	27	28	20
Clarithromycin	18	15	16	8	x	x	30	33	28	13	x
Diclofenac	17	13	15	13	10	12	27	30	25	23	20
Fluconazole	x	x	x	44	x	x	x	x	x	–	x
Gabapentin	49	–	–	40	x	x	60	–	–	45	x
Hydrochlorothiazide	16	–	33	x	x	x	27	–	45	x	x
Levetiracetam	57	–	–	44	x	x	67	–	–	–	x
Mefenamic acid	17	8	15	8	x	x	28	24	25	13	x
Methylbenzotriazole	30	–	44	28	x	x	56	–	–	42	x
Metoprolol	22	–	42	24	x	x	37	–	52	33	x
Metronidazole	x	x	x	40	x	x	x	x	x	45	x
Oxazepam	x	x	x	32	x	x	x	x	x	45	x
Primidone	44	–	54	40	38	x	–	–	–	45	42
Propranolol	17	13	16	14	x	13	28	20	27	27	x
Ritalinic acid	x	x	x	31	x	x	x	x	x	46	x
Sucralose	x	x	x	47	x	x	x	x	x	–	x
Sulfamethoxazole	24	20	23	25	15	12	40	–	47	44	21
Trimethoprim	16	14	17	18	10	12	27	25	29	28	20
Valsartan	45	–	45	32	x	x	58	–	–	45	x
Venlafaxin	17	32	33	20	x	x	27	–	46	28	x

Literature values from [a]Gerity *et al.* (2012) and [b]Nanoboina & Korshin (2010). (x) no measurement for this substance available; (–) the planned degree of elimination was not reached with the applied ozone dosages and therefore no value for ΔAbs is available.

elimination of 50% during ozonation would lead to a required absorbance decrease of 41% at a wavelength of 254 nm and of 70% at 366 nm.

Monitoring

This study clearly showed the benefits of this simple measurement. The decrease of absorbance can be used to evaluate the efficiency of the ozonation process. As soon as the correlation between ΔAbs and the removal of micropollutants in a specific wastewater is known, the elimination process can be monitored and predictions of the achieved water quality can be made. Besides these benefits, the online inlet and outlet measurements of the absorbance should allow an innovative feedback control for the ozone dosage on the basis of an effluent parameter that changes during the process (e.g. ΔAbs) of the ozonation. A stable ΔAbs value throughout a day is a good indicator of a well-implemented control strategy for optimal ozone dosage.

CONCLUSIONS

All the results from this and earlier studies show a clear correlation between ΔAbs and the micropollutant removal efficiency. As the measurement of absorbance is very

simple and stable, the resulting online monitoring system allows a fast insight into the process behaviour.

It was shown that, for the wastewater of a specific WWTP, the correlation between ΔAbs and micropollutant removal must be identified in order to ensure the successful control of ozonation and the corresponding micropollutant removal efficiency.

Different types of feed-forward control strategies for the ozone dosage were tested successfully in earlier pilot studies (Abegglen & Siegrist 2012) on the basis of influent parameters such as the discharge, DOC and nitrite; advantages and disadvantages are shown in Supplementary Information Table S6 (available online at http://www.iwaponline.com/wst/071/053.pdf). (Feed-forward control means adapting a process parameter, such as the ozone dosage, on the basis of an influent parameter, such as the discharge or DOC.) This study gives the background for a feedback control strategy for ozone dosage based on ΔAbs. However, further research on a full-scale WWTP is still required in order to clarify several questions. In particular, storm events and seasonal variations and their effect on ΔAbs have to be identified. To identify the specific parameters for such a feedback control, the corresponding indicator substances and the quality goal of micropollutant removal efficiency must be defined, and the parameters have to be established separately for each WWTP.

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