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MICROSIEVING COUPLED WITH O_3 OR CLO_2 FOR TREATMENT AND DISINFECTION OF COMBINED SEWER OVERFLOWS

MIKROFILTRERING I KOMBINATION MED O_3 ELLER CLO_2 FÖR BEHANDLING OCH DESINFEKTION AV BRÄDDVATTEN

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Abstract

A compact combined sewer overflow (CSO) treatment unit is set up and evaluated in pilot-scale. The pilot-plant consisted of flocculation, coagulation and a microsieving system followed by a disinfection unit with either O_3 or ClO_2. Efficiency of the pilot-plant was evaluated with respect to reduction of Escherichia coli, coliform bacteria and intestinal enterococci as well as removal of biocides. Results showed that 10 mg L^{-1} of ClO_2 as disinfectant was sufficient to meet the European Union (EU) requirements as per Bathing Water Directive (2006/7 EC) while the same results were only achieved when higher O_3 dose (20 mg O_3 L^{-1}) was applied. This study revealed that chlorine dioxide was the most effective disinfectant agent in reducing the number of bacteria to below the limits set by the EU Bathing Water Directive and that the pre-treatment used was highly efficient. Regarding biocides, the efficiency of the removal was highly dependent on the type of substance. However, ozone was found to be able to remove a broader range of the investigated biocides.

Keywords: biocides; chlorine dioxide; CSO; disinfection; microsieving; ozone

Sammanfattning:
Ett kompakt bräddvattenbehandlingsystem ställdes upp och utvärderades i pilotskala. Pilotanläggningen bestod av flockning, koagulering och ett mikrofiltreringssystem följt av en desinfektionsenhet med antingen O_3 eller ClO_2. Pilotanläggningens effektivitet utvärderades med avseende på reduktion av Escherichia coli, koliforma bakterier och intestinala enterokocker samt borttagning av biocider. Resultaten visade att 10 mg L^{-1} av ClO_2 som desinfektionsmedel var tillräckligt för att uppfylla EU:s krav för bakteriellt innehåll enligt Badvattendirektivet (2006/7 EC) medan samma resultat uppnåddes endast när en hög O_3-dos (20 mg O_3 L^{-1}) applicerades. Denna studie visade att klordioxid var det mest effektiva desinfektionsmedlet för att minska antalet bakterier till under de gränser som fastställts i EU-badvattendirektivet. Det visades också att förbehandlingsmetoden (mikrofiltrering) var mycket effektiv. Avskiljningen av biocider berodde i hög grad på typen av biocid, men ozon visade sig kunna ta bort fler av de undersökta ämnena.

Introduction

Combined sewer networks are still in the core of the issues that urban water planners are dealing with. These networks convey substantial loads of surface runoff to wastewater treatment plants (WWTP), which do not necessarily require treatment in the first place. This unwelcomed load of water at the WWTP occupies a substantial proportion of the hydraulic capacity in the treatment process (Bertrand-Krajewski et al., 1995); a capacity which instead could have been utilized to meet the future requirements considering population growth and urbanization. Moreover, combined sewer networks affect the water environment quality by outpouring combined sewer overflows (CSO) under heavy rainfalls. Recent studies showed that in a changed climate, even more frequent and larger volumes of CSO can be expected (Gooré Bi et al., 2015). CSOs contain not only a large amount of bacteria and viruses (Kim et al., 2009; Rechenburg et al., 2006) but also high levels of nutrients (nitrogen and phosphorus), organic matter and solids (Steets and Holden, 2003). Thus, CSOs can deteriorate the quality of waterbodies by introducing pathogens as well as transforming the receiving waters into inhabitable environments for vectors such as Culex quinquefasciatus (Vazquez-Prokopec et al., 2010). Additionally, the high nutrient load in CSOs can also add to heavy eutrophication of waterways (Gervin and Brix, 2001).

It is reportedly possible to alleviate CSO recurrence through upstream measures, e.g. by retrofitting sustainable drainage systems (SuDS) for reduction and/or detention of flows (Vallabhaneni, 2016; Haghighatafshar et al., 2018), but the implementation of these measures is a relatively slow process. Therefore, in the meantime, it is of importance to protect the recipients further downstream by introducing CSO treatment. It should also be noted that in the case of CSOs, the applied treatment technique has to include not only the conventional treatment for removal of nutrients and organic matter but also reduction of pathogenic microorganisms (Lucas et al., 2014). This is especially necessary if the receiving waterbody is used for recreational purposes like bathing. In such cases, the discharged CSO needs to comply with the European Union's Directive 2006/7 EC (Bathing Water Directive, 2006) which imposes delimitations on the concentrations of Escherichia Coli (E. Coli) and intestinal enterococci (Table 1). The concentration of bacteria in this study is expressed as the number of colony-forming units (cfu) per 100 mL sample.

Disinfection of CSOs for removal of pathogenic microorganisms can be done via various chemicals such as ozone, hydrogen peroxide, chlorine or chlorine dioxide. However, it is known that high chemical oxygen demand (COD) and particle content may have negative impact on the effectiveness of the chosen disinfectant agent (Wojtenko et al.,

Table 1. *Limitations suggested by Directive 2006/7 EC on the pathogen content of coastal and transitional waters.*

	Escherichia coli	Intestinal enterococci	Quality class
Maximum concentration allowed (cfu 100 mL^{-1})	500*	185*	Sufficient
	500**	200**	Good
	250**	100**	Excellent

** Based upon a 90-percentile evaluation.*
*** Based upon a 95-percentile evaluation.*

2001; Xu et al., 2002; Gehr et al., 2003). Therefore, it is important to reduce the amount of COD and suspended solids (SS) prior to applying any disinfection stage. Consequently, it is crucial to introduce process setups that can efficiently treat CSO with respect to COD and particle content followed by a disinfection step. In this regard, the application of flocculation/coagulation/disc-filtration (microsieving) as an efficient and robust pre-treatment step with a minimal footprint for CSO treatment is relatively unexplored.

The present study encloses two major objectives:

- to evaluate the effectiveness of flocculation/coagulation/filtration via microsieving as pre-treatment to CSO disinfection.
- to investigate the performance of O_3 and ClO_2 as possible disinfectant agents to meet the stipulated limitations as per the Bathing Water Directive.

Moreover, the effects of the applied treatment processes is also studied on the removal of certain micropollutants such as biocides, which are proven to be contained in urban runoff (Bollmann et al., 2014a)

Materials and Methods

A pilot-plant consisting of flocculation, coagulation and microsieving steps followed by an ozonation unit was installed in the influent line of the Öresundsverket WWTP in Helsingborg, Sweden. In order to mimic the worst possible loading scenario for CSO treatment, the pilot-plant was subjected to raw wastewater inflow to the WWTP.

Pre-treatment in Pilot-scale: Flocculation, Coagulation and Microsieving

To address the problem with high COD, turbidity and nutrient content in the CSO, a pilot-scale pre-treatment consisting of flocculation, coagulation and microsieving was set up according to Figure 1 at Öresundsverket.

A portion (12.6-16.4 m^3 h^{-1}) of the incoming wastewater (after screening and aerated grit chamber) to Öresundsverket was subjected to flocculation and coagulation using 17.4-19.5 mg L^{-1} PAX XL 100 and 3.6-4.1 mg L^{-1} cationic polymer (Kemira 5060). Subsequently, the flow was passed through a disc-filter (provided by Hydrotech, Veolia

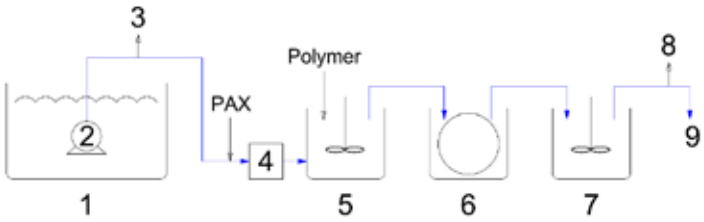

Figure 1. *Schematic illustration of the pilot-plant for pre-treatment of CSO. 1: Incoming wastewater after screening and aerated grit chamber, 2: Submerged centrifugal pump, 3: Sampling point incoming wastewater, 4: Ultra-sound flow meter, 5: Stirred contact chamber, 6: Disc-filter, Hydrotech (microsieving with disc-filter), 7: Stirred equalization tank, 8: Sampling point after pre-treatment, 9: To disinfection.*

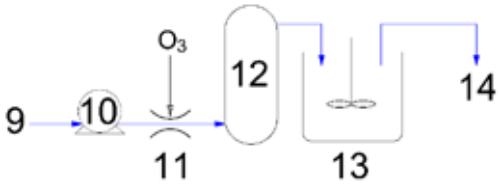

Figure 2. *Schematic setup of the pilot ozonation unit following the pre-treatment step illustrated in Figure 1. 9: Pre-treated wastewater, 10: Booster pump, 11: Venturi injector, 12: Contact tank, 2 minutes HRT, 13: Contact tank, 6 minutes HRT, 14: Sampling point after ozonation.*

Water Technologies) mounted with a woven polyester filter medium of 100-µm pore size. The details of the operational principles of disc-filtration are explained in Ljunggren (2006). The efficiency of pre-treatment by microsieving was investigated by monitoring the chemical oxygen demand (COD), biochemical oxygen demand (BOD_7), suspended solids (SS), total phosphorus (TP), turbidity, E-Coli, coliform bacteria and intestinal enterococci, before and after treatment. The pre-treated wastewater was thereafter treated with chlorine dioxide in laboratory-scale and in pilot-scale with ozone, both utilizing 8 minutes of reaction time.

Pilot-scale Disinfection with Ozone

The pilot-scale ozone disinfection system (Figure 2) was placed after the flocculation, coagulation and microsieving steps according to the recommendations by Väänänen et al. (2014). A Primozone GM 6 ozone generator (Primozone, 2017) was employed for in-situ production and injection of ozone. The utilized ozone generator in principle subjected air (or oxygen) to an electrical discharge while at the same time removed the waste heat by either air or water. The pre-treated wastewater was pumped at a rate of approximately 10 m^3 h-1 through a venturi injector (Figure 2, #11) where five different ozone doses were applied: 3, 6, 9, 12 and 20 mg O_3 L^{-1}. The two reaction vessels (Figure 2, #12, #13) amounted to a total retention time of 8 minutes. Due to practical issues, one ozone dose was applied every day of the pilot-scale study, with replicates of the 9 mg O_3 L^{-1}. The setup ran for 1.5 h to stabilize the whole system before sampling. Cumulative sampling was employed by withdrawing 3 L of wastewater ten times within 1.5 h from each sample point (Figure 1 and 2). From the resulting 30 L cumulative sample, the COD, BOD_7, SS, TP, turbidity, E-Coli, coliform bacteria and intestinal enterococci were analysed.

Laboratory-scale Disinfection with Chlorine dioxide

In this study, chlorine dioxide was synthesized on-site by addition of 25 mL of 9% HCl and 25 mL of 7.5% $NaClO_2$ into 400 mL of distilled water. The mixed solution was then diluted to 1 L, resulting in a concentration of about 1 g ClO_2 L^{-1}. The prepared stock solution was then covered with aluminium foil to avoid any photosynthesis and was left overnight in a +4°C fridge in order to react completely (Hey et al., 2012).

To disinfect the flocculated, coagulated and microsieved wastewater (Figure 1, #9) from Öresundsverket with chlorine dioxide it was necessary to ascertain the minimum dose of disinfectant agent to be used in the study. Based on the initial test, the flocculated, coagulated and microsieved wastewater contained approximately 180 mg L^{-1} COD which in turn consumed 5 mg L^{-1} of chlorine dioxide in 8 minutes. Hence, 5 mg ClO_2 L^{-1} was selected as the lowest dose. For the four disinfection experiments with chlorine dioxide, the setup was as follows: 1 L of pre-treated wastewater was added to three sterilized reactors and chlorine dioxide stock solution was added until the concentrations of 5, 10 and 15 mg ClO_2 L^{-1} were reached. The concentration of chlorine dioxide was measured and controlled by Wallace & Tiernan® Analysers/Controllers P15 plus Photometer, Siemens.

A sodium sulphite solution at about 50 g L^{-1} of Na_2SO_3 was prepared and was used to remove the residual chlorine dioxide in the reactors after

the desired retention time was fulfilled (Hey et al., 2012). The required concentration of the sodium sulphite was calculated according to the following reaction stoichiometry:

$$5Na_2SO_3 + 2ClO_2 + H_2O \rightarrow 5Na_2SO_4 + 2HCl$$

Quantification of Biocides (Sample Preparation and Analysis)

It was hypothesized that both ozone and chlorine dioxide would reduce the biocide content of the wastewater. Therefore, samples were taken before and after the two pre-treatments, two experiments with 20 mg O_3 L^{-1} and one experiment with 10 and 15 mg ClO_2 L^{-1}. The biocides selected for analysis, along with the corresponding abbreviations used throughout this article are presented in Table 2.

Sample extraction was performed following the methods employed by Bollmann et al. (2014b). In a volumetric flask, 100-mL sample was spiked with 50 µL of internal standard solution, containing a mixture of deuterated biocides (1 µg mL^{-1} methanol in gradient grade (LiChrosolv®), Merck, Darmstadt, Germany) isoproturon-D6, terbutryn-D5, cybutryn-D9, tebuconazole-D6, and carbendazim-D4). Then 3 mL of a 0.2M phosphate buffer was added to adjust the pH to 7.0. A Bakerbond SDB-2 (6 mL, 200 mg) SPE-cartridge (*Mallinckrodt Baker*, Deventer, The Netherlands) was conditioned with 12 mL acetonitrile (gradient grade (lichrosolv), Merck, Darmstadt, Germany) and 12 mL Millipore-water successively. After extracting the 100 mL sample (using a velocity of 2 mL min^{-1}) the cartridge was washed with 12 mL Millipore-water and slightly dried with vacuum. The combined eluates of 12 mL acetonitrile and 12 mL methanol were condensed to 1 mL in a BÜCHI Syncore® multiport condenser (Büchi, Flawil, Switzerland) at 50°C, 280 rpm, and 100 mbar for about 90 minutes. The extracts were then transferred to 1.5-mL auto sampler vials.

The analysis of biocides was performed by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) using electrospray ionization in positive mode (ESI(+)) on an Ultimate 3000 HPLC-system (Dionex, Sunnyvale, CA, USA) coupled to an API 4000 triple-quadrupole-MS (AB Sciex, Framingham, MA, USA) according to Bollmann et al. (2014a). The separation was performed at 5°C using Synergy polar-RP

Table 2. *Analyzed biocides, their corresponding abbreviations and CAS Registry Numbers.*

Name	Abbrev.	CAS number
Mecoprop	MCPP	93-65-2
2,4-Dichlorobenzamide*	BAM	2447-79-2
Carbendazim	CD	10605-21-7
Isoproturon	IP	34123-59-6
Diuron	DR	330-54-1
Iodocarb	IPBC	55406-53-6
Terbutryn	TB	886-50-0
N-Octylisothiazolinone	OIT	26530-20-1
Tebuconazole	TBU	107534-96-3
Dichloro-N-octylisothiazolinone	DCOIT	64359-81-5
Propiconazole	PPZ	60207-90-1

** 2,4-Dichlorobenzamide is a degradation product of the pesticide Dichlobenil (DCBN) – CAS number: 1194-65-6*

Table 3. *Average results from the analysis of total phosphorus, SS, COD and turbidity. Values in parenthesis are the standard deviations of the measurements.*

	Incoming (untreated)	Concentration in CSO acc. to Soonthornnonda and Christensen (2008)	Pre-treated (after disc-filter)	Removal efficiency	Expected range acc. to Väänänen et al. (2016)
TP (mg P L^{-1})	7.40 (1.33)	0.82 (0.06)	0.21 (0.07)	97%	TP>95% / <0.3 mg L^{-1}
SS (mg SS L^{-1})	225 (56.5)	86.8 (7.08)	4.4 (1.1)	98%	SS>95% / <20 mg L^{-1}
COD (mg O_2 L^{-1})	504 (129)	N/A	126 (46)	75%	COD>70-95% / 50-200 mg L^{-1}
BOD_7 (mg O_2 L^{-1})	172.7 (66.9)	24.2 (6.35)	40.5 (10.3)	76%	-
Turbidity (FNU*)	266 (83.5)	N/A	2.2 (0.86)	99%	-

FNU: Formazin Nephelometric Unit

column (L=150 mm, ID=2 mm, particles=4 µm, Phenomenex, Torrance, CA, USA). A multi-step gradient of water (A) and methanol (B) was used: 0-3 min 0% B, 3-5 min 0 to 50% B, 5-15 min 50 to 80% B, 15-15.5 min 80 to 100% B, 15.5-19 min 100% B, 19-20 min 100 to 0% B, 20-25 min 0% B. In order to change to acidic conditions for the ionization, 0.03 mL min^{-1} of 0.2% formic acid in water was added post column prior to introduction to the ion source of the mass spectrometer (Bollmann et al. 2014b).

Analytical Methods

TP and COD were measured in the pre-treated samples with HACH LANGE cuvette test tubes LCK-350 and LCK-114, respectively. All the pre-treated samples were also analysed for turbidity with a portable HACH turbidimeter (model 2100Qis). SS content and BOD_7 were analysed according to the standard methods EN 872:2005 and SS 02 81 43 / EN 1899-1:1998, respectively.

All the samples were kept at about 4ºC for maximum 24 hours after disinfection experiments before they were delivered for analysis of their pathogen content. The analyses for pathogen content were performed by ALcontrol laboratories in Malmö, Sweden. The adopted enumeration methods for the bacterial analyses were SS028167-2 MF (for E. Coli and Coliform bacteria) and SS-EN ISO 7899-2:2000 (for intestinal enterococci), according to the guidelines described by the Swedish Standard Institute (SIS) and International Organization for Standardization (ISO), respectively.

Results and Discussion

Pre-treatment Step

(Coagulation, Flocculation and Disc-filter)

The results for the analysis of total phosphorus (TP), SS, COD and turbidity are presented in Table 3 for both incoming (raw) and pre-treated wastewater. It was found that the pre-treatment step (including coagulation, flocculation and disc-filtration) had a considerable effect on the reduction of TP, SS, COD and turbidity by 97%, 98%, 75% and 99%, respectively. The high removal efficiency of the microsieving step is found to be superior to the results obtained from particle settlers in a similar application (Chhetri et al., 2016). The achieved removal efficiencies are in strong agreement with findings from Väänänen et al. (2016). According to them (Väänänen et al., 2016), such high removal efficiencies are only reached when the wastewater is

subjected to coagulant and cationic polymer prior to disc-filtration.

Table 4 presents the bacterial concentration in the incoming and the pretreated wastewater. According to the results from the microbial analyses, it was found that the incoming wastewater contained over 10^5 cfu 100 mL^{-1} (i.e. upper detection limit) of all analysed species i.e. E. Coli, Faecal Coliforms and enterococci. This is in agreement with the results from a recent study carried out by U.S. Geological Survey Scientific Investigations which quantified E. Coli, Faecal Coliforms, and enterococci generally between 10^6 and 10^7 cfu 100 mL^{-1} in primarily-settled wastewater (Francy et al., 2011).

Analysis of wastewater samples after pre-treatment revealed that the number of pathogenic agents decreased after the microsieving step. However, considering the pore size of the applied microsieve which was 100 µm, no significant reduction of the bacteria population should be expected in the screening step since the size of bacteria ranges between 0.5-5 µm (Hammer and Hammer Jr, 2012). Thus, the observed reduction in the quantity of the bacteria can be associated to their flocculation/aggregation properties in the wastewater. It is known that the extracellular polymeric substances (EPS) formed around the bacteria, either loosely-bound or tightly-bound, are mainly in the form of carbohydrates and proteins and have a net negative charge so that the bacteria can be considered as negatively charged colloidal particles (Eboigbodin and Biggs, 2008). Consequently, the addition of positively charged coagulants such as PAX XL 100, as used in this study, would lead to aggregation of bacteria as well as other suspended materials and hence formation of larger flocs and better screening efficiency.

After the pre-treatment step, the levels of E. Coli, intestinal enterococci and coliform bacteria were in average 2703, 25862 and 1877 cfu 100 mL^{-1}, respectively. The standard deviation for the pre-treatment values of E. Coli, intestinal enterococci and coliform bacteria amounted to 2717, 13337 and 1179 cfu 100 mL^{-1}. The large standard deviation observed for the pre-treatment could be due to large variations in the incoming bacteria levels. It can also be seen that coliform bacteria are generally more abundant in the pretreated wastewater than E. Coli and enterococci. However, it is not possible to determine the occurred log-reduction after the pre-treatment step since the exact initial number of

Table 4. *The concentrations of the studied pathogens in the inflow (raw wastewater) and after pretreatment.*

Sample ID	**Influent (raw wastewater)** (cfu 100 mL^{-1})	**Pretreated sample**		
		E. Coli	**Intestinal enterococci**	**Coliform bacteria**
a	>100000	3500	3200	25000
b	>100000	700	920	21000
c	>100000	930	1400	27000
d	>100000	7300	540	35000
e	>100000	610	2000	53000
f	>100000	940	3500	9600
g	>100000	650	360	8300
h	>100000	7000	3100	28000
Average (*standard deviation*)		**2590 (3029)**	**1878 (1261)**	**25863 (14258)**

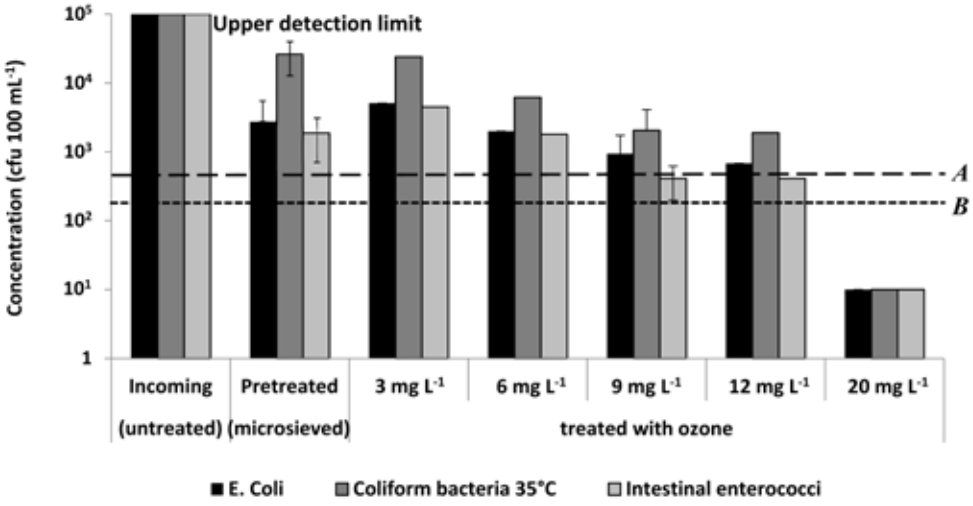

Figure 3. *Pathogen concentrations in logarithmic scale before and after the addition of 3, 6, 9, 12 and 20 mg O_3 L^{-1} in pilot-scale. The lower detection limit was 10 cfu 100 mL^{-1} and the data presented is the average with the standard deviation (where applicable). Dashed line A: EU directive limit for E. Coli, Dashed line B: EU directive limit for Intestinal enterococci.*

bacteria in the raw wastewater could only be determined up to 10^5 cfu 100 mL^{-1} according to the adopted analysis methods.

Disinfection Experiments

Ozone (O_3) in pilot-scale

The levels of E. Coli, coliform bacteria and intestinal enterococci before and after treatment with 3, 6, 9, 12 and 20 mg O_3 L^{-1} are presented in Figure 3. In the case of disinfection with ozone, it was not possible to repeat the dosages except for the 9 mg O_3 L^{-1} dose. For this reason, Figure 3 presents standard deviations for the pre-treated and 9 mg O_3 L^{-1} values while all the other measurements are single values without standard deviation. As seen in Figure 3, the levels of E. Coli, coliform bacteria and intestinal enterococci remain quite stable for the 3, 6, 9 and 12 mg O_3 L^{-1} doses, with all values well above the limits set by the EU bathing water directive. However, when 20 mg O_3 L^{-1} was applied, all microbial levels were reduced to < 10 cfu 100 mL^{-1}, which is well below the directive limits.

The failure of the ozone doses less than 20 mg O_3 L^{-1} in reducing the microbial levels to the directive stipulated limits (presented in Table 1) agrees well with the findings of Gehr et al. (2003) where an ozone dose of at least 30 mg O_3 L^{-1} is needed to reduce coliform bacteria to below 9000 cfu 100 mL^{-1}. It was also observed that ozonation using the applied doses did not have significant effect on TP and SS reduction whereas only a marginal reduction (3-4%) of COD and BOD_7 could be accredited to ozone treatment.

Chlorine dioxide (ClO_2) in laboratory-scale

The average levels of the studied microorganisms before and after the laboratory-scale disinfection with chlorine dioxide are presented with standard deviation in Figure 4. The bacterial composition of the pre-treated and incoming water were the same as in the pilot-scale disinfection with O_3. In the case of 15 mg ClO_2 L^{-1} and the incoming wastewater, the absence of standard deviation is due to the lack of variance in results. The lowest chlorine dioxide dose (5 mg ClO_2 L^{-1}) reduced these levels to (in average): 114, 104 and 71 cfu 100 mL^{-1}

while the 10 mg ClO_2 L^{-1} dose reduced the levels to (in average): <10, 21 and 14 cfu 100 mL^{-1}. The highest dose (15 mg ClO_2 L^{-1}) reduced all microbial levels to below 10 cfu 100 mL^{-1}.

It is apparent that even the lowest chlorine dioxide dose reduces the bacteria levels down to the limits set by the EU bathing water directive. However, the lowest chlorine dioxide dose of 5 mg ClO_2 L^{-1} shows a standard deviation that lies very close to the directive stipulated limit. It was also observed that the COD and SS content of the samples remained intact following the application of chlorine dioxide.

Application of chlorine dioxide as disinfectant agent was found to be more effective than ozone. The hygiene criteria (Directive 2006/7 EC) was achieved just at about 5 mg ClO_2 L^{-1} (minimum concentration tested). Consequently, complete fulfilment of the hygiene criteria with safer margin was met at 10 mg ClO_2 L^{-1}, with approximately 4 mg ClO_2 L^{-1} residual after the detention time of 8 minutes. The reason for the apparent disparity of the two disinfection agents can be explained by comparing their oxidation potentials, ozone has an oxidation potential of 2.07 V while chlorine dioxide has a potential of 0.95 V. The higher oxidation potential of ozone is an indication that ozone is highly capable of oxidizing most of the compounds it interacts with in comparison to chlorine dioxide. In addition, even the pretreated wastewater used in this study contained a large amount of organic compounds besides the microorganisms, ozone reacts quickly as soon as it is dissolved. Chlorine dioxide on the other hand, with its lower oxidation potential, can be expected to be present in the wastewater for a longer time, thus increasing the potential of encountering the microorganisms to inactivate.

Fate of Biocides through the Process

The average effect (with the standard deviation where applicable) of pre-treatment, ozone, and chlorine dioxide on the biocide content of the wastewater is presented in Figure 5. The results show

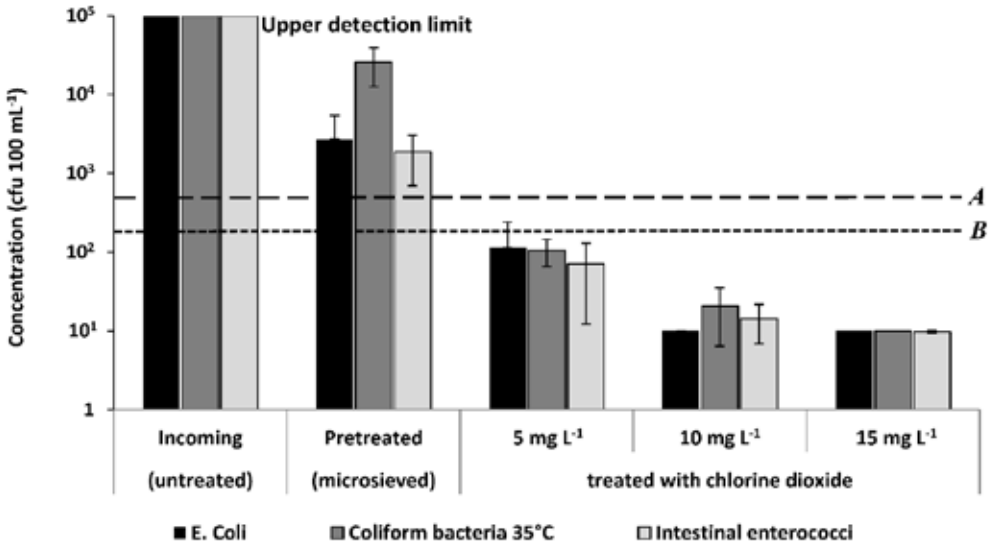

Figure 4. *Pathogen concentrations in logarithmic scale before and after the addition of 5, 10 and 15 mg ClO_2 L^{-1} in laboratory-scale. The lower detection limit was 10 cfu 100 mL^{-1} and the data presented is the average with the standard deviation (where applicable). Dashed line A: EU directive limit for E. Coli, Dashed line B: EU directive limit for Intestinal enterococci.*

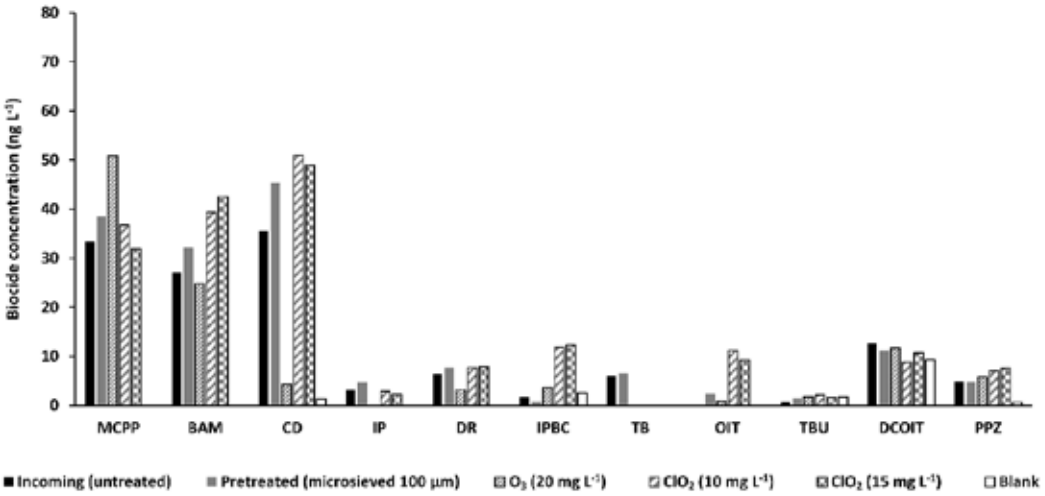

Figure 5. *Analysis results for biocide removal experiment through microsieving, ozonation, and chloride dioxide treatment for the selected substances. The biocide concentrations are expressed in ng L^{-1}. Note that all the results in this figure are subjected to about ±10% uncertainty.*

that the pre-treatment step did not lead to any reduction in the biocides content of the wastewater. Moreover, biocides CD, IP and TB are substantially reduced by ozonation (90-100%) while DR was only reduced by about 60%. On the other hand, chlorine dioxide is only effective in removal of TB (complete removal) and IP (at about 60%). TB is found to be the only biocide affected by both ozone and chlorine dioxide so that no traces of TB were detected in any of the treated samples.

The results show that IPBC, TBU, DCOIT, and PPZ are not affected by any of the treatment processes. However, it should be noted that the blank samples contained relatively high concentrations of IPBC, TBU, and DCOIT and minor amounts of PPZ. The observed increased concentration of BAM, OIT, IPBC and PPZ after the application of chlorine dioxide indicates that those samples could have been subjected to contamination.

Conclusions

The study reveals the applicability of combined coagulation, flocculation and microsieving (with a filter medium of 100 µm in pore size) to remove substantial amount of bacteria along with efficient reduction in COD, total phosphorus, SS and turbidity. The resulting quality of the wastewater makes it feasible for the disinfection agents to inactivate the pathogenic microorganisms with less interference from COD and particles. Since most CSOs are often only partially treated before discharged to the recipient, the achieved 97% reduction in total phosphorus is highly beneficial considering the eutrophication issue in general.

The results show that chlorine dioxide was clearly a more effective disinfectant than ozone. It was proven possible to achieve the required level of disinfection according to the EU bathing water directive with 10 mg ClO_2 L^{-1} by a safe margin. Ozone, on the other hand, did not result in the satisfactory level of disinfection, unless 20 mg O_3 L^{-1} was applied.

Moreover, it was observed that ozone, contrary to chlorine dioxide, was able to reduce the amount of the biocides Carbendazim (CD), Isoproturon (IP) and Diuron (DR) quite substantially, whereas both chlorine dioxide and ozone were found to be effective in complete removal of Ter-

butryn (TB). Other biocides, such as Mecoprop (MCPP), 2.4-Dichlorobenzamide (BAM), Tebuconazole (TBU), Dichloro-N-octylisothiazolinone (DCOIT) and Propiconazole (PPZ) were not removed by either chlorine dioxide or ozone. This study encourages further investigations with respect to the reduction of biocides in wastewater by ozone, and other potential agents and methods.

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References

Bathing Water Directive (2006) Directive 2006/7 EC of The European Parliament and of the Council. Official Journal of the European Union.

Bertrand-Krajewski, J.-L., Lefebvre, M., Lefai, B., and Audic, J.-M. (1995) Flow and pollutant measurements in a combined sewer system to operate a wastewater treatment plant and its storage tank during storm events. Water Science & Technology, 31(7), 1–12.

Bollmann, U. E., Tang, C., Eriksson, E., Jönsson, K., Vollertsen, J., and Bester, K. (2014a) Biocides in urban wastewater treatment plant influent at dry and wet weather: concentrations, mass flows and possible sources. Water research, 60, 64–74.

Bollmann, U. E., Vollertsen, J., Carmeliet, J., and Bester, K. (2014b) Dynamics of biocide emissions from buildings in a suburban stormwater catchment – Concentrations, mass loads and emission processes. Water Research, 56, 66–76.

Chhetri, R. K., Bonnerup, A., and Andersen, H. R. (2016) Combined Sewer Overflow pretreatment with chemical coagulation and a particle settler for improved peracetic acid disinfection. Journal of Industrial and Engineering Chemistry, 37, 372–379.

Eboigbodin, K. E. and Biggs, C. A. (2008) Characterization of the Extracellular Polymeric Substances Produced by Escherichia coli Using Infrared Spectroscopic, Proteomic, and Aggregation Studies. Biomacromolecules, 9(2), 686–695.

Francy, D. S., Stelzer, E. A., Bushon, R. N., Brady, A. M. G., Mailot, B. E., Spencer, S. K., Borchardt, M. A., Elber, A. G., Riddell, K. R., and Gellner, T. . (2011) Quantifying Viruses and Bacteria in Wastewater—Results, Interpretation Methods, and Quality Control. U.S. Geological Survey Scientific Investigations Report 2011–5150, 44.

Gehr, R., Wagner, M., Veerasubramanian, P., and Payment, P. (2003) Disinfection efficiency of peracetic acid, UV and ozone after enhanced primary treatment of municipal wastewater. Water Research, 37(19), 4573–4586.

Gervin, L. and Brix, H. (2001) Removal of nutrients from combined sewer overflows and lake water in a vertical-flow constructed wetland system. Water Science & Technology, 44(1), 171–176.

Gooré Bi, E., Monette, F., Gachon, P., Gaspéri, J., and Perrodin, Y. (2015) Quantitative and qualitative assessment of the impact of climate change on a combined sewer overflow and its receiving water body. Environmental Science and Pollution Research, 22(15), 11905–11921.

Haghighatafshar, S., Nordlöf, B., Roldin, M., Gustafsson, L.-G., la Cour Jansen, J., and Jönsson, K. (2018) Efficiency of blue-green stormwater retrofits for flood mitigation – Conclusions drawn from a case study in Malmö, Sweden. Journal of Environmental Management, 207.

Hammer, M. J. and Hammer Jr, M. J. (2012) Water and Wastewater Technology, Seventh Edition. Pearson Education, 528.

Hey, G., Ledin, A., Jansen, J. la C., and Andersen, H. R. (2012) Removal of pharmaceuticals in biologically treated wastewater by chlorine dioxide or peracetic acid. Environmental Technology, 33(9), 1041–1047.

Kim, W. J., Managaki, S., Furumai, H., and Nakajima, F. (2009) Diurnal fluctuation of indicator microorganisms and intestinal viruses in combined sewer system. Water Science & Technology, 60(11), 2791.

Ljunggren, M. (2006) Micro screening in wastewater treatMent – an overview. VATTEN - Journal of Water Management and Research, 62, 171–177.

Lucas, F. S., Therial, C., Gonçalves, A., Servais, P., Rocher, V., and Mouchel, J.-M. (2014) Variation of raw wastewater microbiological quality in dry and wet weather conditions. Environmental Science and Pollution Research, 21(8), 5318–5328.

Primozone (2017) Data Sheet for Primozone® GM2-GM6-GM12-GM18 - ozone generators.

Rechenburg, A., Koch, C., Claßen, T., and Kistemann, T. (2006) Impact of sewage treatment plants and combined sewer overflow basins on the microbiological quality of surface water. Water Science & Technology, 54(3), 95–99.

Soonthornnonda, P. and Christensen, E. (2008) Source apportionment of pollutants and flows of combined sewer wastewater. Water Research, 42(8–9), 1989–1998.

Steets, B. M. and Holden, P. A. (2003) A mechanistic model of runoff-associated fecal coliform fate and transport through a coastal lagoon. Water Research, 37(3), 589–608.

Väänänen, J., Cimbritz, M., and la Cour Jansen, J. (2016) Microsieving in primary treatment: effect of chemical dosing. Water Science and Technology, 74(2), 438–447.

Väänänen, J., Nilsson, F., la Cour Jansen, J., Hörsing, M., Hagman, M., and Jönsson, K. (2014) Discfiltration and ozonation for reduction of nutrients and organic micro-pollutants from wastewater – a pilot study. Water Practice and Technology, 9(4), 475–482.

Vallabhaneni, S. (2016) Wastewater Collection Systems. Water Environment Research, 88(10), 953–965.

Vazquez-Prokopec, G. M., Vanden Eng, J. L., Kelly, R., Mead, D. G., Kolhe, P., Howgate, J., Kitron, U., and Burkot, T. R. (2010) The Risk of West Nile Virus Infection Is Associated with Combined Sewer Overflow Streams in Urban Atlanta, Georgia, USA. Environmental Health Perspectives, 118(10), 1382–1388.

Wojtenko, I., Stinson, M. K., and Field, R. (2001) Performance of Ozone as a Disinectant for Combined Sewer Overflow. Critical Reviews in Environmental Science and Technology, 31(4), 295–309.

Xu, P., Janex, M.-L., Savoye, P., Cockx, A., and Lazarova, V. (2002) Wastewater disinfection by ozone: main parameters for process design. Water Research, 36(4), 1043–1055.