Elimination of micropollutants during post-treatment of hospital wastewater with powdered activated carbon, ozone and UV

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ABSTRACT:

A pilot-scale hospital wastewater treatment plant consisting of a primary clarifier, membrane bioreactor and five post-treatment technologies including ozone (O_3), O_3/H_2O_2, powdered activate carbon (PAC), and low pressure UV light with and without TiO_2 was operated to test the elimination efficiencies for 56 micropollutants. The extent of the elimination of the selected micropollutants (pharmaceuticals, metabolites and industrial chemicals) was successfully correlated to physical-chemical properties or molecular structure. By mass loading, 95% of all measured micropollutants in the biologically treated hospital wastewater feeding the post-treatments consisted of iodinated contrast media (ICM). The elimination of ICM by the tested post-treatment technologies was 50- 65% when using 1.08 g O_3/gDOC, 23 mg/L PAC, or a UV dose of 2400 J/m^2 (254 nm). For the total load of analyzed pharmaceuticals and metabolites excluding ICM the elimination by ozonation, PAC, and UV at the same conditions was 90%, 86%, and 33%, respectively. Thus, the majority of analyzed substances can be efficiently eliminated by ozonation (which also provides disinfection) or PAC (which provides micropollutants removal, not only transformation). Some micropollutants recalcitrant to those two post-treatments, such as the ICM diatrizoate, can be substantially removed only by high doses of UV (96% at 7200 J/m^2). The tested combined treatments (O_3/H_2O_2 and UV/TiO_2) did not improve the elimination compared to the single treatments (O_3 and UV).

INTRODUCTION

Hospital wastewater contains pharmaceuticals and disinfectants[1-4], as well as pathogens and antibiotic resistant bacteria[5-7] in high concentrations. Some of the environmentally relevant groups of pharmaceuticals used in relatively high amounts in hospitals are antibiotics which contribute to the spread of antibiotic resistance[2], cytostatics which are potentially ecotoxic[8-10] and X-ray contrast media which are used in high quantities[11, 12], but many more pharmaceuticals are present for which not sufficient information is available for a risk assessment.

Treatment of the hospital wastewater at the source has advantages of avoiding dilution due to mixing with the municipal sewage, avoiding losses into environment due to leaks and combined sewer overflows, and preventing pathogens and antibiotic multi-resistant bacteria to enter the environment.[11, 13, 14] Biological treatment of hospital wastewater on site showed to be feasible and efficient to remove dissolved organic carbon (DOC) and chemical oxygen demand (COD) significantly to >90%, as well as nitrogen (>99% N-elimination by denitrification).[11, 15] Nevertheless, any biological treatment (conventional activated sludge or membrane bioreactor, MBR) is typically insufficient to eliminate the majority of micropollutants.[11, 16, 17] Therefore, additional oxidative or other physical-chemical post-treatments are necessary. Good results in municipal wastewater treatment were obtained with ozone[18-22], activated carbon[23-26], UV/H_2O_2[27, 28], and nanofiltration or reverse osmosis[29-33].

Three post-treatment technologies, namely, ozonation (and O_3/H_2O_2), UV in absence and presence of TiO_2 and powdered activated carbon (PAC) were selected in this study to estimate the efficiency for hospital wastewater treatment. 56 target analytes including pharmaceuticals, human metabolites, and industrial chemicals were chosen as elucidated in our earlier publication on their behavior during treatment with MBR. [11] The main objectives of our study were to (1) determine elimination efficiencies for 56 organic micropollutants by the selected post-treatment technologies, treating an effluent of an MBR fed with raw hospital wastewater, and compare them to municipal wastewater treatment; to (2)

compare and predict the elimination efficiency of the selected micropollutants by the selected post-treatment technologies; and to (3) evaluate feasibility, energy consumption and costs.

MATERIALS AND METHODS

Wastewater Treatment Setup. A pilot plant was installed at the cantonal hospital in Baden, Switzerland (346 beds, water consumption 673 L per bed and day). First, the wastewater was treated by a MBR (Picatech Huber AG, Kriens, Switzerland), as described elsewhere.[11] MBR effluent water quality was as follows: 6-8 mg/L DOC, 30 mg/L dissolved COD, 3.7 mg NO_3-N/L, pH 8.1-8.5, temperature 27-28 °C, 30-40 µg/L bromide. The MBR permeate was collected in a 1 m^3 tank and disconnected from the MBR for individual post-treatment experiments with activated carbon, ozone or UV (SI, Figure S3). Experiments were performed in two replicates with different MBR permeate composition. The removal efficiency was calculated as the average of the two replicate experiments.

Activated carbon treatment. Post-treatment of the MBR-permeate with PAC (Norit SAE Super, surface area 1300 m^2/g, particle size d_{50}15µm, pH_{PZC} 9.8, Norit, Amersfoort, The Netherlands) took place in a 180-L reactor. The constant MBR-permeate flow of 180 L/day resulted in a hydraulic residence time of 1 day. The effluent of the PAC reactor was filtered through a flat sheet ultrafiltration membrane (Martin System, siClaro FM 611, pore size 0.04 micrometer, and membrane surface 6.2 m^2). 90 L/day of filtered PAC effluent was removed, while also 90 L/day of loaded PAC in solution was withdrawn (5 L every 80 min) to keep the PAC retention time at 2 days (exception: experiments in June 2009 were setup for 5 days of PAC retention time). For the required PAC doses of 10, 20, and 40 mg/L, the start-up concentration in the PAC reactor was 20, 40, and 80 mg/L for PAC retention time of 2 days. The dosing frequency of 150 mg PAC from a stock solution of 2 g/L was adjusted to 120, 60 or 30 min, to achieve the three different carbon doses. The reactor was emptied and cleaned before switching to the next carbon concentration. The actual PAC concentration in the PAC-reactor, as well as temperature, pH and DOC were regularly measured and recorded (Table S7). The influent of the first replicate

(Monday-Friday) was sampled before the start of the experiment and after 2 and 4 days (concentrations stayed constant over the time, the average taken as influent). The corresponding effluent was sampled after 2 and 4 days (average taken as effluent). For the second replicate (Friday-Monday) the influent was sampled before the start of the experiment and after 3 days (average taken as influent). The corresponding effluent was sampled after 3 days. Equilibrium was found to be reached after 2 days. Campaigns were run with 8±4 mg/L PAC, 23±7 mg/L PAC, and 43±14 mg/L PAC.

Ozone Treatment. A counter current bubble column of 2 m height and 4.5 L volume was used for the post-treatment of the MBR-permeate with ozone. The ozone was produced from oxygen in the air with the Chemodata 1.0 g/Hmax ozone generator (Chemonorm AG, Altendorf, Switzerland), with an ozone production of 0.1 - 0.15 g O_3/h. The ozone concentration was regulated by adjustment of the wastewater flow. The MBR-permeate flows of 12-23 L/h resulted in the required ozone doses in the column (hydraulic residence time of 12-23 min). An ozone analyzer BMT 964 (BMT Messtechnik Gmbh, Stahnsdorf, Germany) provided online measurement. The transferred ozone dose was calculated from the difference of the applied dose and the ozone in the off-gas (ozone transfer efficiency 66-78%). The three tested transferred ozone doses of 4.2, 5.8, and 7 mg/L resulted in specific ozone concentrations of 0.64, 0.89, and 1.08 g O_3/g DOC (Table S8). Additional experiments were conducted with the advanced oxidation process O_3/H_2O_2. For these experiments, the MBR permeate was pre-treated with 1.2 g O_3/g DOC, followed by addition of 2.5 mg/L H_2O_2 and 0.8 g O_3/g DOC (H_2O_2:O_3 molar ratio approx. 1:2). In a parallel run, the same pre-treated wastewater was treated with 0.8 g O_3/g DOC without an addition of H_2O_2.

UV treatment. A commercially available setup from UBE Industries (Model 3 m^3/h, UBE corporation Europe, S.A., Castellon, Spain) with a volume of 3.3 L and a water flow of 0.6 m^3/h was used for the post-treatment of the MBR-permeate by UV (Table S9). The reaction column was positioned around a low pressure UV lamp (254 nm, 220 V, 100-400 W overall energy consumption including the 40 W lamp power consumption). A nominal fluence rate of 10 mW/cm^2 and a hydraulic residence time of 20 s resulted in a nominal fluence of 2 000 J/m^2. The effective fluence rate of UV

treatment was calculated from the observed elimination rates of two compounds (diclofenac and iopromide) for which fluence-based rate constants are available from literature[34] (SI, Pages S21-S22). An effective fluence rate of 4 mW/cm^2 was calculated for the reactor with hospital wastewater (39.8 W/m^2 for diclofenac, 40.5 W/m^2 for iopromide). The effective fluence rate is lower by a factor of 2.5 than the nominal fluence rate value (10 mW/cm^2), probably due to the absorption of light by the wastewater in which the optical density is not negligible. The calculated effective fluence rate corresponds to a fluence of 800 J/m^2 for a single treatment. Typically 3 treatment cycles were applied with a cumulative dose of 2400 J/m^2.

The UV/TiO_2 experiments were performed with the same setup from UBE Industries after inserting four conical cartridges around the UV lamp consisting of a photo-catalytic fiber (titanium-dispersed silica-based fiber with a sintered anatase-TiO_2 layer on the surface[35]). The column volume of this setup was 3.0 L with a hydraulic residence time of 18 s. The calculated fluence rate with the photocatalytic fiber was only 1.7 mW/cm^2 (fluence of 306 J/m^2 after a single treatment), less than half of the values obtained for the reactor without the photocatalytic fibers.

The MBR-permeate was pre-filtered by a polypropylene filter (30 μm, Positech, Switzerland) prior to UV treatment to retain particles. Further, two pre-filters with pore sizes of 25 μm and 5 μm, located just before the UV reactor, were part of the commercial setup. Because of the short hydraulic residence time of the wastewater in the UV system, the experiments were conducted as follows. 200 L MBR permeate was treated with UV and collected into another tank (called “first run”). Then the collected water was recirculated through the UV reactor for 180 minutes, which is equivalent to 9 cycles , as one cycle of 200 L at a flow rate of 600 L/h takes 20 minutes. The samples were taken at the start of each experiment and after 1, 2, 3, 6, and 9 cycles. The removal efficiencies were calculated for the first run and after 3 and 9 cycles.

Sample Preparation and Analysis of Micropollutants. A detailed description of the sample preparation and analysis can be found elsewhere.[11] Shortly, samples were filtered with a 0.7 μm GF/F glass–fiber filter (Whatman, Dassel, Germany) and further through a 0.2 μm regenerated cellulose filter

(Sartorius AG, Göttingen, Germany), spiked with isotope labeled internal standards and analyzed by on-line SPE-HPLC-MS/MS with a Triple Quadrupol mass spectrometer (TSQ Quantum Ultra, Thermo Fisher Scientific). Limits of quantification are listed in the Supporting Informations (SI, Table S4).

Other measurements. The adsorbable organic halogen compounds (AOX) of three grab samples (effluents of: MBR, 43 mg/L PAC, and 1.08 g O_3/g DOC) were determined coulometrically after incineration according to DIN EN 1485-H14 and DIN EN ISO 9562 (by Bachema AG, Schlieren, Switzerland).

Chemical oxygen demand (COD) was measured by a Dr. Lange test kit (Hach Lange GmbH, Düsseldorf, Germany). Dissolved organic carbon (DOC) was determined using a Shimadzu TOC analyzer. Bromate in the samples of high ozone dosages was measured by ion chromatography.[36] For gadolinium and platinum measurements, samples were acidified with 60% nitric acid (1%, v/v), and analyzed by ICP-MS (Thermo Scientific, Element 2).

3. RESULTS AND DISCUSSION

3.1. Occurrence and Post-treatment Elimination Efficiencies. From the 67 target analytes (SI, Table S1, S2), 9 were not detected in the raw hospital wastewater prior to the MBR treatment (SI, Table S5), while cilastatin and paracetamol were removed during MBR treatment to non-detectable residues.[11] The concentrations of the remaining 56 micropollutants after MBR treatment are listed in Table 1, together with elimination efficiencies for the three post-treatments. Even after biological treatment, concentrations are very high, e.g. at 3.4 mg/L for the iodinated contrast media (ICM) iopamidol, and for several other compounds higher than 10 µg/L (other ICM, 4/5 Methylbenzotriazole, benzotriazole, the metabolites of aminopyrine 4-AAA and 4-AA, ciprofloxacin, gabapentin). In total, ICM occur with a concentration of 4.6 mg/L, from which a C-concentration of 1.2 mg/L was calculated (15-20% fraction of DOC). Elimination efficiencies were evaluated for the three different post treatments with PAC, ozone and UV, each with three different dosages. Most compounds are eliminated well with PAC and ozone, while elimination is much lower with UV. Due to low concentration or low frequency of

detection, only partial information on elimination efficiencies was obtained for bezafibrate, ifosfamide, morphine, oseltamivir, oseltamivir carboxylate, ritonavir, sulfadiazine, thiopental, trimethoprim, and verapamil. Based on the results, we selected the doses 23 mg/L, 1.08 gO_3/gDOC and 2400 J/m^2 for PAC, ozone and UV, respectively, for the further discussions in the following chapters, because they showed relatively good abatement of micropollutants and are reasonable in the context of cost constrains (see chapter 3.5.2). Elimination efficiencies with PAC and ozone normalized to DOC compare very well with efficiencies in municipal wastewater treatment, as shown in Table S10 and S11 in a literature overview.

Table 1. Post-treatment (O_3, PAC, UV) elimination efficiencies (%) for 56 micropollutants

	Influent[(1)] (µg/L)	PAC (dose in mg/L)[(2)]			O_3 (dose in g O_3/g DOC)[(3)]			UV (fluence in J/m^2)[(4)]		
		8	23*	43	0.64	0.89	1.08	800	2 400	7 200
1. 4-AAA[c]	11.3 ± 5.0	**30 ± 6**	**73 ± 4**	**90 ± 2**	99 ± 1	99 ± 0	99 ± 0	**42 ± 0**	**87 ± 1**	99 ± 0
2. 4-AA[d]	17.2 ± 8.0	**92 ± 0**	**95 ± 2**	**99 ± 0**	>83	>83	>83	**53 ± 4**	**41 ± 6**	**55 ± 5**
3. 4-FAA[c]	4.79 ± 1.33	**40 ± 1**	**81 ± 5**	**93 ± 2**	96 ± 2	98 ± 1	98 ± 1	**43 ± 4**	**85 ± 0**	98 ± 1
4. 4-MAA[d]	2.18 ± 3.01	**68 ± 6**	**75 ± 4**	**67 ± 1**	96 ± 0	97 ± 0	97 ± 1	**25 ± 0**	**9 ± 16**	**25 ± 10**
5. 4/5-TTri[d]	40.2 ± 29.7	**85 ± 4**	**93 ± 2**	**97 ± 0**[a]	**90 ± 4**	**98 ± 0**	**100 ± 0**	**1 ± 5**	**6 ± 4**	**5 ± 5**
6. Atenolol[a]	0.023 ± 0.024	28 ± 0	>88	>88	>23	>23	>23	5 ± 2	-3 ± 1	-9 ± 7
7. Atenolol acid[a]	1.87 ± 0.46	**76 ± 1**	**94 ± 2**	98 ± 0	97 ± 2	99 ± 1	>99	**-4 ± 2**	**7 ± 4**	**12 ± 3**
8. Azithromycin[b]	0.11 ± 0.18	20 ± 0[e]	100 ± 0[e]	100 ± 0[e]	>91	>91	>91	**5 ± 1**	**14 ± 4**	**23 ± 5**
9. Benzotriazole[b]	10.1 ± 4.2	**69 ± 4**	**84 ± 2**	**94 ± 1**	**66 ± 5**	**82 ± 0**	**90 ± 0**	**2 ± 1**	**4 ± 2**	**8 ± 2**
10. Bezafibrate[a]	<LOQ – 0.150	68 ± 12	>86	>86	n.a.	87 ± 4[(s)]	n.a.	n.a.	n.a.	n.a.
11. Carbamazepine[b]	0.235 ± 0.128	98 ± 0	99 ± 1	100 ± 0	>99	>99	>99	**1 ± 2**	**1 ± 0**	**1 ± 2**
12. Ciprofloxacin[c]	15.7 ± 8.0	100 ± 0	>99[e]	>99[e]	100 ± 0	100 ± 0	100 ± 0	**15 ± 0**	**29 ± 4**	**57 ± 3**
13. Clarithromycin[a]	1.28 ± 0.84	100 ± 0	100 ± 0[e]	100 ± 0[e]	100 ± 0	100 ± 0	100 ± 0	**6 ± 3**	**5 ± 1**	**14 ± 1**
14. Clindamycin[c]	1.16 ± 1.18	96 ± 2[e]	>99[e]	100 ± 0[e]	>98	>98	>98	**1 ± 9**	**8 ± 4**	**15 ± 6**
15. Cyclophosph.[a]	0.185 ± 0.064	**41 ± 6**	**73 ± 7**	>73	**33 ± 3**	**47 ± 0**	**57 ± 0**	**3 ± 2**	**0 ± 3**	**-2 ± 1**
16. D617[b]	0.143 ± 0.115	100 ± 0	>99	>99	99 ± 0	>99	>99	**7 ± 1**	**6 ± 2**	**12 ± 2**
17. Diatrizoate[c]	366 ± 259	**1 ± 1**	**14 ± 2**	**18 ± 9**	**7 ± 2**	**10 ± 2**	**16 ± 2**	**30 ± 1**	**72 ± 2**	**96 ± 0**
18. Diclofenac[b]	0.858 ± 0.186	96 ± 1	98 ± 0	99 ± 0	100 ± 0	100 ± 0	100 ± 0	**47 ± 1**	88 ± 1	>98
19. Erythromycin[c]	<LOQ – 0.140	>95[e]	>88[e]	>88[e]	>93	>93	>93	**10 ± 0**	**3 ± 0**	**10 ± 1**
20. Fluconazole[a]	3.72 ± 1.71	**87 ± 3**	95 ± 2	99 ± 0	**27 ± 6**	**37 ± 2**	**47 ± 2**	**1 ± 0**	**3 ± 0**	**1 ± 0**
21. Furosemide[b]	2.46 ± 0.75	98 ± 1	>97	>97	>98	>98	>98	**10 ± 0**	**13 ± 3**	**35 ± 6**
22. Gabapentin[b]	14.9 ± 18.7	**23 ± 1**	**42 ± 4**	**47 ± 1**	**47 ± 10**	**61 ± 4**	**74 ± 1**	**5 ± 6**	**1 ± 6**	**-3 ± 4**
23. Hydrochloroth.[a]	1.84 ± 0.52	**88 ± 2**	97 ± 2	98 ± 0	>98	>98	>98	**1 ± 7**	**14 ± 3**	**50 ± 2**
24. Ifosfamide[b]	<LOQ – 0.600	24 ± 0	>60	>60	20	41	62	n.a.	n.a.	n.a.
25. Indometacin[a]	0.064 ± 0.080	>90	>91	>91	>97	>97	>97	6 ± 5	9 ± 13	24 ± 5
26. Iomeprol[d]	430 ± 466	**20 ± 4**	**65 ± 10**	**90 ± 3**	**29 ± 6**	**40 ± 1**	**52 ± 3**	**20 ± 5**	**65 ± 0**	**90 ± 2**
27. Iopamidol[d]	3353 ± 5993	**18 ± 2**	**69 ± 11**	**80 ± 2**	**31 ± 2**	**43 ± 2**	**55 ± 1**	**28 ± 4**	**66 ± 0**	**92 ± 1**
28. Iopromide[c]	118 ± 108	**47 ± 5**	**85 ± 8**	**91 ± 0**	**37 ± 3**	**49 ± 2**	**60 ± 2**	**28 ± 10**	**59 ± 3**	**92 ± 0**
29. Ioxitalamic a.[c]	342 ± 204	**2 ± 2**	**9 ± 12**	**1 ± 16**	**2 ± 2**	**13 ± 1**	**25 ± 7**	**34 ± 3**	**52 ± 5**	**94 ± 2**
30. Levetiracetam[a]	0.551 ± 0.345	**64 ± 7**	**73 ± 2**	**70 ± 2**	**43 ± 9**	**44 ± 9**	**54 ± 3**	**10 ± 5**	**7 ± 10**	**0 ± 13**
31. Lidocaine[a]	4.02 ± 3.74	99 ± 0	100 ± 0	100 ± 0	>98	>98	>98	**6 ± 0**	**5 ± 3**	**5 ± 3**
32. Mefenamic a.[a]	0.491 ± 0.142	>99	>99	>99	>99	>99	>99	**5 ± 1**	**8 ± 1**	**21 ± 5**
33. Metoprolol[a]	0.596 ± 0.227	>98	>99	>99	98 ± 1	>97	>97	**2 ± 0**	**0 ± 1**	**4 ± 0**
34. Metronidazole[c]	1.86 ± 2.03	**3 ± 22**[e]	**67 ± 9**[e]	**78 ± 5**[e]	**4 ± 0**	**25 ± 3**	**49 ± 4**	**-9 ± 15**	**-2 ± 36**	**22 ± 8**
35. Morphine[b]	<LOQ – 0.280	n.a.	>63	>63	n.a.	n.a.	n.a.	**26 ± 0**	>66	>66
36. *N4*-Ac-SMX[a]	0.455 ± 0.44	72 ± 3	92 ± 2	97 ± 1	**57 ± 3**	71 ± 0	80 ± 0	**7 ± 1**	**14 ± 4**	**33 ± 1**
37. Norfloxacin[c]	3.14 ± 1.82	99 ± 1[e]	>99[e]	>99[e]	>99	>99	>99	**14 ± 1**	**40 ± 1**	**63 ± 2**
38. Oseltamivir[c]	0.036 ± 0.045	n.a.	>63	>63	n.a.	n.a.	n.a.	3 ± 4	19 ± 1	40 ± 0
39. Oseltamivir car.[b]	0.124 ± 0.115	12 ± 0	36 ± 4	>36	n.a.	n.a.	n.a.	**3**	**6**	**-2**
40. Oxazepam[a]	1.06 ± 0.34	98 ± 0	99 ± 0	100 ± 0	**61 ± 5**	**73 ± 1**	83 ± 1	**1 ± 0**	**5 ± 2**	**12 ± 2**
41. Phenazone[c]	0.418 ± 0.259	**25 ± 8**	88 ± 11	97 ± 1	71	>9	>9	**45 ± 3**	**49 ± 6**	64 ± 5
42. Primidone[b]	0.601 ± 0.697	2 ± 0	79 ± 10	88 ± 0	49	68	78	8 ± 2	-5 ± 4	0 ± 1
43. Propranolol[b]	0.139 ± 0.067	>91	>94	>94	>92	>92	>92	**10 ± 3**	**12 ± 1**	**22 ± 3**
44. Ranitidine[b]	0.454 ± 0.247	>97	>96	>96	>98	>98	>98	**15 ± 5**	**41 ± 1**	**71 ± 1**
45. Ritalinic acid[b]	0.212 ± 0.103	8 ± 6	40 ± 4	57 ± 8	84 ± 6	95 ± 1	99 ± 0	**0 ± 1**	**8 ± 4**	**6 ± 3**
46. Ritonavir[b]	0.024 ± 0.021	n.a.	>87	>87	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47. Sotalol[a]	0.574 ± 0.467	91 ± 1	96 ± 1	99 ± 0	>94	>94	>94	**24 ± 2**	79 ± 1	>94
48. Sulfadiazine[a]	2.33 ± 6.64	0 ± 0[e]	40 ± 15[e]	>40[e]	>47	>47	>47	10 ± 2	>25	>25
49. SMX[a]	3.23 ± 4.70	**2 ± 8**[e]	**33 ± 9**[e]	**62 ± 11**[e]	**96 ± 1**	**98 ± 0**	99 ± 0	**17 ± 1**	**55 ± 2**	**85 ± 3**
SMX+Ac-SMX	3.76 ± 3.66	**7 ± 7**	**39 ± 8**	**67 ± 9**	**94 ± 2**	**96 ± 1**	**98 ± 1**	**16 ± 0**	**50 ± 3**	**78 ± 5**
50. Sulfapyridine[c]	0.251	85 ± 0[e]	95 ± 2[e]	>95[e]	>96	>96	>96	**-1 ± 3**	25 ± 7	69 ± 3
51. Thiopental[c]	0.069 ± 0.079	n.a.	>66	>66	n.a.	n.a.	n.a.	8	35	47
52. Tramadol[a]	0.891 ± 0.295	98 ± 0	100 ± 0	100 ± 0	>99	>99	>99	**3 ± 1**	**14 ± 1**	**26 ± 1**
53. Trimethoprim[c]	0.037 ± 0.037	n.a.[e]	>83[e]	>83[e]	n.a.	n.a.	n.a.	**5 ± 8**	**-12 ± 10**	**-8 ± 21**
54. Valsartan[b]	0.455 ± 0.202	89 ± 2	99 ± 1	99 ± 0	61 ± 3	69 ± 1	78 ± 2	**0 ± 2**	**4 ± 2**	**5 ± 3**
55. Venlafaxine[a]	0.681 ± 0.275	99 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	**-1 ± 7**	**2 ± 2**	**-1 ± 7**
56. Verapamil[a]	0.005 ± 0.004	>85	>88	>88	>76	>76	>76	12 ± 7	19 ± 4	40 ± 5

[(1)] Post-treatment influent (MBR effluent) [(2)]Doses of PAC Norit SAE Super: 8 ± 4 mg/L; 23 ± 7 mg/L; and 43 ± 14 mg/L. [(3)]Doses of ozone: 0.64 ± 0.01 g O_3/g DOC; 0.89 ± 0.03 g O_3/g DOC; and 1.08 ± 0.05 g O_3/g DOC. [(4)]Applied fluence of 800 J/m^2 in 1 run, 2400 J/m^2 in 3 cycles, 7200 J/m^2 in 9 cycles. * n=4 (otherwise n=2). [(s)] spiked. [a-d] Analytical quality control label (see Table S4). [e] As reviewed in [37] **Bold font**: post-treatment effluent concentration is above 100 ng/L. **Bold font, grey background**: effluent concentration is above 10 µg/L. 4-AAA: 4-Acetamidoantipyrine, 4-AA: 4-Aminoantipyrine, 4-FAA: 4-Formylaminoantipyrine, 4-MAA: 4-Methylaminoantipyrine, 4/5-Ttri: 4/5-Methylbenzotriazole, Cyclophosph.: Cyclophosphamide, Hydrochloroth.: Hydrochlorothiazide, a.: acid, *N4*-Ac-SMX: *N4*-acetylsulfamethoxazole, Oseltamivir car.: Oseltamivir carboxylate, SMX: sulfamethoxazole, SMX+Ac-SMX: sum of sulfamethoxazole and *N4*-acetylsulfamethoxazole. More on nomenclature and classification in Tables S1-S2.

3.2. Prediction of the micropollutants' elimination from physical-chemical properties

3.2.1. Ozone. The reactivity of micropollutants with ozone at a certain pH (apparent second order rate constant, $k''_{O3,app}$) can be estimated based on their molecular structures and pK_a values, and roughly divided into three classes[38]: (i) low or no reactivity with ozone ($k''_{O3,app} < \sim 10\ M^{-1}s^{-1}$): nitro group, amides, *N*-phenyl amides; (ii) intermediate reactivity with ozone ($\sim 10 > k''_{O3,app} > \sim 1\times10^5\ M^{-1}s^{-1}$): primary amines, protonated secondary amines, thioethers, anisols, quinones, naphtalenes, non-dissociated phenols; and (iii) high reactivity with ozone ($k''_{O3,app} > \sim 1\times10^5\ M^{-1}s^{-1}$): olefins, dissociated phenols (phenolates), anilines, thiophenols, deprotonated thiols, and tertiary amines. The reactivity of ozone-reactive moieties (ORMs) increases or decreases by neighbouring electron donating or electron withdrawing groups, respectively. Molecules without ORMs are typically oxidized by hydroxyl radicals ($^{\bullet}OH$) which are formed as secondary oxidants during ozonation. [38, 39] In a recent study we showed that it is possible to predict the abatement of ozone-resistant micropollutants by measuring $^{\bullet}OH$ exposures [40].

This theoretical approach is well applicable to predict elimination. O_3 reactivity estimations are described in Table S6 and presented in comparison with the achieved eliminations in Table S11. All the compounds that showed ≥ 97% or higher elimination from the hospital wastewater at an ozone dose of 1.08 $gO_3/gDOC$ contained moieties with high or intermediate reactivity with ozone (Tables S11-A, S11-B). Although the range for intermediate reactivity is relatively large with its five orders of magnitude, only < 20% of the target micropollutants belong to this group. For compounds without ORMs reactivity with $^{\bullet}OH$ is typically high (second-order rate constant typically in the range of $10^9 - 10^{10}\ M^{-1}s^{-1}$), although the $^{\bullet}OH$ concentration is very low compared to the ozone concentration and most of the $^{\bullet}OH$ are scavenged by the matrix prior to reacting with micropollutants. [38, 39]

Further to the correlation of the elimination to the molecular structure, a comparison to known ozonation rate constants from literature was performed (Figure 1, Table S11). For compounds for which ozone rate constants were not available (e.g. ritonavir), the reactivity range with ozone (none/low, intermediate and high reactivity) was estimated based on the structure (Table S6) and indicated in Figure 1 with open symbols at an arbitrary log k''_{O3} within the appropriate reactivity range. The

compounds with apparent ozonation rate constants at pH 8-8.5 $>10^5$ $M^{-1}s^{-1}$ (carbamazepine, ciprofloxacin, clarithromycin, diclofenac, furosemide, lidocaine, mefenamic acid, ranitidine, sulfamethoxazole, and tramadol), show removal above 97%. As the ozone rate constants decrease a decrease in transformation is observed.

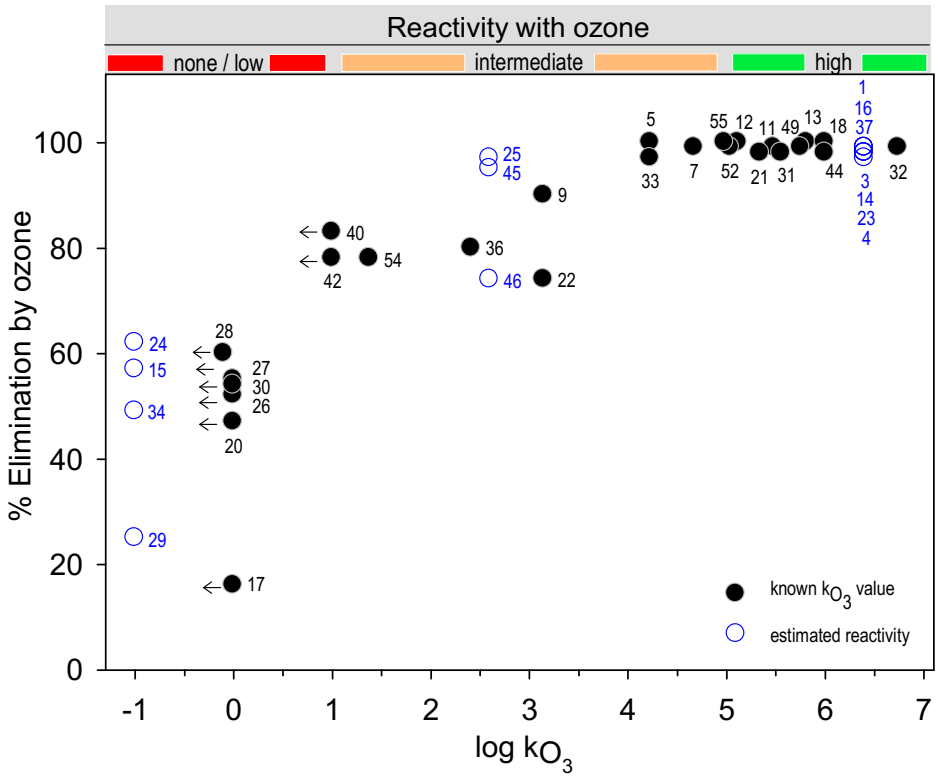

Figure 1 Elimination of micropollutants during ozonation of hospital wastewater (1.08 $gO_3/gDOC$, 7 mg/L O_3, pH 8.5) versus ozonation rate constants from literature ($M^{-1}s^{-1}$, Table S11) or estimated reactivity at pH 8-8.5 (Table S6) if k_{O3} is not available. Arrows represent log k_{O3}<1 or 10, respectively. See Table 1 for micropollutant numbering. Micropollutants for which quantification of elimination was limited by LOQ (2, 6, 8, 10, 19, 35, 38, 39, 41, 43, 47, 48, 50, 51, 53, and 56) are not included.

3.2.2. PAC

Adsorption is depicted relative to the D_{ow} of the adsorbates (micropollutants) in Figure 2. As the adsorption to activated carbon depends on multiple properties of micropollutants and carbon, prediction for adsorption is not as accurate as for ozonation (Table S10). Interactions between the adsorbent (PAC) and adsorbate are controlled by non-specific dispersive interactions. In case of charged adsorbates also electrostatic interactions with a charged adsorbent surface can be important. Properties of an adsorbate

that mainly influence the adsorption process are its octanol-water distribution coefficient (K_{ow}, or D_{ow} when accounting for acid-base speciation), pK_a, molecular size, aromaticity versus aliphaticity, and presence of specific functional groups. Properties of an adsorbent that mainly influence the adsorption process are its surface area, pore size and texture, surface chemistry (functional groups, point of zero charge pH_{PZC}), and mineral matter content.[41, 42] Despite of complex interactions, all compounds in our data set with $logD_{ow} > 2$ were removed completely (Figure 2) or to below their LOQs (Table S10-C). Furthermore, for uncharged compounds with $logD_{ow} \sim 2$ and smaller, a decreasing trend in adsorption efficiency with decreasing $logD_{ow}$ values was observed. A good estimation for uncharged compounds was possible, as no electrostatic interactions with the functional groups on the surface of the activated carbon occur and only dispersive forces are present. As also shown in Figure 2, a simple estimation from $logD_{ow}$ values for charged polar compounds does not work and leads to an underestimation of elimination efficiencies for many compounds (e.g. ciprofloxacin, furosemide, atenolol acid). At the working pH 8.8, the surface of the utilized activated carbon with pH_{PZC} 10 is predominantly positively charged. This may explain the strong sorption of some compounds with anionic functional groups (e.g. furosemide), others, however, show much lower elimination (e.g. sulfamethoxazole). The same observation is made for polar zwitterionic compounds. For polar cationic compounds, a general statement is difficult since only compounds with $logD_{ow} \sim 0$ and higher were analyzed for which a certain adsorption is expected. Although the pH_{PZC} of the carbon is known, the actual functional groups responsible for electrostatic interaction are not known and this can be a possible explanation for the varying behavior of individual charged compounds.

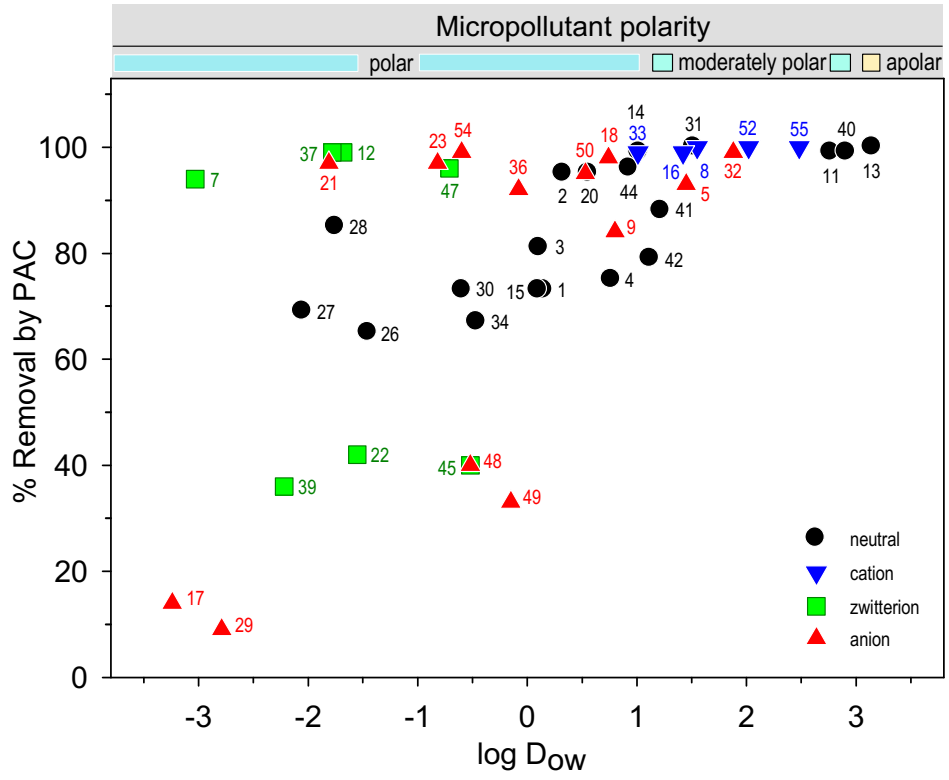

Figure 2 Removal of micropollutants from hospital wastewater (23±7 mg/L PAC, pH 8.8) as a function of $logD_{ow}$ at pH 9 (Table S3). See Table 1 for micropollutant numbering. Micropollutants for which quantification of the elimination was limited by LOQ (6, 10, 19, 24, 25, 35, 38, 43, 46, 51, 53, and 56) are not included.

3.2.3. UV No quantitative structure activity relationship (QSAR) to the fluence-based photolysis rate constants of homologous compounds is known. Therefore, a prediction of the elimination efficiency by UV from molecular structures or physical chemical properties is currently not possible. Elimination of a contaminant by photolysis was shown to be predictable only when experimentally determined fluence-based rate constants are available.[34]

3.3. Elimination efficiencies of different classes of analytes

3.3.1. Iodinated X-ray Contrast Media (ICM). Within the group of ICM, different elimination behavior of uncharged ICM (iomeprol, iopamidol, and iopromide) compared to the charged diatrizoate and ioxitalamic acid were observed. Adsorption of ICM to PAC is expected to be low (low $logK_{ow}$ values, SI, Table S6). Charged ICM are even more polar ($logD_{ow}$ values in Table S3) and are eliminated

significantly less than uncharged ICM. For ICM, elimination by ozonation is comparable, or less efficient than by adsorption (Figure 3 shows a comparison of the removal efficiencies of ozonation and PAC). ICM have second-order rate constants <1 $M^{-1}s^{-1}$ and elimination is dominated by oxidation by $^{\bullet}OH$. [39] Concentrations in the µg/L to low mg/L range could still be found in the effluent. Removal by UV for uncharged ICM is relativly high, comparable to removal by high PAC doses. For the two charged ICM, only UV proved to be efficient, at the investigated doses for each treatment. The maximum tested UV dose (9 cycles, fluence 7200 J/m^2), though energetically very demanding, can remove around 95% of diatrizoate and ioxitalamic acid, although the remaining concentrations in the UV effluent of up to 20 µg/L are still considerable.

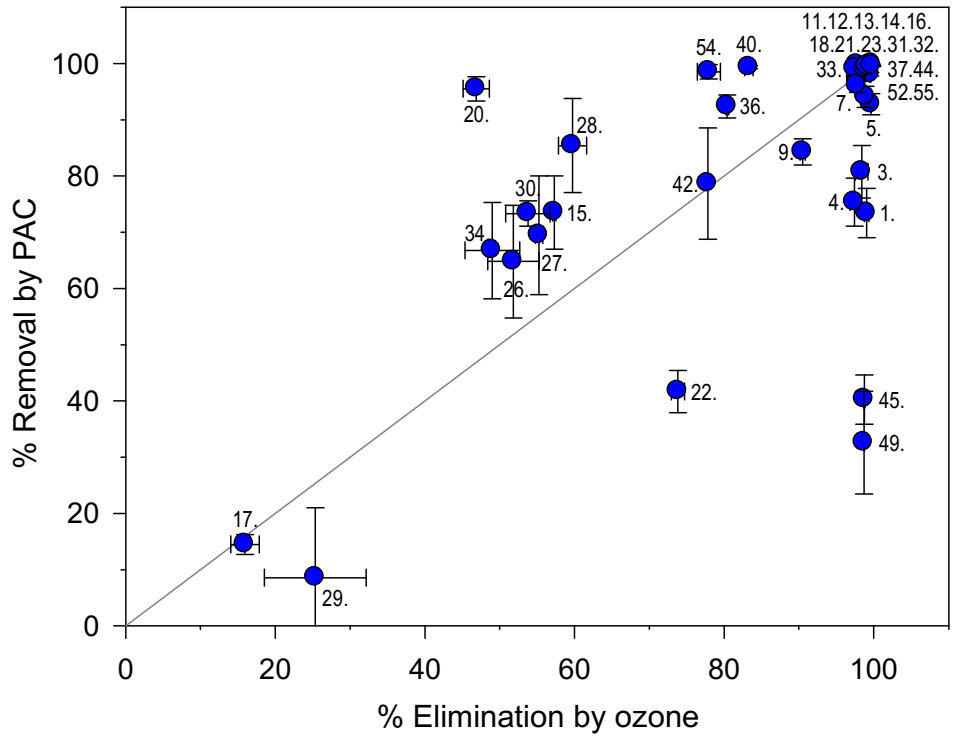

Figure 3. Comparison of micropollutants' elimination by ozone and PAC. Ozone dose: 7 mg/L (1.08 gO_3/gDOC, pH 8.5); PAC dose: 23±7 mg/L, pH 8.8. See Table 1 for micropollutant numbering.

3.3.2. Corrosion inhibitors. Methylbenzotriazole and benzotriazole are relatively well eliminated by adsorption to PAC as well as by ozonation. Nevertheless, concentrations of 200-1000 ng/L still remain

even after application of the highest tested doses due to high inflow concentrations of these compounds. Both compounds are moderately polar with methylbenzotriazole slightly more hydrophobic than benzotriazole (SI, Tables S3, S6), which resulted in 97 and 94% elimination at the highest tested PAC dose for the two compounds, respectively. Ozone rate constants of the two structurally similar compounds are in the intermediate range, with higher value for methylbenzotriazole (10^4 $M^{-1}s^{-1}$ for anion[38], pK_a 8.9*)* due to the presence of an electron donating methyl group that increases the reactivity compared to benzotriazole (2650 $M^{-1}s^{-1}$ for anion[38], pK_a 8.6*)*. No significant elimination by UV was observed up to an applied dose of 7200 J/m^2.

3.3.3. Metamizole metabolites. Four human metabolites of the analgesic metamizole (aminopyrine) were abundant in the MBR-treated hospital wastewater: 4-methylaminoantipyrine (4-MAA, hydrolysis product of metamizole), 4-aminoantipyrine (4-AA, second generation TP), 4-acetamidoantipyrine (4-AAA, third generation TP), and 4-formylaminoantipyrine (4-FAA, third generation TP). These moderately hydrophilic pyrazolone derivates are well removed by ozonation due to an olefin group, which has a high ozone reactivity. Only partial elimination could be achieved by adsorption to PAC and UV treatment. This resulted in effluent concentrations between ~500 and 3000 ng/L after treatment with PAC, and up to above 20 µg/L for 4-AA after the treatment with the highest tested UV dose (7200 J/m^2).

3.3.4. Cyclophosphamide. Cyclophosphamide is a polar uncharged cytostatic with a similar persistence to PAC and ozone treatment as uncharged ICM. The concentration of cyclophosphamide is about 3 orders of magnitude lower than the concentrations of ICM, however, its toxicity is considerably higher. With a $\log K_{ow}$ value ~0, no active sites for ozone attack, and no photochemical removal, the resulting final concentration of cyclophosphamide is often >100 ng/L, despite its relatively low influent concentrations. The structurally related cytostatic ifosfamide shows similar removal trends, although it was rarely detected in the wastewater.

3.3.5. Gabapentin and levetiracetam. The two structurally unrelated compounds are both antiepileptic preparations occurring in raw hospital wastewaters in µg/L levels.[11] Gabapentin is a very polar

carboxylic acid ($logD_{ow}$ -1.6 at pH 9) that shows only poor adsorption. At pH 8-8.5 it contains a protonated primary amine, which shows intermediate reactivity with ozone. Levetiracetam is a polar and uncharged compound with a higher log D_{ow} than gabapentin, which results in a slightly higher PAC adsorption compared to gabapentin (Figure 3). Levetiracetam has no ozone-reactive moieties (two amides), which leads to only a partial removal due to reaction with $^{\bullet}OH$. Therefore, the two antiepileptics are not removed satisfactorily by any of the tested post-treatment technologies. The remaining concentrations are >100 ng/L and in case of gabapentin, µg/L levels (Table 1).

3.3.6. Fluconazole, metronidazole, and sulfonamides. Anti-infectives discussed here in detail don't include antivirals or antibiotics which are either not frequently detected in the post-treatment influent (e.g. ritonavir, roxithromycin) or are well removed by both PAC and ozonation (e.g. ciprofloxacin, clarithromycin). The moderately hydrophilic antimycotic fluconazole, a triazole derivative, has no active sites for ozone attack and therefore exhibits similar elimination efficiency by ozonation as ICM due to only $^{\bullet}OH$ oxidation. Elimination by adsorption to PAC is better, 95% at a PAC dose of 23 mg/L (Figure 3). Metronidazole is polar and uncharged, similar to levetiracetam, which resulted in a comparable elimination efficiency (~75%) with the highest PAC dose of 43 mg/L. It contains a nitro group, which deactivates the molecule for ozone attack, resulting in elimination efficiencies comparable to compounds which were eliminated only by $^{\bullet}OH$. No significant elimination by UV was observed for fluconazole and metronidazole. The sulfonamides sulfadiazine and sulfapyridine were found in the influent of the post-treatments only in low concentrations. Sulfamethoxazole was always detected in the range of 1-10 µg/L in the influent, and mostly above 100 ng/L in the effluent of the three post-treatments. The three sulfonamides differ in their pK_a values and slightly in polarity (SI, Table S3), which influences their adsorption behavior. At the working pH 8.8, the least charged and at the same time the most hydrophobic of the three – sulfapyridine - shows the highest elimination efficiency by PAC (Table 1). Due to the aniline functional group, the three sulfonamides react very fast with ozone.[20] As most of the attack occurs at the aniline ring, *N4*-acetylated metabolites of sulfonamides, e.g. *N4*-acetylsulfamethoxazole, exhibit lower reactivity with ozone due to deactivation due to the presence of

the *N*-acetyl instead of a NH_2 functional group. The three sulfonamides are also to a lower extent sensitive to UV treatment.

3.3.7 Gadolinium and platinum. Additionally to organic micropollutants, the two metals were measured. They occur in raw wastewater of the studied hospital mainly due to gadolinium complexes used as magnetic resonance imaging (MRI) contrast media and platinum containing cytostatics (see SI, Figures S1-S2), in average concentrations of 13.4 µg/L and 220 ng/L, respectively. After the MBR treatment, average concentrations of 12.9 µg/L for Gd and 130 ng/L and for Pt were found. Platinum-containing cytostatics were previously reported to sorb to 60% to activated sludge of a hospital wastewater.[43] Metals are principally not removed by ozonation or photolysis. The results for the PAC dose of 10 mg/L and the ozone dose of 0.64 g O_3/ g DOC show 47% elimination of platinum by PAC, but no significant elimination neither of platinum by ozonation nor of gadolinium by any of those treatments. Gadolinium-containing contrast media are therefore very stable against oxidation and are not adsorbing to PAC.

3.4. Options to enhance the post-treatment steps *3.4.1. Ozone.* Further experiments were performed by adding hydrogen peroxide. This accelerates ozone decomposition and partially increases the $^{\bullet}OH$ exposure in the system.[38] Thus, the elimination of micropollutants with low reactivity with ozone may be enhanced.[44] To minimize the consumption of ozone by the background organic matter, the MBR permeate was pre-treated with ozone prior to the O_3/H_2O_2 experiment. Results from this first treatment with 1.2 g O_3/gDOC agreed well with the previously shown data. Micropollutant elimination after the post-ozonation with hydrogen peroxide was not significantly improved (±10%) compared to ozone alone (SI, Figure S4). This is in agreement with previous studies, where only little improvement was found for O_3/H_2O_2 compared to O_3 alone, especially in waters with high DOC.[44]

3.4.2. PAC. Elimination efficiencies of the PAC process could potentially be improved if it is combined with nanofiltration (instead of ultrafiltration), which would additionally retain micropollutants by the membrane.[45] However, due to its high micropollutant concentration, the nanofiltration

concentrate has to be treated or otherwise taken care of.[46] Alternatively, loaded activated carbon from PAC post-treatment can be pumped to the MBR for recycling and thereby significantly increase the elimination in the bioreactor.[23] No additional experiments on any of those processes were performed in this study.

3.4.3. UV. The photocatalytic treatment of hospital wastewater MBR permeate by UV with a TiO_2 photocatalyst showed lower elimination than UV treatment alone (SI, Table S12). With the photocatalytic TiO_2 fibers, there might be an additional indirect phototransformation, however the screening and absorption of the light by the fibers proved to be higher than the possible indirect phototransformation. The calculated fluence rate with the photocatalytic fiber was only 1.7 mW/cm^2, less than half of the value for the reactor without the photocatalytic fibers (4.0 mW/cm^2) (SI, Page S21-S22). Heterogeneous advanced oxidation by UV/TiO_2 involves direct and indirect photolysis. A micropollutant is adsorbed and attacked by $^{\bullet}OH$ formed on the TiO_2 surface. Unfortunately, the quantum yield for the reaction of $^{\bullet}OH_{TiO2}$ formation is very low and the whole process could suffer from a disadvantage of this inefficient step.[47] Another process that is known to significantly improve UV treatment of micropollutants is addition of hydrogen peroxide. It was shown before that the elimination of atenolol, carbamazepine, primidone, and trimethoprim can be significantly improved by the addition of hydrogen peroxide. Using a low pressure UV lamp at 700 J/m^2, the elimination of trimethoprim with addition of 20 mg/L H_2O_2 was enhanced from <10% to 92%.[27] Good elimination was also shown for sulfamethoxazole, clarithromycin, and lidocaine using a low pressure UV lamp with addition of H_2O_2.[28]

3.5. Overall comparison of the three post-treatment technologies. *3.5.1. DOC Removal.* The difference between the tested technologies in removal of dissolved organic carbon (DOC) is very significant. A decrease of 60% in DOC levels was observed after the treatment of MBR permeate by 23 mg PAC/L (SI, Table S7). The highest tested dose of 43 mg PAC/L removes around 70% of DOC and improves the wastewater quality of the MBR permeate from 6.3 mg C/L to 2.0 mg C/L. The decrease in DOC levels after ozonation and UV treatment is less than 15% at any tested conditions (SI, Tables S8-

S9). While PAC removes DOC efficiently by adsorption, mineralization of dissolved organic matter during ozonation and UV treatment is small.

3.5.2. Organic micropollutants. For this comparison, a realistic dose was selected for each treatment: 7 mg/L ozone (1.08 gO3/gDOC ozone; higher doses could produce an excess of bromate); 23 mg/L PAC (upper margin of range commonly used at full-scale without recycling to the biological reactor [23]); and 3 cycles for UV treatment (2400 J/m^2; a higher fluence is unrealistic due to high energy consumption, see section 3.5.4). An evaluation of the three tested technologies with regard to micropollutant removal is summarized in Table 2. For comparison, the overall elimination efficiencies of the combined treatments with MBR are also shown. Removal efficiencies for the sum of the load of all target analytes (52-63%) are close to ICM removal efficiencies (50-65%) for the three single post-treatments, because the MBR effluent before the post-treatment consists of over 95% of ICM by load. Thus, it is more meaningful to evaluate elimination efficiencies in sub-groups: 1) iodinated X-ray contrast media (ICM); 2) pharmaceuticals and metabolites excluding ICM; and 3) industrial chemicals.

Table 2 Comparison of MBR and the three post-treatment technologies (O_3, PAC, UV) for groups of micropollutants: elimination of micropollutant loads.

		Single treatments				**Combined treatments** (same doses as for the single treatments)		
		MBR*	**1.08 $gO_3/gDOC$ O_3**	**23 mg/L PAC**	**2400 J/m^2 UV**	**MBR+O_3**	**MBR+PAC**	**MBR+UV**
Iodinated X-ray contrast media, ICM	Load before (mg/d)	943'060	922'888	922'888	922'888	943'060	943'060	943'060
	Load after (mg/d)	922'888	462'479	361'360	324'696	462'479	361'360	324'696
	Elimination (%)	**2**	**50**	**61**	**65**	**51**	**62**	**66**
Pharmaceuticals (without ICM) + metabolites	Load before (mg/d)	211'205	21'603	21'603	21'603	211'205	211'205	211'205
	Load after (mg/d)	21'603	2'103	2'991	14'511	2'103	2'991	14'511
	Elimination (%)	**90**	**90**	**86**	**33**	**99**	**99**	**93**
Industrial chemicals	Load before (mg/d)	81'602	16'190	16'190	16'190	81'602	81'602	81'602
	Load after (mg/d)	16'190	320	1'418	15'226	320	1'418	15'226
	Elimination (%)	**80**	**98**	**91**	**6**	**100**	**98**	**81**
Sum of all analyzed micropollutants	Load before (mg/d)	1'235'867	960'681	960'681	960'681	1'235'867	1'235'867	1'235'867
	Load after (mg/d)	960'681	464'901	365'768	354'433	464'901	365'768	324'696
	Elimination (%)	**22**	**52**	**62**	**63**	**62**	**70**	**71**

*as in [11]

As discussed in 3.3.1, ICM are very difficult to remove by any of the three tested technologies, although adsorption to PAC (61%) and UV treatment with very high doses (65%) show a slightly better performance than ozonation (50%). An alternative and more efficient solution to remove ICM is probably by collecting and incinerating the patients' urine in hospitals and from out-patients.

For the sub-group of pharmaceuticals and metabolites excluding ICM, performance of ozonation (90%) is slightly better compared to PAC (86%), while UV (33%) is not satisfactory. A similar trend and an even stronger difference between ozonation (98%), PAC (91%) and UV (6%) is observed for the sub-group of industrial chemicals. Micropollutants of those two sub-groups, containing the majority of analyzed substances, can thus be treated most efficiently by ozonation or PAC. Most of the target micropollutants have similar elimination efficiencies by ozonation and PAC (Figure 3). Few exceptions are gabapentin, oseltamivir carboxylate, ritalinic acid, sulfadiazine, and sulfamethoxazole – for which ozonation is more efficient, or fluconazole, iopromide, levetiracetam, metronidazole, 4-MAA, and 4-AAA – for which PAC is more efficient. The anionic ICM diatrizoate and ioxitalamic acid show unsatisfactory removal by either ozone or PAC, and were the only compounds for which direct phototransformation by UV at high doses of 2400 J/m^2 turned out to be most efficient.

3.5.3 Energy consumption. For the analysis of energy consumption of the different post-treatments, calculations for municipal wastewater treatment can be used. For ozonation, an energy consumption of 0.02 kWh/g ozone is needed for the generation of ozone from oxygen, including the production and transport of oxygen.[19, 48] When using 5-10 mg/L ozone, the total energy consumption is 0.1 - 0.2 kWh/m^3. Energy consumption at the municipal wastewater treatment plant would rise by about 20-40% when using ozonation. For PAC treatment, the energy consumption at the plant is only around 0.05 kWh/m^3, so lower than for ozonation.[48, 49] However, the production of PAC is energy intensive, what is reflected in the high costs of PAC (2 €/kg PAC). The UV reactor has a total energy consumption of 100-400 W, depending on the selection of the pump, including a lamp power consumption of 40 W. In a single treatment with a flow rate of 1000 L/h the energy consumption of the photocatalytic reactor is 0.1-0.4 kWh/m^3 and with nine cycles 0.9-3.6 kWh/m^3. Therefore, the energy consumption in a single

UV treatment is in a similar range as with 7 mg/L ozone (0.12 kWh/m^3), however, with much lower elimination efficiencies. Even with nine cycles the elimination by UV is lower than with ozone for most compounds except for ICM. UV/H_2O_2 was found to efficiently oxidize micropollutants but energy requirements were substantially higher compared to ozonation. [28, 50]

3.5.4 Cost. The treatment of hospital wastewater with ozone or PAC following an MBR would cost 2.90 or 3.20 CHF (2.40 or 2.70 €) per m^3, respectively (details of the calculation are given in Tables S14-S16). In Switzerland, municipal wastewater treatment costs about 2 CHF (1.70 €) per m^3 wastewater (median), and with an additional treatment with ozone or PAC costs are estimated to be around 2.20 CHF (1.80 €) per m^3. The costs per m^3 wastewater for the treatment of hospital wastewater (i.e. requiring biological treatment followed by either ozonation or PAC) is slightly higher than for the treatment of the whole wastewater stream at the central municipal wastewater plant with the same technology. If the hospital has a separate treatment and discharges the treated wastewater directly to the receiving water, the investment cost for the municipal wastewater treatment will hardly change; only the operation cost is reduced, which is in the range of 1-1.50 CHF (0.80-1.20 €) per m^3 (for BOD, nutrient and micropollutant removal, depending on the size of the plant). The hospital has the advantage of reusing the treated wastewater for gardening, which would then additionally reduce the drinking water cost. Additionally there is no loss of raw hospital wastewater by combined sewer overflows and exfiltration from sewer systems.

3.5.5. Other important aspects. The main advantage of PAC over ozonation and UV is the "true removal" of chemicals from the wastewater by adsorption to carbon (that can be incinerated after use), rather than transformation to oxidation or photodegradation products. Those transformation products are often unknown and have a potential to also have ecotoxicological effects.[51, 52] It is recommended that after oxidative treatments a sand filter (biofilter) is installed to eliminate well degradable transformation products. It was shown that sand filtration is an effective barrier to toxic oxidation byproducts originating mainly from the matrix. [53, 54] Furthermore, ozonation can produce bromate, which is formed in bromide-containing waters and is the ozonation by-product of major concern.[55] In our study, the

bromide level in the MBR effluent was 30-40 μg/L, representative for municipal wastewater treatment plants in Switzerland. Bromate was never found in quantifiable concentrations above 1 μg/L even for a high ozone dose of 1.08 g ozone/g DOC (7 mg/L ozone), thus it is well below the drinking water standard of 10 μg/L.[56]

A value to consider to fulfill requirements of municipal wastewater treatment plant effluents is AOX (adsorbable organic halogen compounds). AOX typically consists of compounds formed during chlorination, which are potentially toxic. Hospital wastewater, however, is special due to the high concentrations of non-toxic X-ray contrast media, which contain iodine. Organic iodine compounds may account for about 50% of AOX input into municipal wastewater.[57] The AOX value, measured in this study only once (SI, Table S13), was decreased from 0.56 mg/L in the MBR permeate better by PAC (around 70%) than by ozonation (40%). The AOX in the final effluent after post-treatments, however, can be above requirements for wastewater treatment plant effluent (requirement for Switzerland: 0.08 mg/L).[58]

Another important issue, specific for hospital wastewaters, is preventing input of pathogenic or (multi-)resistant bacteria and other potentially dangerous microorganisms and parasite eggs further into the environment. Even though the MBR is a good barrier, a further disinfection step is advisable. For inactivation of pathogens and possibly removal of antibiotic resistance, UV or ozonation are more efficient compared to PAC.

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SUPPORTING INFORMATION: Analyzed micropollutants, analytical method, gadolinium and platinum measurements, parameters of the post-treatment plants, more information on elimination of micropollutants and comparison with literature, AOX, cost evaluation (Tables S1−S16, Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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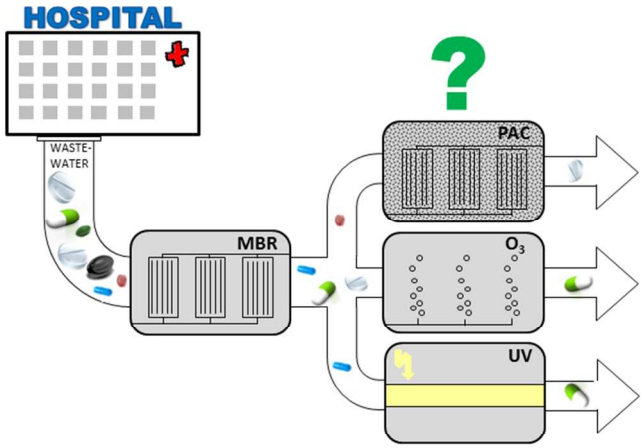

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