ORGANICS REMOVAL AND MINIMIZATION OF DEGRADATION PRODUCTS DURING TREATMENT OF PHARMACEUTICAL WASTEWATER

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FOCUSING THE PROBLEM

- The removal of residual pharmaceutical compounds from industrial pharmaceutical wastewater is very challenging due to:
  - Presence of non-biodegradable solvents and synthesis intermediate;
  - The simultaneous presence of high fraction of easily biodegradable carbon and lower amounts of recalcitrant organics;
  - A high saline content.
- Combination of biological and AOPs are then necessary to reach the target discharge limits.
- If AOP is used as a post-treatment step, organic by-products are likely to be present in the final effluent.

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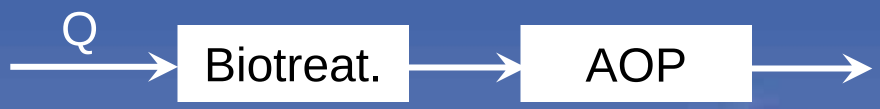
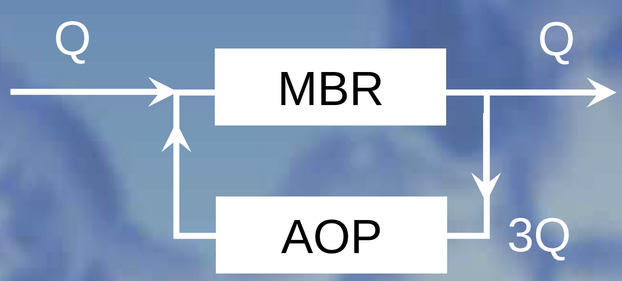
How is it possible to limit the formation of by-products ?

- **Long contact time of the AOP step (high operational costs).**



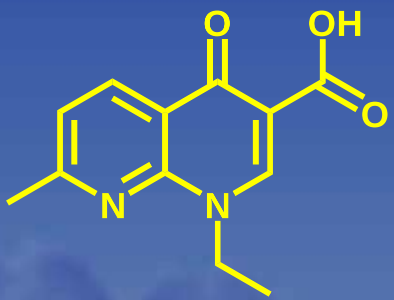
- **Integration of biological treatment and AOP (the investigated approach that was employed for two different pharmaceutical wastewaters within the project).**



A Membrane BioReactor (MBR) was used with both O_3 or UV/H_2O_2 step; Organics and by-products were identified by LC/MS and LC/MS-MS.

Composition of pharmaceutical wastewater

Parameter	Unit	Amount
pH		4
Conductivity	mS cm^{-1}	7
DOC	mg L^{-1}	775
COD	mg L^{-1}	2660
NH_4^+	mg_N L^{-1}	<0.1
Acetate	mg L^{-1}	1900
Nalidixic acid	mg L^{-1}	**45**
Cl^-	mg L^{-1}	2.8
PO_4^{3-}	mg L^{-1}	<0.1
$SO_4^{=}$	mg L^{-1}	0.16
Na	mg L^{-1}	2
TSS	mg L^{-1}	496
VSS	mg L^{-1}	264



nalidixic acid

(a synthetic antibacterial agent)

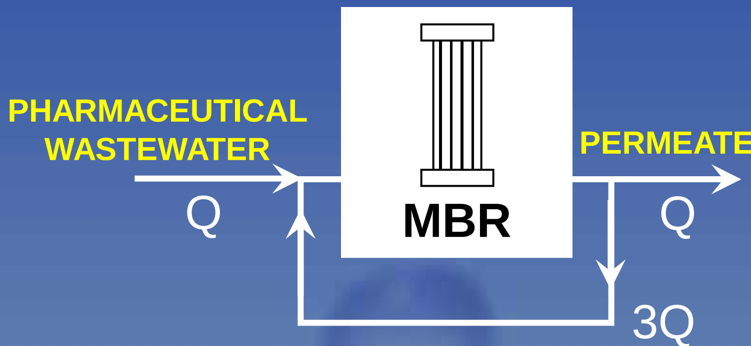
concentration of added nutrients

PO_4^{3-} = 18.9 mg L^{-1}

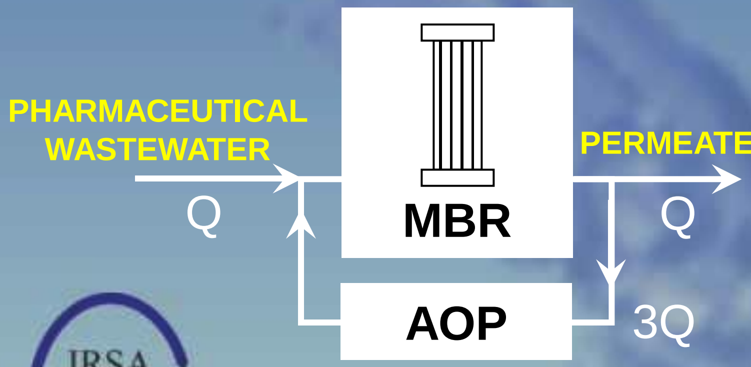
NH_4^+ = 49.2 mg L^{-1}

Lab-scale plant set-up: operational conditions

1° phase: MBR alone



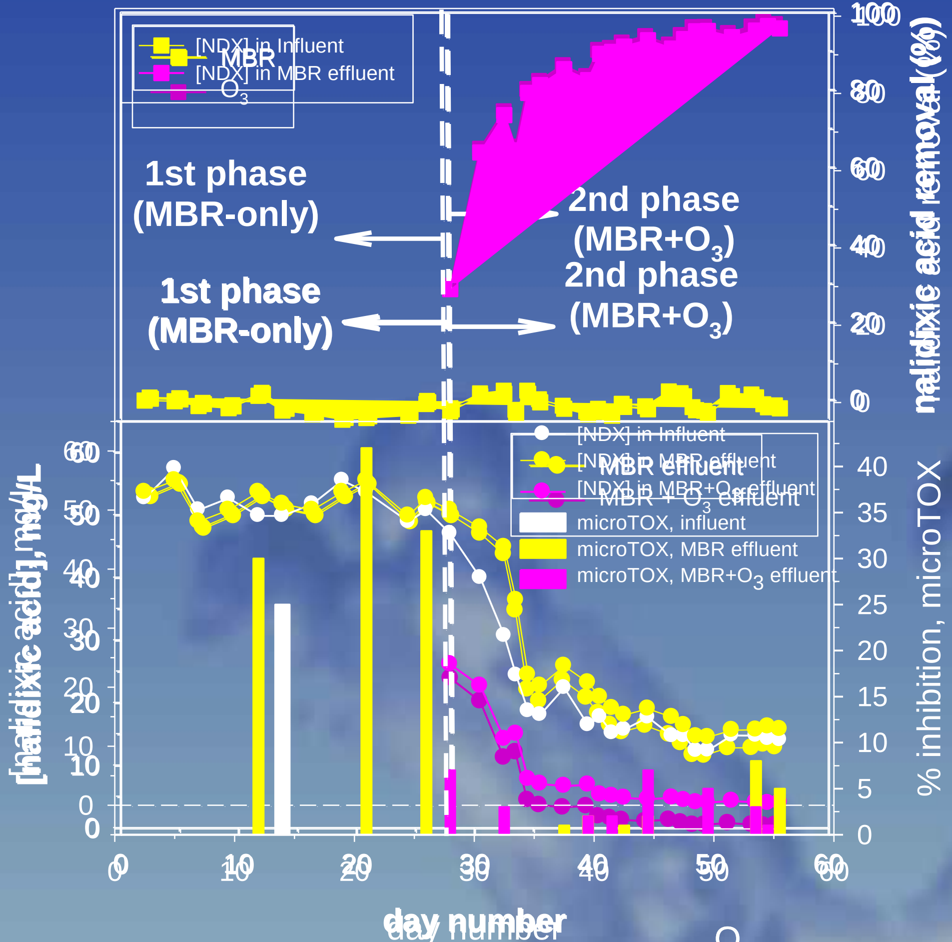
2° phase: MBR/AOP

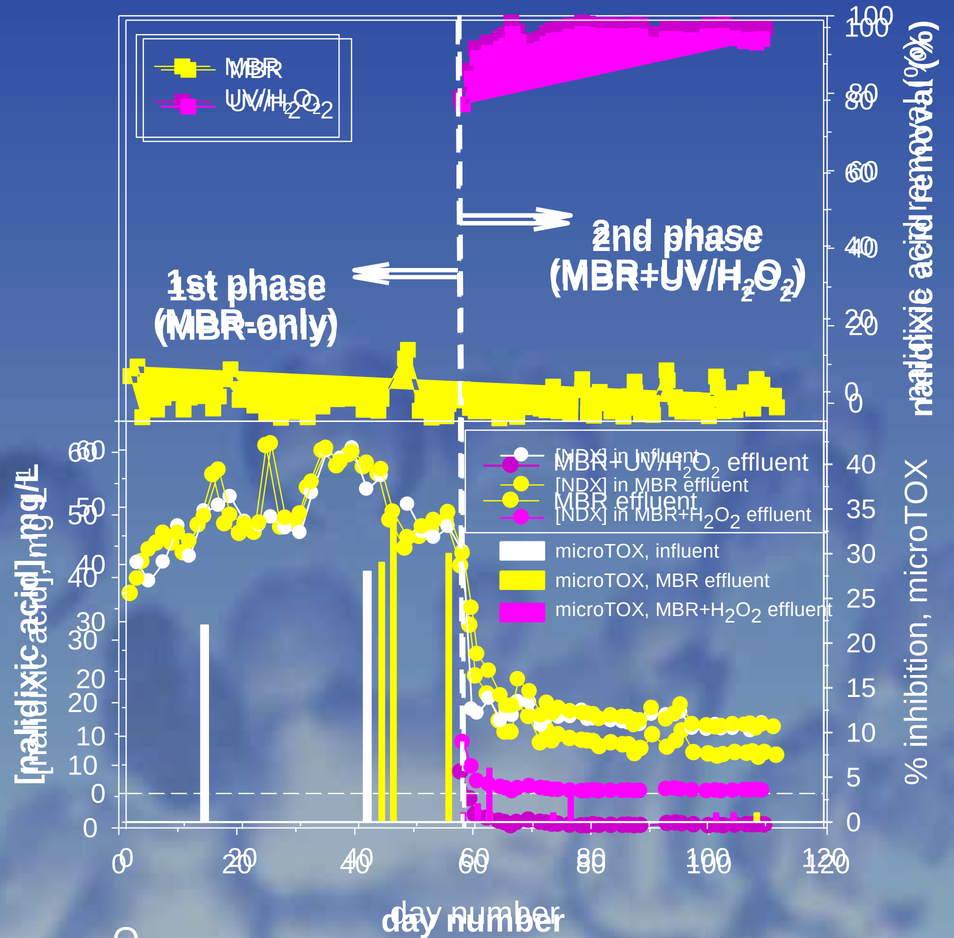


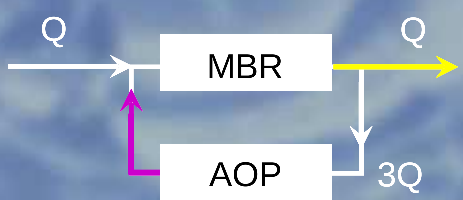
Parameter	Unit	Amount
MBR reactor	L	6
Feed flow rate Q	L d^{-1}	1.6
Hydraulic Retention Time	d	3.75
Sludge Residence Time	d	30
Volumetric Loading Rate	g_{COD} L_{react}^{-1} d^{-1}	1.3
Membrane flux	L m^{-2} h^{-1}	5.7
Relaxation cycle	15 min every 3 h	
Ozone dosed	mg L^{-1}	103
Ozone dosed	mg mg_{COD}^{-1}	0.22
UV dose	W h L^{-1}	20.8
UV lamp (254 nm)	W	40
H_2O_2	mM	0.5

No significant sludge reduction was observed after integration with AOP

Nalidixic acid concentration in the effluent, % of removal

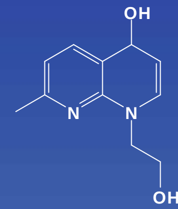






Characterization of nalidixic acid real wastewater: 48 organics identified

compound number	MW	ret. time (min)
1, 4	152	1.4, 1.9
2	108	1.5
3, 6	206	1.5, 2.2
5, 17	208	1.9, 5.3
7, 12	136	2.6, 4.1
8, 10, 39	190	2.9, 3.6, 8.1
9	166	3.1
11	157	3.9
13	224	4.1
14	180	4.5
15, 42	188	4.6, 8.5
16, 18	164	5.3, 5.8
19, 35	222	5.9, 7.9
20	295	6.1
21, 26	230	6.3, 6.9
22, 27, 34	204	6.6, 7.0, 7.9
23	210	6.6
24, 31, 41, 43	218	6.6, 7.7, 8.3, 8.5
25	220	6.6
28, 48	234	6.9, 7.2, 9.2
29	266	7.3
30	186	7.7
32, 38, 44	248	7.7, 8.0, 8.8
33, 37	264	7.8, 7.9
36, 45	246	7.9, 8.9
40	276	8.1
46	260	8.9
47	216	9.1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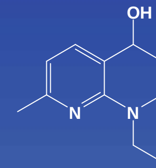
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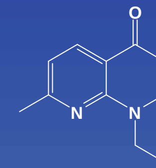
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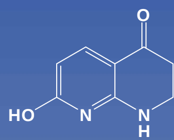
organic n. 13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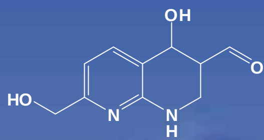
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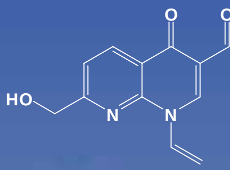
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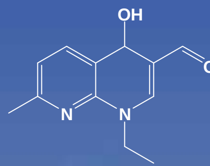
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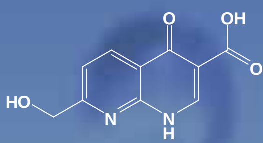
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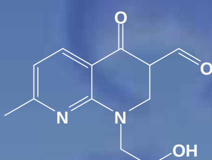
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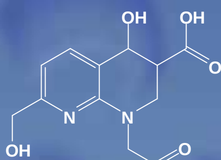
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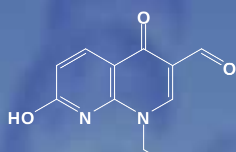
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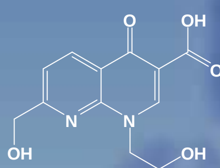
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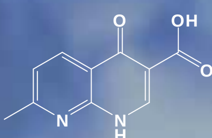
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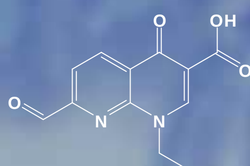
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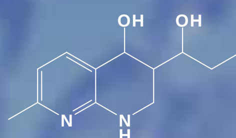
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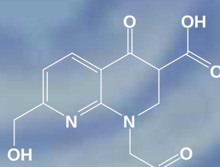
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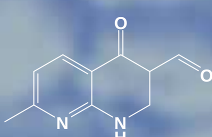
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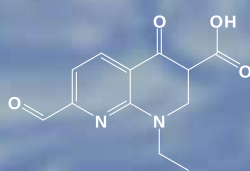
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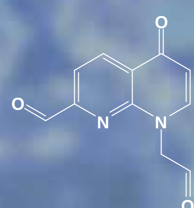
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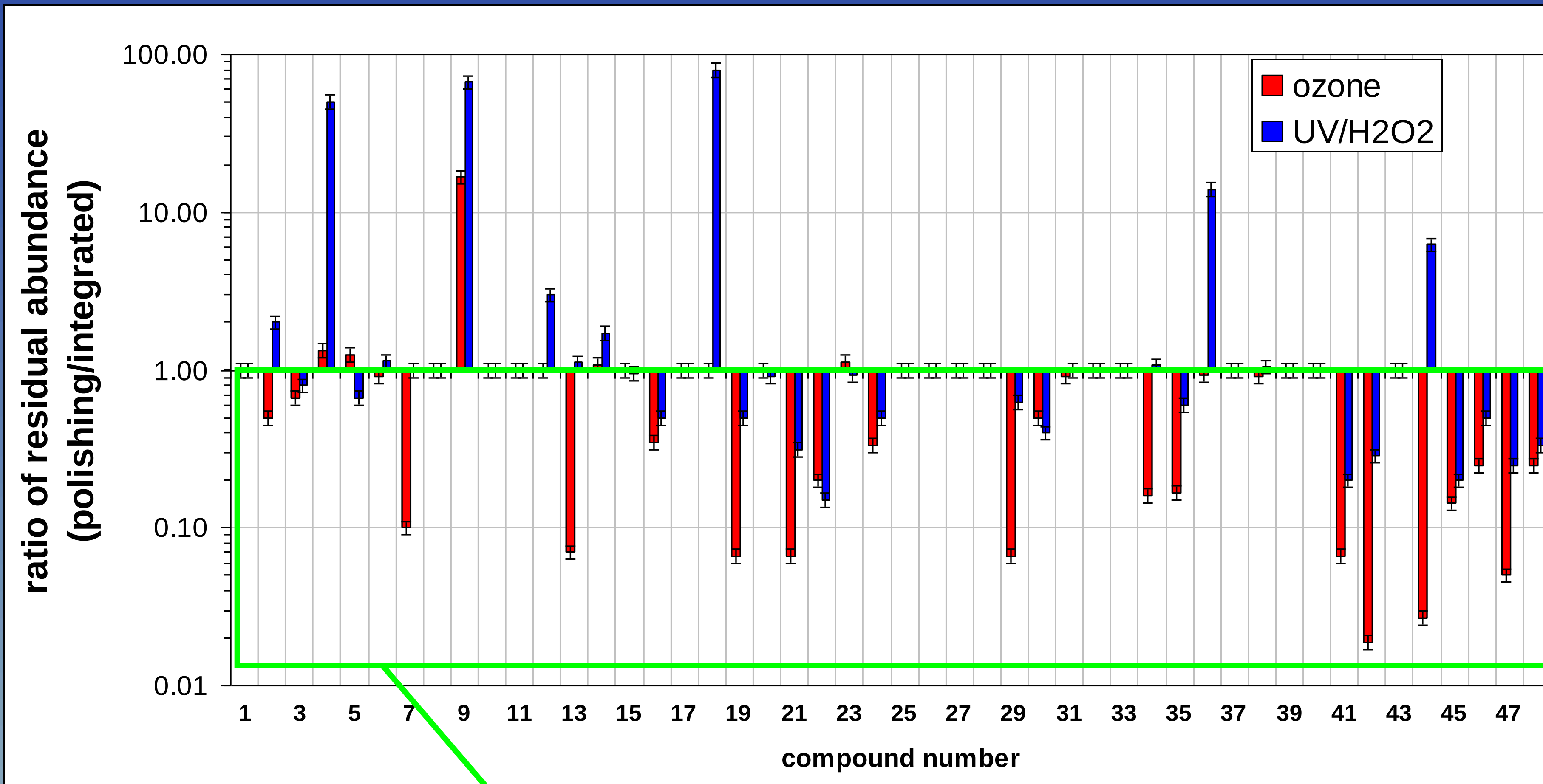
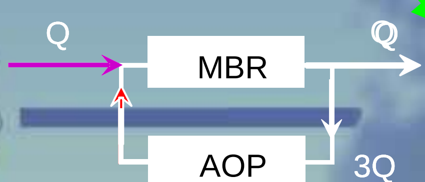
Organics degradation: comparison of the two integrated set-ups vs standard polishing set-up

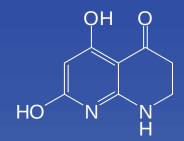




Ratio < 1: Integrated MBR/AOP < MBR→AOP

Nalidixic acid real wastewater: 55 by-products identified

compound number	MW	ret. time (min)
1	116	1.0
2, 5	180	1.0, 1.7
3, 16, 37	194	1.4, 3.3, 6.9
4	200	1.5
6, 8	254	1.7, 1.9
7, 19, 29	184	1.9, 3.9, 5.9
9, 17	210	2.2, 3.6
10, 31, 50	208	2.6, 6.2, 7.9
11, 21, 33	224	2.6, 4.4, 6.3
12	196	2.9
13	268	2.9
14, 22, 27, 34	238	3.0, 4.9, 5.4, 6.3
15	188	3.3
18	212	3.6
20	166	4.2
23	290	5.1
24	216	5.2
25, 39, 52	222	5.2, 7.1, 8.2
26	130	5.3
28, 54	178	5.9, 8.5
30, 36	266	6.1, 6.4
32	236	6.2
35	316	6.3
38	252	7.0
40	289	7.1
41	250	7.2
42, 45	206	7.3, 7.6
43, 48	264	7.5, 7.7
44	189	7.6
46	220	7.6
47	262	7.7
49	192	7.8
51, 53	278	8.0, 8.3
55	234	9.3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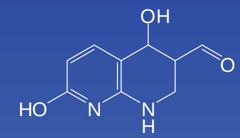
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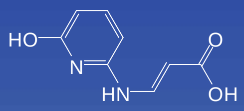
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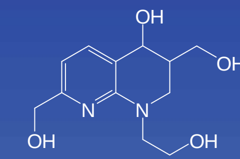
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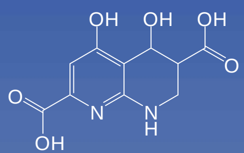
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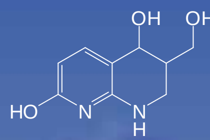
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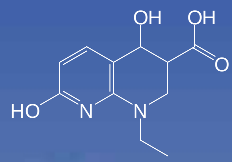
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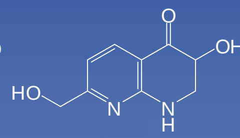
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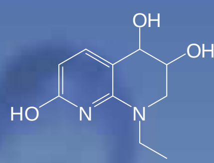
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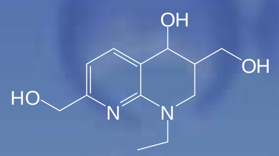
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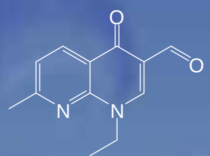
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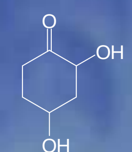
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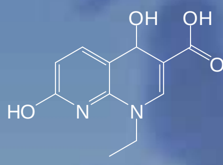
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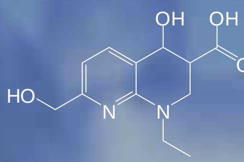
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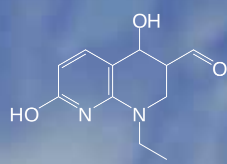
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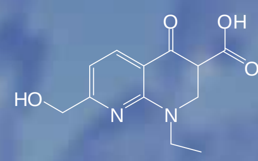
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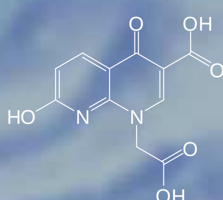
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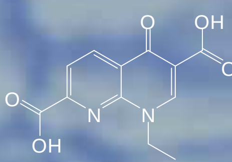
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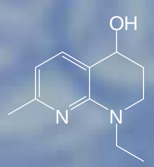
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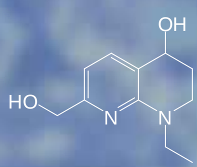
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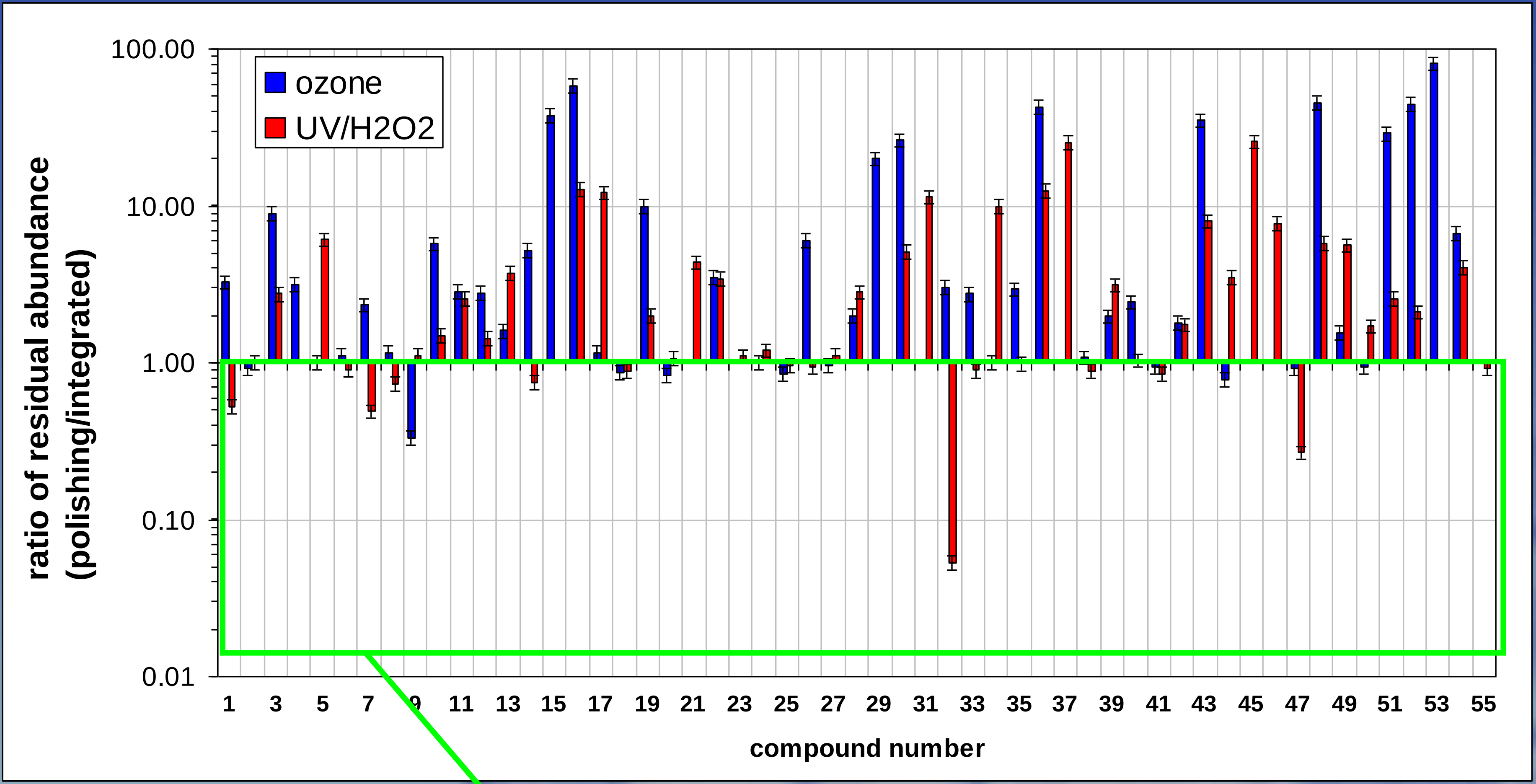
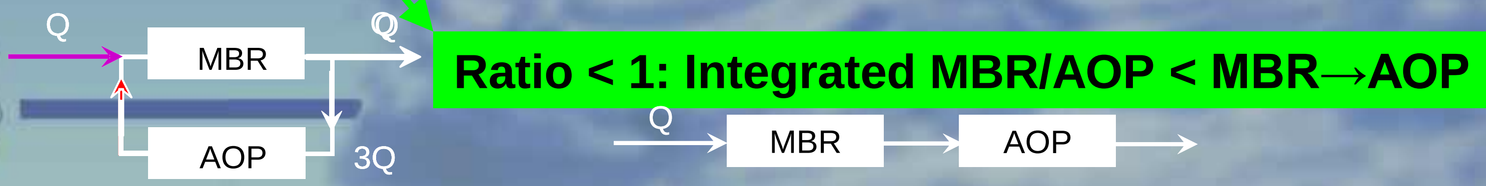
By-products minimization: comparison of the two integrated set-ups vs standard polishing set-up





Conclusions

- gross-parameters (COD, CST, nitrification, etc.). The efficiency of MBR was not affected by the integration with AOP (for both O_3 or UV/H_2O_2);
- organics removal. Performance of the sequential MBR/AOP system was comparable or even better than the integrated one. Just for few compounds the efficiency of MBR treatment improved by integration with AOP (O_3 or UV/H_2O_2);
- By-products removal. For most compounds the integrated MBR/AOP system was more effective than the sequential one. Integration with O_3 was generally better than that with UV/H_2O_2.
- More information ? ES&T, 2012, 46, 1010−1018.

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