

# Integrated MBR and AOP processes for organics removal from pharmaceutical wastewater

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# Presentation outline

- Focusing the problem;
- Potential benefits of integrating biological processes and AOPs;
- Results obtained treating a real pharmaceutical wastewater (using  $O_3$  or  $UV/H_2O_2$ ) as AOP:
  - Process performance through gross-parameters monitoring
  - removal of main organics;
  - by-products formation;
  - by-products degradation;
  - integrated vs sequential MBR/AOP configuration;
- Conclusions.

# FOCUSING THE PROBLEM

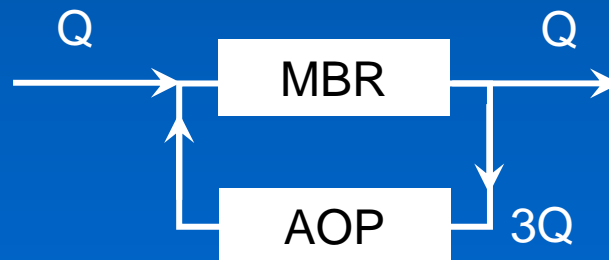
- **The removal of residual pharmaceutical compounds from industrial pharmaceutical wastewater is very challenging due to:**
  - **Presence of non-biodegradable solvents and synthesis intermediate;**
  - **The simultaneous presence of high fraction of easily biodegradable carbon and lower amounts of 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.**

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

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



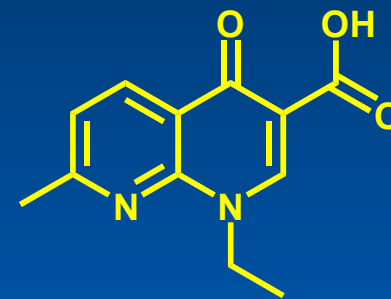
- **Integration of biological treatment and AOP** (the investigated approach that was employed for two different pharmaceutical wastewaters within the project).



**A Membrane BioReactor (MBR) was used with both O<sub>3</sub> or UV/H<sub>2</sub>O<sub>2</sub> 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 <sup>-1</sup>	7
DOC	mg L <sup>-1</sup>	775
COD	mg L <sup>-1</sup>	2660
NH <sub>4</sub> <sup>+</sup>	mg <sub>N</sub> L <sup>-1</sup>	<0.1
Acetate	mg L <sup>-1</sup>	1900
<b>Nalidixic acid</b>	mg L <sup>-1</sup>	<b>45</b>
Cl <sup>-</sup>	mg L <sup>-1</sup>	2.8
PO <sub>4</sub> <sup>3-</sup>	mg L <sup>-1</sup>	<0.1
SO <sub>4</sub> <sup>=</sup>	mg L <sup>-1</sup>	0.16
Na	mg L <sup>-1</sup>	2
TSS	mg L <sup>-1</sup>	496
VSS	mg L <sup>-1</sup>	264



**nalidixic acid**  
 (a synthetic antibacterial agent)

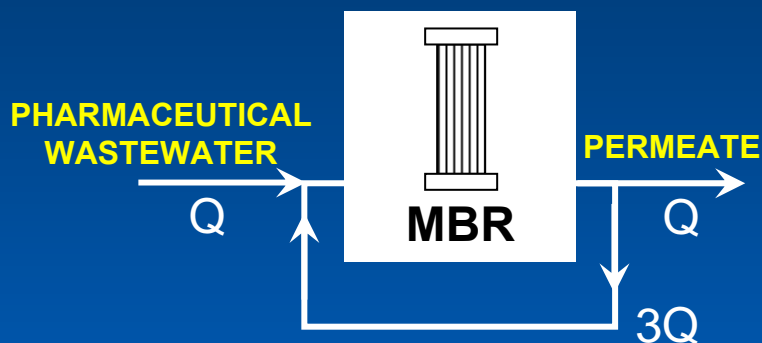
concentration of added nutrients

PO<sub>4</sub><sup>3-</sup> = 18.9 mg L<sup>-1</sup>

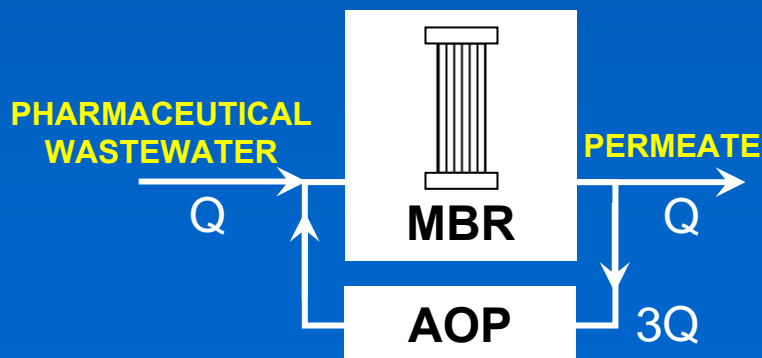
NH<sub>4</sub><sup>+</sup> = 49.2 mg L<sup>-1</sup>

# Lab-scale plant set-up: operational conditions

1° phase: MBR alone



2° phase: MBR/AOP

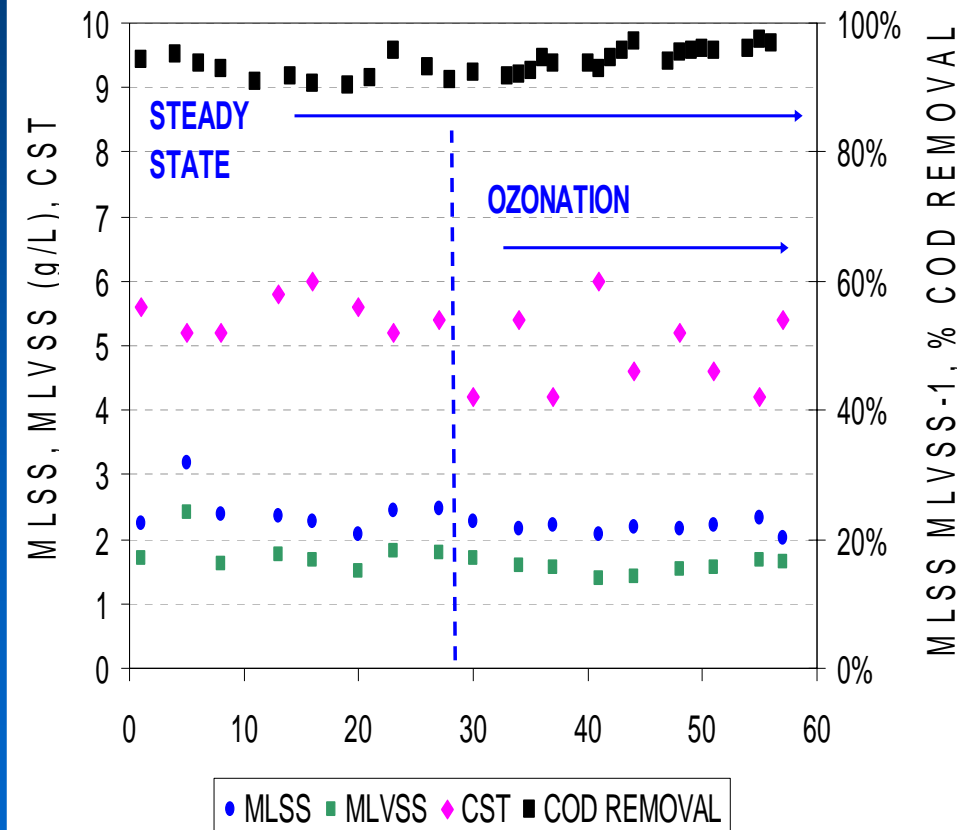


Parameter	Unit	Amount
MBR reactor	L	6
Feed flow rate $Q$	$L d^{-1}$	1.6
HRT	d	3.75
SRT	d	30
VLR	$g_{COD} L_{react}^{-1} d^{-1}$	1.3
Membrane flux	$L m^{-2} h^{-1}$	5.7
Relaxation cycle		15 min every 3 h
Ozone dosed	$mg L^{-1} min^{-1}$	2.2
Ozone dosed	$mg mg_{COD}^{-1}$	0.22
Ozonation time	min	15
UV lamp (254 nm)	W	40
UV reaction time*	min	5
$H_2O_2$	mM	0.5

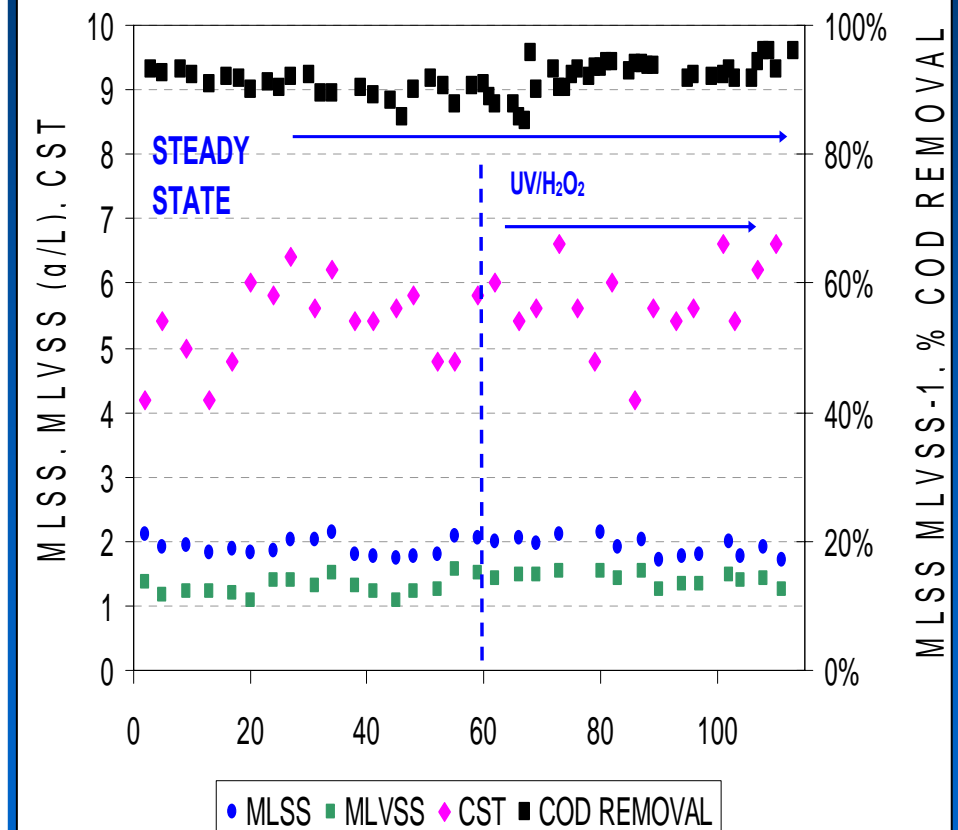
\*UV reactor volume: 0.5 L

## Gross parameters

### MBR integrated with O<sub>3</sub>



### MBR integrated with UV/H<sub>2</sub>O<sub>2</sub>



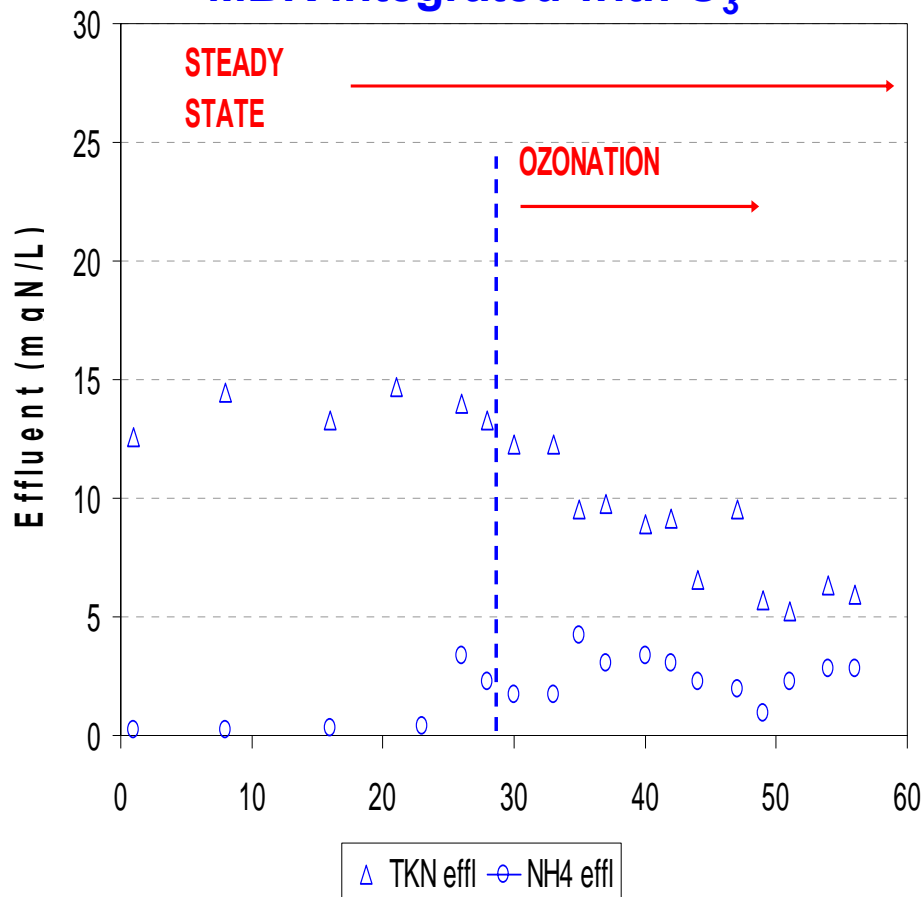
**No significant sludge reduction was observed after integration with AOP**

## TKN and $\text{NH}_4^+$ removal

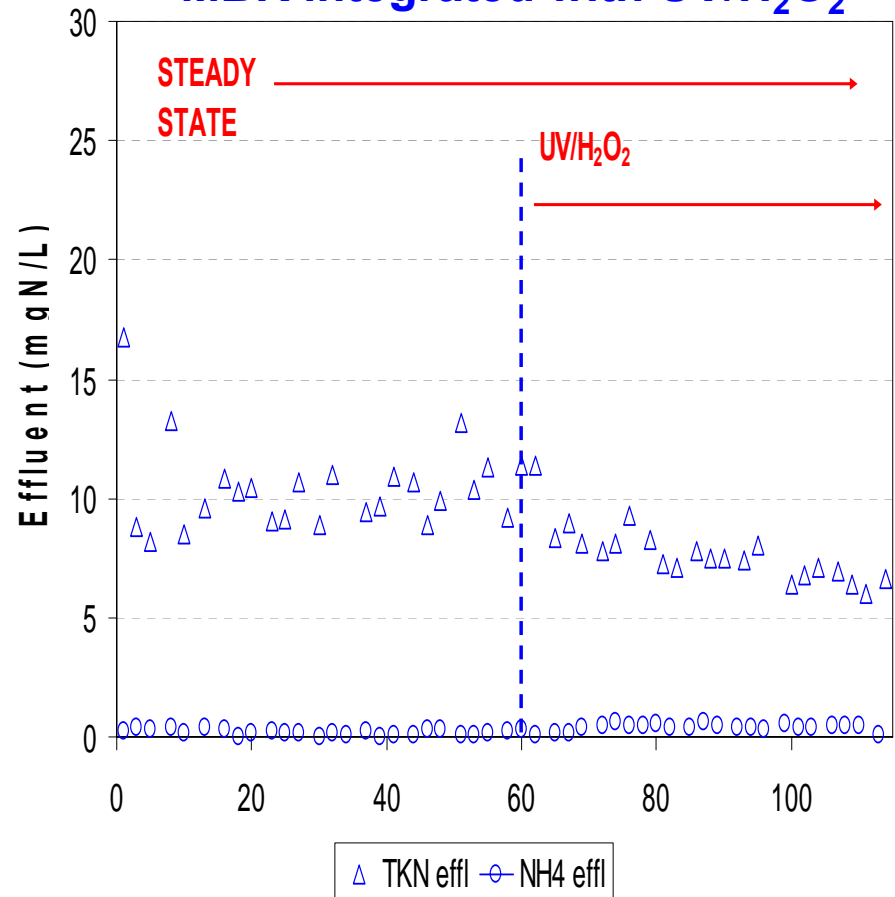
$\text{TKN}_{\text{inf}} = 59.1 \text{ mg}_\text{N}/\text{L}$ ,  $\text{NH}_{4,\text{inf}} = 37.8 \text{ mg}_\text{N}/\text{L}$

$\text{TKN}_{\text{inf}} = 51.5 \text{ mg}_\text{N}/\text{L}$ ,  $\text{NH}_{4,\text{inf}} = 31 \text{ mg}_\text{N}/\text{L}$

### MBR integrated with $\text{O}_3$

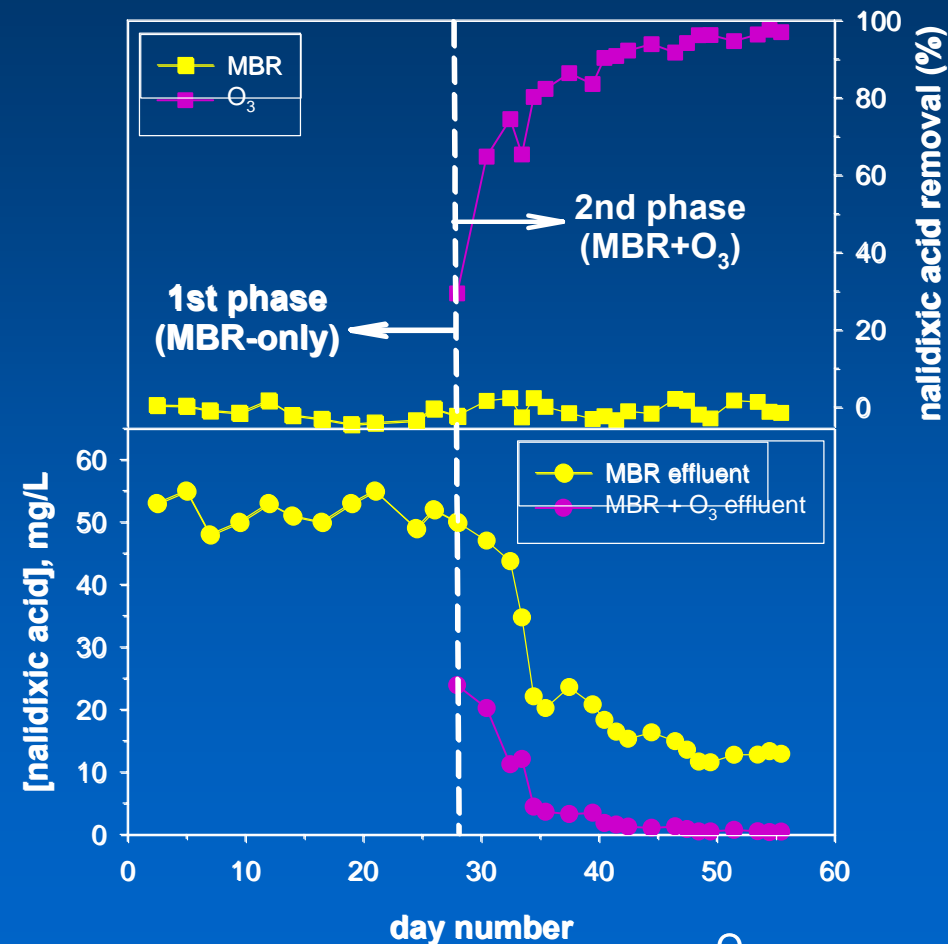


### MBR integrated with UV/ $\text{H}_2\text{O}_2$

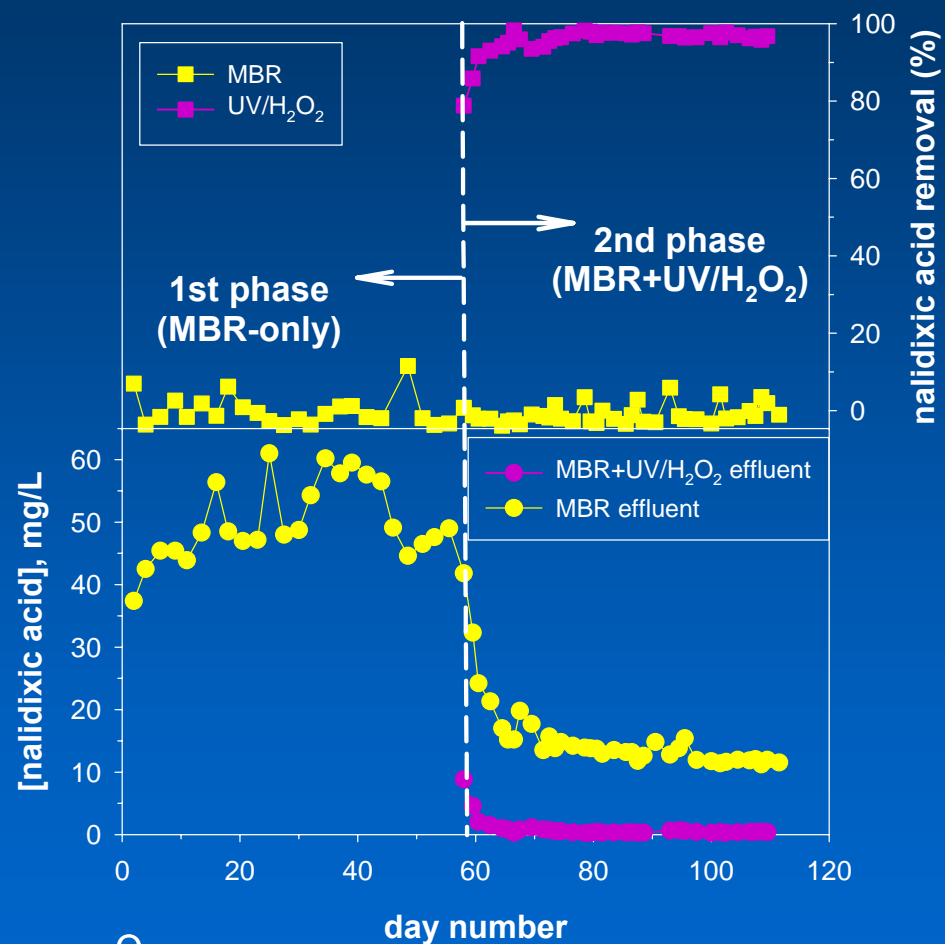
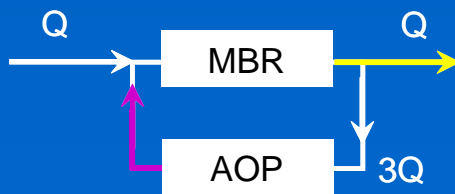




## Concentration of nalidixic acid in the effluent and % of removal

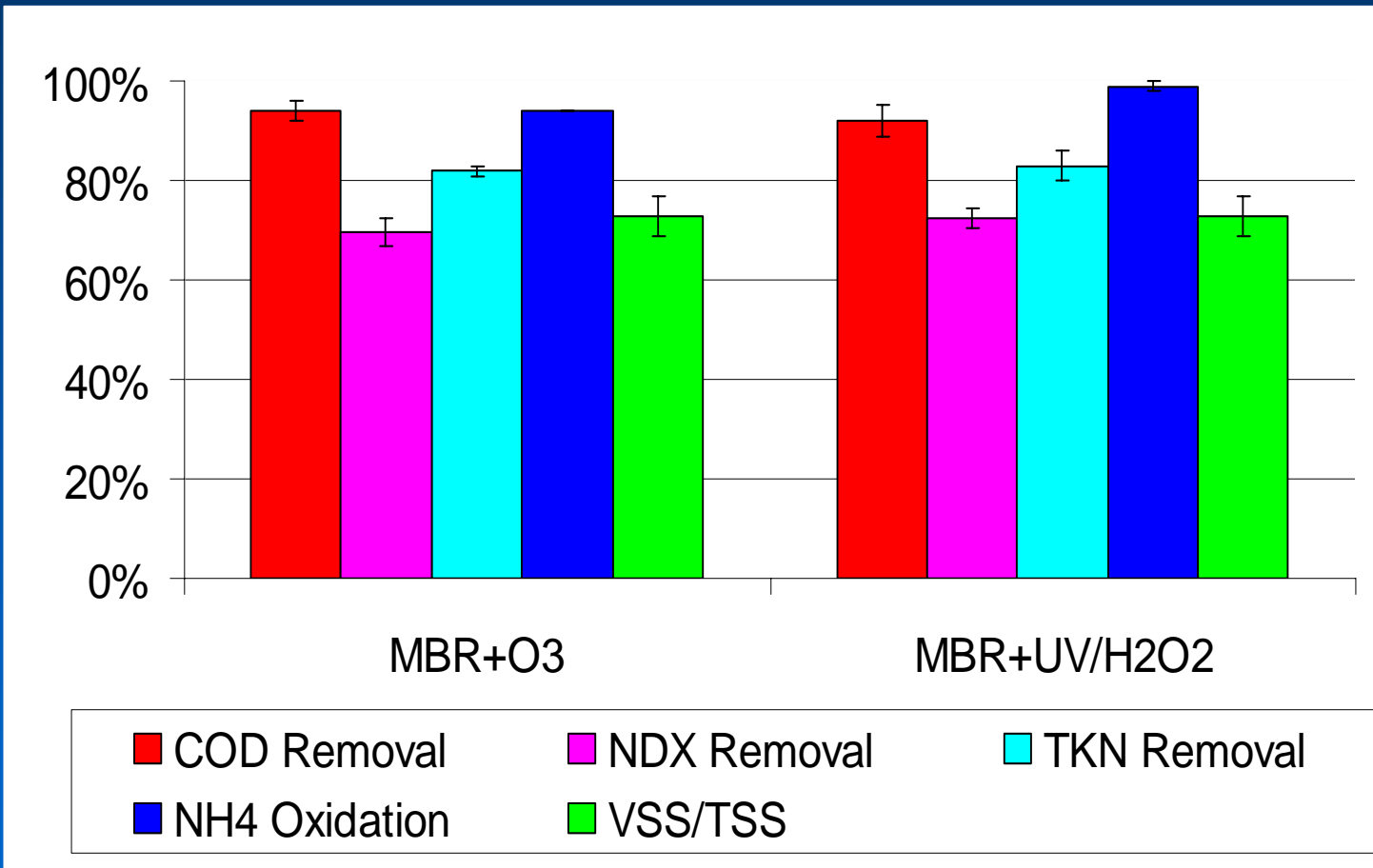


ozonation time:  
15 min



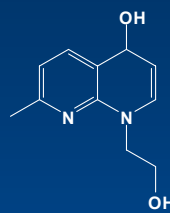
UV/H<sub>2</sub>O<sub>2</sub> reaction time:  
5 min

## Performance of the two investigated integrations

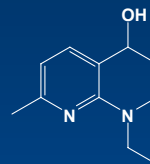


## Characterization of nalidixic acid real wastewater: 48 organics identified

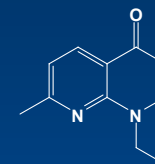
compound number	MW	ret. time (min)
1, 4	152	1.4, 1.9
2	108	1.5
3, 6	206	1.5, 2.2
5, 17	208	1.9, 5.3
7, 12	136	2.6, 4.1
8, 10, 39	190	2.9, 3.6, 8.1
9	166	3.1
11	157	3.9
13	224	4.1
14	180	4.5
15, 42	188	4.6, 8.5
16, 18	164	5.3, 5.8
19, 35	222	5.9, 7.9
20	295	6.1
21, 26	230	6.3, 6.9
22, 27, 34	204	6.6, 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



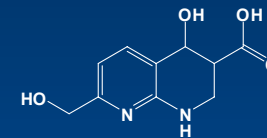
organic n. 6



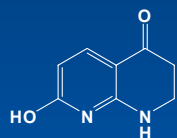
organic n. 8



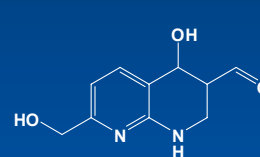
organic n. 10



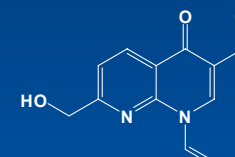
organic n. 13



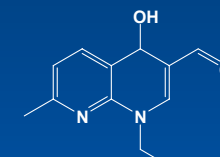
organic n. 16



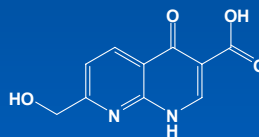
organic n. 17



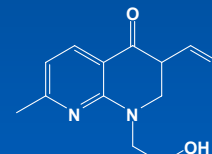
organic n. 21



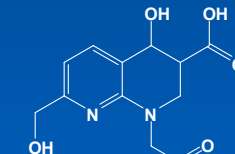
organic n. 24



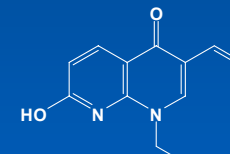
organic n. 25



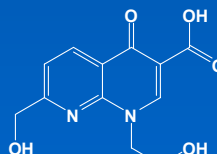
organic n. 28



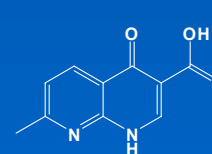
organic n. 29



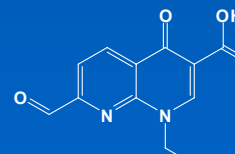
organic n. 31



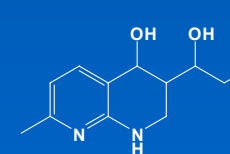
organic n. 33



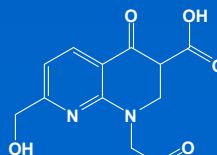
organic n. 34



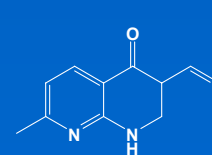
organic n. 36



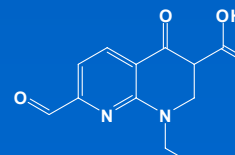
organic n. 35



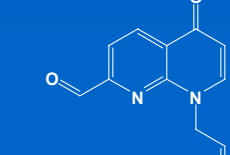
organic n. 37



organic n. 39

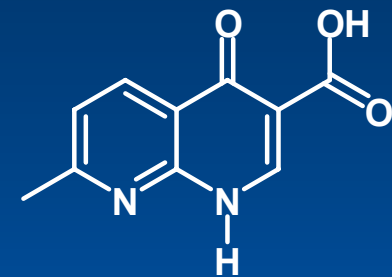
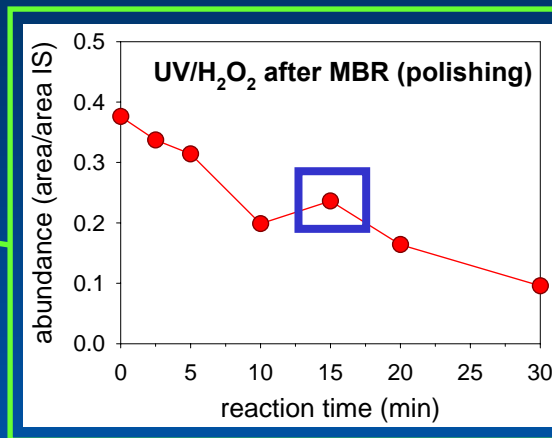
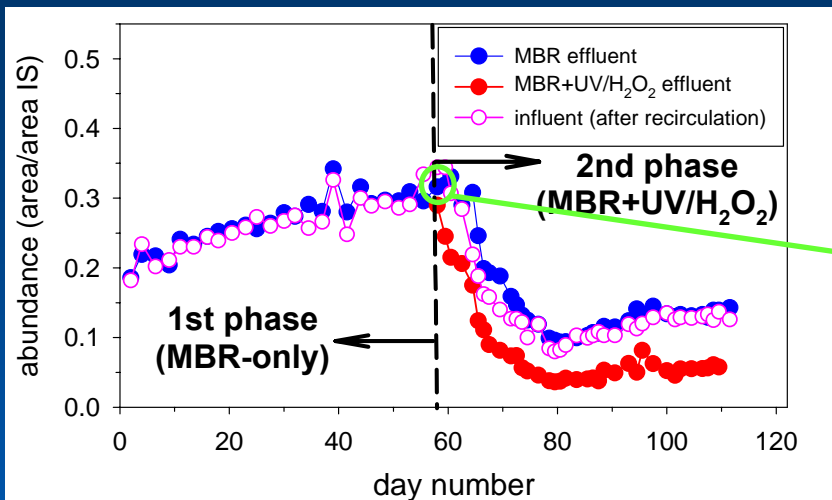


organic n. 44

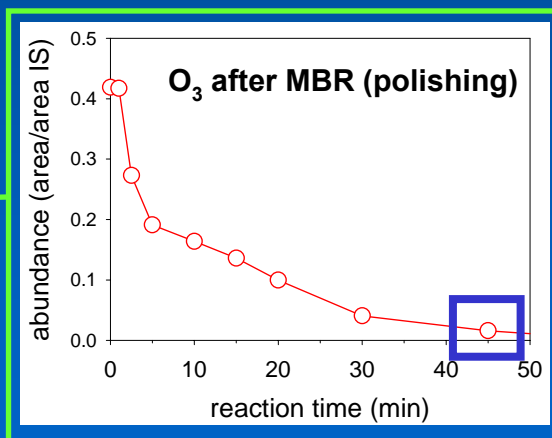
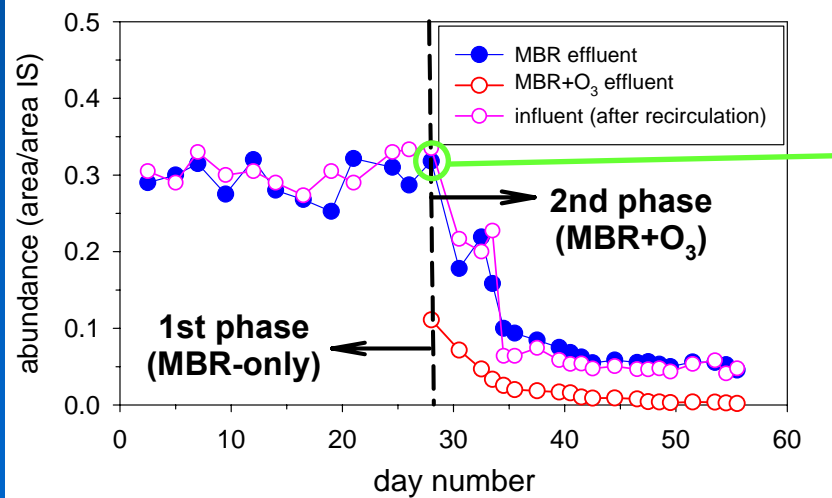


organic n. 47

## Integration of MBR/AOP: organics degradation



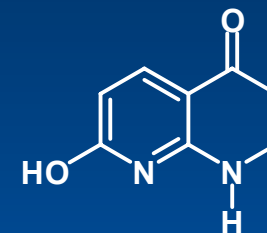
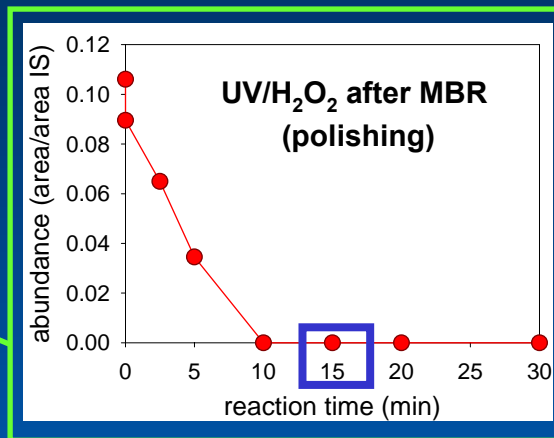
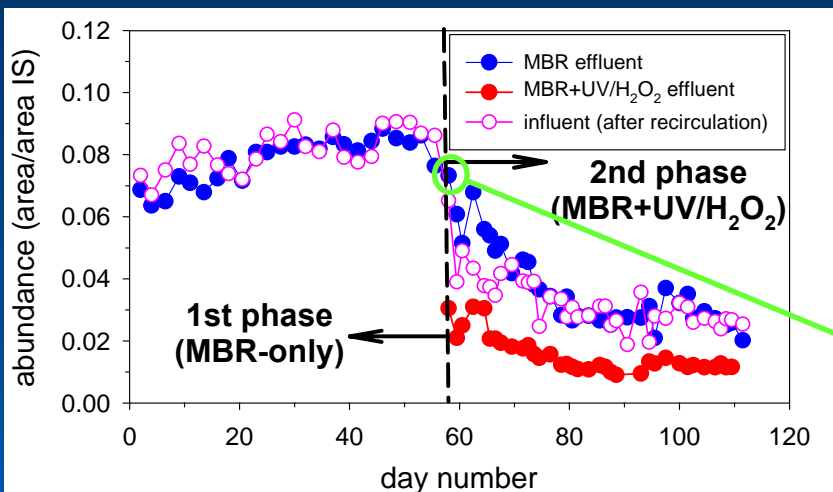
organic n. 34



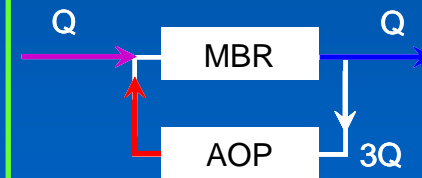
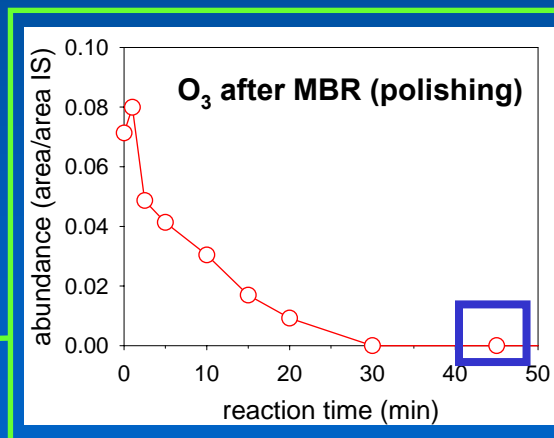
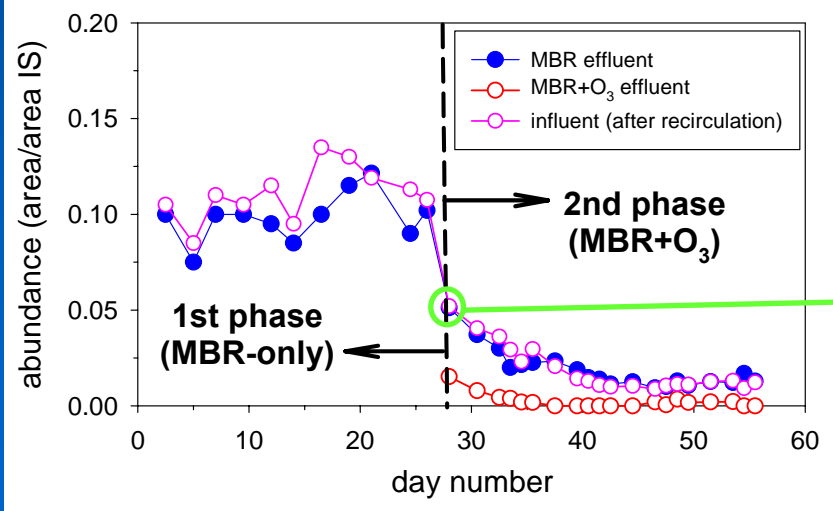
Integration: O<sub>3</sub> better than UV/H<sub>2</sub>O<sub>2</sub>  
 Polishing: O<sub>3</sub> better than UV/H<sub>2</sub>O<sub>2</sub>

Removal of this organic: integrated MBR/AOP (with O<sub>3</sub> and UV/H<sub>2</sub>O<sub>2</sub>)  $\cong$  MBR  $\rightarrow$  AOP

## Integration of MBR/AOP: organics degradation



organic n. 16

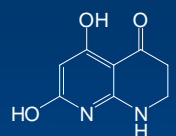


Integration: O<sub>3</sub> better than UV/H<sub>2</sub>O<sub>2</sub>  
 Polishing: O<sub>3</sub> comparable to UV/H<sub>2</sub>O<sub>2</sub>

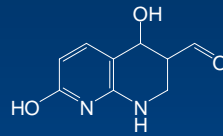
Removal of this organic: integrated MBR/AOP (with O<sub>3</sub> and UV/H<sub>2</sub>O<sub>2</sub>) < MBR→AOP

## Nalidixic acid real wastewater: 55 by-products identified

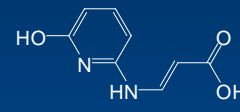
compound number	MW	ret. time (min)
1	116	1.0
2, 5	180	1.0, 1.7
3, 16, 37	194	1.4, 3.3, 6.9
4	200	1.5
6, 8	254	1.7, 1.9
7, 19, 29	184	1.9, 3.9, 5.9
9, 17	210	2.2, 3.6
10, 31, 50	208	2.6, 6.2, 7.9
11, 21, 33	224	2.6, 4.4, 6.3
12	196	2.9
13	268	2.9
14, 22, 27, 34	238	3.0, 4.9, 5.4, 6.3
15	188	3.3
18	212	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



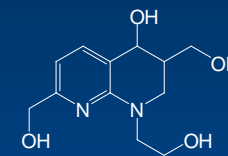
by-product n. 2



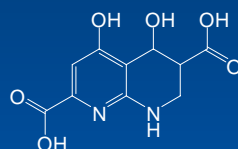
by-product n. 3



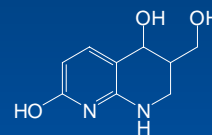
by-product n. 5



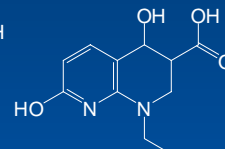
by-product n. 6



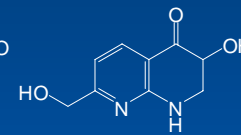
by-product n. 8



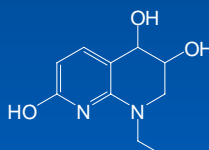
by-product n. 12



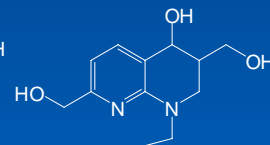
by-product n. 14



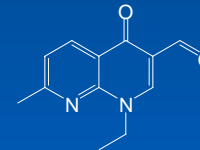
by-product n. 16



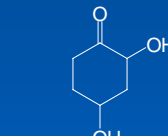
by-product n. 17



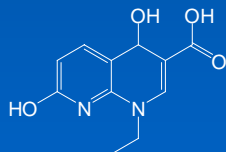
by-product n. 22



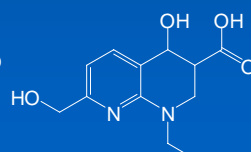
by-product n. 24



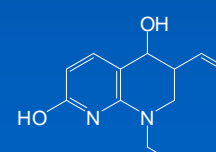
by-product n. 26



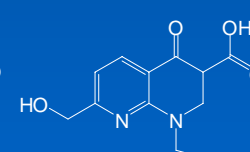
by-product n. 32



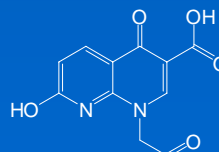
by-product n. 38



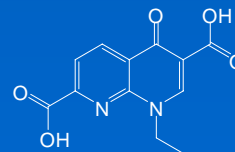
by-product n. 39



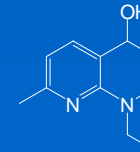
by-product n. 41



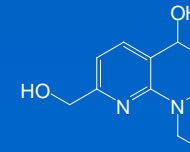
by-product n. 43



by-product n. 47

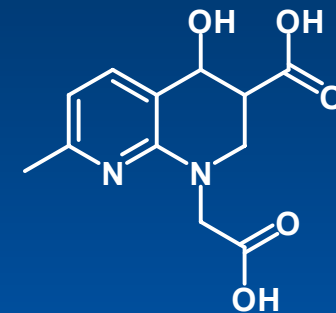
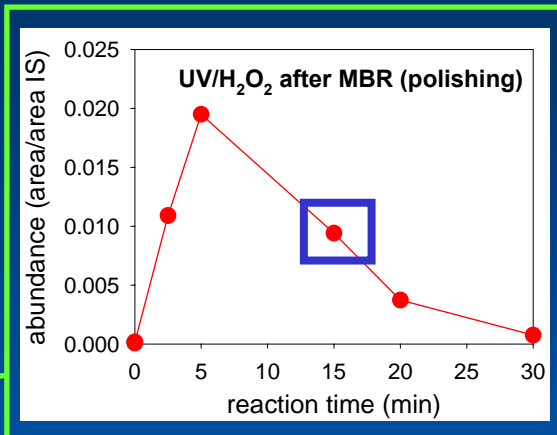
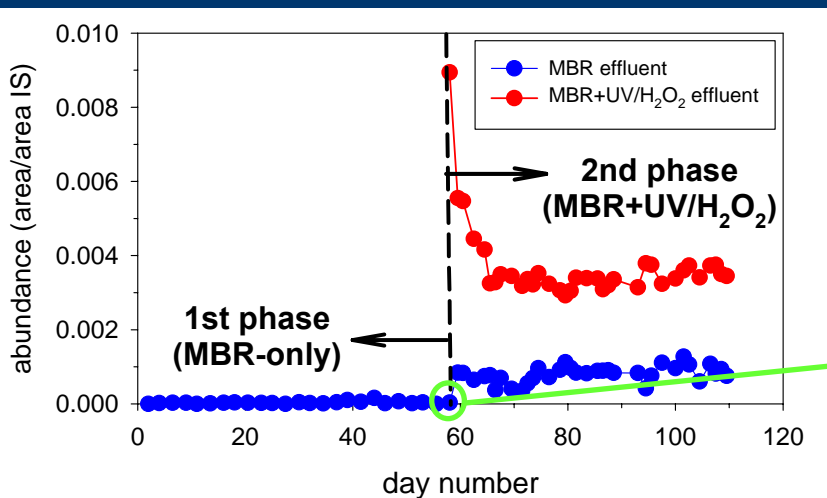


by-product n. 49

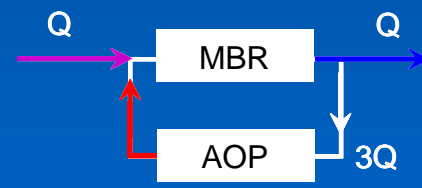
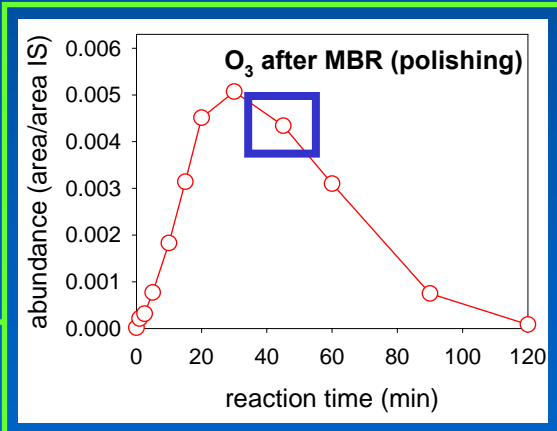
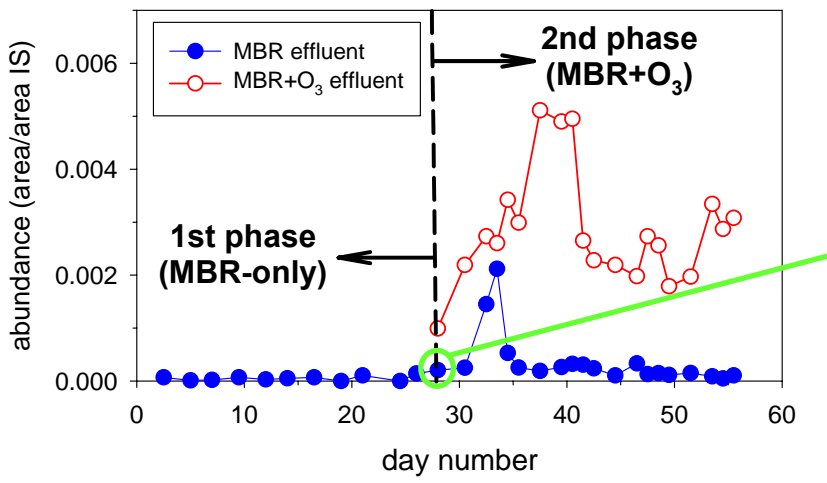


by-product n. 50

## Integration of MBR/AOP: by-products formation/degradation



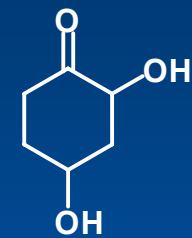
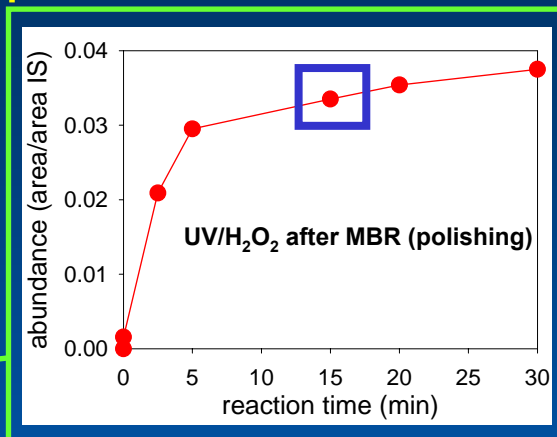
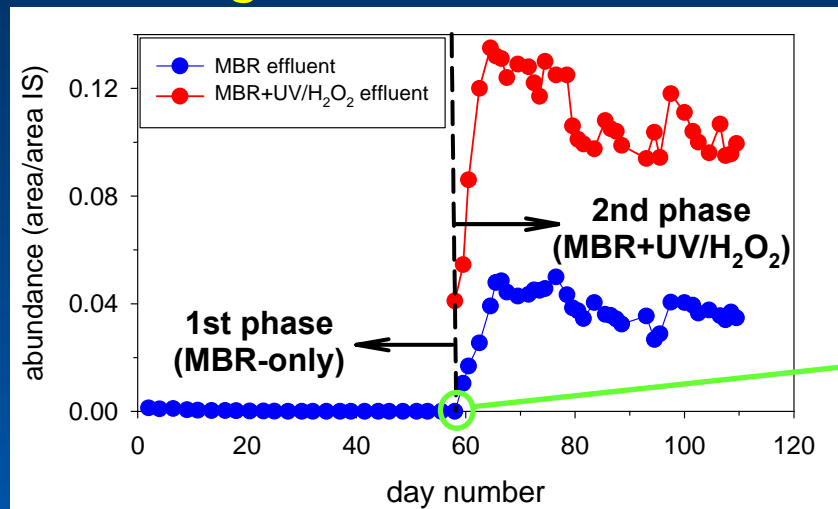
by-product n. 36



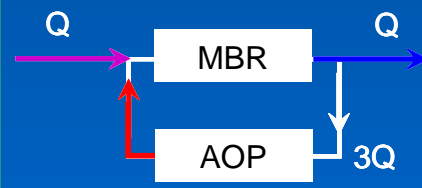
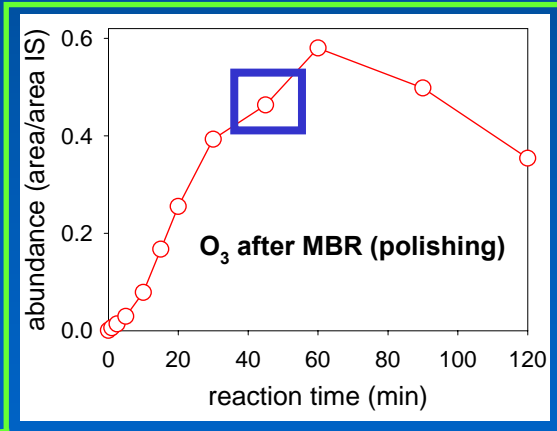
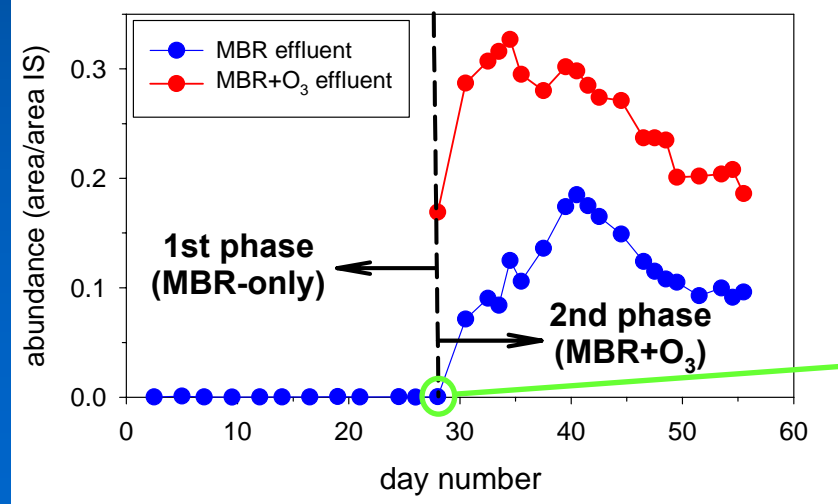
Integration: O<sub>3</sub> slightly better than UV/H<sub>2</sub>O<sub>2</sub>  
 Polishing: O<sub>3</sub> better than UV/H<sub>2</sub>O<sub>2</sub>

Formation of this by-product: integrated MBR/AOP (with O<sub>3</sub> and UV/H<sub>2</sub>O<sub>2</sub>) < MBR→AOP

## Integration of MBR/AOP: by-products formation/degradation



by-product n. 26

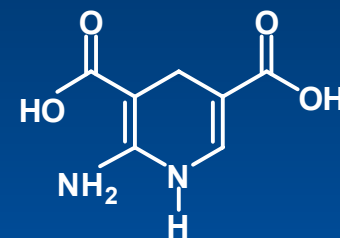
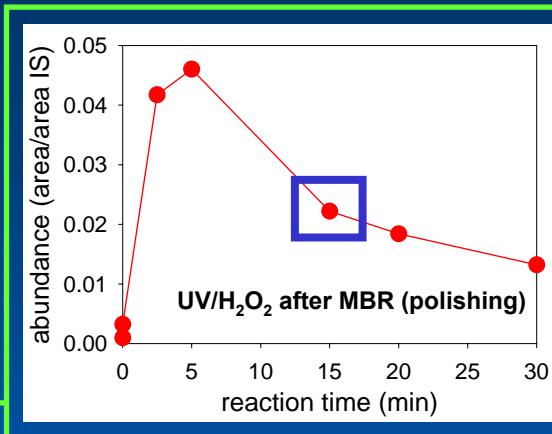
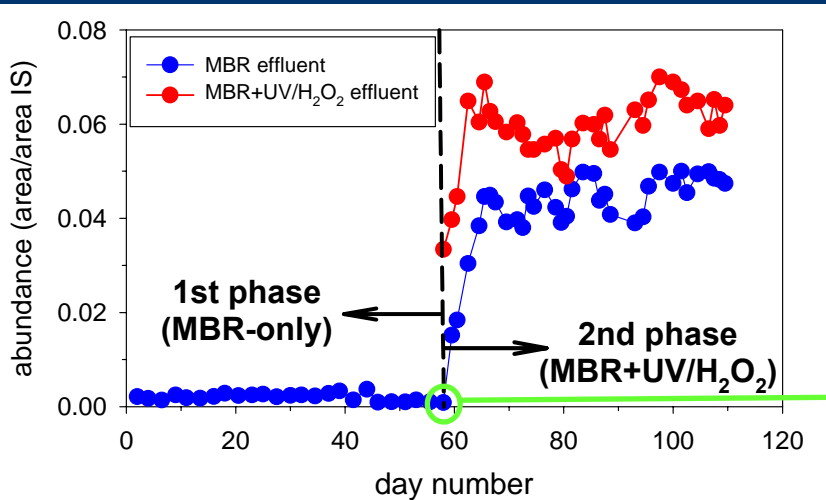


Integration: UV/H<sub>2</sub>O<sub>2</sub> better than O<sub>3</sub>  
 Polishing: UV/H<sub>2</sub>O<sub>2</sub> better than O<sub>3</sub>

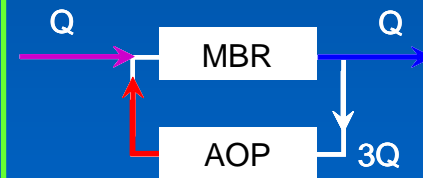
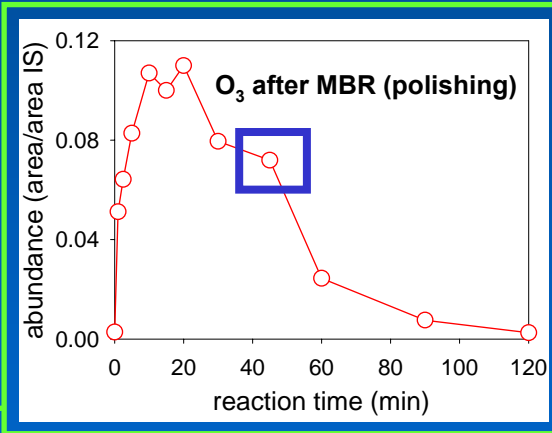
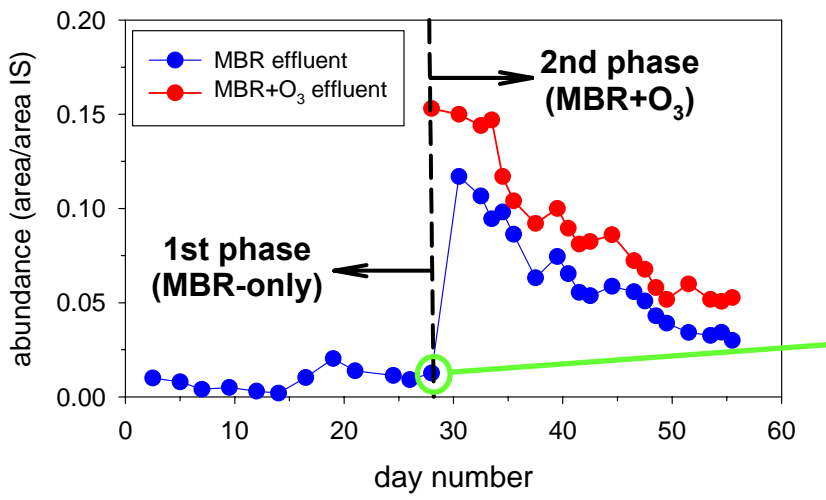
Formation of this by-product: integrated MBR/AOP (with O<sub>3</sub> only) < MBR→AOP



## Integration of MBR/AOP: by-products formation/degradation



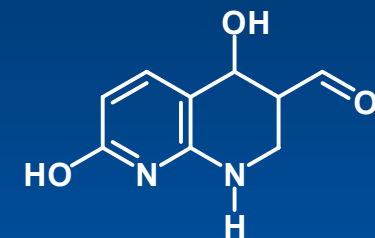
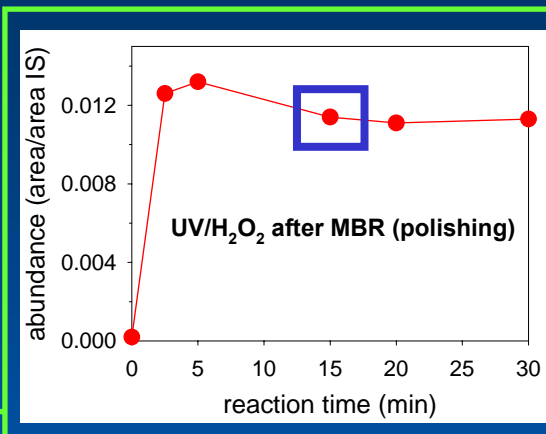
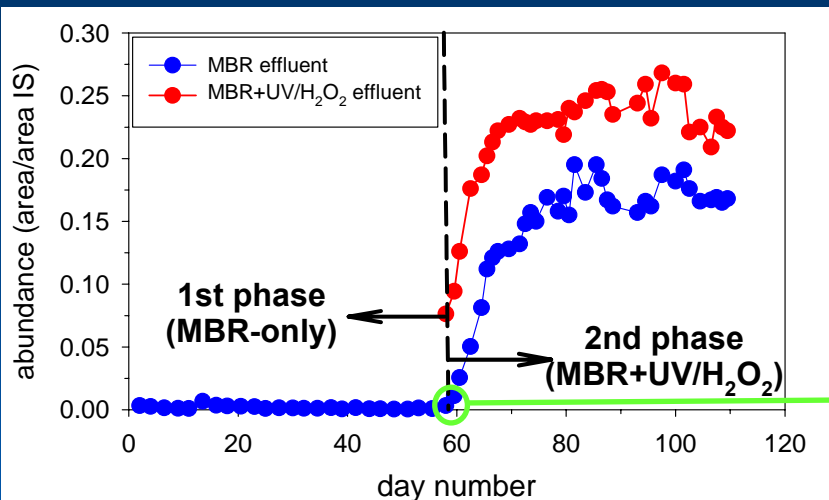
by-product n. 7



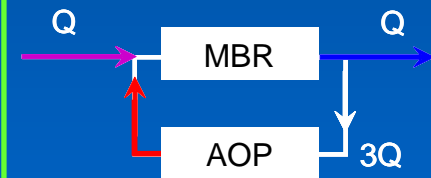
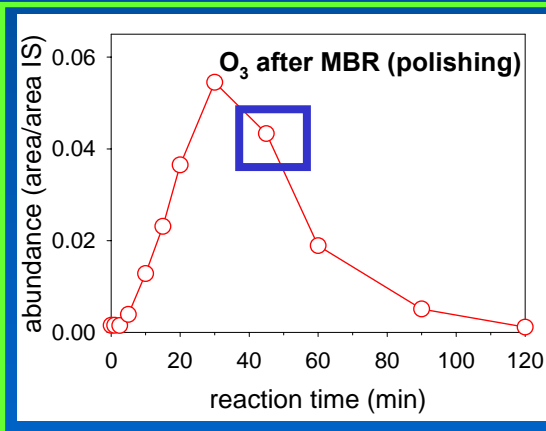
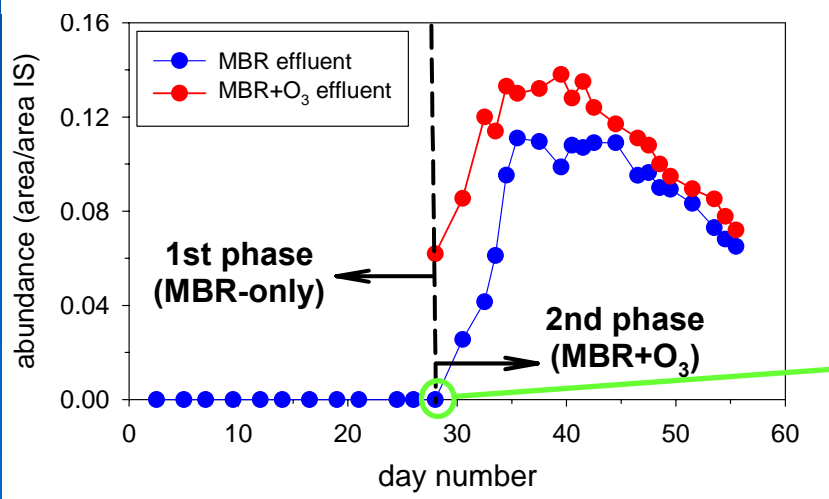
Integration: O<sub>3</sub> better than UV/H<sub>2</sub>O<sub>2</sub>  
 Polishing: UV/H<sub>2</sub>O<sub>2</sub> better than O<sub>3</sub>

Formation of this by-product: integrated MBR/AOP (with UV/H<sub>2</sub>O<sub>2</sub> only) > MBR→AOP

## Integration of MBR/AOP: by-products formation/degradation



by-product n. 3



Integration: O<sub>3</sub> better than UV/H<sub>2</sub>O<sub>2</sub>  
 Polishing: UV/H<sub>2</sub>O<sub>2</sub> better than O<sub>3</sub>

Formation of this by-product: integrated MBR/AOP (with O<sub>3</sub> and UV/H<sub>2</sub>O<sub>2</sub>) > MBR→AOP

# 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  $UV/H_2O_2$ .

## Acknowledgment



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