Evaluation of Fenton and modified Fenton oxidation coupled with membrane distillation for produced water treatment: Benefits, challenges, and effluent toxicity

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SUPPLEMENTARY MATERIAL for

Evaluation of Fenton and modified Fenton oxidation coupled with membrane distillation for produced water treatment: Benefits, challenges, and effluent toxicity

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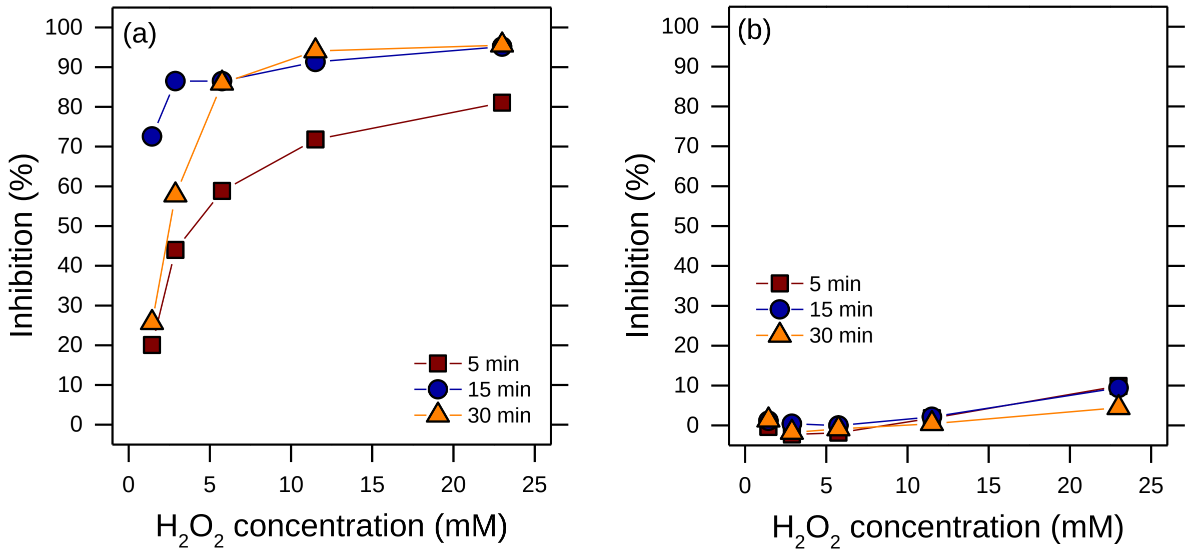


Figure S1 (a) Effect of hydrogen peroxide on bioluminescence . (b) Effect of hydrogen peroxide quenched with catalase. The acute toxicity was measured after 5, 15, and 30 minutes of contact (in red, blue, and orange, respectively) with the *Vibrio Fischeri* culture.

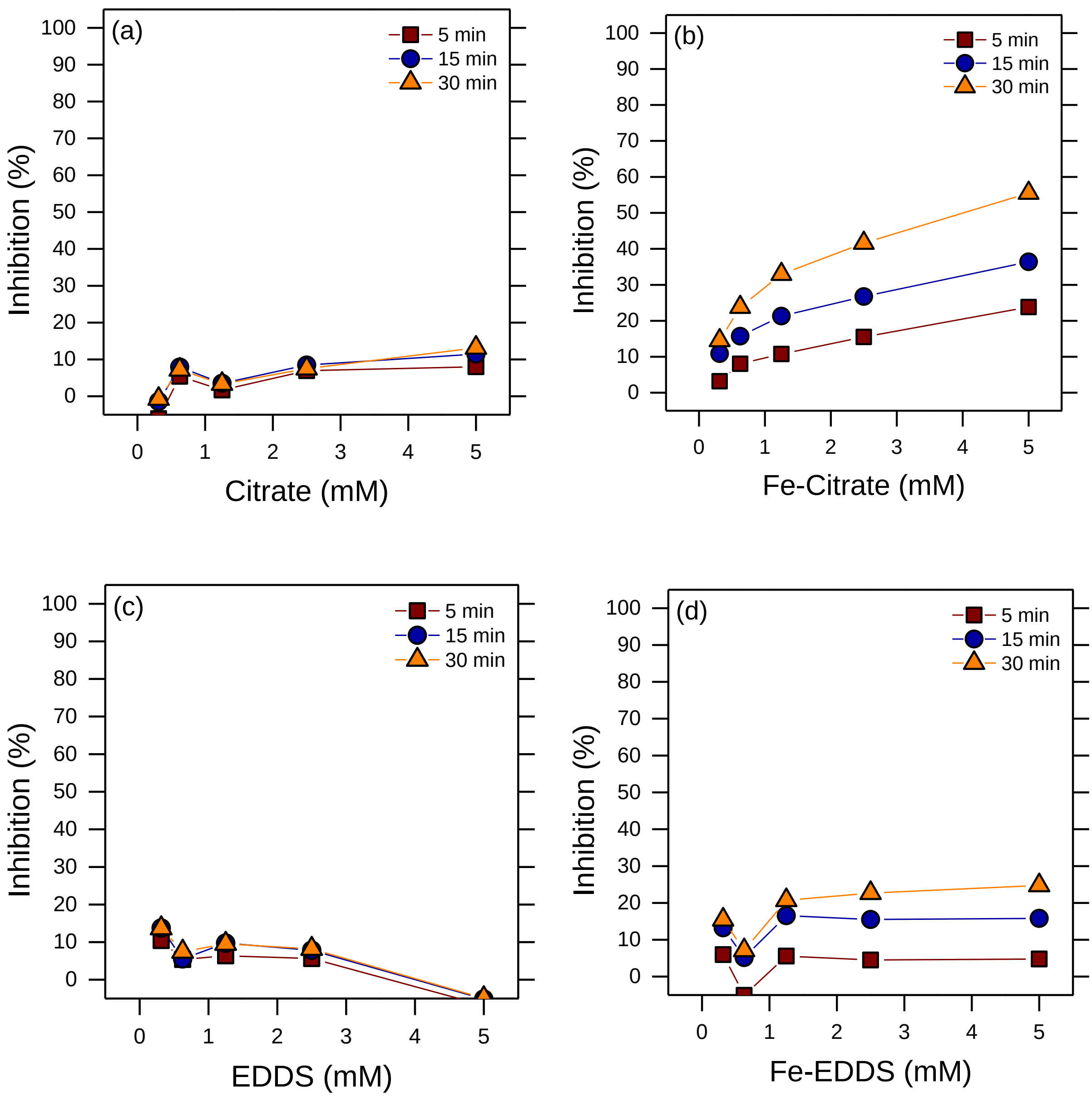
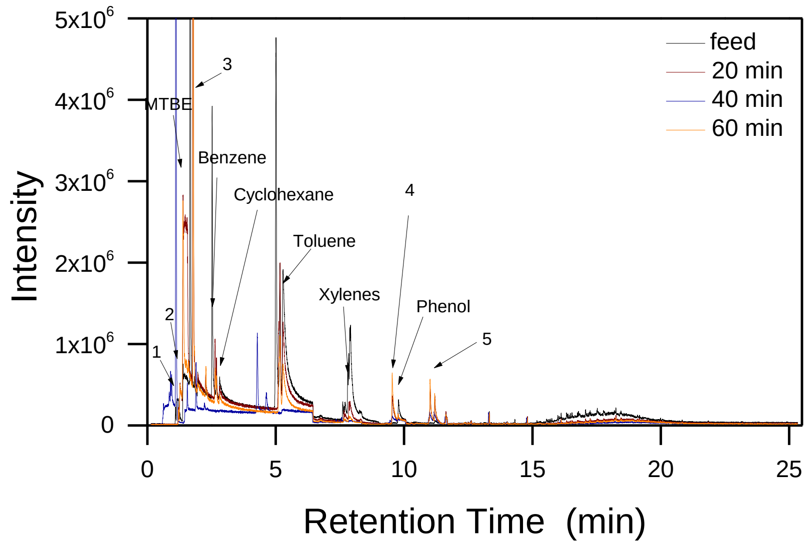
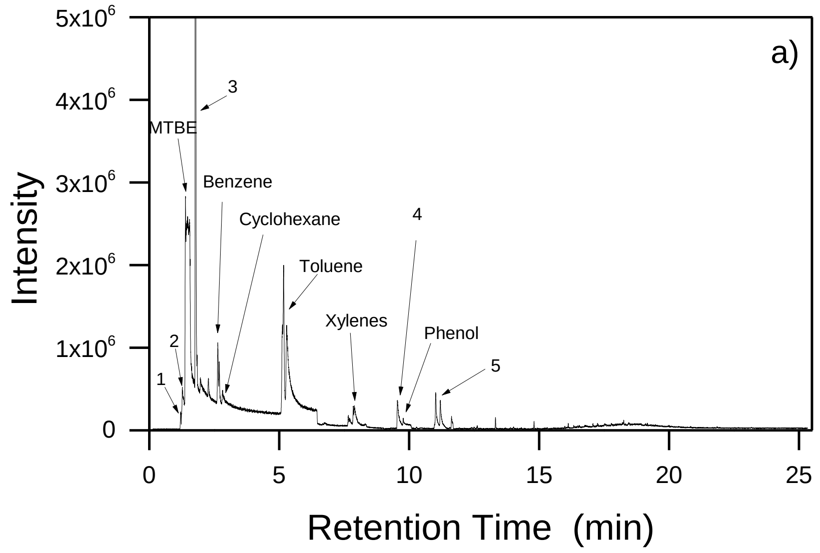


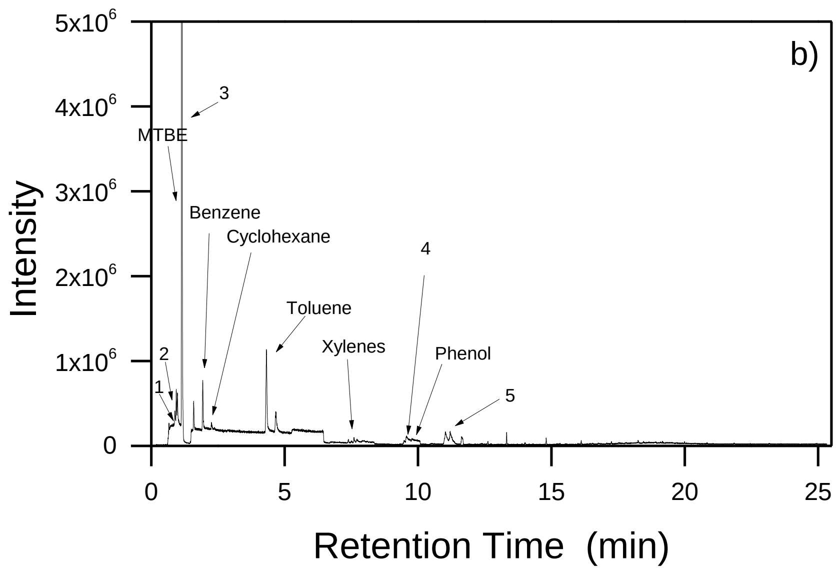
Figure S2 Toxicity curves of (a) citrate, (b) Fe-citrate system, (c) EDDS, and (d) the Fe-EDDS system as a function of concentration. The toxicity was measured after 5, 15, and 30 minutes of contact (in red, blue, and orange, respectively) with the *Vibrio Fischeri* culture.



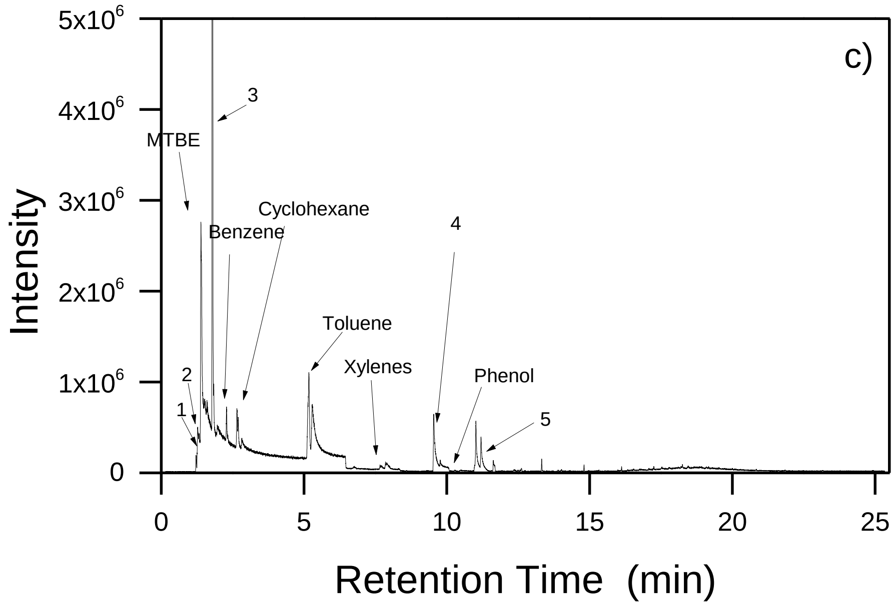
5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
Intensity
0
5
10
15
20
25
Retention Time (min)
feed
20 min
40 min
60 min
MTBE
1
2
3
Benzene
Cyclohexane
Toluene
Xylenes
4
Phenol
5



a)
5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
Intensity
0
5
10
15
20
25
Retention Time (min)
MTBE
1
2
3
Benzene
Cyclohexane
Toluene
Xylenes
4
Phenol
5



b)
5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
Intensity
0
5
10
15
20
25
Retention Time (min)
MTBE
1
2
3
Benzene
Cyclohexane
Toluene
Xylenes
4
Phenol
5



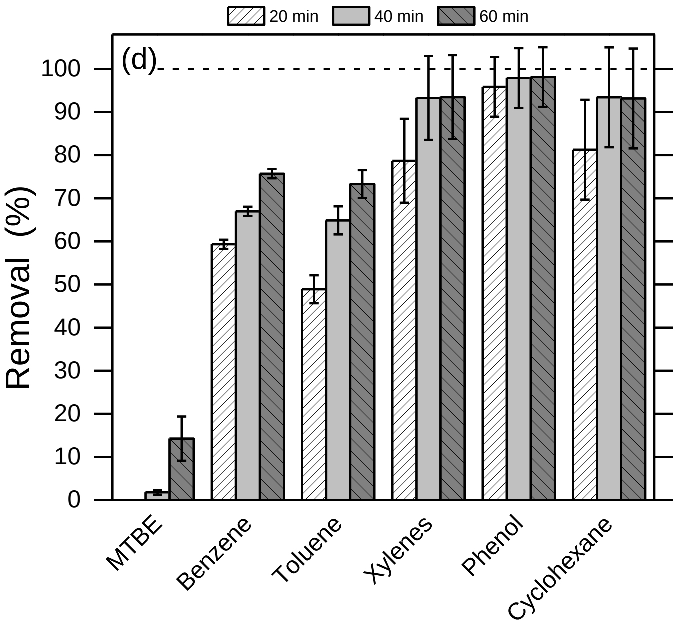


Figure S3 Chromatograms of the solutions upon Fenton oxidation carried out for (a) 20, (b) 40, and (c) 60 minutes. The numbers are related to the by-products illustrated in Figure 1 of the main manuscript. All the non-targeted are column related compounds. (d) Degradation rate of each organic compound in the synthetic produced water after 20, 40, and 60 minutes of Fenton treatment.

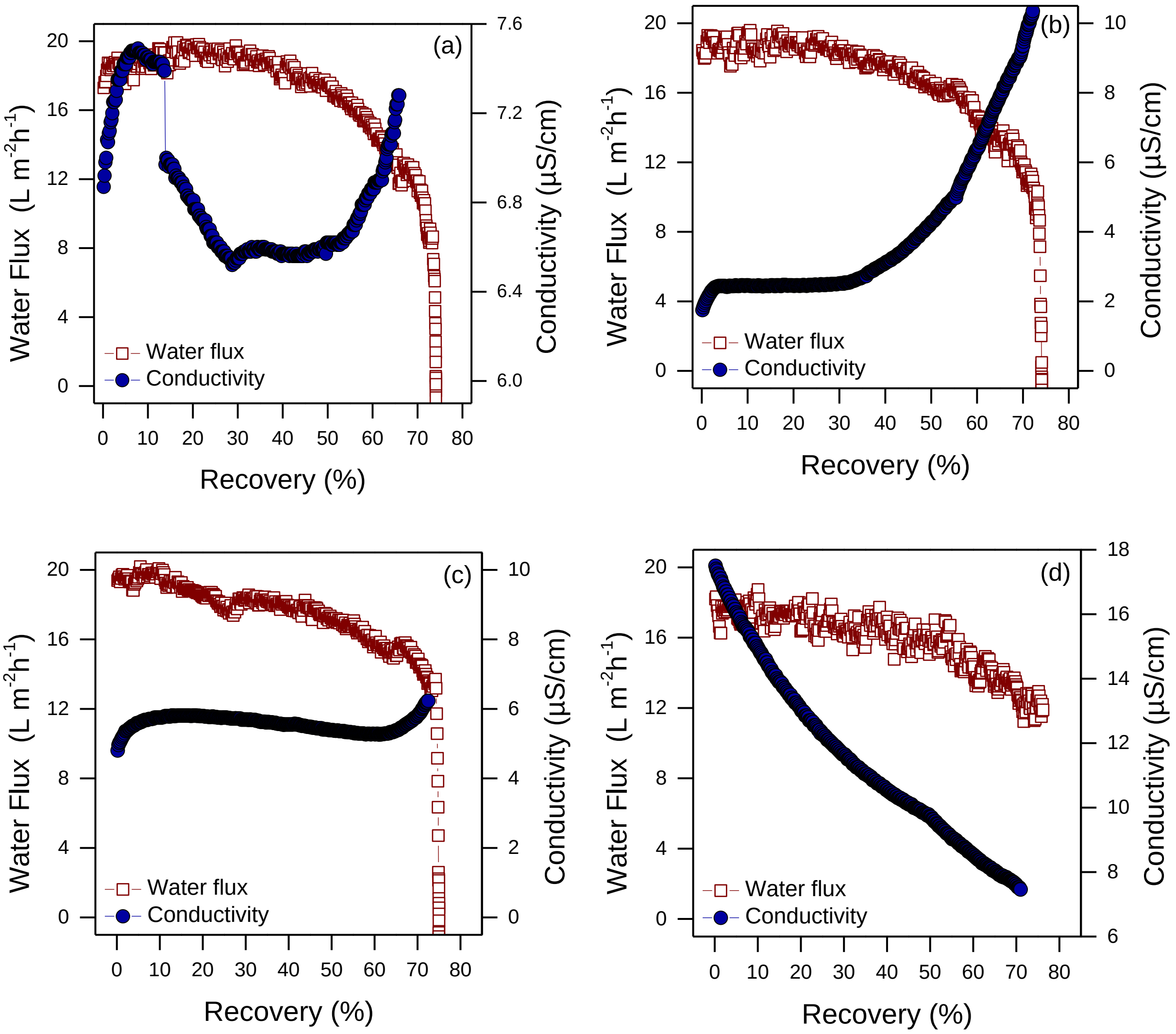


Figure S4 Water flux and conductivity of the distillate tank during the membrane distillation of (a) the synthetic produced water,(b) the synthetic produced water pre-treated with Fenton oxidation, (c) the salts of the synthetic produced water and (d) the organics of the synthetic produced water.

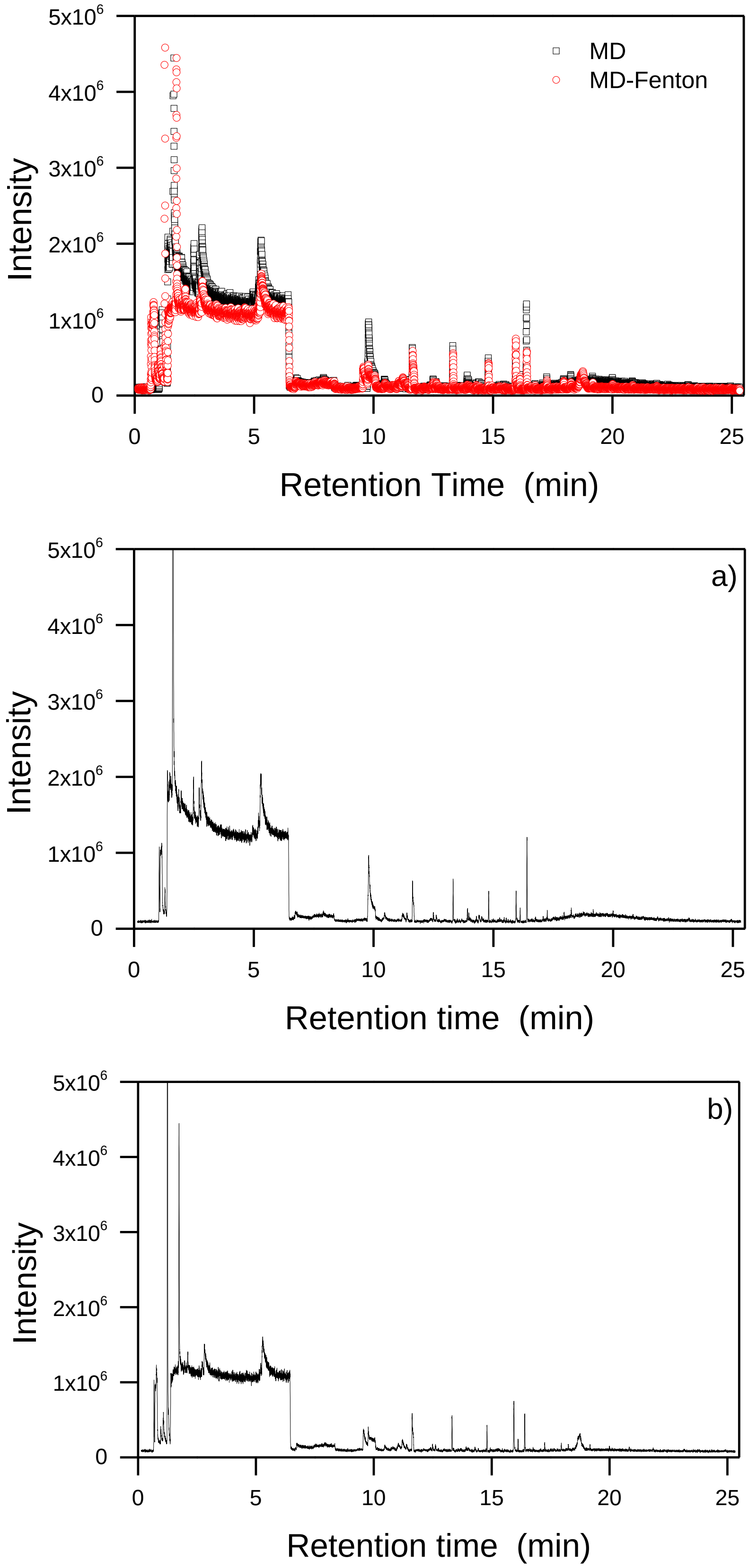


Figure S5 (a) Chromatogram of the final effluent after treatment with membrane distillation. (b) Chromatogram of the final effluent after treatment with both Fenton and membrane distillation.

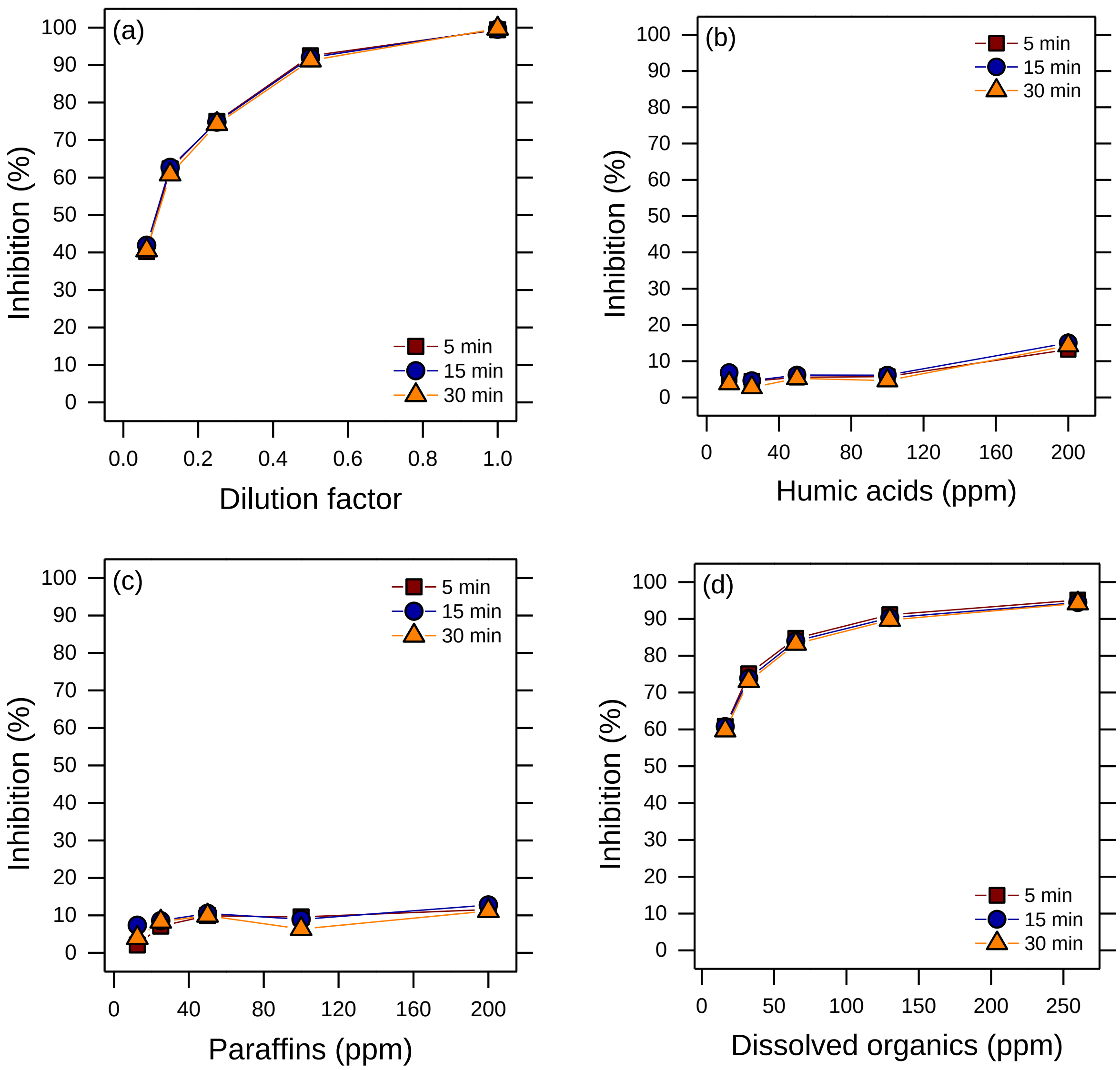


Figure S6 Toxicity curves of the (a) non-treated synthetic produced water, (b) humic acids, (c) paraffins, and (d) dissolved organic compounds as a function of concentration. The toxicity was measured after 5, 15, and 30 minutes of contact (in red, blue, and orange, respectively) with the *Vibrio Fischeri* culture.

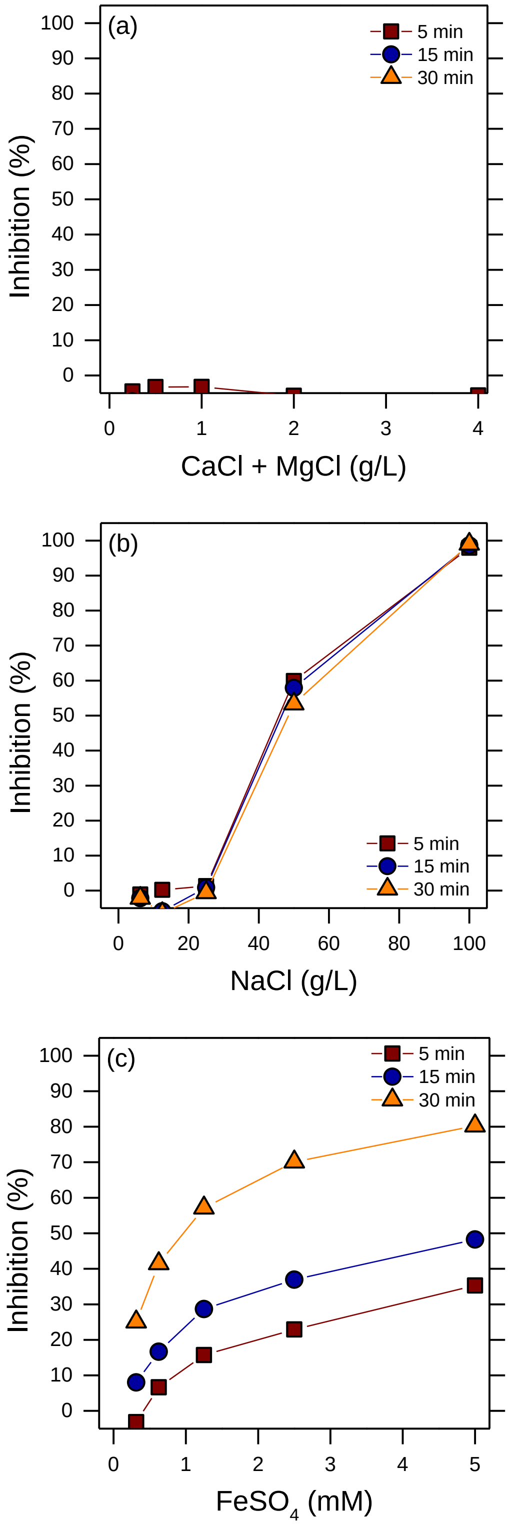
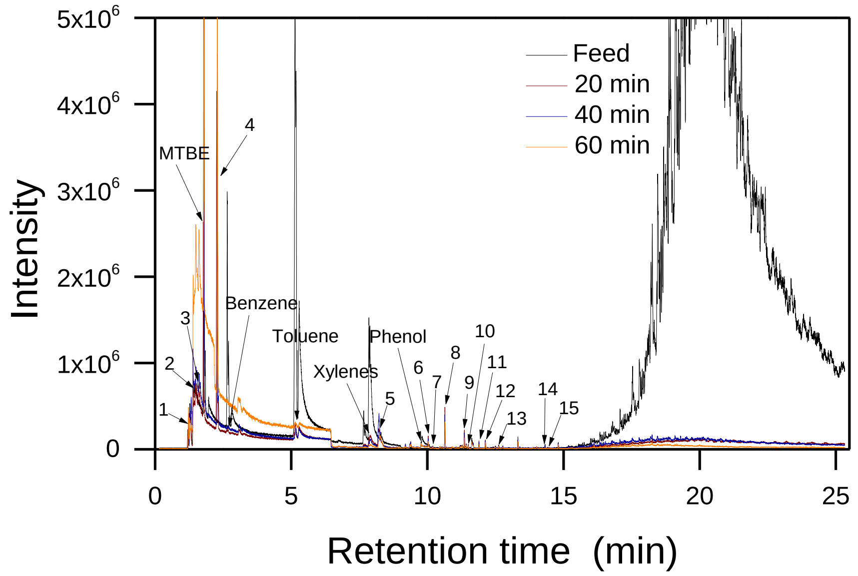
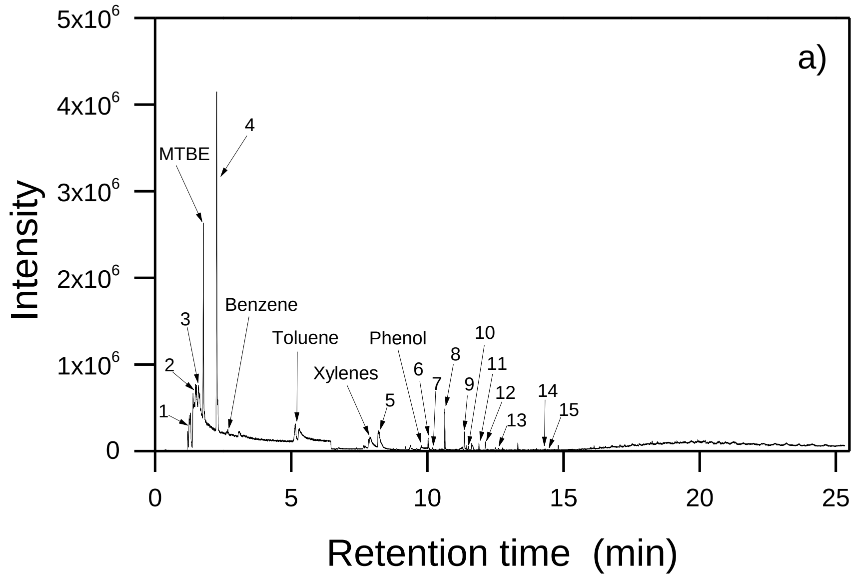


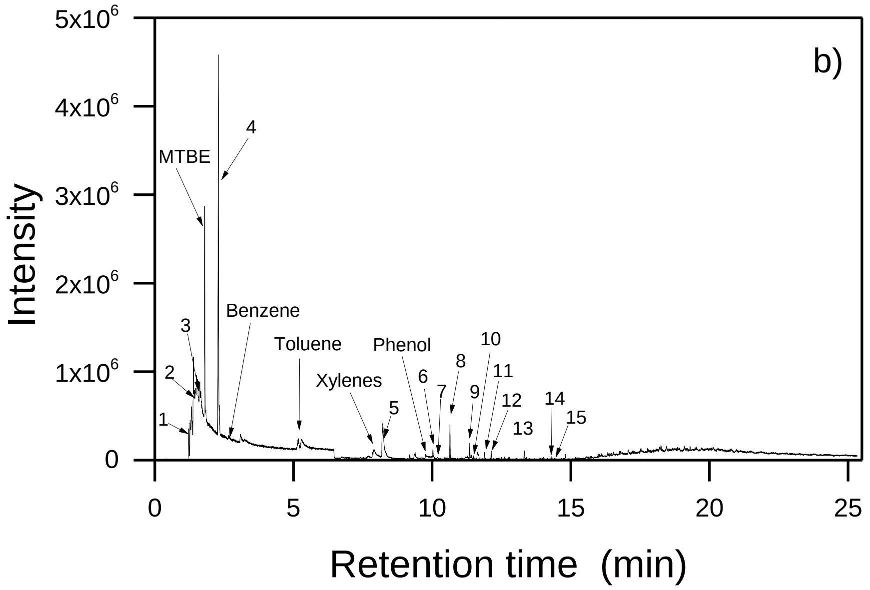
Figure S7 Toxicity curves of (a) calcium and magnesium, (b) sodium chloride, and (c) iron sulfate as a function of concentration. The toxicity was measured after 5, 15, and 30 minutes of contact (in red, blue, and orange, respectively) with the *Vibrio Fischeri* culture.



Feed
20 min
40 min
60 min
MTBE
1
2
3
4
Benzene
Toluene
Xylenes
Phenol
5
6
7
8
9
10
11
12
13
14
15
Intensity
Retention time (min)



a)
MTBE
1
2
3
4
Benzene
Toluene
Xylenes
Phenol
5
6
7
8
9
10
11
12
13
14
15
Intensity
Retention time (min)



b)
MTBE
1
2
3
4
Benzene
Toluene
Xylenes
Phenol
5
6
7
8
9
10
11
12
13
14
15
Intensity
Retention time (min)

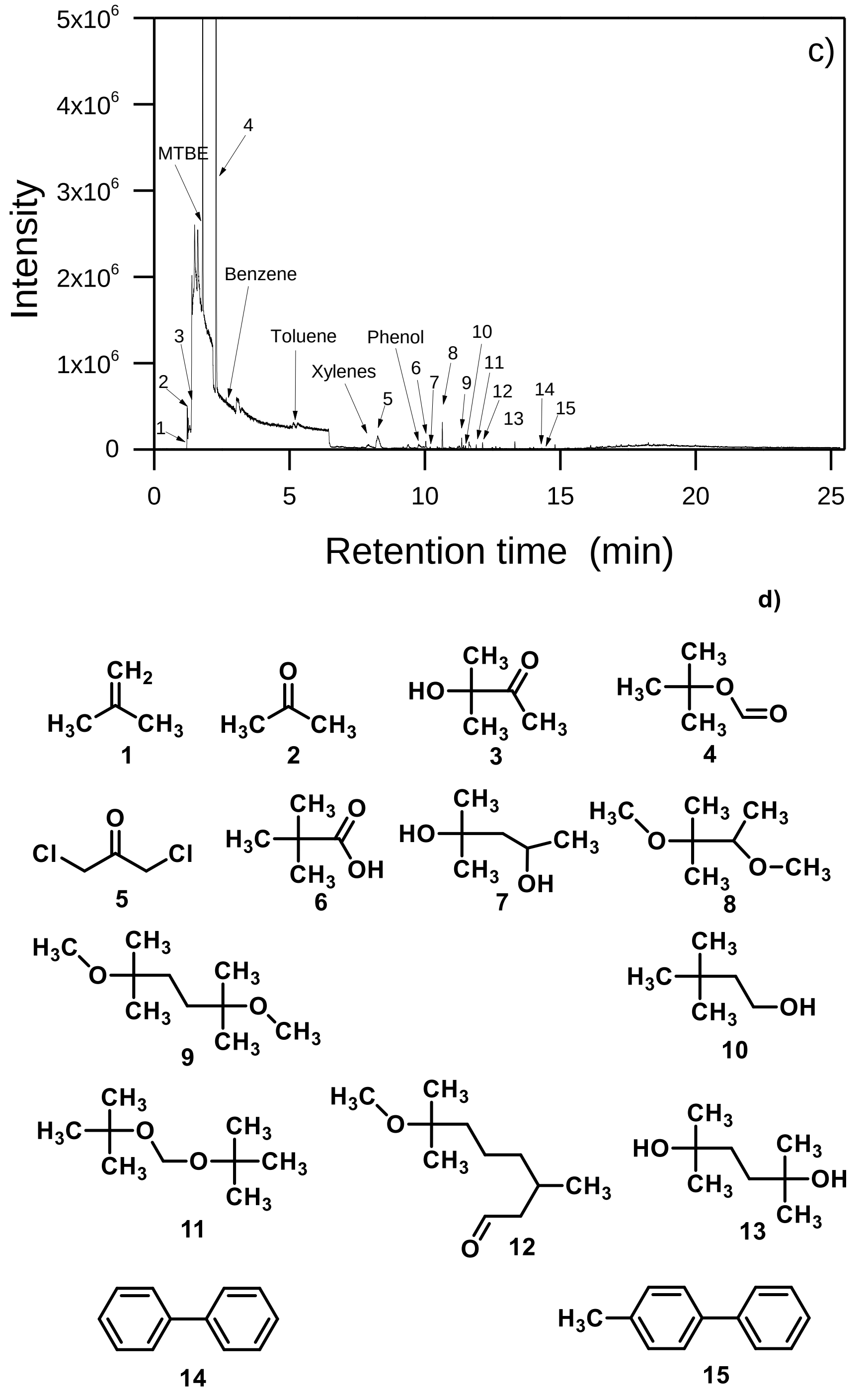
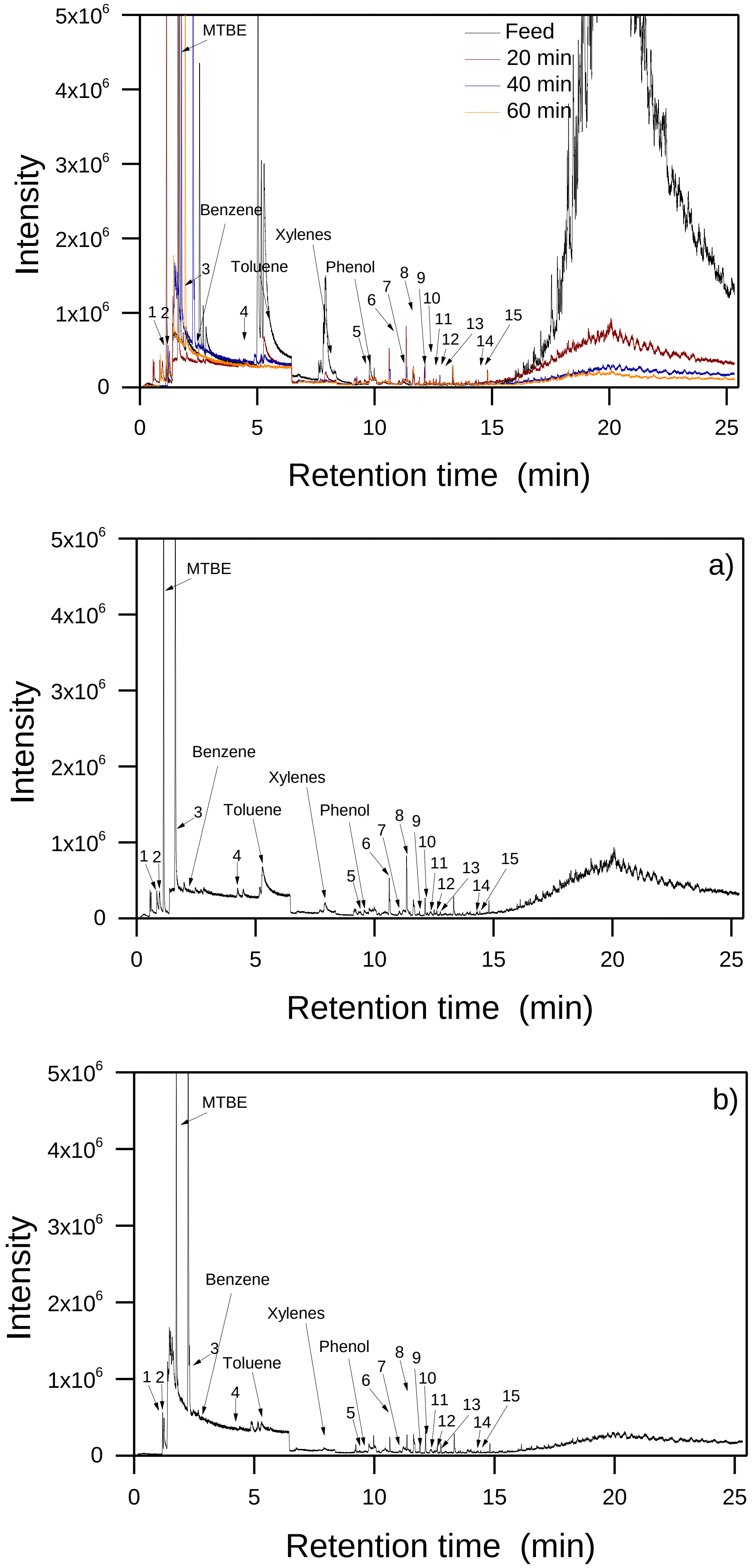
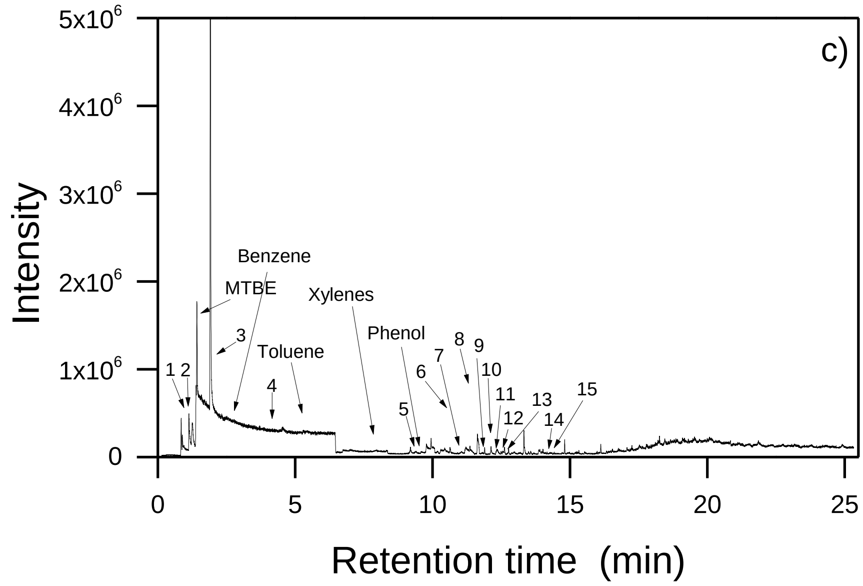


Figure S8 Chromatograms of the solution after treatment by the Fe-citrate oxidation system after (a) 20, (b) 40, and (c) 60 minutes. The numbers are related to the by-products detected and illustrated in (d). All the non-targeted are column related compounds. (d) Chemical structures of the residual by-products adsorbed onto the fiber during the SPME extraction and detected by GC-MS at the end of the reaction with the Fe-citrate system as catalyst.



Feed
20 min
40 min
60 min
MTBE
Benzene
Toluene
Xylenes
Phenol
Intensity
Retention time (min)
a)
b)



d)

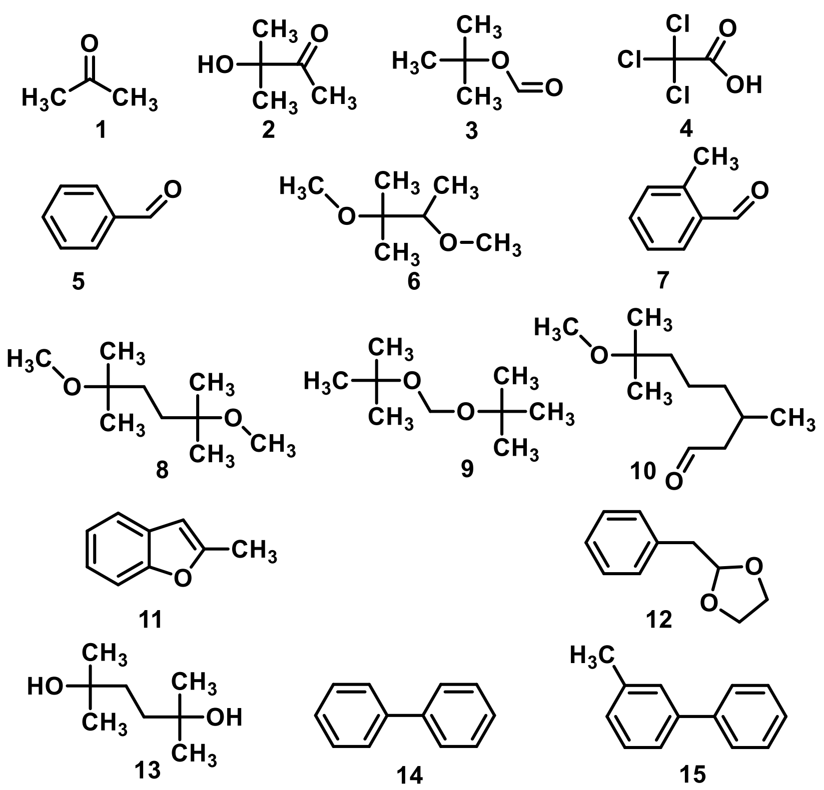


Figure S9 Chromatograms of the solution after treatment by the Fe-EDDS oxidation system after (a) 20, (b) 40, and (c) 60 minutes. The numbers are related to the by-products detected and illustrated in (d). All the non-targeted are column related compounds. (d) Chemical structures of the residual by-products adsorbed onto the fiber during the SPME extraction and detected by GC-MS at the end of the reaction with Fe-EDDS system as catalyst.

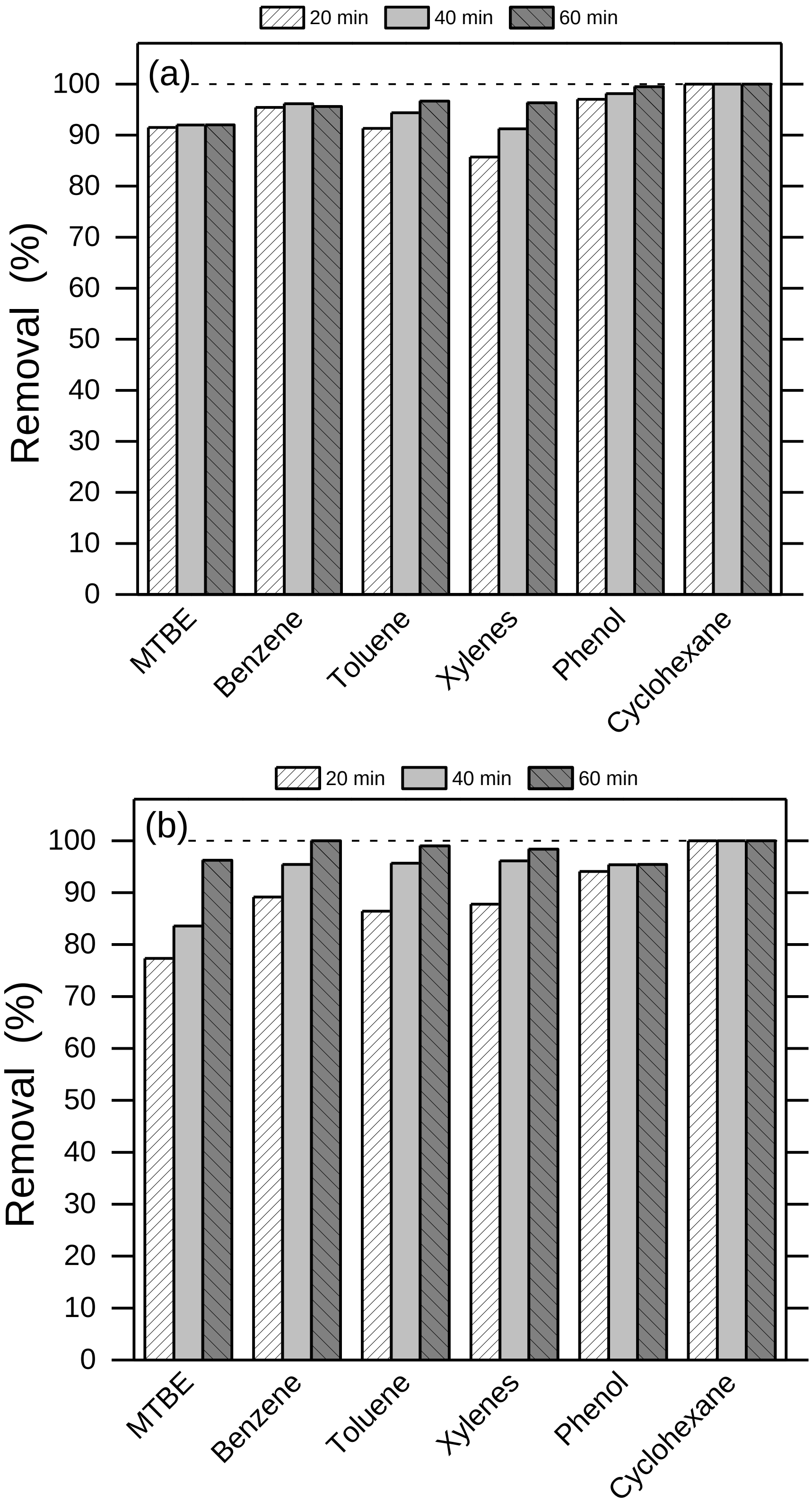
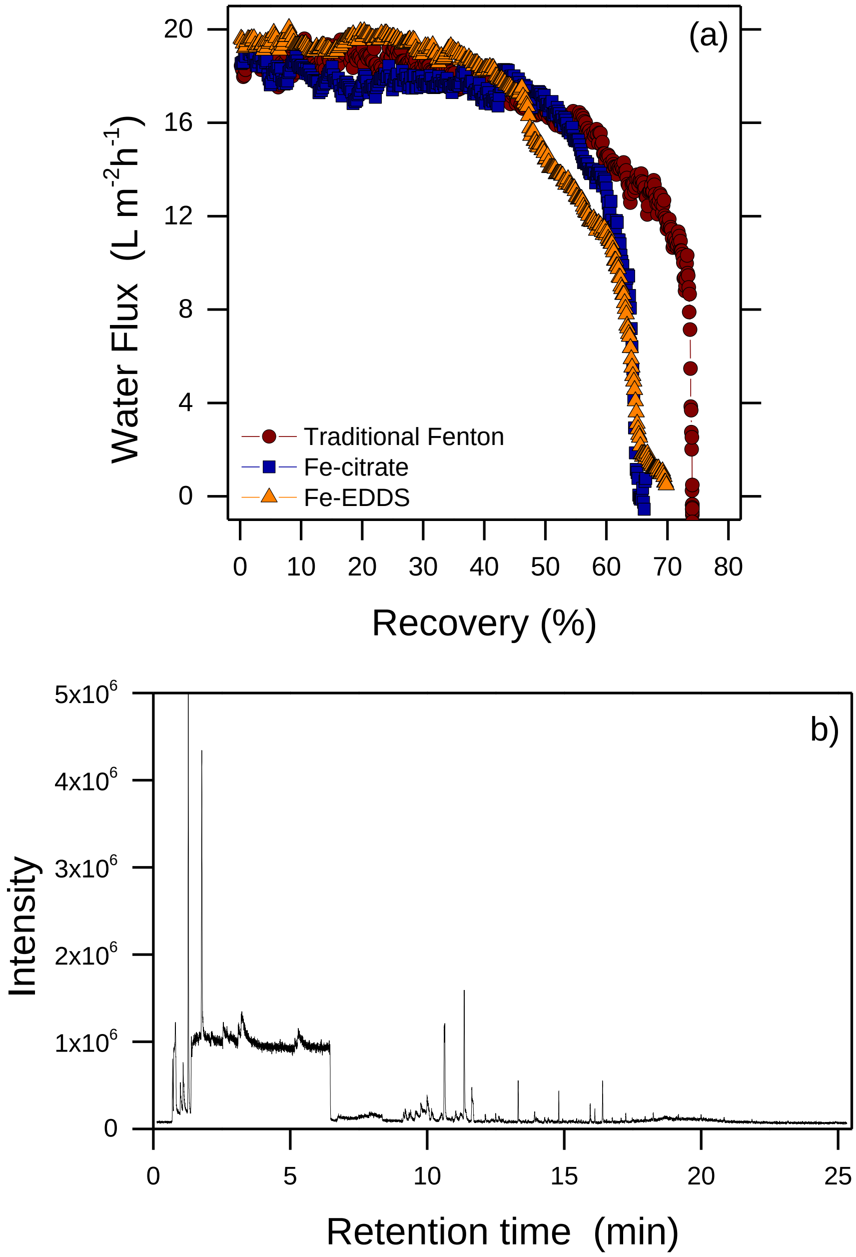


Figure S10 (a) Degradation rate of various organic compounds after 20, 40, and 60 minutes of modified Fenton treatment with (a) the Fe-citrate system and the (b) Fe-EDDS system.



(a)
Water Flux (L m-2h-1)
20
16
12
8
4
0
Traditional Fenton
Fe-citrate
Fe-EDDS
0 10 20 30 40 50 60 70 80
Recovery (%)
b)
Intensity
5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
0 5 10 15 20 25
Retention time (min)

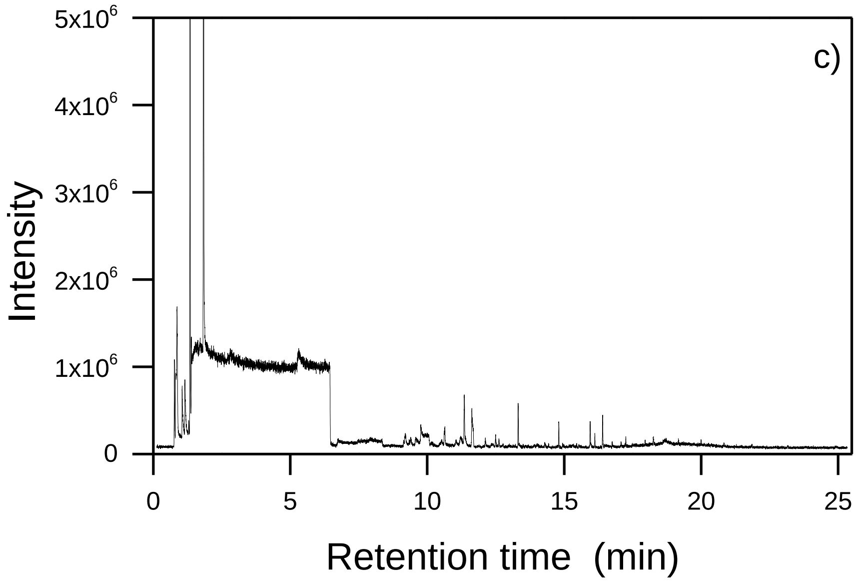


Figure S11 (a) Results of the MD filtration tests at high water recovery with different feed solutions: feed solution pre-treated by (red circles) traditional Fenton process, (blue squares) Fe-citrate system, and (orange triangles) Fe-EDDS system. Chromatograms of the final effluent after treatment with both modified-Fenton and membrane distillation for the (b) Fe-citrate oxidation pre-treatment and (c) Fe-EDDS oxidation pre-treatment. Please note that the lower recovery in the case of Fe-citrate and Fe-EDDS systems is imputable to the lower initial volume of feed, namely ~1.7 L rather than ~1.9 L as in Fenton system. A lower volume stopped the process before since the pump was not able anymore to take feed solution.