

Supplementary Material

for

Evaluation of heterogenous catalytic ozonation for micropollutants' removal from wastewater. Application of a pre-industrial level unit.

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Contents of the Supplementary Material

Supplementary Tables

Table S1 Specifications of the membrane module used	2
Table S2 Main physicochemical characteristics of materials tested as catalysts.....	2
Table S3 Chemical composition of zeolite	2
Table S4 Sampling Points.....	3
Table S5 Physicochemical characteristics of selected micropollutants at 20°C.	3

Supplementary Figures

Figure S1 Diagram (a) and view (b) of wastewater treatment plant "AINEIA"	4
Figure S2 Variation of BOD ₅ , COD, SS, T-N, NH ₄ -N, NO ₃ -N and T-P in the influent of WWTP for 2018-2021	5
Figure S3 Variation of BOD ₅ , COD, SS, T-N, NH ₄ -N, NO ₃ -N and T-P in the treated effluent of WWTP for 2018-2021	6
Figure S4 Detailed flowchart of the pre-industrial level unit.....	7
Figure S5 Photograph of the pre-industrial level unit.....	8
Figure S6 Chemical structures of selected micropollutants.....	8

Supplementary Tables

Table S1 Specifications of the membrane module used

Membrane	PTFE Hollow Fiber
Inner Diameter (mm)	1.47
Outer Diameter (mm)	1.88
Density (g/cm ³)	0.97
Porosity (%)	53
Pure Water Flux (L/min/m ² @ 2 bar)	180
Water Entry Pressure (bar)	1.93
Maximum Pore Diameter (μm)	0.741
Mean Pore Diameter (μm)	0.589
Minimum Pore Diameter (μm)	0.52
Length, L (m)	0.96
Effective Contact Area (m ²)	4.8
Number of fibers	846

Table S2 Main physicochemical characteristics of materials tested as catalysts

Zeolite	
PZC	6.8
IEP	2.2
S _{BET} , m ² /g	21
Pore volume, mL/g	0.164
PET (Polyethylene terephthalate)	
PZC	6.2
Granule size, mm	0.8-2.5
Granule Density, g/mL	0.79
Specific Surface Area, m ² /m ³	405

Table S3 Chemical composition of zeolite

%								mg/Kg	
SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Fe ₂ O ₃	LOI	NiO	Cr ₂ O ₃
70.5	12.1	0.58	2.91	1.45	2.82	0.67	8.9*	ND	ND

*Determination at 900 °C as clarified by TG-DTA

Table S4 Sampling Points

Symbol	Name	Description
P0	Secondary effluent	- Secondary treatment effluent wastewater before conventional disinfection (simple ozonation) and - Influent wastewater to the pre-industrial pilot unit
P1	1 st Bed effluent	Effluent wastewater after the post filtration (1 st Fix-Bed) in the pre-industrial pilot unit
P2	Membrane	Effluent wastewater after the membrane in the pre-industrial pilot unit
P3	2 nd Bed effluent	Effluent wastewater after the catalytic ozonation (2 nd Fix-Bed) in the pre-industrial pilot unit
P4	3 rd Bed effluent	Effluent wastewater after the biological stabilization (3 rd Fix-Bed) in the pre-industrial pilot unit

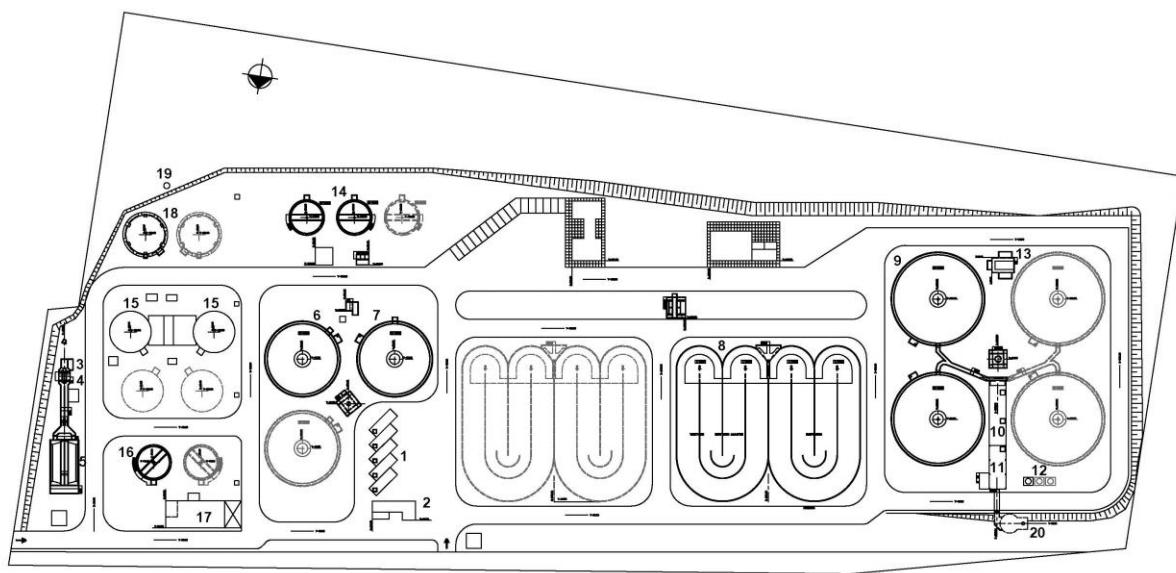
Table S5 Physicochemical characteristics of selected micropollutants at 20°C.

Micropollutant	Molecular weight	Log D at pH 8	pK_a	k_{O3} (M⁻¹s⁻¹)	k_{OH} (M⁻¹s⁻¹)	Reference
p-CBA	156.6	-1.15	4.07	0.15	5*10 ⁹	[1,2]
Benzotriazole	119.1	1.21	9.04	20	7.6*10 ⁹	[1,3]
Paracetamol	151.2	0.91	9.5	2.57*10 ⁶	7.1*10 ⁹	[1,4]
Caffeine	194.2	-0.55	14	650	4.1*10 ⁹	[1,5]

References

1. Mandal, S. Reaction rate constants of hydroxyl radicals with micropollutants and their significance in advanced oxidation processes. *J. Adv. Oxid. Technol.* 2018, 21, 178-195.
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4. El Najjar, N.H., Touffet, A., Deborde, M., Journel, R., Vel Leitner, N.K. Kinetics of paracetamol oxidation by ozone and hydroxyl radicals, formation of transformation products and toxicity. *Sep. Purif. Technol.* 2014, 136, 137-143.
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Supplementary Figures



GENERAL ARRANGEMENT PLAN LEGEND

- | | | | |
|---|-------------------------------------|----|----------------------------|
| 1 | SEPTIC WASTEWATER RECEPTION STATION | 10 | OZONE CONTACT UNIT |
| 2 | SEPTIC WASTEWATER PRETREATMENT UNIT | 11 | OZONE PRODUCTION STATION |
| 3 | INFLOW CHAMBER | 12 | LIQUID OXYGEN STORAGE TANK |
| 4 | SCREENING STATION | 13 | RAS & SAS PUMPING STATION |
| 5 | GRIT & GREASE REMOVAL | 14 | SLUDGE THICKENERS |
| 6 | PST (PRIMARY SEDIMENTATION TANK) | 15 | ANAEROBIC SLUDGE DIGESTERS |
| 7 | SEPTIC WASTEWATER BALANCING TANK | 16 | SLUDGE POST-THICKENER |
| 8 | BIOREACTOR | 17 | SLUDGE DEWATERING STATION |
| 9 | FST (FINAL SEDIMENTATION TANK) | 18 | GAS HOLDER |
| | | 19 | GAS FLARE |
| | | 20 | EFFLUENT CHAMBER |

LINE'S LEGEND

- | | |
|---|-----------------|
| — | OPERATING UNITS |
| — | FUTURE UNITS |

(a)



(b)

Figure S1 Diagram (a) and view (b) of wastewater treatment plant "AINEIA"

Influent of WWTP

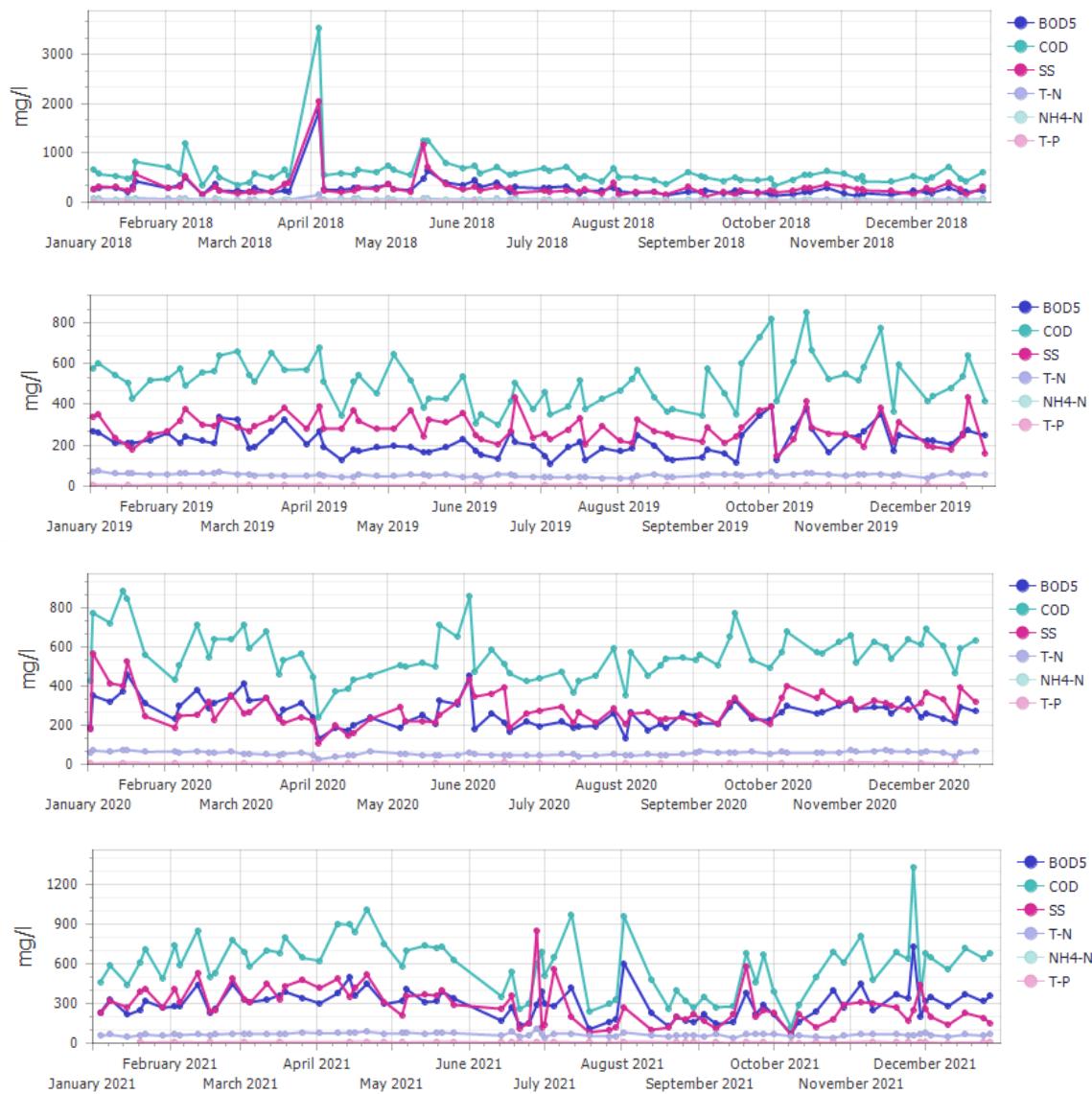


Figure S2 Variation of BOD₅, COD, SS, T-N, NH₄-N, NO₃-N and T-P in the influent of WWTP for 2018-2021 (*Data obtained from <http://astikalimata.ypeka.gr/Services/Pages/WtpViewApp.aspx#>*)

where,

BOD₅: Biological oxygen demand (in five days)

COD: Chemical oxygen demand

SS: Suspended solids

T-N: Total nitrogen

NH₄-N: Ammonium nitrogen

NO₃-N: Nitrate nitrogen

T-P: Total phosphorus

Treated effluent of WWTP

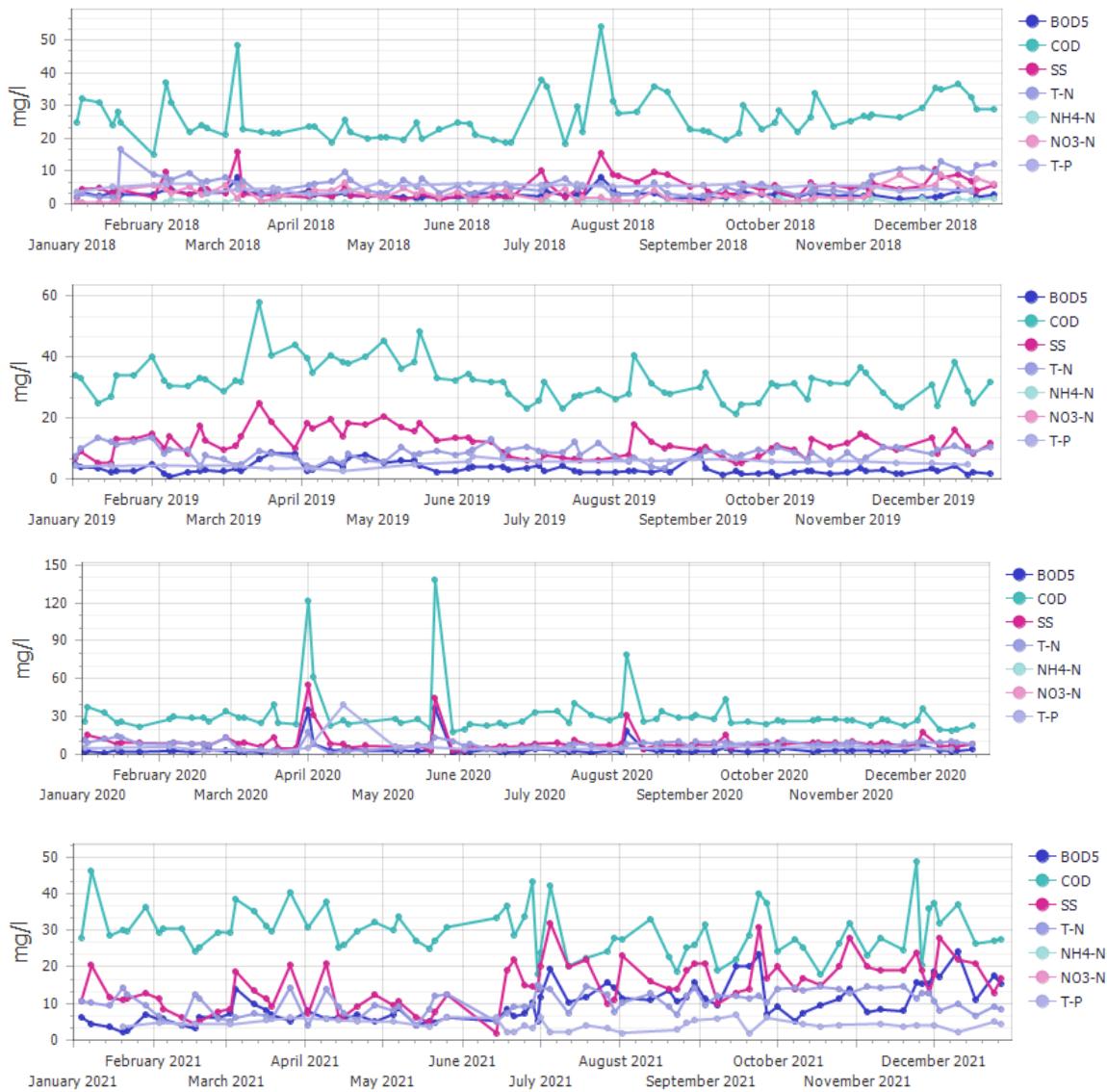


Figure S3 Variation of BOD₅, COD, SS, T-N, NH₄-N, NO₃-N and T-P in the treated effluent of WWTP for 2018-2021 (*Data obtained from <http://astikalimata.ypeka.gr/Services/Pages/WtpViewApp.aspx#>*)

where,

BOD₅: Biological oxygen demand (in five days)

COD: Chemical oxygen demand

SS: Suspended solids

T-N: Total nitrogen

NH₄-N: Ammonium nitrogen

NO₃-N: Nitrate nitrogen

T-P: Total phosphorus

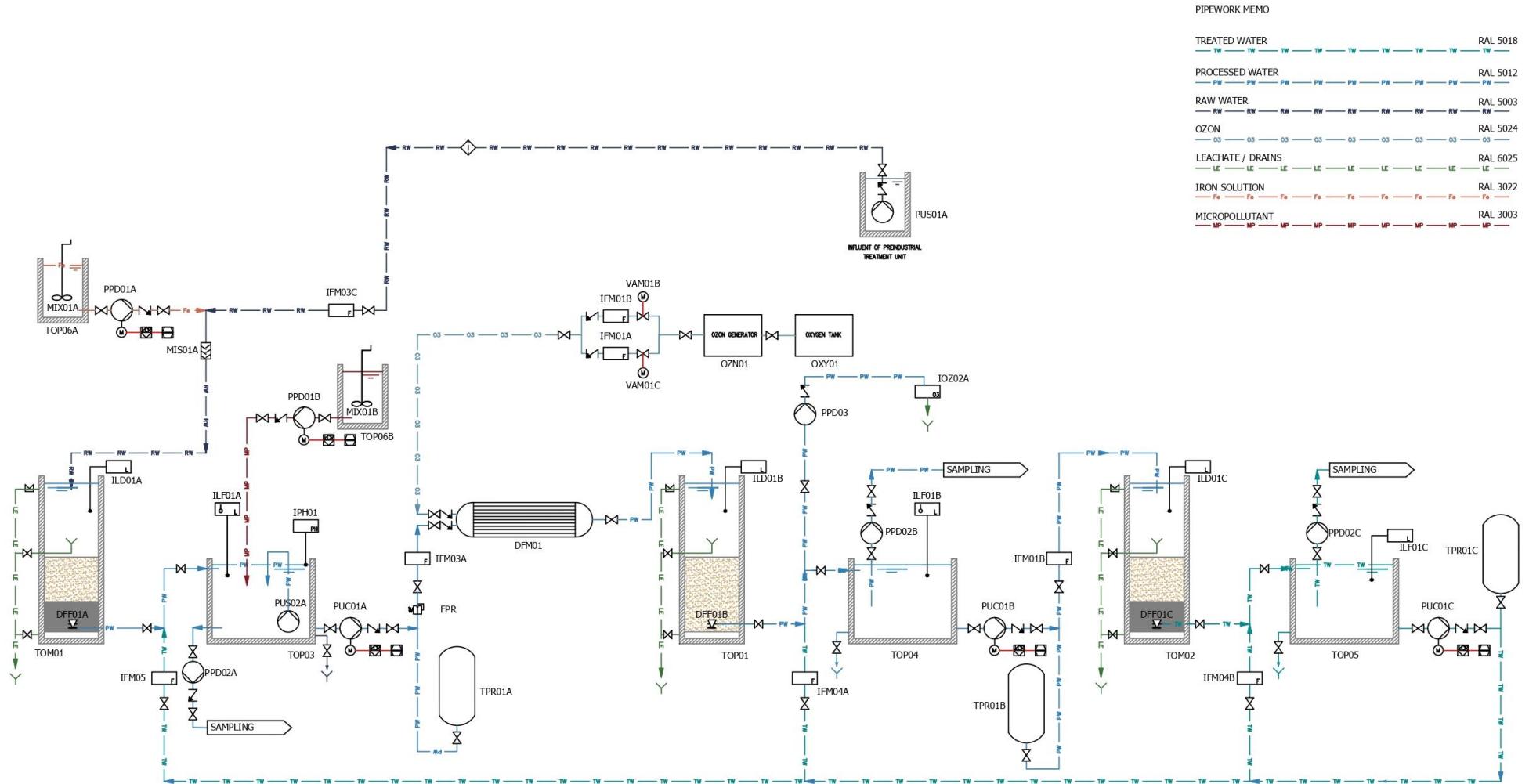


Figure S4 Detailed flowchart of the pre-industrial level unit



Figure S5 Photograph of the pre-industrial level unit

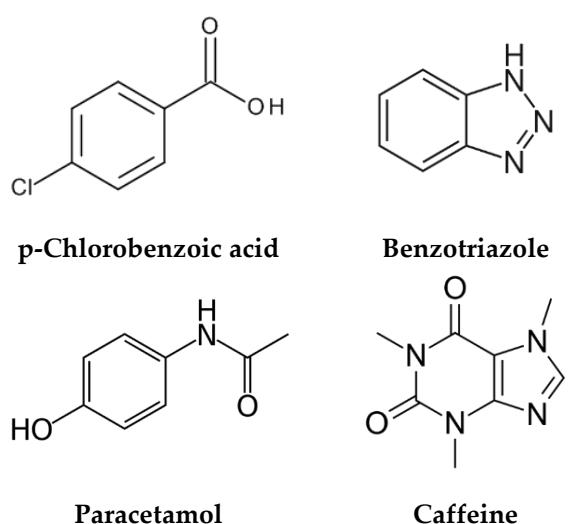


Figure S6 Chemical structures of selected micropollutants