



Sveučilište u Zagrebu
Fakultet kemijskog
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Davor Dolar



**Reuse of municipal wastewater for agricultural irrigation
by membrane processes**

**Oporaba komunalne otpadne vode za navodnjavanje
membranskim procesima**



Water for all 2019

March 21-22. 2019., Osijek, Croatia





Government
of the Republic
of Croatia

**Direct reuse of municipal wastewater for agriculture irrigation with membrane technologies
(ReHOHMem)**

Project is financed within the Program for encouraging research and development activities in the field of climate change for period 2015 and 2016

**Content of this publication is responsibility of Faculty of chemical engineering and technology*



REPUBLIC OF CROATIA

MINISTRY OF ENVIRONMENTAL
AND NATURE PROTECTION



ministry of science
education and sports



FOND ZA ZAŠTITU OKOLIŠA I
ENERGETSKU UČINKOVITOST



hrzz
Croatian Science
Foundation

■ ReHOHMem project

- » Financed (1.492.908,72 HRK) by:
 - » Government of Republic of Croatia and partner institutions:
 - » Ministry od Science and Education
 - » Ministry of Environment and Energy
 - » Environmental Protection and Energy Efficiency Fund
 - » Croatian Science Foundation
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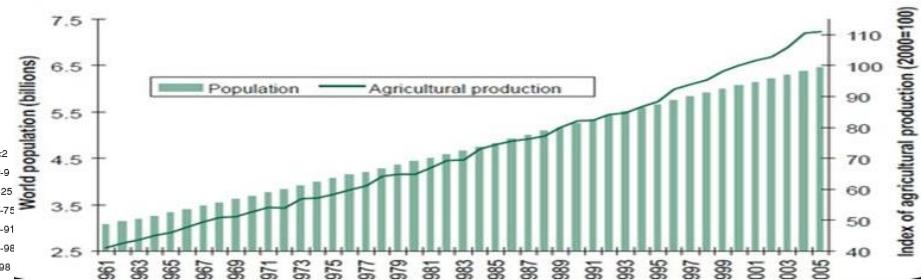
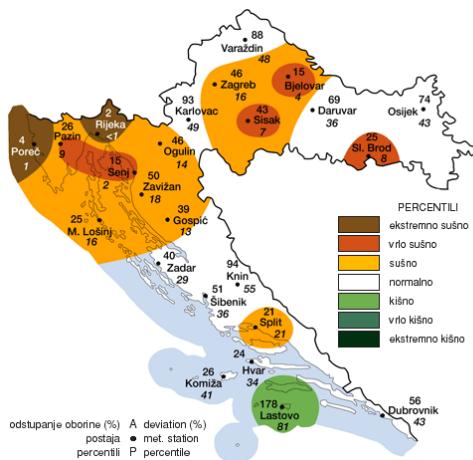
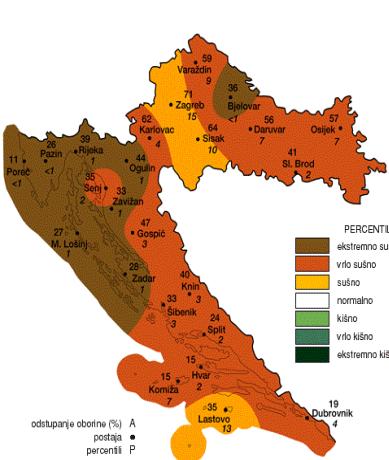
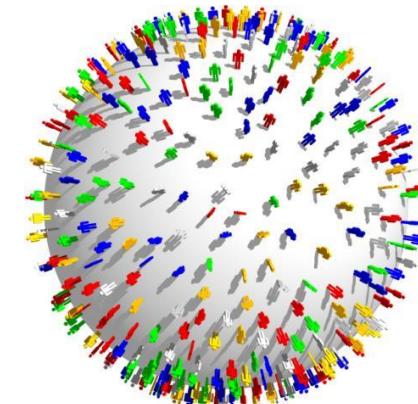
- Treat municipal wastewater (MWW) with membrane bioreactor (MBR), nanofiltration (NF), and reverse osmosis (RO)
- Physico-chemical and microbiological parameters compared to WHO and EU guidelines
- Removal of contaminants of emerging concern (CEC) from Watch List (WL)
- Reuse effluent for agricultural irrigation



FKIT MCMXIX



Introduction





APPROPRIATE
TREATMENT





FKIT MCMXIX



Introduction

Croatia

- No regulations for reuse
- No wastewater reuse
- 150 WWTP – 4.33 million PE

	2008.	2009.	2010.	2011.	2012.	2013.	2014.	2015.	2016.	2017.
Otpadne vode, tis. m³ <i>Waste water, '000 m³</i>										
Ukupno <i>Total</i>	322 718	324 781	301 030	342 800	328 553	393 544	363 353	366 872	364 790	378 398
Kućanstva <i>Households</i>	128 403	127 033	189 332	182 646	184 408	194 052	175 708	179 586	174 203	178 382
Djelatnosti <i>Activities</i>	100 803	99 883	54 656	86 335	62 477	71 318	62 351	72 528	77 227	76 800
Komunalne usluge <i>Public utilities services</i>	-	-	-	-	-	-	-	-	-	-
Ostale vode <i>Other waters</i>	93 512	97 865	57 042	73 819	81 668	128 174	125 294	114 758	113 360	123 216





Materials and methods



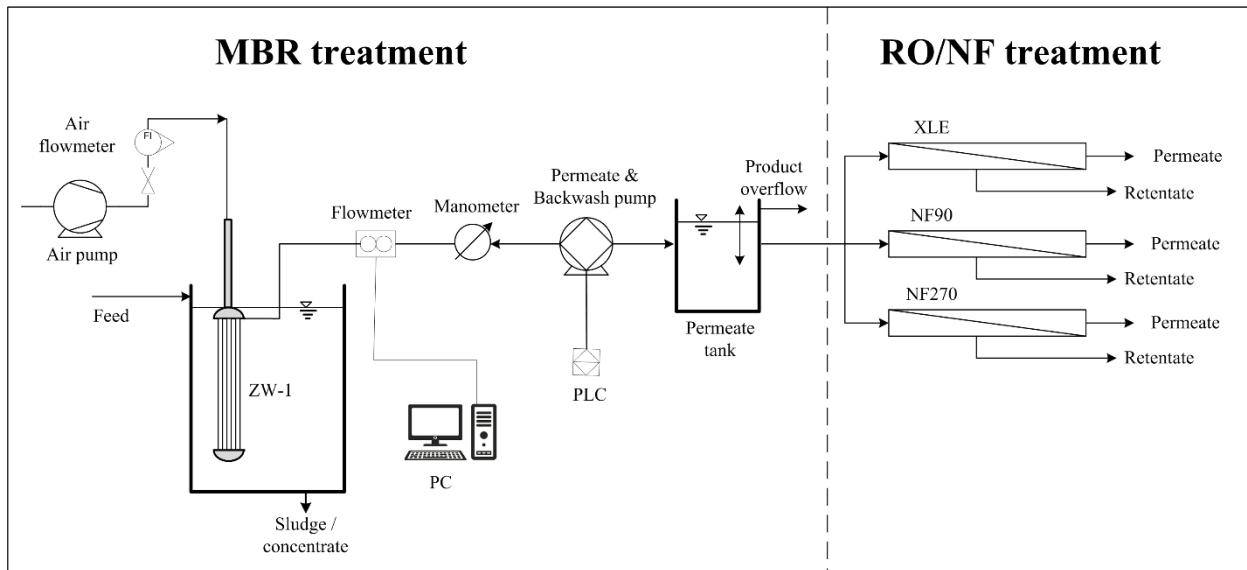
WWTP Čakovec (red dot sampling point)

Physico-chemical: electrical conductivity (EC_w); pH; turbidity; chemical oxygen demand (COD); biological oxygen demand (BOD_5); dissolved organic carbon (DOC); total suspended solids (TSS); total nitrogen (TN), content of PO_4^{3-} , NO_3^- , NO_2^- , NH_4^+ , F^- , Cl^- , Br^- , SO_4^{2-} , Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}

Trace elements: Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, V, and Zn

Microbiological analysis: total coliforms (TC), *Escherichia coli* (EC), *Enterococcus* (ENT), Total colony count at 36 °C (TC36), Total colony count at 22 °C (TC22), and *Pseudomonas aeruginosa* (PA)

CEC: diclofenac, erythromycin, clarithromycin, azithromycin, methiocarb, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid, oxadiazon, tri-allate



	Period I	Period II
Temperature, °C	24.15±1.09	22.84±1.50
TMP, bar	-0.02	-0.04
Permeate flux, L m ⁻² h ⁻¹	12.26±3.99	24.67±2.67
HRT, h	8.7	4.4
MLSS, g L ⁻¹	9.34±1.71	12.47±1.38
Air supply, L min ⁻¹	20	

12 bar

RO – XLE

NF – NF90 and NF270



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Results and discussion

Real MWW characteristics during the monitoring of six months

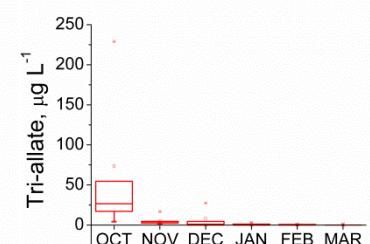
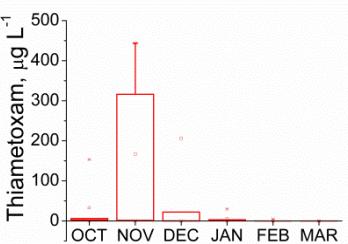
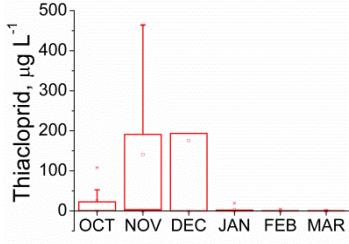
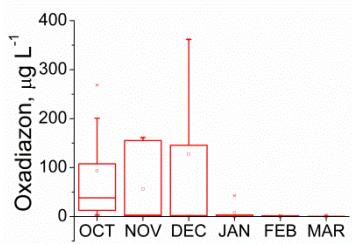
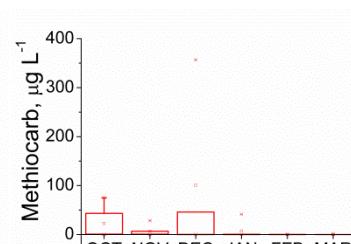
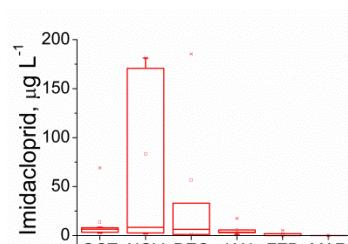
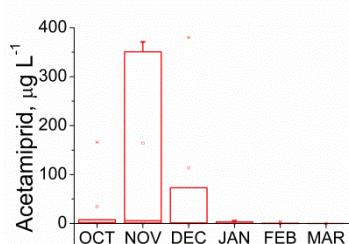
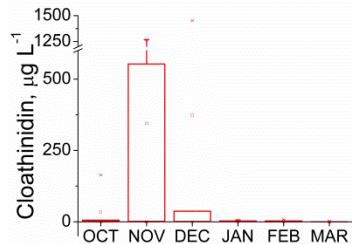
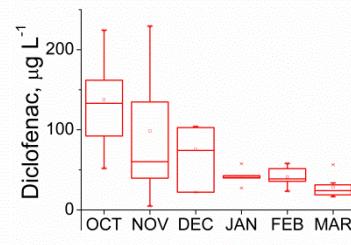
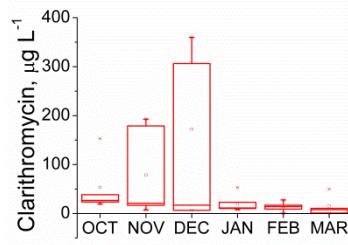
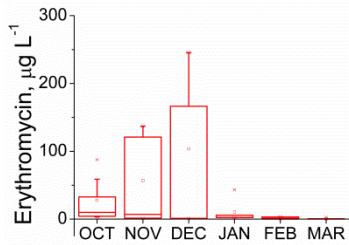
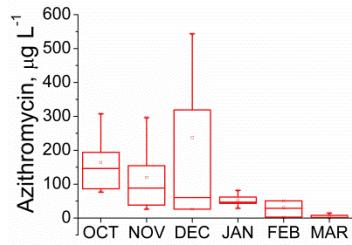
Months Parameter	Unit	October	November	December	January	February	March	Yearly Average
Physico-chemical characteristics								
<i>t</i>	°C	17.2	12.6	10.2	11.2	10.2	9.7	14.6±4.0
turbidity	NTU	83.8	57.3	56.4	21.5	15.7	7.65	62.6±37.2
pH	-	7.64	7.73	7.76	7.78	7.82	7.82	7.7±0.1
EC _w	µS cm ⁻¹	1200	713	816	726	711	634	871.7±177.1
COD	mg L ⁻¹	857	491	444	212	137	110	551±298
BOD	mg L ⁻¹	451	241	233	93	60	35	265±150
TSS	mg L ⁻¹	273	137	138	44	29	42	182±129
PO ₄ ³⁻	mg L ⁻¹	5.79	7.59	3.20	1.84	1.63	1.08	3.77±1.93
TP	mg L ⁻¹	7.50	5.08	4.26	2.58	2.12	1.25	4.67±1.98
TN	mg L ⁻¹	62.30	39.35	43.36	21.10	19.26	12.49	38.38±14.69
NO ₂ ⁻	mg L ⁻¹	0	0.04	0.04	0.34	0.26	0.44	0.10±0.15
DOC	mg L ⁻¹	101.6	57.2	10.5	42.2	61.1	15.0	64.0±29.5
F ⁻	mg L ⁻¹	0.410	0.26	0	0	0	0	0.331±0.398
Cl ⁻	mg L ⁻¹	155.4	70.37	82.56	87.28	116.2	118.2	113.6±42.47
Br ⁻	mg L ⁻¹	0	1.920	4.57	0	0	1.48	0.721±1.376
NO ₃ ⁻	mg L ⁻¹	0.85	31.59	2.17	0.50	0.88	21.75	53.15±112.74
SO ₄ ²⁻	mg L ⁻¹	116.8	31.42	34.60	58.36	66.74	65.00	53.86±24.97
Na ⁺	mg L ⁻¹	124.7	63.95	70.61	29.30	36.60	33.21	72.71±33.53
NH ₄ ⁺	mg L ⁻¹	21.93	6.85	0.02	10.59	11.22	7.11	19.73±15.07
K ⁺	mg L ⁻¹	24.15	3.67	0	7.14	7.72	6.51	12.66±8.25
Mg ²⁺	mg L ⁻¹	20.59	3.29	0	14.20	17.04	18.75	16.38±8.68
Ca ²⁺	mg L ⁻¹	75.60	16.83	3.20	37.13	44.89	50.32	51.68±26.37

Concentrations (Log ₁₀) of bacterial indicators								
Total coliforms	cfu 100 mL ⁻¹	7.63	6.93	7.12	6.50	6.57	6.19	6.92±0.58
<i>Escherichia coli</i>	cfu 100 mL ⁻¹	6.93	6.05	6.52	6.05	5.79	5.44	6.21±0.72
Enterococco	cfu 100 mL ⁻¹	5.81	5.39	5.82	5.35	5.30	4.86	5.53±0.37
Total colony count at 37 °C	cfu 1 mL ⁻¹	6.88	6.17	6.31	5.77	5.35	4.84	6.23±0.67
Total colony count at 22 °C	cfu 1 mL ⁻¹	7.10	6.54	6.81	6.16	6.13	5.63	6.65±0.51
Pseudomonas aeruginosa	cfu 100 mL ⁻¹	-	-	-	0	-	0	0

Trace elements								
Al	µg L ⁻¹	75.8	61.4	48.4	21.1	11.7	10.3	47.4±22.9
As	µg L ⁻¹	0.714	0.763	0.521	0.476	0.541	0.980	0.651±0.205
Cd	µg L ⁻¹	0.030	0.025	0.026	0.016	0.014	0.014	0.023±0.005
Co	µg L ⁻¹	0.332	0.374	0.648	0.508	0.408	0.381	0.416±0.096
Cr	µg L ⁻¹	0.887	0.691	0.668	0.423	0.296	0.250	0.633±0.196
Cu	µg L ⁻¹	7.48	6.24	5.42	2.84	2.42	12.5	6.30±2.85
Fe	µg L ⁻¹	181	202	213	136	95.3	50.6	178±85
Li	µg L ⁻¹	5.55	3.40	3.46	2.83	2.66	2.73	3.61±0.82
Mn	µg L ⁻¹	65.6	67.7	60.6	37.9	43.3	24.5	53.7±13.7
Mo	µg L ⁻¹	1.92	0.911	0.620	0.597	0.643	0.630	0.971±0.425
Ni	µg L ⁻¹	2.57	1.87	1.64	1.06	0.880	0.918	1.84±0.60
V	µg L ⁻¹	0.427	0.691	2.42	0.423	0.296	0.250	0.597±0.562
Zn	µg L ⁻¹	42.6	31.0	19.4	15.8	23.9	21.9	28.0±13.0

Results and discussion

Concentration of CECs during the six months of monitoring





Results and discussion

MWW and MBR effluent characteristics during the two experimental periods with removal efficiencies.

	Period I			Period II		
	MWW	MBR effluent	R, %	MWW	MBR effluent	R, %
DOC, mg L⁻¹	87.41±19.09	15.41±4.84	82.21	112.05±19.87	21.02±3.20	80.66
COD, mg O₂ L⁻¹	438.71±264.17	36.40±13.74	89.83	765.50±422.25	24.66±4.79	95.80
BOD₅, mg O₂ L⁻¹	589.64±378.29	25.00±14.15	94.12	792.14±518.60	15.07±6.01	97.38
TN, mg N L⁻¹	n.a.	n.a.	-	71.09±11.90	44.96±9.31	36.56
pH	7.34±0.16	7.68±0.23	-	7.19±0.11	7.79±0.07	-
EC_w, µS cm⁻¹	1378±196	1150±150	16.41	1267±45	1025±38	19.09
Turbidity, NTU	116.26±103.21	0.79±0.54	98.52	233.97±97.51	0.50±0.34	99.75
Ions, mg L⁻¹						
F⁻	0.37±0.40	0.12±0.02	66.69	0.60±1.04	0.13±0.02	77.81
Cl⁻	158.23±48.01	153.68±47.69	2.88	75.30±23.30	83.32±13.29	-10.66
NO₂⁻	0.00±0.00	3.66±4.55	-	0.06±0.08	1.60±0.50	-2405.82
Br⁻	0.05±0.09	0.00±0.00	99.83	0.01±0.03	0.00±0.00	100.00
NO₃⁻	1.68±0.79	226.87±60.75	-	2.36±3.11	189.83±18.38	-
PO₄³⁻	44.88±18.05	58.66±36.46	-30.70	19.18±5.34	11.74±9.89	38.79
SO₄²⁻	45.16±16.75	58.40±14.42	-29.32	21.04±9.42	40.16±4.27	-90.87
Li⁺	0.00±0.00	0.00±0.00	-	0.00±0.00	0.00±0.00	-
Na⁺	98.14±30.25	97.57±27.77	0.58	69.28±18.61	74.05±5.58	-6.88
NH₄⁺	17.42±2.40	0.00±0.00	100	16.48±4.59	0.63±0.85	96.18
K⁺	28.67±10.63	31.92±4.47	-11.34	20.12±5.52	21.77±3.53	-8.21
Mg²⁺	21.15±1.34	23.79±3.96	-12.47	19.72±5.00	20.28±1.02	-2.84
Ca²⁺	93.38±2.77	81.25±4.98	12.98	88.96±22.54	92.89±1.25	-4.41
SAR	2.39±0.76	2.45±0.70	-	1.72±0.36	1.83±0.14	-
PAR	0.41±0.15	0.47±0.06	-	0.29±0.06	0.31±0.05	-



Results and discussion

Concentration of CEC detected in the MWW and in the MBR effluent.

CEC, $\mu\text{g L}^{-1}$	Period I		Period II			
	MWW	MBR effluent	R, %	MWW	MBR effluent	R, %
Azithromycin	0.68 \pm 0.23	0.32 \pm 0.02	52.62	11.90 \pm 16.19	9.13 \pm 7.08	23.25
Erythromycin	0.044 \pm 0.062	0.06 \pm 0.09	-44.44	0.11 \pm 0.16	0.30 \pm 0.23	-167.95
Clarithromycin	6.08 \pm 3.74	1.56 \pm 1.14	74.25	1.54 \pm 0.22	0.43 \pm 0.06	71.87
Diclofenac	87.80 \pm 25.14	80.71 \pm 19.81	8.07	36.04 \pm 6.78	28.06 \pm 10.57	22.13
Imidacloprid	1.44 \pm 2.03	1.70 \pm 2.40	-18.07	n.d.	n.d.	-
Methiocarb	0.228	<LOQ	>99.9	n.d.	n.d.	-
Clothianidin	3.99 \pm 4.79	0.46 \pm 0.25	88.37	n.d.	n.d.	-
Acetamiprid	2.32 \pm 3.22	1.40 \pm 1.99	39.36	n.d.	n.d.	-
Thiamethoxam	3.18 \pm 4.79	3.14 \pm 3.79	1.05	n.d.	n.d.	-
Oxadiazon	1.72 \pm 1.28	1.15 \pm 0.88	33.15	0.114.	0.110	-
Tri-allate	0.29	<LOQ	>99.9	n.d.	n.d.	-



Results and discussion

MBR effluents (feed) and NF270, NF90, and XLE permeate together with removal efficiencies.

	NF270			NF90			XLE		
	feed	permeate	R, %	feed	permeate	R, %	feed	permeate	R, %
DOC, mg L ⁻¹	27.01	0.962	96.43	16.09	2.1338	86.74	17.42	2.1662	87.6
COD, mg O ₂ L ⁻¹	22.7	<5	>77,97	25.8	5.7	77.91	23.8	6.67	72
BOD ₅ , mg O ₂ L ⁻¹	13	<4	>69.23	15	<4	>73.33	13	<4	>69.23
TN, mg N L ⁻¹	46.7	39.2	16.06	49.9	12.6	73.13	49.6	<5	>89.92
pH	7.81	7.82	-	7.9	7.33		7.84	7.15	
EC _w , µS cm ⁻¹	1000	444	55.60	1083	69.7	93.56	1083	55.5	94.90
Turbidity, NTU	0.298	0.13	56.37	0.406	0.2	50.74	0.404	0.436	-7.92
Ions, mg L ⁻¹									
F ⁻	8.96	0.28	96.91	0.20	0.05	73.06	0.19	0.06	67.88
Cl ⁻	18.62	31.04	-66.68	108.72	3.55	96.73	103.59	2.59	97.50
NO ₂ ⁻	0.42	0.90	-111.35	2.53	0.25	90.03	2.16	0.18	91.76
Br ⁻	0.00	0.00		0.00	0.00		0.00	0.00	
NO ₃ ⁻	49.65	168.21	-238.81	240.73	25.11	89.57	238.24	20.65	91.33
PO ₄ ³⁻	1.94	0.00	>99.99	21.66	0.00	>99.99	18.26	0.69	96.20
SO ₄ ²⁻	8.35	0.46	94.50	44.46	0.22	99.50	45.35	0.41	99.10
Li ⁺	0.00	0.00		0.00	0.00		0.00	0.00	
Na ⁺	70.68	40.87	42.18	80.29	9.41	88.28	80.77	6.84	91.54
NH ₄ ⁺	0.00	0.73		0.00	0.29		0.00	0.93	
K ⁺	20.13	11.15	44.60	22.18	3.20	85.57	23.97	3.23	86.51
Mg ²⁺	20.55	3.44	83.26	22.06	0.15	99.31	21.76	0.25	98.86
Ca ²⁺	96.37	30.51	68.34	95.22	1.06	98.89	94.91	1.40	98.53
SAR	1.71	1.87	-	1.93	0.31	-	1.94	0.34	-
PAR	0.29	0.30	-	2.26	0.45	-	1.40	0.39	-



Results and discussion

Concentrations of CEC in NF270, NF90, and XLE feed and permeate with removal efficiencies.

CEC, $\mu\text{g L}^{-1}$	NF270			NF90			XLE		
	feed	permeate	R, %	feed	permeate	R, %	feed	permeate	R, %
Azithromycin	0.1933	0.0385	80.08	0.2145	<LOQ	>99.9	0.1405	<LOQ	>99.9
Clarithromycin	0.3596	0.0868	75.88	0.2865	<LOQ	>99.9	0.2617	<LOQ	>99.9
Diclofenac	40.29	3.585	91.10	47.76	<LOQ	>99.9	40.16	<LOQ	>99.9



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Results and discussion

WHO guidelines

Parameter	Unit	Degree of restriction on use			
		None	Slight to moderate	Severe	
Salinity	κ (EC_w) or $\mu S\text{ cm}^{-1}$	<700	700 – 3000	>3000	
	TDS mg L^{-1}	<450	450 – 2000	>2000	
Infiltration (affects infiltration rate of water into soil. Evaluate using EC_w and SAR together)					
SAR	=0 – 3	EC_w =	>700	700 – 200	<200
	=3 – 6	EC_w =	>1200	1200 – 300	<300
	=6 – 12	EC_w =	>1900	1900 – 500	<500
	=12 – 20	EC_w =	>2900	2900 – 1300	<1300
	=20 – 40	EC_w =	>5000	5000 – 2900	<2900
Na^+	Surface irrigation	mg L^{-1}	<69	69 – 207	>207
	Sprinkle irrigation	mg L^{-1}	<69	>69	
Cl ⁻	Surface irrigation	mg L^{-1}	<142	142 – 354	>354
	Sprinkle irrigation	mg L^{-1}	<106.5	>106.5	
Total nitrogen (TN)		mg L^{-1}	<5	5 – 30	>30
		mg L^{-1}	<5	5 – 30	>30
Nitrogen (NO_3^- -N)		mg L^{-1}	<50	50 – 100	>100
TSS		mg L^{-1}	<50	50 – 100	>100

pH	-	6.5 – 8 (8.5)
turbidity	NTU	<2
DOC	mg L^{-1}	-
COD	mg L^{-1}	-

Anions and cations		
NO_2^-	mg L^{-1} (meq L^{-1})	-
SO_4^{2-}	mg L^{-1} (meq L^{-1})	960 (20)
Mg^{2+}	mg L^{-1} (meq L^{-1})	61 (5)
Ca^{2+}	mg L^{-1} (meq L^{-1})	400 (20)
Nutrients		
NO_3^-	mg L^{-1} (meq L^{-1})	140 (10)
NH_4^+	mg L^{-1} (meq L^{-1})	90 (5)
PO_4^{3-}	mg L^{-1} (meq L^{-1})	194 (2)
K^+	mg L^{-1} (meq L^{-1})	78 (2)



Results and discussion

Classes of reclaimed water quality, and the associated agricultural use and irrigation method considered

Crop category	Minimum reclaimed water quality class	Irrigation method
All food crops, including root crops consumed raw and food crops where the edible portion is in direct contact with reclaimed water	Class A	All irrigation methods allowed
Food crops consumed raw where the edible portion is produced above ground and is not in direct contact with reclaimed water	Class B	All irrigation methods allowed
	Class C	Drip irrigation only
Processed food crops	Class B	All irrigation methods allowed
	Class C	Drip irrigation only
Non-food crops including crops to feed milk- or meat-producing animals	Class B	All irrigation methods allowed
	Class C	Drip irrigation only
Industrial, energy, and seeded crops	Class D	All irrigation methods allowed

Reclaimed water quality criteria for agricultural irrigation

Reclaimed water quality class	Water quality class Indicative technology target	E.coli (cfu 100 mL ⁻¹)	BOD ₅ (mg L ⁻¹)	TSS (mg L ⁻¹)	Turbidity (NTU)	Additional criteria
Class A	Secondary treatment, filtration, and disinfection (advanced water treatments)	≤10 or below detection limit	≤10	≤10	≤5	Legionella spp.: ≤1,000 cfu L ⁻¹ when there is risk of aerosolization.
Class B	Secondary treatment, and disinfection	≤100	≤25	≤35	-	Intestinal nematodes (helminth eggs): ≤1 egg L ⁻¹ when irrigation of pastures or fodder for livestock.
Class C	Secondary treatment, and disinfection	≤1,000	≤25	≤35	-	
Class D	Secondary treatment, and disinfection	≤10,000	≤25	≤35	-	



Conclusion

- According to EU and WHO guidelines NF/RO permeate satisfied the requirements for reuse.
- Depending on the membrane type the resulting permeate could be reused without restrictions according to EU guidelines (Class A), but for WHO guidelines the SAR and ECw of the permeate should be adjusted.
- All detected CECs were completely removed by hybrid MBR-NF/RO process.





FKIT MCMXIX



Thank you very much
for your attention

