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Challenges of municipal wastewater reclamation for irrigation by MBR and NF/RO: Physico-chemical and microbiological parameters, and emerging contaminants

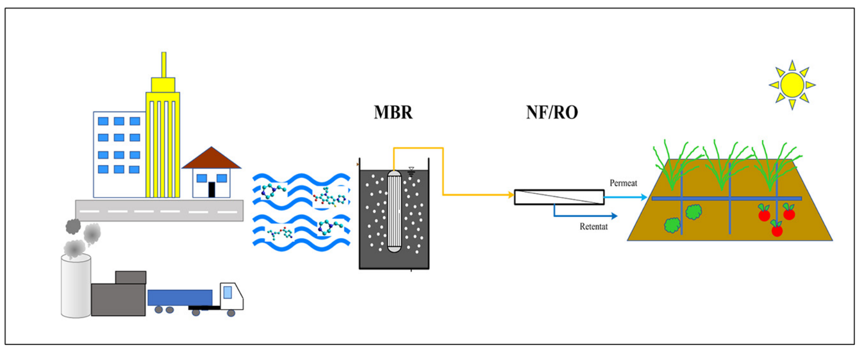
M. Racar [a], D. Dolar [a,*], K. Karadakić [a], N. Čavarović [a], N. Glumac [b], D. Ašperger [a], K. Košutić [a]

[a] University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, HR-10000 Zagreb, Croatia
[b] Međimurske vode d.o.o., Matice hrvatske 10, HR-40000 Čakovec, Croatia

HIGHLIGHTS

- Municipal wastewater reclamation for irrigation by membrane processes was examined.
- NF/RO permeate satisfied EU and WHO guidelines for irrigation.
- Wastewater was analyzed for twelve contaminants of emerging concern (CEC).
- Eleven CECs were found in municipal wastewater during the monitoring.
- MBR-NF/RO coupled system removed in high percentage the detected CECs.

GRAPHICAL ABSTRACT



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ABSTRACT

Climate change and the increased demand for food amplified the global problem with water supply for irrigation. This work deals with the reclamation of municipal wastewater (MWW) for irrigation by a membrane bioreactor (MBR), nanofiltration (NF), and reverse osmosis (RO). The emphasis was on the comparison of physico-chemical and microbiological parameters with the World Health Organization (WHO) and the European Union (EU) guidelines. In addition, the detection and removal of contaminants of emerging concern (CEC) from the Watch List (EU Decision 2015/495) were examined. Firstly, the MWW was monitored (physico-chemical and microbiological parameters, trace elements, and occurrence of CECs) for six months. Thereafter, the MWW was treated with MBR, NF, and RO. The reclaimed water satisfied the physico-chemical and microbiological quality requirements only after additional NF/RO treatment. Membrane bioreactor efficiently removed methiocarb (>99.9%), tri-allate (>99.9%), clothianidin (88.0%), and clarithromycin (71.9–74.2%), while the removal of azithromycin, acetamiprid, and oxadiazon was around 30%. The low and even negative removal during MBR treatment was observed for diclofenac (15%), clothianidin (−14%), imidacloprid (−18%), and diclofenac (−157%). Additional treatment of MBR effluent with NF90 and XLE membranes resulted in complete rejection of detected CECs, while NF270 membrane achieved results between 75% and 91%.

* Corresponding author.
E-mail address: dolar@fkit.hr (D. Dolar).

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1. Introduction

The lack of water for irrigation is one of the main challenges of agricultural production. This is the result of unevenly distributed water sources, seasonal droughts, and climate change. Nowadays, when all water supplies must be considered, wastewater represents a reliable and relatively untapped source of water (UN, 2017) that is increasingly being reclaimed for irrigation (Tram Vo et al., 2014). The advantage of using municipal wastewater (MWW) for irrigation is its continuous generation and independence from seasonal droughts. To be safe for reuse, reclaimed wastewater should comply with the physico-chemical and microbiological quality criteria defined by the guidelines for water use in irrigation (Alcalde-Sanz LaG, 2017; WHO, 2006). However, these guidelines do not mention organic micropollutants, which is concerning considering that crops can absorb organic micropollutants through roots (Hurtado et al., 2016; Wu et al., 2015), and some of these compounds might be translocated to other parts of the plant (Goldstein et al., 2014; Piña et al., 2018), entering the human food network (Christou et al., 2017). Organic micropollutants can cause problems by disrupting the soil microbiology (Cao et al., 2016; Toth et al., 2011), inhibiting crop growth, lowering the rates of germination, causing tissue deformation, etc. (Piña et al., 2018; Wu et al., 2015). In addition, antibiotic-resistant bacteria can be carried along with the micropollutants in the environment (Christou et al., 2017). Conventional wastewater treatment plants (WWTPs) are not designed for organic micropollutants removal (Tijani et al., 2013) and their efficiency differs for each compound and applied treatment (Barbosa et al., 2016; Sousa et al., 2019). Even if the treated MWW meets the set quality requirements, its use may contribute to an increased and non-accounted exposure to organic micropollutants such as antibiotics, pesticides, hormones, etc. representing a worrying concern for public health, agricultural production, and the environment (Christou et al., 2017; Piña et al., 2018).

To tackle the problem of unregulated organic micropollutants, the European Union (EU) created a strategy enacted by a series of decisions (2013/39/EU, 2013; 2015/495/EU, 2015) to strengthen the risk assessment of a number of micropollutants in the aquatic environment. The main goal of revising the current legislative framework was to protect the aquatic environment and human health (Ribeiro et al., 2015). A crucial step has been made with the Decision 39/2013/EU (2013/39/EU, 2013), where the first Watch List (WL) was proposed and later published in the Decision 2015/495/EU (2015/495/EU, 2015). The WL contains a series of substances for which monitoring data should be gathered throughout the EU (Sousa et al., 2019). In Decision 2015/495/EU, 2015, the WL consisted of 17 contaminants of emerging concern (CEC). The CECs from the WL are especially important for wastewater reclamation in irrigation, as they pose a risk of contamination for food, soil, and the aquatic ecosystem.

An adequate treatment is required to ensure that the reclaimed wastewater does not contain mentioned CECs. Different advanced treatment processes (membrane processes, advanced oxidation processes, and adsorption) were applied for the removal of numerous organic micropollutants as reviewed in Barbosa et al., 2016. However, there is still the need for more investigations with real wastewaters, under realistic conditions, on the performance of different treatments for the removal of substances included in the WL. This is especially true for methiocarb, neonicotinoids (imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid), along with oxadiazon and tri-allate, that were removed from the WL, as they are still of great interest (Barbosa et al., 2016; Krzeminski et al., 2019). Furthermore, there is no study on the removal efficiency of methiocarb, tri-allate, clothianidin, and acetamiprid in membrane processes such as membrane bioreactor (MBR), nanofiltration (NF), and reverse osmosis (RO) (Barbosa et al., 2016; Krzeminski et al., 2019).

According to authors knowledge there is no papers were real MWW influent was treated by MBR-NF and MBR-RO hybrid processes and includes monitoring of physico-chemical and microbiological parameters, trace elements, and concentrations of CECs. Thus, the main goal of this work was to evaluate the raw MWW reclamation for irrigation by a MBR-NF/RO hybrid process. This goal was accomplished by comparing effluent/permeate characteristics to the World Health Organization (WHO) (WHO, 2006) and EU guidelines (Alcalde-Sanz LaG, 2017) for water reuse in irrigation. In order to decrease the uptake of CEC to the food chain, their occurrence was analyzed and the efficiency of their removal with the hybrid MBR-NF/RO process was evaluated. In should be emphasized that the examined CEC were from the WL (diclofenac, azithromycin, clarithromycin, erythromycin, methiocarb, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid, oxadiazon, and tri-allate) and some of them were not yet investigated.

2. Materials and methods

2.1. MBR, NF, and RO experiments

This study was conducted on a laboratory MBR and NF/RO system presented in Fig. 1. The MWW was sampled after large screening (removal of large floating objects) and grit chamber (removal of sand and grease) in a WWTP, with a potential of 75,000 population equivalent (pe), located in Čakovec, Croatia. A third of the MWW is of industrial and two-thirds of domestic origin. The MWW was monitored from October 2017 until March 2018, and the results are presented in Table S1 as monthly average values measured in the daily composite samples.

The laboratory MBR (details in Dolar et al., 2019), with the hydraulic volume of 5 L, used an immersed ultrafiltration (UF) hollow fiber module ZeeWeed 1 (ZW-1) from GE Water & Process Technologies (Hungary). The membrane is made of polyvinylchloride (PVDF) with nominal characteristics: membrane surface area of 0.046 m^2, the membrane pore size of 0.02 μm, and molecular weight cut-off (MWCO) of 200 kDa.

The MBR experiments were carried out two times (each lasting 2 weeks). For the first period (Period I) the MWW was sampled in October 2018; while for the second period (Period II), it was sampled in November 2018. The membrane was cleaned between the two periods and fresh sludge from WWTP Čakovec was added to the MBR. The MBR operational conditions during the two periods are given in Table 1. The fresh MWW sampled in WWTP Čakovec was brought three times during each experimentation period. The MWW and sludge were sampled from the same WWTP and experiments were run maximum 1 h after sampling. Therefore, acclimation period was not included into experiment. The operation mode consisted of 10 min of outside-in suction and 1 min of backwash. Sludge retention time (SRT) is not mentioned here since no sludge was removed from the reactor throughout the experimentation periods (except small samples for sludge analysis). During MBR treatment, sludge was microscopically examined and typical microorganisms for MWW treatment were found, namely microorganisms from the order *Rotaria*, *Suctorida*, and *Vorticella* sp. (Fig. S1).

NF/RO experiments were done in batch mode (permeate and retentate were recirculated to the feed tank) and were performed at Period II. When enough MBR permeate (10–15 L for each membrane) was collected it was treated with NF/RO membranes. NF was performed with NF270 and NF90, and RO with XLE membranes, all from Dow-Filmtec (USA), at 12 bar in a laboratory set-up as described in Racar et al., 2020. The membrane characteristics are listed in Table S2. The feed from a 10 L tank recirculated through the cell at a flow rate of 3 L min^{-1} (fluid velocity 0.75 m s^{-1}). Prior to the experiment, the pristine membranes were washed with demineralized water (5 L) to remove the conserving agents, precompressed for 1 h at 15 bar, and stabilized for 30 min at working pressure. NF/RO experiments were carried out in batch recirculation mode for 3 h.

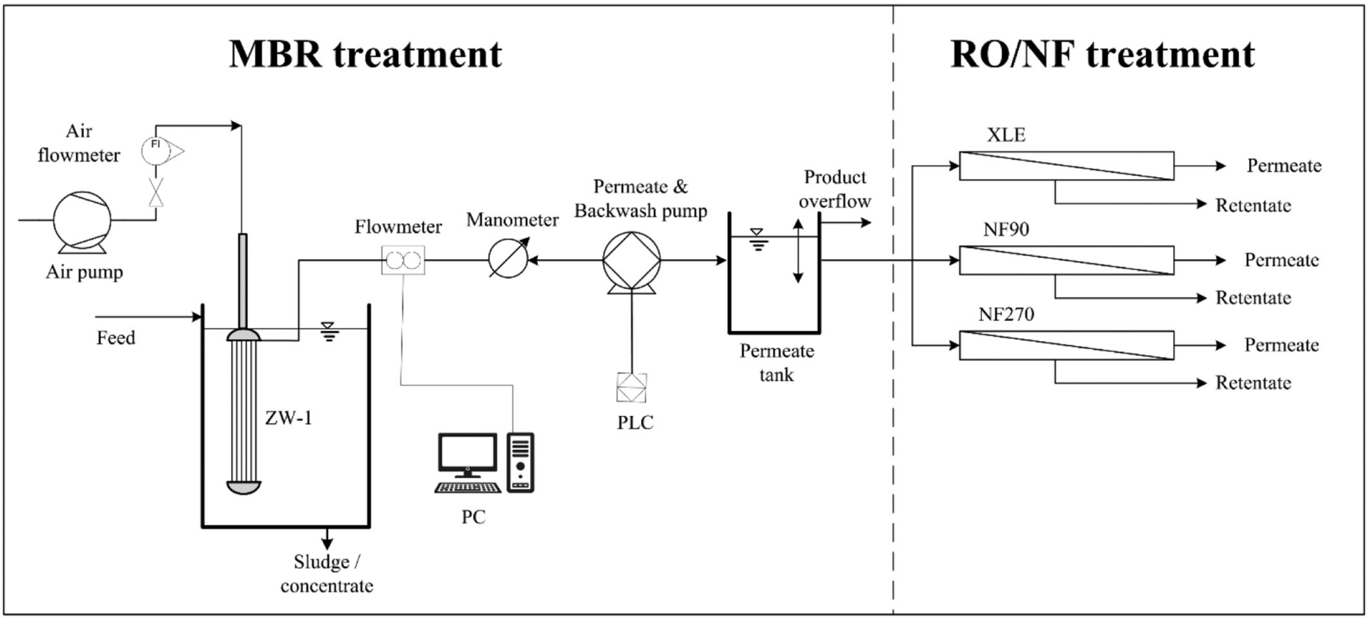

Fig. 1. Schematic representation of MBR-RO/NF treatment.

2.2. Analytical methods and water analysis

The water analysis was conducted for the main wastewater parameters according to Standard Methods (APHA/AWWA/WEF, 1995), which includes 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). Moreover, the content of PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+, F^-, Cl^-, Br^-, SO_4^{2-}, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, V, and Zn was determined. The microbiological analysis included the determination of 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).

The content of carbon was measured with Carbon Analyzer Shimadzu TOC-V_{WS} (Japan); turbidity with WTW Turb 430 (Germany); conductivity and pH with SI Analytics HandyLab680 (Germany); TN, COD, and BOD_5 with Hach Lange DR3900 (Germany); ion content with Ionic chromatograph DIONEX ICS-3000 Thermo Fischer Scientific (SAD); and trace metals content with ICP-MS (Element 2, Thermo Finnigan, Germany).

Bacterial indicators were quantified with 10^{-3} to 10^{-6} dilution by membrane filtration using cellulose ester filters with a pore size of 0.45 μm (Membrane solutions, China). TC and EC were cultured on Chromogenic coliform agar (Biolife, Italy) for 24 h on 36 °C and 24 h on 44 °C, respectively. The colonies of EC underwent biochemical identification tests using *Bactident EC* (Merck, Germany). ENT was cultured on Slanetz-Bartley agar (Biolife, Italy) for 48 h at 36 °C and presumptive colonies were confirmed by growth on Bile aesculin agar (Biolife, Italy). TC36 and TC22 were cultured on Yeast extract agar (KOMED, Croatia) for 48 h at 36 °C and 72 h at 22 °C, respectively. The detection limits were 1 CFU/100 mL for TC, EC, ENT, and PA, and 1 CFU/1 mL for TC36 and TC22.

Table 1
MBR operational conditions for the two experimental periods.

	Period I	Period II
	1–2 weeks	3–4 weeks
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	

2.3. Determination of CECs concentration

During the CECs (diclofenac, erythromycin, clarithromycin, azithromycin, methiocarb, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid, oxadiazon, and tri-allate) monitoring, samples were also taken for 6 months (October 2017 to March 2018). Number of samples varied per month and they are presented in Fig. 2. The concentration of CECs was measured three times in each experimental period and the CECs characteristics are given in Table S3. Fresh batches of MWW were brought three times during each experimentation period. A sample of MWW was taken from each batch, while samples of MBR effluent were taken 18 h after the treatment of a new batch of MWW started.

All samples were filtered with Munktell 391 filter paper (Sweden) and the substances were enriched by solid-phase extraction (SPE) on Strata-X 33 μm polymeric reversed phase cartridges (Phenomenex, USA). SPE cartridges were conditioned with 2 mL of acetonitrile followed by 3 mL of water. After the conditioning step, water samples were percolated through the cartridge. Afterward, the cartridge was rinsed with 3 mL methanol:water (40:60) and then dried under vacuum for 20 min, to remove the excess of water. Elution was performed with a mixture of 1.5 mL acetonitrile and 1.5 mL methanol. The extract was evaporated on a rotary evaporator and reconstituted with methanol-water (50:50). Liquid chromatography (LC) analysis was performed using HPLC Agilent Technologies 1200 Series (USA) coupled with an Agilent Technologies 6420 Triple Quad LC/MS (USA). Chromatographic separation was achieved with a SynergyTM Fusion-RP Phenomenex (USA) column. For the analysis of pesticides, eluent A was 0.1% formic acid and eluent B was methanol at a flow rate of 0.3 L min^{-1}. For the analysis of pharmaceuticals eluent A was 0.3% formic acid and 0.1% ammonium formate and eluent B methanol:ethanol (1:1), also at a flow rate of 0.3 mL min^{-1}. The limit of quantifications (LOQ) of azithromycin, erythromycin, clarithromycin, diclofenac, imidacloprid, methiocarb, clothianidin, acetamiprid, oxadiazon, and tri-allate were 9.23 ng L^{-1}, 34.18 ng L^{-1}, 18.70 ng L^{-1}, 791.07 ng L^{-1},

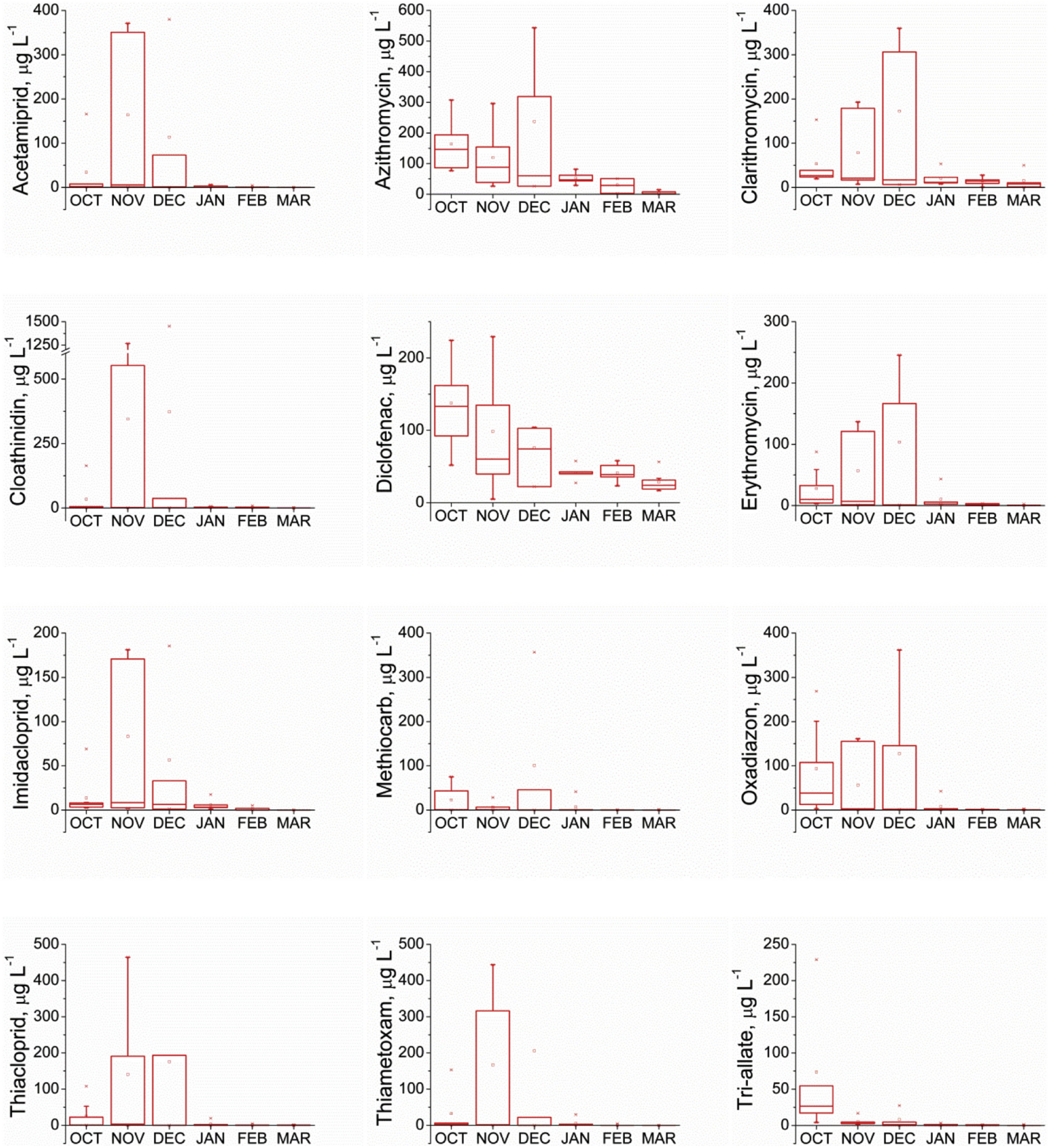

Fig. 2. The concentration of CECs (diclofenac, azithromycin, clarithromycin, erythromycin, methiocarb, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid, oxadiazon, and tri-allate) during the six months of monitoring.

122.43 ng L^{-1}, 3.09 ng L^{-1}, 34.99 ng L^{-1}, 4.63 ng L^{-1}, 23.70 ng L^{-1}, 9.27 ng L^{-1}, and 52.93 ng L^{-1}, respectively.

3. Results and discussion

3.1. Municipal wastewater monitoring

The MWW was monitored for six months for the main physico-chemical parameters (Table S1) and occurrence of the selected CECs (diclofenac, erythromycin, clarithromycin, azithromycin, methiocarb, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid, oxadiazon, and tri-allate) (Fig. 2). Azithromycin (92.54 ± 113.90 μg L^{-1}), clarithromycin (50.49 ± 80.95 μg L^{-1}), and diclofenac (71.57 ± 57.41 μg L^{-1}) were the most prevalent, while the other measured CECs were found with great variation in concentration, especially acetamiprid, clothianidin, imidacloprid, and thiamethoxam with high concentration in November while the other months had substantially lower concentrations. As seen in Fig. 2, the months with the highest concentrations of CEC during the monitoring were October, November, and December. Thus, the two experimentation periods were conducted during these months. Higher concentrations in the case of macrolide antibiotics (azithromycin, clarithromycin, and erythromycin) and diclofenac can be explained with winter period and sickness of the people. On the other hand, concentrations of detected neonicotinoids were also high during October, November, and December due to weed control in winter grains (like wheat, barley, rye, and triticale) which are grown in this area.

3.2. Municipal wastewater and MBR, NF, and RO performances

Seasonal variations of the MWW parameters measured throughout the six months period is given in Table S1 as average values by month. The characteristics of MWW used in this research (Period I and II) (Table 2) were within the typical parameter range for MWW treated in October and November in WWTP Čakovec. This means that average values (Period I and Period II) of turbidity, COD, EC_w, TN, and TSS for real MWW used in this study were 116.26 and 233.97 NTU, 589.64 and 765.50 mg L^{-1}, 1378 and 1267 μS cm^{-1}, 71.09 mg L^{-1}, and 320 and 510 mg L^{-1}, respectively. Concentration profiles of COD/DOC, ammonia, nitrite, and nitrate during the experimentation periods are presented in Fig. S2. The content of metals (Al, As, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Se, V, and Zn) was within the acceptable range for all the samples and throughout the months (Table S1) according to WHO guidelines (WHO, 2006). Among the 12 CECs analyzed in this study, 5 CECs (azithromycin, erythromycin, clarithromycin, diclofenac, and oxadiazon) were detected in both periods, while imidacloprid, methiocarb, clothianidin, acetamiprid, thiamethoxam, and tri-allate were detected only in Period I (Table 3). Methiocarb, tri-allate (in Period I), and oxadiazon (Period II) were detected in one sample with the average concentration of 0.228 μg L^{-1}, 0.29 μg L^{-1}, and 0.114 μg L^{-1}, respectively. Concentrations of detected CECs were between 0.08 μg L^{-1} and 11.90 μg L^{-1}, except for diclofenac (87.80 μg L^{-1} in Period I and 36.04 μg L^{-1} in Period II). In general, concentrations of all detected compounds were in the concentration range for MWW as presented in Krzeminski et al., 2019.

During Period I and II, MBR was effective in retaining TSS (100.0%) and decreasing turbidity (98.52 ± 1.36%, 99.75 ± 0.18%), DOC (82.21 ± 4.50%, 80.66 ± 4.28%), COD (89.83 ± 4.64%, 95.80 ± 2.27%), and BOD_5 (94.12 ± 2.35%, 97.38 ± 1.84%) (Table 2). The conductivity was lowered (16.41 ± 2.18%, 19.09 ± 1.04%), while the pH slightly increased (Table 2). The microbiological analysis of the MWW and the permeate during Period II showed that the TC was lowered by 4.1 $\log_{10}$ (from $2.8 \cdot 10^6$ to 240 CFU/100 mL), EC by 4.6 $\log_{10}$ (from $2.4 \cdot 10^6$ to 56 CFU/100 mL), ENT by 4.0 $\log_{10}$ (from $6.0 \cdot 10^4$ to 6 CFU/100 mL), TC37 by 3.8 $\log_{10}$ (from $1.8 \cdot 10^6$ to 282 CFU/100 mL), and TC22 by 3.9 $\log_{10}$ (from $1.8 \cdot 10^6$ to 236 CFU/100 mL), while PA was not found.

Quality of MBR effluent was additionally improved after the NF/RO treatment. NF270 achieved a high decrease of DOC (96.43%) and COD (>77.97%), but lower retention of salts (55.60% decrease in EC_w) (Table 4). On the other hand, NF90 and XLE achieved similar results with a decrease in conductivity of 93.56% and 94.90%, COD of 77.91% and 72.00%, and DOC of 86.74% and 87.60% (Table 3).

3.3. CECs removal by MBR and NF/RO

Macrolide antibiotics showed different degrees of removal with MBR treatment. The highest removal rates were for clarithromycin (74.06% and 71.87%) and azithromycin (52.62% and 23.25%) (Table 4). Relatively high removal of these antibiotics could be attributed to hydrophobic interactions due to their high log *D* and negative charge of the compound and positive charge of biomass (Dolar et al., 2012). This leads to the adsorption of these compounds to the biomass via cation exchange processes (Dolar et al., 2012). In the case of erythromycin, its concentration increased after MBR treatment. Compounds, like erythromycin, with low biodegradation constant (k_{biol} = 0.31 L g_{SS}^{-1} d^{-1}) are partially removed or biotransformed (Abegglen et al., 2008; Reif et al., 2013). According to Joss et al., 2006 compounds with k_{biol} between 0.1 and 10 L g_{SS}^{-1} d^{-1} are partially removed, i.e. removal is between 20% and 90%. The concentration of erythromycin in MBR effluent increased and the reason could be the presence of metabolites and biodegradation transformation products. In our case, erythromycin-H_2O can be converted to erythromycin in the aquatic environment (Hirsch et al., 1999).

Diclofenac was recalcitrant (removal 15.10%) to MBR treatment since it has strong electron-withdrawn group (EWG) such as the carboxylic group (Table S3). Compounds possessing EWG are more resistant to elimination through MBR showing removal <20% (Tadkaew et al., 2011). In addition, the presence of chlorine in the chemical structure made this compound more resistant to biological degradation (Nguyen et al., 2013; Tadkaew et al., 2011). Therefore, this confirms that compounds with low biological degradation constants

Table 2
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 O_2 L^{-1}	438.71 ± 264.17	36.40 ± 13.74	89.83	765.50 ± 422.25	24.66 ± 4.79	95.80
BOD_5, mg O_2 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
TSS, mg L^{-1}	320 ± 150	0	100.0	510 ± 198	0	100.0
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
NO_2^-	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
NO_3^-	1.68 ± 0.79	226.87 ± 60.75	–	2.36 ± 3.11	189.83 ± 18.38	–
PO_4^3	44.88 ± 18.05	58.66 ± 36.46	−30.70	19.18 ± 5.34	11.74 ± 9.89	38.79
SO_4^{2-}	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
NH_4^+	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
Mg^{2+}	21.15 ± 1.34	23.79 ± 3.96	−12.47	19.72 ± 5.00	20.28 ± 1.02	−2.84
Ca^{2+}	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	–

n.a. – not available.

Table 3
Concentration of CEC detected in the MWW and in the MBR effluent.

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

n.d. – not detected.
$N = 3$, for methiocarb and tri-allate (Period I) and oxadiazon (Period II) $N = 1$, and erythromycin $N = 2$.

($k_{biol} < 0.10$ L g_{SS}^{-1} d^{-1}) (Reif et al., 2013) (Table S3) are not removed or biotransformed during MBR treatment.

There is a lack of literature on the removal of clothianidin, acetamiprid, methiocarb, oxadiazon, and tri-allate (Krzeminski et al., 2019). Therefore, their removal will be explained according to their structure and familiar physico-chemical characteristics. In this study, MBR removed methiocarb, clothianidin, acetamiprid, oxadiazon, and tri-allate 100%, 88.37%, 39.36%, 33.15%, and 100%, respectively (Table 3).

Removal of methiocarb, tri-allate, and clothianidin with MBR was high (>88%) and according to their characteristics, it can be assumed that methiocarb and tri-allate were adsorbed on sludge due to high log $K_{O/W}$ which is 2.92 and 4.60, respectively (Table S3). In the case of clothianidin the removal mechanism could be via biodegradation as the adsorption on activated sludge is not expected (Log $K_{O/W} = 0.70$) (Table S3). These removal mechanisms were assumed because, according to Rogers, 1996, compounds with log $K_{O/W} < 2.5$ have low sorption potential, between 2.5 and 4.0 medium sorption potential, and with log $K_{O/W} > 4.0$ high sorption potential compounds.

Acetamiprid and oxadiazon are compounds with chlorine in their structure, which could explain its recalcitrant behavior during MBR treatment (Tadkaew et al., 2011). In addition, acetamiprid has low log $K_{O/W}$, expecting low sorption on activated sludge (Table S3). The incomplete removal (33.15%) of oxadiazon could be due to low biodegradability as its structure, with chlorine, also has -OR group as an electron-donating group (EDG) (Tadkaew et al., 2011) (Table S3). Therefore, the overall removal of oxadiazon could be a result of its adsorption on activated sludge due to its high hydrophobicity (log $K_{O/W} = 4.80$) (Table S3).

As mentioned before in Period II only azithromycin, erythromycin, clarithromycin, diclofenac, and oxadiazon were detected and treated with NF/RO (Table 5). As can be seen, azithromycin, clarithromycin, and diclofenac were completely removed with tight nanofiltration NF90 and RO XLE membranes, while with loose NF270 membrane removal was 80.08%, 75.88%, and 91.10%, respectively. Oxadiazon was detected only in one sample at the beginning of Period II. Samples of MBR effluent for NF/RO treatment were taken at the end of Period II; therefore, oxadiazon was not present in NF/RO feed.

3.4. Municipal wastewater reclamation

According to the reclaimed water quality criteria for agricultural irrigation defined by the Joint Research Center (JRC) of the European Commission (Tables S4 and S5) (Alcalde-Sanz LaG, 2017), the MBR permeate satisfies the Reclaimed water quality class B after disinfection. This means that reclaimed water can be used for food crops consumed raw where the edible portion is produced above ground and is not in direct

Table 4
Characteristics of 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^-	31.04	16.62	40.01	108.72	3.55	96.73	103.59	2.59	97.50
NO_2^-	0.90	0.42	53.33	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^-	168.21	49.65	70.48	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^+	0.73	0.00	>99.99	0.29	0.00	>99.99	0.93	0.00	>99.99
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	–

Table 5
Concentrations of CEC in NF270, NF90, and XLE feed and permeate with removal efficiencies.

CEC, μg 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

contact with reclaimed water (Table S5) (Alcalde-Sanz LaG, 2017). Without disinfection, the permeate would fall into Class C, which means that it can be used for the irrigation of the same crops as with Class B but only with drip irrigation or crops with less restriction for irrigation (Table S5) (Alcalde-Sanz LaG, 2017). On the other hand, the NF/RO permeates fall into Class A, and can be used for irrigation without restriction.

However, according to WHO guidelines (Table S6) (WHO, 2006) the MBR effluent falls in the category of "Severe restriction to use" in regard to the water infiltration because the TN is higher than 30 mg L^{-1}. However, this problem was resolved by additional NF/RO treatment. In NF90 and XLE permeates the TN was lowered to acceptable values (<5 mg N L^{-1} for XLE and 12.6 mg N L^{-1} for NF90), while NF270 permeate did not satisfy these requirements (46.7 mg N L^{-1}). On the other hand, because the SAR values are <3 mg L^{-1} and EC_w are <700 μS cm^{-1} the NF90 and XLE permeates are still in the category of "Severe restriction to use". This problem can be solved by adding calcium or magnesium salts in the reclaimed water increasing the EC_w and lowering the SAR. With the correction of SAR and EC_w, the NF90 permeate falls in the "Slight to moderate restriction to use", while XLE permeate would fall into the "None restriction to use" regarding water infiltration. With regard to WHO guidelines on salinity, which is connected to the crop sensibility to the content of salts, the MBR permeate falls into the category of "Slight to moderate restriction to use", while NF/RO into the "None restriction to use".

Reclamation of MWW for agricultural irrigation could directly increase agricultural production, increase water availability, integrated and sustainable use of water resources, avoid using drinking water for irrigation, reduce over-abstraction of surface and groundwater, decrease water scarcity and stress, and decrease their dependence on climate change. Croatia is rich country with fresh water since the average volume of the country's own and transit waters is 25,160 m^{-3} cap^{-1} $year^{-1}$ of which the own waters account for 5880 m^3 cap^{-1}- $year^{-1}$. Nevertheless, there is no doubt that the changes in climate characteristics and that the future climate changes will considerably reflect on the water resources and their availability (ClimateChangePost, 2019). For example in Croatia the amount of produced MWW, in the last 10 years, varied between 300 and 400 Mm^3 yr^{-1} (Ostroški, 2018) confirming MWW as a reliable source of water.

Municipal wastewater is reliable source of the water and irrigation is becoming very important in order to increase food growth. Implementation of membrane technology instead of classical comes down to money. Main problems in MBR are energy consumption and membrane fouling, while the high quality effluent, reduced sludge volumes, and reduced plant footprint are the benefits. MBR require around 0.4–0.6 kWh m^{-3}, instead of 0.3–0.6 kWh m^{-3} for the classical activated sludge process (CAS) (Krzeminski et al., 2017). Nevertheless, Judd, 2017 summarized differences between MBR and CAS. The main conclusion was that the MBR showed overall cost benefits over CAS technology despite the higher operating expenditure (OPEX) for the MBR. One of the examples is that the whole life cost of immersed flat sheet membranes has decreased from \$400 m^{-2} in 1992 to <\$50 m^{-2} in 2005 with a similar trend for immersed hollow fiber (Judd, 2017). For RO treatment Sarai Atab et al., 2016 showed economic study of RO desalination system for potable water and land irrigation. The study showed the reduction of power energy consumption from 2.8 kWh m^{-3} to a more economical 0.8 kWh m^{-3} by feed water temperature increase, feed water pressure decrease, and the average pore size diameter increase.

4. Conclusion

Twelve monitoring CECs were detected in the real MWW with high variation in their concentration. The highest concentrations (up to 500 μg L^{-1}) were found in winter period (October 2017–December 2017). Eleven and five CECs were detected in the real MWW in Period I and Period II, respectively. The concentrations were at relatively high concentration (even up 87.80 ± 25.14 μg L^{-1}).

High removal rates (till levels below LOQ) were achieved with the combination of MBR-XLE and MBR-NF90 treatment for all CECs determined in influent. Removal with MBR-NF270 was between 90 and 99%. Removal efficiency of MBR varied quite significantly (−105–99.9%) depending on the compound due to diverse physico-chemical properties of the target compounds. Additional treatment with RO XLE and nanofiltration NF90 membrane showed excellent removal rates (>99%) for all compounds, while for loose nanofiltration NF270 membrane between 75% and 91%.

According to the EU and WHO guidelines, only the permeate after NF/RO satisfied the requirements for reuse, and 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 EC_w of the permeate should be adjusted by adding calcium salts.

Abbreviations

BOD_5	biological oxygen demand [mg L^{-1}]
CAS	Classical activated sludge process
CEC	contaminants of emerging concern
COD	chemical oxygen demand [mg L^{-1}]
DOC	dissolved organic carbon [mg L^{-1}]
EC	*Escherichia coli* [1 CFU 100 mL^{-1}]
EC_w	electrical conductivity [μS cm^{-1}]
EDG	electron-donating group
ENT	*Enterococcus* [1 CFU 100 mL^{-1}]
EU	European Union
EWG	electron-withdrawn group
HPLC	high pressure liquid chromatography
JRC	Joint Research Center
LC	liquid chromatography
LOQ	limit of quantification [ng g^{-1}]
MBR	membrane bioreactor
MWCO	molecular weight cut-off [Da]
MWW	municipal wastewater
NF	nanofiltration
OPEX	operating expenditure
PA	*Pseudomonas aeruginosa* [1 CFU 100 mL^{-1}]
PVDF	polyvinylchloride
RO	reverse osmosis
SPE	solid-phase extraction
SRT	solid retention time [h]
TC22	Total colony count at 22 °C [1 CFU 1 mL^{-1}]
TC36	Total colony count at 36 °C [1 CFU 1 mL^{-1}]
TC	total coliforms [1 CFU 100 mL^{-1}]
TN	total nitrogen [mg L^{-1}]

TSS	total suspended solids [mg L^{-1}]
UF	ultrafiltration
WHO	World Health Organization
WL	Watch List
WWTP	conventional wastewater treatment plant
ZW-1	ZeeWeed 1

CRediT authorship contribution statement

M. Racar: Investigation, Writing - original draft, Formal analysis.**D. Dolar:**Conceptualization, Investigation, Writing - original draft, Project administration.**K. Karadakić:**Investigation.**N. Čavarović:**Investigation.**N. Glumac:**Investigation.**D. Ašperger:**Investigation.**K. Košutić:**Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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