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Reuse of quaternary treated wastewater for agricultural irrigation, reality or fantasy?

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Key words: crops, irrigation, quaternary water treatment, wastewater reuse

Abstract

Human activities significantly impact environmental conditions, leading to challenges such as biodiversity loss and water scarcity, particularly manifested through increased water stress. One promising solution to mitigate these challenges is the reuse of treated wastewater (TWW) for agricultural irrigation. However, using TWW for this purpose raises concerns regarding soil quality, crop health, and consumer safety. This study explored a quaternary wastewater treatment process employed at a wastewater treatment plant (WWTP) in Trnava at Zeleneč, Slovakia, with purpose of making the TWW safe for irrigation, while monitoring the water, soil and crop quality. For the purpose of the study, various agricultural crops, including onions, potatoes, carrots, and parsley were grown by using quaternary treated wastewater. The study implemented advanced water treatment methods such as coagulation, ultrafiltration, adsorption, and disinfection to elevate the quality of treated wastewater. The results demonstrated a significant improvement in the quality of the treated wastewater, indicating its suitability for agricultural use. Specifically, there was a reduction in chemical oxygen demand (COD) from 34.5 mg/L in the raw effluent to 24.5 mg/L post-treatment, representing a removal efficiency of 63%. Regarding nitrogen, TN and it's the effect of quaternary wastewater treatment was also assessed for pharmaceuticals and drugs, which showed remarkable reduction of 99.2% for methamphetamine and over 50% removal efficiency for additional pharmaceuticals detected in the raw WWTP effluent. Importantly, no harmful antibiotic residues were found in the quaternary treated wastewater, confirming that the treatment process effectively mitigated potential health risks associated with the use of wastewater in agriculture. These findings suggest that treated wastewater is a viable option for sustainable agricultural practices, enhancing food safety and addressing water scarcity issues.

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Introduction

The impact of human activity on the environment can be seen all around us, from changes in climatic conditions to micro/nanoplastics in the seas [1, 2]. In addition to the change in biodiversity, the effect of these changes is also manifested in the form of water stress. Examples of this are the scarcity of drinking water, decreasing water levels of surface and ground water. Water reuse is a way we can alleviate the stress on water resources. However, the application of treated wastewater (TWW) for irrigation of crops is very irresponsible and risky. The content of micropollutants, heavy metals and other pollutants in irrigation water could adversely affect the soil, crops and of course, the end consumers. When recycled water is used for irrigation, treated wastewater from the WWTP is often used as a resource. Not from industrial WWTP. However, such water can still contain a high degree of chemical and microbial contamination, which means that if disinfection is not done sufficiently, it is at risk of recontamination. [3, 4].

Materials and methods

The quaternary water treatment plant (ASIO, s.r.o., Czech Republic) was designed to additionally treat effluent coming from wastewater treatment plant (WWTP). After applying advanced water purifying methods, the water should not pose any threat to growing vegetables on the field. Subsequently, the water was applied for irrigation of crops of specific variety such as onions (Crockett), potatoes (Laura), carrots (Romance) and parsley (Efez). The wastewater was treated right at the Zeleneč WWTP and then pumped to a storage tank. Water quality parameters such as microbiology and basic indicators were carried out in the laboratories of SL TAVOS, a. s. Results of microbiology, nitrates and heavy metals in crops and soil were carried out in accredited Eurofins laboratories.

Pretreatment and coagulation

The TWW from the tank was pumped through an Azud modular 100 (SISTEMA AZUD, S.A., Spain) disc filter with a pore diameter of 130 μ m. The inclusion of a disc filter is needed to protect the rest of the equipment from mechanical damage. The mechanical pretreatment was followed by addition of ferric sulfate, which is a common coagulant under commercial name PREFLOC – PIX113 (Kemifloc, a.s., Czech Republic). Depending on the pH of the TWW, the pH was adjusted either by addition of H₂SO₄ or NaOH. This step is important for better iron precipitation conditions and economic efficiency.

Ultrafiltration

After coagulation, the TWW was subsequently pumped through Inge Dizzer P4040–6 ultrafiltration (UF) unit (BASF, USA). The flow rate across the membrane was constant and when the transmembrane pressure increased, the system's backwash was activated, with a backwash flow rate ranging from 50 to $100 \text{ L/m}^2/\text{h}$. More information about the UF unit is shown in the

Tab. 1.

Tab. 1 Parameters of UF unit

Parameter	Unit	Value
Membrane surface area	m ²	6.00
Length	mm	960
Outer diameter of membrane	mm	100
Inner diameter of membrane	mm	28.40
Weight	kg	4.50
Unit performance	L/h/1pc	300
Maximum pressure	bar	1.50
Maximum working pressure	°C	40
Material	_	PVC-U

Adsorption

The UF permeate was retained in an accumulation tank and passed to an Aquasorb 6300 activated carbon filter column (The Jakobi Carbons Group, Sweden). The activated carbon parameters are shown in the

Tab. 2.

Parameter	Jednotka	Hodnota	
Iodine number	mg/g	min. 970	
Humidity	%	5	
Ash	%	13	
Wetting	%	99	
Hardness	%	90	
Bulk density	kg/m ³	430	
pH	_	8-11	

Disinfection

After the activated carbon column, the purified TWW entered the column with UV lamp (Aquaterm C800, Slovakia) with a power of 65 W and a maximum flow rate of 2800 L/h. Recommended working conditions for temperature and pressure are 2-40 °C and 7 bar. The quaternary treated water after UV disinfection was discharged into a secondary storage tank from which it was subsequently applied onto the planted crops.

Results and discussion

The results of COD monitoring are shown in Fig. 1 The median COD concentration has a value of 34.50 mg/L for WWTP effluent and 24.50 mg/L for the irrigation effluent. The lowest recorded and achieved COD concentrations were 16 mg/L and 10 mg/L. When assessing the removal efficiency of COD, the highest recorded value was at a date 16.7.2024, peaking at 63 %. The lowest

value did not exceed 2 % (7.5.2024) and the median COD removal efficiency was 33.33 %. The BOD₅ value remained basically constant throughout the whole monitoring, settling at a value of 3 mg/L even in the outflow from the WWTP and to irrigation.

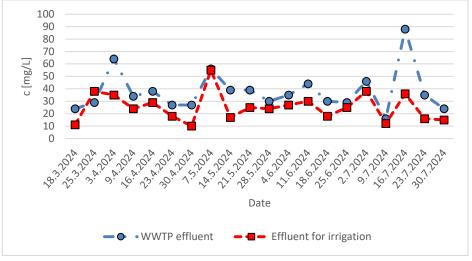


Fig. 1 COD change in the effluent sample of WWTP and for irrigation

Nitrogen in form of the N–NH₄⁺ that was present in the effluent from the WWTP and for irrigation, did not exceed a value greater than 1 mg/L. As for TN, it had relatively high fluctuation in values in the individual effluents. In the effluent from the WWTP, the median TN was equal to 6.65 mg/L. The median value of TN in the irrigation water was not significantly lower and its value was equal to 6.35 mg/L. N–NO₃⁻ concentration shows a slightly decreasing trend for both outflows, this phenomenon can be seen in Fig. 2. The value remains more or less constant, and the median removal efficiency was 0.59 %. Removing a substantial part of the N–NO₃⁻ by coagulation and UF may be problematic. Firstly, membrane modification is needed, and pH also acts as an important parameter. Based on a study by Morteza K. A. et al. from 2016 [5], we can conclude that even adsorption may not be effective for the removal of N–NO₃⁻ under certain conditions. The optimum pH is 5.5 to 6, however, the efficiency also depends on the preparation of activated carbon in which functional groups are formed/destroyed. The pH value of the water that has been leaving UF unit with a value around 7.39.

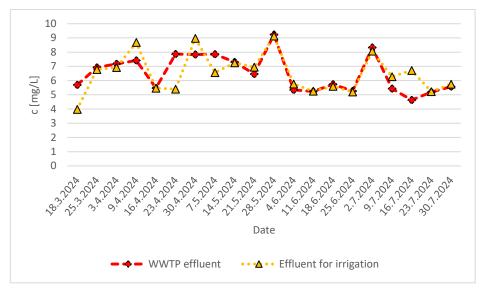


Fig. 2 Change of N–NO3⁻ in the effluent sample of WWTP and for irrigation

Soil

A summary of the data on soil pollutants concentrations is given in

Tab. 3. As we can see, the concentration of arsenic did not show any significant changes for reference and project soil samples. Also, cadmium in both soils did not exceed 0.4 mg/kg dry weight. However, as can be noticed, the most significant difference of heavy metals between the reference and the project sample was for onion and parsley. A smaller difference was in soils where carrots were planted, and the lowest was in the soil with potatoes. $N-NO_3^-$ concentration had the greatest difference in parsley. According to Annex 7 in Decree No 508/2004 Coll. of the Ministry of Agriculture of the Slovak Republic on the use of agricultural land [6], we can say that none of the values of heavy metal concentration exceeded the relevant limit value in agricultural soil. *Tab. 3 Chemical parameters for reference and experiment soil*

	Onion		Potato		Carrot		Parsley		
	mg/kg dry weight, % weight (TS)								
	Ref.	Exp.	Ref.	Exp.	Ref.	Exp.	Ref.	Exp.	
Arzén	8.90	9.50	6.80	7.20	7.00	7.10	8.80	6.40	
N-NO ₃ ⁻	3.15	2.80	2.13	<1,30	<1,30	<1,30	6.55	<1,30	
Chrome	35.20	23.00	31.40	28.90	38.00	25.30	32.40	24.00	
Cadmium	<0,40	<0,40	<0,40	<0,4	<0,40	<0,40	<0,40	<0,40	
Copper	30.00	18.70	21.70	21.50	23.10	20.50	25.30	17.80	
Nikel	32.20	20.50	27.80	25.40	30.10	22.70	26.90	21.50	
Lead	17.80	12.10	14.60	13.60	17.00	13.10	16.10	10.80	
Mercury	0.05	0.04	0.05	0.03	0.05	0.04	0.05	0.03	
pН	8.85	8.99		9.11		9.07		9.23	
Selene	0.62	0.76	0.39	0.47	0.35	0.53	0.40	0.46	
Dry weight at									
105 °C	84.90	84.70	84.70	82.00	82.90	86.30	89.90	83.70	

Crops

Increase in nitrate (NO₃⁻) concentration in the monitored crops, except parsley, was either zero or relatively negligible. In parsley, a more than threefold increase was detected from a value below 100 mg/L to a value of 387.1 mg/L. This trend can be seen in Fig. 3. In a study by Kara M. in 2020 [7], it is reported that some crops such as spinach and parsley can accumulate nitrate up to the range of 1000–2500 mg/kg, this fact partially explains the high NO₃⁻ content. This type of irrigation could also have an effect on NO₃⁻ concentration in crops, as drip irrigation is concentrated on the plant or close to the root of the plant [8]. For this reason, parsley in the project could probably have accumulated more NO₃⁻ than the reference sample. This theory is also supported by the above–mentioned article on page 2 by Morteza K. A. [5], that the mobility of NO₃⁻ in soil is high, while the ammonium cation NH₄⁺ and free ammonia NH₃ bind to soil particles and cannot percolate into groundwater. The presence of parsley in the reference soil is likely to cause accumulation, whereas the soil in the experiment had low concentrations (due to drip irrigation).

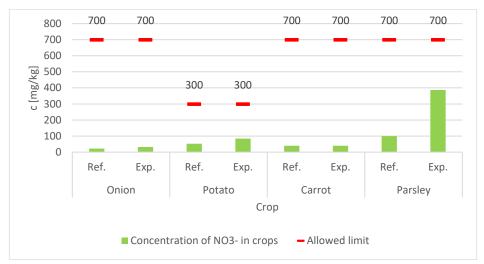
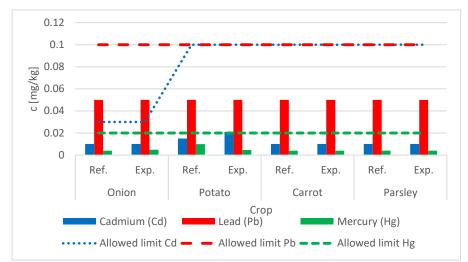


Fig. 3 Content of NO₃⁻ in reference soil compared to experimental one

The given experimental varieties of onion, potato, carrot and parsley did not show the ability to accumulate heavy metals, the values for cadmium were below 0.01 mg/kg and only the value in the reference sample for potato was 0.015 mg/kg with a minimal increase in the experimental sample to 0.021 mg/kg. Lead was in all crops below 0,05 mg/kg. Mercury was higher in potatoes compared to the other crops, settling at value of 0.0099 mg/kg and 0.0046 mg/kg for reference and experimental samples respectively. The pesticide content was higher in some of the tested crops, but the maximum permissible level was not exceeded by any of them. In most cases, the quantities of pesticides as a whole were below the limit of quantification. The only pesticide that had an elevated concentration approaching the maximum permitted level is flonicamid, which was present in the reference potato sample at value of 0,056 mg/kg out of the allowed limit of 0.09



mg/kg. Crops watered with quaternary treated wastewater were not treated with pesticides and therefore none were detected. Results for the heavy metare shown in the Fig. 4.

Fig. 4 Content of heavy metals in reference and experimental samples of crops

A total of 46 drugs and 70 pharmaceuticals (and their metabolites) were determined in the TWW, from this number drugs and pharmaceuticals were selected to serve to show the efficacy of the process. It can be seen in Fig. 5 and Fig. 6 that the different technological processes, except for adsorption, do not have a significant effect on the content of drugs and pharmaceuticals in the TWW. As we can notice, the quaternary TWW at the effluent has significantly lower concentrations of drugs and pharmaceuticals, and this reduction was achieved using an activated carbon column. For drugs, there was a reduction of more than 50 % of their original concentration. Methamphetamine was essentially completely removed at both low and high initial concentrations, with efficiency of reduction of 99.2 %. The initial concentration of drugs and medications seem to affect the efficiency of their removal. While sometimes it is affected negatively and sometimes not at all. This phenomenon can be observed for example with methamphetamine (neutral) and carbamazepine (negative).

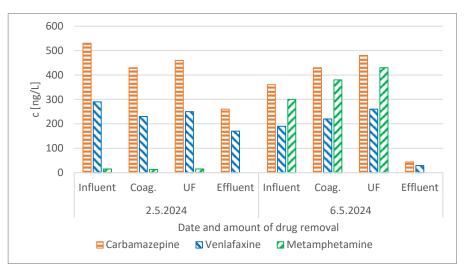


Fig. 5 Drugs and their concentrations during each step of quaternary treatment

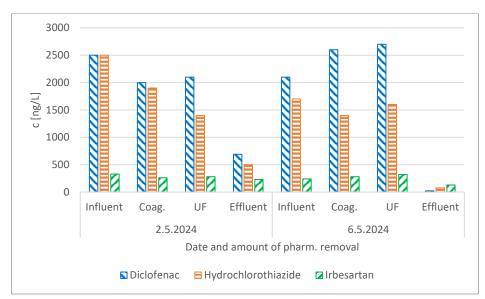


Fig. 6 Pharmaceuticals and their concentrations during each step of quaternary treatment

Disinfection

Based on the obtained data, it can be stated that the numbers of microorganisms in crops at the wastewater treatment plant were higher than in the reference field, with the exception of potato soil, where the difference was minimal. The explanation is likely that the accumulation tank for the treated wastewater was above ground, where during the summer heat, the temperature was +25 °C, making it nearly impossible to keep microbial activity under control. At the same time, the drip irrigation pipes were exposed to high temperatures and became contaminated with microorganisms after a certain period, even though spot samples taken at the outlet did not show microbial contamination. As a result, increased amounts of microorganisms also entered the soil and onto the surface of the crops. However, E. coli and Salmonella were not present anywhere in

the soil. Similarly to what was observed in soil, we also observed higher levels of microorganisms in the tested crops than in the reference crops when analyzing the microorganisms. Enterococci were at very low levels (<10 CFU/g, Salmonella negative, elevated values were only present for coliforms at 103 CFU/g, and when compared to the units of CFU/g TS in the reference samples. The elevated parameter values were also caused by the fact that the crop analysis was done with crops that were not washed extensively. The bacteria cannot get inside the crops being monitored unless the surface of the crop is damaged.

Conclusion

The project offers valuable insights into water reuse in agriculture and its effects on crop quality. According to Regulation (EU) 2020/741 of the European Parliament and of the Council [9], the reclaimed water achieved class A quality, as E. coli was absent at the outlet, BOD₅ was maintained at 3 mg/L, turbidity remained below 2 NTU (with minimal exceptions), and suspended solids were below 10 mg/L. Ammoniacal nitrogen did not exceed 1 mg/L, and technology had a negligible effect on nitrate nitrogen levels. Soil analysis showed significant differences in heavy metal concentrations, with lower levels at the experimental site compared to reference soil. As for nitrate content in crops, the levels were negligible in both sample groups, while only the experimental parsley sample showed a difference of almost 300 mg/kg compared to reference. Heavy metal accumulation in crops was minimal with all values below allowed limits. Lastly, drug and pharmaceutical monitoring indicated that most treatment processes had little impact on their removal, with adsorption being the most effective method, notably removing substances like methamphetamine and diclofenac almost entirely.

Acknowledgement

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