

Modelling of sanitary wastewater composition and operation of a small membrane bioreactor wastewater treatment plant with denitrification and nitrification

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Abstract

The ratio of concentrations of total nitrogen and five-day biochemical oxygen demand in the sanitary wastewater of an energy infrastructure facility in Serbia is many times higher than usual, resulting in only half of the total nitrogen being eliminated in wastewater treatment plants (membrane bioreactor with anoxic and aerobic reactors) by denitrification. The first step of analysis was mathematical modelling of the composition and origins of the input wastewater. The model was developed based on the scientific literature data on composition of human excrement and the data on composition of water used for sanitary purposes. Next, it was successfully verified by comparisons to the experimental data of the wastewater composition. In the next step, a model for wastewater treatment simulation was created by using the BioWin software (Envirosim Associates, USA) in order to examine functioning of the plant and test the effects of several possible modifications of the process. A good agreement with the qualities of the influent and effluent determined by laboratory analyses was achieved after model calibration. The results of simulations showed a tenfold decrease in the total nitrogen concentration and a fortyfold decrease in the total phosphorous concentration in the effluent after introducing the following modifications to the simulated process: ferric chloride dosing, increasing dosing of acetate in the anoxic reactor by a factor of seven, increasing of the waste activated sludge rate by a factor of four and increasing the recirculation flow rate by a factor of three.

Keywords: Wastewater treatment simulation software; excrement; urine; acetate; nitrogen.

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1. INTRODUCTION

Mathematical modelling of wastewater composition and biological treatment processes is a powerful tool for predicting effluent quality. It can be used in the design process, or even more importantly, in the analysis of the performance of the existing wastewater treatment plants (WWTPs). The performance of plants can be unsatisfactory mostly due to the flaws in the design or substantially different influent quality than that envisaged by the design. Because of the significant impact the effluent characteristics have on the environment and the status of water bodies, and penalties imposed through legislation for non-conformance with emission limit values, finding the most efficient way to improve the functioning of the underperforming WWTPs is of great importance. Modelling of treatment processes is a valuable tool for testing different solutions and choosing the optimal one.

Quality and quantity of the influent is a key input for the design of WWTPs. Often, especially for design of new WWTPs, the influent quality is presumed using expert judgement or an engineering standard [1]. Even when the measurements, sampling and laboratory analyses have been performed on existing facilities, data sets are often quite limited due to the high financial and temporal costs of extended dynamic influent dataset, hindering the widespread utilization of WWTP models [2] and increasing the risk for errors in the design. In the case of sanitary wastewater, various factors influence its composition [3], as there are different uses of drinking water, different efficiencies of

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drinking water use, cultural differences in food diet (ranges of average daily consumption of foods in 266 countries in 2010 were 19.2 to 325.1 g per day for fruits, 34.6 to 493.1 g per day for vegetables, 3.0 to 124.2 g per day for unprocessed red meat and 2.5 to 66.1 g per day for the processed one) [4] and water consumption [5], *etc.*

In order to address the mentioned issues regarding the influent quality and quantity input for the design and modelling, several approaches [6] have been suggested and tested:

- software tools for deriving WWTP influent data given selected properties of the catchment area and the distribution and kinds of emission sources [7,8],
- simple models for generating temporal distribution of influent data for urban WWTPs using available average quantity and quality data, using statistical distributions [9],
- the Fourier-based models, which are generally used to describe the patterns of the wastewater under dry weather conditions; these models are very useful to interpolate hourly values given average daily data, *e.g.* [9-11],
- simple spreadsheet type of calculation of influent quality and quantity, as a part of the analysis of different options for the treatment of source-separated components of wastewater (usually separately collected urine) depending on their composition and level of dilution [12,13], or the analysis of the influence of the quality and quantity of basic components of wastewater on its composition for special cases and specific diets like for example in the envisaged planetary space bases [14]; these kinds of analyses pertain by definition to small numbers of people.

The present study focused on the performance of a small WWTP, designed for 70 population equivalents (PEs), discharging effluent into a small watercourse with intermittent flow (average $0.16 \text{ m}^3 \text{ s}^{-1}$). The wastewater treatment process is based on a membrane bioreactor (MBR) preceded by denitrification and nitrification reactors, with recirculation to the denitrification reactor, organic substrate addition and chemical removal of phosphorous (simulated process is shown in Fig. 1). The process was simulated for several variants of chemicals and organic substrate dosing, recycle ratio and waste activated sludge (WAS) discharge rate. The starting points of the applied calculation were data on basic human physiology and human habits and preferences, with focus on determining the quantity, quality and share of each source of wastewater resulting from all identified drinking water uses, using new model for the calculation of wastewater quality. Founded on those bases, a method for calculation of the composition of sanitary wastewater was developed and tested.

WWTPs comprise two main types of biological processes – suspended growth processes with microorganisms responsible for the treatment maintained in liquid suspension by appropriate mixing methods and attached growth (biofilm) processes [15]. Treated water is separated from the liquid suspension by using settlers or membranes. Performance of the complex array of treatment processes (biological, chemical and physical) applied in WWTPs can be analysed in detail only by using simulation software based on complex set of equations describing the processes. BioWin (Envirosim Associates, USA) is one of the most frequently used software packages, and one of the very few that are based on a coherent set of equations for all main processes in both suspended and attached growth as well as all the processes in the sludge [16-19].

In this work, the BioWin software coupled with the simulation of wastewater production was used to predict effectiveness and potentials for use of a MBR WWTP in treating of real sanitary wastewater. For the scientific analysis a case was chosen based on the composition of wastewater very different from the usual sanitary wastewater, especially regarding the concentration of total nitrogen (TN), which has significant repercussions on the treatment effects and efficiency in this, and future similar facilities.

Mathematical modelling of the composition and origins of wastewater was based on the composition of human excrement and urine reported in literature and data on the composition of water used for sanitary purposes, and on the average daily consumption of sanitary water per person and the share of defecations during work hours in the daily defecation occurrences, which were determined through the calibration. The aim of the study was to provide a helpful asset for mathematical simulation of wastewater composition based on its constituents derived from sanitary water uses, and for simulation of wastewater treatment using specialised software like BioWin, which helps design, improve, and optimize wastewater treatment processes.

1. 1. Legislation on effluent quality

The limits for the effluent quality were adopted according to the Regulation on emission limit values of polluting substances in waters and deadlines for achieving them of the Republic of Serbia [20]. In addition, Regulation on the limit values of pollutants in surface and ground waters and sediment and deadlines for reaching them of the Republic of Serbia [21] specifies the limits of water quality classes of surface water bodies. Wastewater treatment, as stipulated in the Law on Water [22], Article 98, shall be carried out to the level that corresponds to the emission limit values [20] or to the level that does not violate the quality standards of the recipient's environment [21], adopting a more rigorous criterion.

In this case the recipient watercourse is a small intermittent stream for which data on quality were lacking and a mixing zone could not be defined. Due to the vagueness of Article 98 [22], the only criterion that would undoubtedly be in line with legislation is that the effluent quality should correspond to the class II of quality for the type 6 surface water bodies (as per Rule book for determination of ecological and chemical status parameters for surface waters and determination of chemical and quantitative status parameters for groundwater of the Republic of Serbia [23]), which is significantly more stringent than the emission limits.

1. 2. The analyses performed

As mentioned above, the first step was mathematical modelling of the composition and origins of wastewater. The next step was analysis of the possibilities to achieve the limit values for five day biochemical oxygen demand (BOD₅), chemical oxygen demand (COD) and TN and total phosphorus (TP) concentrations for the class II of quality for type 6 surface water bodies and this required modification and optimisation of the WWTP operation. So, in this step, the effects of modifications to the facility operation were tested using the system model created in the software package BioWin 6.0 (Envirosim Associates, USA).

2. Materials and methods

2. 1. Composition of wastewater

The composition of sanitary wastewater of an energy infrastructure facility in Serbia, was expected to be similar to the composition of standard sanitary wastewater – the mixture of toilet, washbasin, shower, laundry and kitchen wastewaters, in the quantity corresponding to 70 workers present at any time, and the existing WWTP (three reactors in series: anoxic, aerobic and MBR) was designed accordingly.

The assumed quality of the untreated wastewater (Table 1) was similar to the average domestic wastewater, as for example defined by the ATV DVWK A 131E standard [1].

Table 1. Quality of the untreated sanitary wastewater from the ToR

Parameter	
Total content of suspended solids, mg dm ⁻³	500
BOD ₅ , mg O ₂ dm ⁻³	500
TN content, mg N dm ⁻³	53
TP content, mg P dm ⁻³	13
pH	6.5 tpo 9.0
Temperature, °C	5 to 45

According to [1], the COD is typically two times larger than BOD₅, while the ratio of BOD₅ to TN is approximately 5.

Effluent and wastewater samples were collected and analyzed within five campaigns, in the February 2022 to March 2023 period (Table 2). pH value, electrochemical conductivity, temperature and dissolved oxygen concentration were measured *in situ*, using the calibrated probes. The physico-chemical analysis and microbiological testing were conducted following the standard procedures outlined by the American Public Health Association (APHA) and the American Water Works Association (AWWA). All applied procedures from water sampling, water quality testing and reporting followed the requirements of the ISO 17025:2015 standard. The results of the WWTP influent and effluent sampling and laboratory analyses show very low BOD₅/TN ratio of close to 1. The effective removal of nitrogen (over 90 %) is possible only when

this ratio is over 4 [24]. The wastewater composition listed in Table 2 is different from the typical compositions as in [1] and Table 1. The difference is particularly obvious in the BOD₅/TN ratio, and to some extent in the COD to BOD₅ ratio, which is high, close to 3, indicating that organic matter in wastewater has a lower biodegradability than expected.

Table 2. Quality parameters of the untreated sanitary wastewater and of the WWTP effluent

Parameter	Untreated sanitary wastewater		WWTP effluent	
	Mean*	Standard deviation	Mean*	Standard deviation
Temperature, °C	18.5	5.9	23.1	7.0
Smell	faecal		none	
Visible subst.	none		none	
pH	7.90	0.28	7.30	0.35
Specific conductivity, $\mu\text{S cm}^{-1}$	2799	542.8	2194	437.4
Dissolved O ₂ , mg O ₂ dm ⁻³	0.7	0.37	7.8	0.43
Colour, °Pt-Co**	557.7	200.7	190.7	96.2
Ammonium ion content, mg N dm ⁻³	139.4	62.4	10.8	6.3
Nitrites content, mg N dm ⁻³	0.041	0.02	0.69	0.82
Nitrates content, mg N dm ⁻³	0.3	0.12	97.7	44.82
Kjeldahl nitrogen content, mg N dm ⁻³	186.3	33.3	11.6	5.9
TN content, mg N dm ⁻³	186.6	33.4	109.9	47.6
Organophosphates content, mg P dm ⁻³	11.6	8.4	10.7	4.9
TP content, mg P dm ⁻³	12.8	8.2	11.8	4.8
Chlorides content, mg dm ⁻³	185.2	66.9	167.3	30.8
Sulphates content, mg dm ⁻³	145.1	37.5	163.3	47.6
Content of settleable matter (Imhoff), ml dm ⁻³	2.1	2.1	<0.7	
Content of total suspended solids, mg dm ⁻³	121.7	48.2	11.1	12.9
Ignition weight loss at 550°C, mg dm ⁻³	109.1	44.3	10.4	12.6
Ignition residue at 550 °C, mg dm ⁻³	3.8	1.5	0.8	0.1
Evaporation residue at 105 °C, mg dm ⁻³	1514	275.6	1624	143.1
COD, mg O ₂ dm ⁻³	451.4	154.7	70.9	46.6
BOD ₅ , mg O ₂ dm ⁻³	168.3	69.2	7.7	2.1
TOC, mg dm ⁻³	88.5	46.6	13.8	4.7

*if the value of parameter was below the quantification limit, it was taken as half of quantification limit in calculation of means; **°Pt-Co – platinum-cobalt scale degrees

2. 2. Mathematical modelling of composition of influent wastewater

The actual number of workers in the facility is several times smaller than the planned one, and kitchen and showers for staff are not available or used. The ratio of concentration of TN and BOD₅ is many times higher than that envisaged in ToR, resulting in only half of the TN being eliminated by denitrification (Table 2).

Composition of the influent wastewater was explained through its constituents' origins and the scientific literature data. The base assumption was that the only sources of wastewater were washbasins and toilets.

The composition of human urine and excrement (average values) adopted from the literature sources [25-27] is shown in Table 3. The quality parameter mass generated per person is divided by the sanitary water volumetric consumption and summed with the parameter concentration in the sanitary water used for washing and toilet flushing (samples were collected at the groundwater treatment plant outlet in February, March and April 2022, Table 4) to calculate the composition of wastewater by Eqs. (1) and (2).

In order to calculate the excrement contribution to the wastewater composition, the share of defecations during work hours in the daily defecation occurrences in a person had to be determined. If, for example, an average person working one eight-hour shift a day defecates when at work in 20 % of cases, then in three eight-hour shifts in one day, only 60 % of average daily excrement quantity per person is generated per workplace. Considering that the COD to BOD₅ ratio in excrement (which dominates regarding the organic matter in comparison to urine) is approximately 2 based on data shown in Table 3, biodegradability of the excrement organic matter is reduced by a fitting factor in comparison to that ratio to achieve a good fit. Calculation of wastewater BOD₅, and all other parameter concentrations (represented here by COD), is given by Eqs. (1) and (2), respectively:

Table 3. Composition of human urine and excrement adopted from scientific literature sources [25-27]

Parameter	Content, mg dm ⁻³ (for urine quantity, dm ³ /c/d*)	Content per dry mass of excrement, mg g _{dry} ⁻¹	Quantity, g/c/d*
	Urine	Excrement	
COD	12968 ¹	1275 ¹	65.5 ¹
BOD ₅	2552 ³		31.7 ¹
TN	8858 ¹		1.8 ¹
Total phosphorus	1200 ¹	4.29 ¹	0.814 ¹
Potassium	1362 ¹	3.85 ¹	0.919 ¹
Calcium	111 ¹	3.57 ¹	1.103 ¹
Magnesium	95 ¹	1.71 ¹	0.213 ¹
Chlorides	4190 ²	0.6 ¹	0.09 ¹
Sulphur	810 ²	0.87 ¹	0.165 ¹
Sodium	2820 ²	2.87 ¹	0.1 ¹
Sulphates	1180 ²		
Urine daily quantity (UQ _{c,d})	1.4 ¹		
Excrement (dry mass)			29 ¹
Excrement (wet mass)			128 ¹

* /c /d - per caput per diem (latin for per head per day); ¹from [25]; ²from [26]; ³from [27]

Table 4. Experimentally determined composition of sanitary water (treated groundwater)

Parameter	Mean	Standard deviation
Specific electric conductivity at 20°C, µS cm ⁻¹	1365	425
Temperature, °C	23.4	0.54
Colour, °Pt-Co*	<5	
Smell	none	
Taste	none	
Turbidity, NTU**	<1	
pH	7.69	0.081
COD (KMnO ₄), mg O ₂ dm ⁻³	1.42	0.78
Ammonia content, mg dm ⁻³	<0.03	
Nitrites content, mg dm ⁻³	<0.003	
Nitrates content, mg dm ⁻³	2.21	0.55
Chlorides content, mg dm ⁻³	135.3	98
Total iron content, mg dm ⁻³	<0.09	
Active chlorine content, mg dm ⁻³	<0.05	
Manganese content, mg dm ⁻³	<0.05	
Total hardness, mg Ca dm ⁻³	130.6	4.7
Calcium content, mg dm ⁻³	49.4	12.4
Magnesium content, mg dm ⁻³	48.9	14.8
Sulphates content, mg dm ^{-3***}	68.4	7.2
Bicarbonates content, mg dm ^{-3***}	369.0	14.3
Potassium, mg dm ^{-3***}	0.78	0.18
Sodium content, mg dm ^{-3****}	100.5	
Total mineralization, mg dm ⁻³	775.5	

*°Pt-Co - platinum-cobalt scale degrees; **NTU – nephelometric turbidity unit; ***taken from the data on untreated groundwater quality;

****calculated based on electric charge balance

$$\text{BOD}_{5\text{ww}} = \frac{m(\text{BOD}_5)_{\text{e,c,d}} \times \frac{24}{8} \times \text{SDW} \times \text{BRF} + UQ_{\text{c,d}} \times \text{BOD}_{5\text{u}}}{Q_{\text{sw,c,d}}} + \text{BOD}_{5\text{sw}} \quad (1)$$

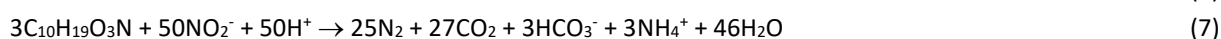
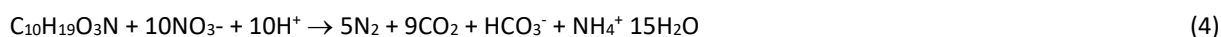
$$\text{COD}_{\text{ww}} = \frac{m(\text{COD})_{\text{e,c,d}} \times \frac{24}{8} \times \text{SDW} + UQ_{\text{c,d}} \times \text{COD}_{\text{u}}}{Q_{\text{sw,c,d}}} + \text{COD}_{\text{sw}} \quad (2)$$

where BOD_{5ww} and COD_{ww} are BOD₅ and COD in wastewater, $m(\text{BOD}_5)_{\text{e,c,d}}$ and $m(\text{COD})_{\text{e,c,d}}$ are daily BOD₅ and COD quantities in human excrement, SDW is a share of defecations during work hours in the daily defecation occurrences, BRF is the biodegradability reduction factor, BOD_{5u} and COD_u are BOD₅ and COD in urine, BOD_{5sw} and COD_{sw} are BOD₅ and COD in sanitary water, UQ_{c,d} is a daily urine quantity, and Q_{sw,c,d} is a daily consumption of sanitary water.

Cations like potassium and sodium, and anions like sulphates and bicarbonates were not a part of the laboratory analyses performed on sanitary water. Concentrations of these ions in sanitary water were derived directly from the data on untreated groundwater quality (except for sodium which was calculated), in order to calculate total mineralization, which is referenced in key legislation [20]. The ion exchanger (regenerated by sodium chloride) is used in the facility for groundwater treatment to lower the magnesium concentration below the limit set by legislation [28] on drinking water quality. Probably due to the use of sodium chloride for ion exchanger regeneration, the chloride ions average concentration was higher in sanitary water than in groundwater by almost 120 mg dm⁻³. The sodium concentration in sanitary water was calculated based on electric charge balance of the solution (*i.e.* for the calculated sodium concentration net charge of the solution is zero).

2. 3. Wastewater treatment plants treatment process simulation

As the quality of effluent (Table 2) implies, low BOD₅ value in particular, oxidation of biodegradable organic carbon and organic nitrogen by oxygen, and oxidation of biodegradable organic carbon through denitrification and denitrification practically proceed to the end. About a half of total nitrogen in wastewater, 90 % comprised of nitrate, remains in the effluent as there is not enough biodegradable organic carbon for complete nitrogen reduction. The nitrate and nitrite ions are reduced to nitrogen gas by electron donors like wastewater complex organics represented by formula C₁₀H₁₉O₃N (Eqs.(4) and (7)), or basic ions or molecules like acetate (Eqs.(5) and (8)) and glucose (Eqs.(6) and (9)) which can be added if there is insufficient organic carbon for complete denitrification and denitrification in wastewater [29,30].



After the analysis of the wastewater and effluent compositions, the treatment process and the resulting effluent quality were analysed by using modelling. The system model was created with the use of the software BioWin 6.0, which uses a general activated sludge/anaerobic digestion (ASDM) model, referred to as the BioWin ASDM. The BioWin ASDM has more than fifty state variables and over eighty process expressions [31]. These expressions are used to describe the following biological processes (including substrate and electron-acceptors consumption, hydrolysis, biomass growth) and chemical reactions typically occurring in wastewater treatment plants [31]:

- growth and decay of ordinary heterotrophic biomass,
- growth and decay of methylotrophic biomass,
- growth and decay of ammonia oxidizing biomass,
- growth and decay of nitrite oxidizing biomass,
- growth and decay of anaerobic ammonia oxidizing biomass,
- growth and decay of phosphorus accumulating biomass,
- growth and decay of sulphur oxidizing biomass,
- growth and decay of sulphur reducing biomass,
- hydrolysis, fermentation, oxidation/reduction, adsorption, ammonification and assimilative denitrification processes,
- chemical phosphorus removal with iron and aluminium salts,
- chemical phosphorus removal with salts,
- iron redox reactions and precipitation of vivianite and FeS,
- modelling of pH and alkalinity,
- liquid – gas interaction.

To simulate the enumerated processes, input data have to be set such as flow rate and composition of the influent, geometries of reactors and clarifiers, flow rates in pumps, flow rates of inputs like air or solutions of chemicals *etc.* Composition of influent, in addition to the standard quality parameters, is defined also by wastewater (WW) fractions,

like the fractions of soluble, colloidal and particulate matter, their readily biodegradable, slowly biodegradable and nonbiodegradable fractions *etc.*, and rates (for BOD₅ calculation) of degradation of colloidal slowly biodegradable COD, particulate slowly biodegradable COD and degradable external organics COD. Delimiting the organic matter in this fashion can be important in the analyses of the performance of WWTPs and finding causes of underperformance, especially when there is a significant share of pretreated industrial wastewater in the influent [3].

The simulations can be dynamic and steady state. In the present case, the simulations were performed in the steady state mode, with input defined based on average values of the flow rate and parameters of wastewater quality.

The WWTP configuration is replicated in the model (Figure 1) by using elements enumerated and described in Table 5. The parameter values in the model were, whenever possible, taken from the available data on the WWTP and influent.

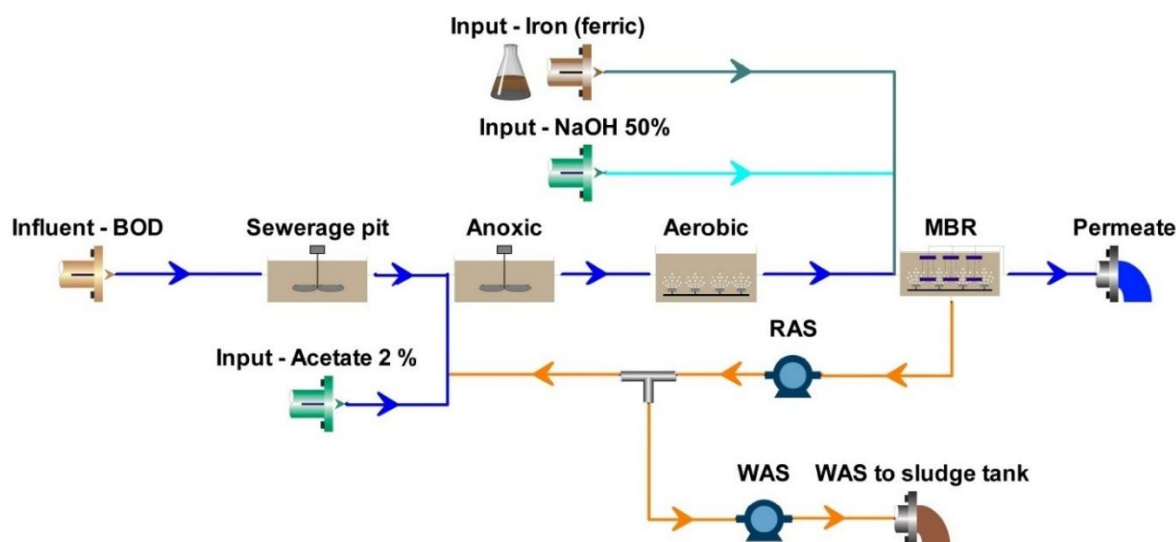


Figure 1. BioWin model flowsheet simulating the WWTP process flowsheet

Table 5. Description of the elements in the BioWin model simulating the current state of the system

Element	Description of the model input
Influent defined with BOD ₅ and other parameters (COD is calculated by BioWin)	Flow rate 1.32 m ³ day ⁻¹ (1.53·10 ⁻⁵ m ³ s ⁻¹), BOD ₅ 168.3 mg O ₂ dm ⁻³ , TSS 121.7 mg dm ⁻³ , VSS 90.0 mg dm ⁻³ , TKN 186.3 mg N dm ⁻³ , nitrates 0.3 mg dm ⁻³ , TP 12.8 mg dm ⁻³ , pH 7.9, alkalinity 7.4 mmol dm ⁻³ , calcium 52 mg dm ⁻³ , magnesium 51 mg dm ⁻³ . WW fractions are default ones, except for the share of nonbiodegradable soluble COD (0.225 instead of 0.1300), and share of non-colloidal slowly biodegradable COD (0.1015 instead of 0.750). The three rates of degradation (for BOD ₅ calculation) are all set to 0.2865 instead of default 0.5000. Changes were made in order to replicate the COD of 451.4 mg O ₂ dm ⁻³
Sewerage pit	Volume 30 m ³ , depth 3 m, width 2.5 m, nonaerated
Anoxic suspended growth bioreactor	Volume 4 m ³ , depth 3 m, width 1 m, nonaerated
Aerobic suspended growth bioreactor	Volume 3.7 m ³ , depth 3 m, width 1 m, aerated (dissolved oxygen setpoint 1.5 mg dm ⁻³ , density of diffusers 10 % (share of active area of diffusers in aeration tank in the area of aeration tank), α 0.500 and β 0.950 (parameters connected to mass transfer calculations)
Suspended growth MBR	Volume 3.5 m ³ , depth 3 m, width 1 m, aerated (dissolved oxygen setpoint 6.0 mg dm ⁻³ , density of diffusers 10 %, α 0.500 and β 0.950 (parameters connected to mass transfer calculations), number of cassettes 6, displaced volume per cassette 0.043 m ³ , membrane surface area per cassette 6.25 m ² . Flow split 7.2 (as return mixed liquor to permeate (effluent) ratio)
Flow splitter for waste activated sludge	Rate in side stream to waste activated sludge tank 10 dm ³ d ⁻¹ (1.16·10 ⁻⁴ dm ³ s ⁻¹)
Input for dosing of ferric chloride solution	32 wt.% ferric chloride solution, no flow (not added)
Input for dosing of sodium hydroxide solution	50 wt.% sodium hydroxide solution for pH regulation, flow 1 dm ³ day ⁻¹ (1.16·10 ⁻⁵ dm ³ s ⁻¹)
Input for dosing of acetate salt solution	2 wt.% sodium acetate solution as a carbon source for denitrification (equivalent to 1.5 wt.% glucose solution). Acetate is used in the model as it is available in the BioWin software along with methanol and propionate, glucose is used in the WWTP. Flow rate was 7.3 dm ³ day ⁻¹ (8.45·10 ⁻⁵ dm ³ s ⁻¹)

The model was tested and calibrated using data on wastewater quality and quantity, and the quality of the effluent, determined by laboratory analyses. The calibrated model described in Table 5 is a representation of the system in its current state.

The simulations were performed in the steady state mode due to the small average flow rate (approximately $1.3 \text{ m}^3 \text{ day}^{-1}$) and a large volume of the system (approximately 40 m^3), as well as due to the limited number of temporal data on the qualities of the influent and effluent.

If the legislation is interpreted in the most stringent way (as elaborated in section 1.1), the operation of the WWTP could be modified and optimised to achieve values for BOD_5 , COD and nutrients concentrations as close to, or under the limit values for the class II of quality for the type 6 surface water bodies. The effects of modifications to the facility operation were tested using the calibrated model. Testing included several variants of dosing of the 2 wt.% (10, 20, 30, 40, 50, 60, $70 \text{ dm}^3 \text{ day}^{-1}$, with 50 found optimal) acetate in the anoxic reactor for denitrification, 32 wt.% ferric chloride dosing for phosphorus elimination (1, 2, 3, 5, 2.2, 2.4, $2.6 \text{ dm}^3 \text{ day}^{-1}$, with $2.4 \text{ dm}^3 \text{ day}^{-1}$ found optimal) and 50 % sodium hydroxide solution dosing for pH regulation in the MBR (1, 1.5, 2, $3 \text{ dm}^3 \text{ day}^{-1}$, with $1.5 \text{ dm}^3 \text{ day}^{-1}$ found optimal), as well as different recirculation rates of mixed liquor from the MBR to the anoxic reactor set as return mixed liquor to permeate (effluent) ratio (5, 10, 15, 20, 25, with 20 found optimal) and rates in the side stream to the waste activated sludge tank ($0.01, 0.02, 0.03, 0.04, 0.05, 0.06 \text{ m}^3 \text{ day}^{-1}$, with $0.04 \text{ m}^3 \text{ day}^{-1}$ found optimal). The best performing set of flow and dosing rates values in a sense of minimization of TN, TP and COD in the effluent was determined and is shown in the Results section along with the respective effluent quality.

The BioWin model generates output for every model element, down to the effluent discharge. The output is comprised of quality parameters, which are derived from the parameters defining the composition of inputs, by calculation at every successive element.

Other parameters relevant for the comparison with limits set by legislation [20,21] that could not be calculated from the inputs within the BioWin model itself, were calculated by using a Microsoft Excel spreadsheet. Chlorides and sodium ions concentrations are calculated by adding contributions of ferric chloride and sodium hydroxide to contents of chlorides and sodium in wastewater, Eqs. (10) and (11), total mineralization is calculated by summing the dissolved matter, and total organic carbon (TOC) is calculated by using a correlation with COD, Eq. (12) [32].

$$c(\text{Cl}^-)_e = c(\text{Cl}^-)_{\text{ww}} + Q_{\text{FeCl}_3, \text{d}} \rho(\text{FeCl}_3 (32 \text{ wt.}\%)) 0.32 \frac{3M(\text{Cl})}{M(\text{FeCl}_3)} \quad (10)$$

$$c(\text{Na}^+)_e = c(\text{Na}^+)_{\text{ww}} + Q_{\text{NaOH}, \text{d}} \rho(\text{NaOH} (50 \text{ wt.}\%)) 0.50 \frac{M(\text{Na})}{M(\text{NaOH})} \quad (11)$$

$$c(\text{TOC}) = \frac{\text{COD}_e - 7.25}{2.99} \quad (12)$$

where $M(\text{Cl}^-)$, $M(\text{Na}^+)$, $M(\text{NaOH})$ and $M(\text{FeCl}_3)$ are the molar masses of chlorine, sodium, sodium hydroxide and ferric chloride respectively, $\rho(\text{FeCl}_3 (32 \text{ wt.}\%))$, $\rho(\text{NaOH} (50 \text{ wt.}\%))$, $Q_{\text{FeCl}_3, \text{d}}$ and $Q_{\text{NaOH}, \text{d}}$ are the densities and flow rates of ferric chloride and sodium hydroxide solutions respectively. Subscript e denotes effluent.

3. RESULTS

3. 1. Results of wastewater quality modelling

By using Eqs. (1) and (2) and data from Table 3, the values of key wastewater parameters (BOD_5 , COD, TN, TP) and chlorides were calculated, juxtaposed with laboratory analyses results, as those parameters were covered by the analyses performed on the wastewater samples, and values of SDW, BRF and $UQ_{c, \text{d}}$ parameters calibrated. The best fitting calculated values are shown in Table 6. The total calcium, magnesium, sodium and potassium concentrations were also calculated in order to calculate total mineralization for the purpose of comparison with the limit set by legislation [20] but were not used for the calibration.

The results presented in Table 6 show a very good fit of calculated to measured values for the key quality parameters of influent wastewater (root-mean-square deviation is 14.7 mg dm^{-3}). The values of BRF, SDW and $Q_{\text{sw}, \text{c}, \text{d}}$ that were fitted

in order to achieve the best agreement of calculated with the measured values, are all within the logical and acceptable ranges (biodegradability smaller than average by a third, and defecation two times less likely at work than at home).

Table 6. Results of parameter fitting and wastewater quality calculation

Parameter	Calculated	Average	Fitted
COD, mg O ₂ dm ⁻³	452	451.4	
BOD ₅ , mg O ₂ dm ⁻³	168	168.3	
TN content, mg N dm ⁻³	172	186.6	
TP content, mg P dm ⁻³	23	12.8	
Chlorides content, mg dm ⁻³	212	185.2	
Calcium content, mg dm ⁻³	52		
Magnesium content, mg dm ⁻³	51		
Sulphur content, mg dm ⁻³	38	48.4 (SO ₄ ²⁻)	
Sodium content, mg dm ⁻³	152		
Potassium content, mg dm ⁻³	26		
$Q_{sw,c,d} / l / c / d^*$			77
BRF, %			66
SDW, %			15

* $l / c / d$ – per caput per diem (latin for per head per day)

3. 2. Wastewater treatment plants treatment process simulations

The system model was first tested and calibrated by using data from the laboratory testing of influent and effluent quality, and then its parameters modified to achieve the optimal performance of the simulated WWTP (Table 7). A good agreement with the quality of the effluent determined by laboratory analyses was achieved in the model (Table 8, columns 2 and 3). In order to achieve values for BOD₅, COD and nutrients concentrations as close as possible, or under the limit values for the class II of quality for the type 6 surface water bodies (Table 8, column 6), modifications in the operation of the WWTP were proposed to optimise it, especially in the sense of maximizing nutrients reduction. The effects of modifications to the facility operation were tested by using the model. The values of optimised parameters (flow rates of inputs of solutions, recirculation ratio and discharge of waste activated sludge) are shown in Table 7. The composition of the effluent is shown in Table 8, column 4.

Table 7. Description of the elements in the BioWin model of the optimized system with regard to parameters that were changed in comparison with the current state (Table 5)

Element	Description of model input
Suspended growth MBR	Flow split 20 instead of 7.2 (as return mixed liquor to permeate (effluent) ratio)
Flow splitter for waste activated sludge	Rate in side stream to waste activated sludge tank is 0.04 m ³ day ⁻¹ (4.63·10 ⁻⁴ dm ³ s ⁻¹) instead of 0.01 m ³ day ⁻¹ (1.16·10 ⁻⁴ dm ³ s ⁻¹)
Input for dosing of ferric chloride solution	32 wt.% ferric chloride solution, 2.4 dm ³ day ⁻¹ (2.78·10 ⁻⁵ dm ³ s ⁻¹) instead of no flow (not added)
Input for dosing of sodium hydroxide solution	50 wt.% sodium hydroxide solution for pH regulation, flow 1.5 dm ³ day ⁻¹ (1.74·10 ⁻⁵ dm ³ s ⁻¹) instead of 1 dm ³ d ⁻¹ (1.16·10 ⁻⁵ dm ³ s ⁻¹)
Input for dosing of acetate salt solution	2 wt.% sodium acetate solution as carbon source for denitrification (equivalent to 1.5 wt.% glucose solution). Flow is 50 dm ³ day ⁻¹ (5.79·10 ⁻⁴ dm ³ s ⁻¹) instead of 7.3 dm ³ d ⁻¹ (8.45·10 ⁻⁵ dm ³ s ⁻¹)

Table 8. Results of the effluent quality obtained experimentally and by the calibrated BioWin model simulations for the current and optimized states of the system along with the limits set by legislation

1	2	3	4	5	6	7
Parameter	Effluent, current state, laboratory results (Reduction, %)	Effluent, current state, simulation (Reduction, %)	Effluent, best performance, simulation (Reduction, %)	Change between the current (3) and optimized (4), %	Values for class II from Regulation on the limit values of pollutants [21]	Regulation on emission limit values (Reduction, %) [20]
pH ¹	7.3	7.51	7.29	-3	6.5 8.5	
TSS ¹ , mg dm ⁻³	11.1	0.0	0.0	0	25 + ✓	100 + ✓
BOD ₅ ¹ , mg O ₂ dm ⁻³	7.7 (95.4)	0.71 (99.6)	0.63 (99.6)	-11	4.0 + ✓	80 (75) + ✓
COD (bichromate) ¹ , mg O ₂ dm ⁻³	70.9 (84)	23.4 (95)	27.93 (94)	19	15	70 + ✓
TOC ² , mg C dm ⁻³	13.8	5.41	6.92	30	5.0	

1	2	3	4	5	6	7
Parameter	Effluent, current state, laboratory results (Reduction, %)	Effluent, current state, simulation (Reduction, %)	Effluent, best performance, simulation (Reduction, %)	Change between the current (3) and optimized (4), %	Values for class II from Regulation on the limit values of pollutants [21]	Regulation on emission limit values (Reduction, %) [20]
TN content ¹ , mg N dm ⁻³	109.9	109.9	11.27	-90	2,0	
Nitrates content ¹ , mg N dm ⁻³	97.7	105.5	6.83	-94	3,0	
Nitrites content ¹ , mg N dm ⁻³	0.688	0.007	0.016	129	0.03 ✓	
Ammonium ion content ¹ , mg N dm ⁻³	10.8	0.032	0.065	103	0.1 ✓	
Molecular ammonia content ¹ , mg NH ₃ dm ⁻³		0.000025	0.00003	20	0.025 ✓	
TP content ¹ , mg P dm ⁻³	11.8	10.4	0.25	-98	0.15	
Orthophosphates content ¹ , mg P dm ⁻³	10.7	10.4	0.25	-98	0.1	
Chlorides content ² , mg dm ⁻³	167.3	211.7	726.7	243	100	
Sulphates content ² , mg dm ⁻³	163.3	90.3	90.3	0	100 + ✓	
Total mineralization ² , mg dm ⁻³		1865	2065	34	1000	

✓ - under the limit (for the optimized WWTP simulation results); + - under the limit (for the current state WWTP simulation results);

¹BioWin simulation results; ²Spreadsheet calculation results (Eqs. (10) to (12) and summing for total mineralization)

The results for the best performing variant showed a tenfold decrease in the TN concentration and a fortyfold decrease in the TP concentration in the effluent in comparison to the current state.

4. DISCUSSION

4. 1. Wastewater quality modelling

The results present a very good fit of calculated to measured values for the key quality parameters of the influent wastewater, which points strongly to the usefulness of the presented model for the calculation of wastewater quality. As expected, share of defecations during work hours in the total defecation occurrences (15 %) is much smaller than the share of working hours in 24 hours (33 %), as most people obviously prefer using the toilet at home. Biodegradability reduction factor (66 %) reflects the higher COD to BOD₅ ratio than the standard one for sanitary wastewater. It is quite possible that this reflects the diet that deviates from the average one in a number of workers, as this is possible within a small group of people. The daily sanitary water consumption per person of 77 dm³ is in accordance with the very limited number of waters uses in the facility – drinking, hand washing and toilet and urinal flushing, as it is a half of the standard domestic daily consumption per person [1].

4. 2. Wastewater treatment plants treatment process simulations

Despite the tenfold decrease in the TN concentration and a fortyfold decrease in the TP concentration in the effluent in comparison to the current state (after the changes in dosing rates of input solutions, recirculation rate and waste activated sludge discharge rate), concentrations of nutrients are still somewhat above the very stringent limits for the class II quality. Even if they could be reached with further adjustments to the WWTP, the best results would be near the limits, and compliance with the Regulation on the limit values of pollutants in surface and ground waters and sediment and deadlines for reaching them of the Republic of Serbia [21] could not be guaranteed. The large volume of 32 wt.% ferric chloride needed for almost complete phosphorus removal creates problems as it releases large quantities of chlorides (for the set of model parameters given in Table 7 it is 515 mg dm⁻³ in addition to the influent concentration, Eq. (10)). The alternative of adding ferric sulphate would create similar problem with the sulphates. The large increase in the contents of chlorides and sulphates would cause the equivalent increase in specific electric conductivity and mineralization (2065 mg dm⁻³), too. Even without the modifications, the use of sodium hydroxide for pH control causes a high sodium concentration, which together with nitrate and chloride ions originating from the human waste raise the total mineralization to 1865 mg dm⁻³. The limits of class II quality from the Regulation on the limit values of pollutants of the Republic of Serbia [21] obviously could not be reached by any modification to the existing equipment.

5. CONCLUSIONS

Wastewater composition in the case of small facilities, as demonstrated in this paper, especially with the restricted number of sanitary waters uses, can be very different than the typical domestic, or more generally, communal wastewater. To set the appropriate baseline quality and quantity of wastewater for the WWTP design purposes, the recommendation based on the analysis performed in this paper is that the data on per person excrement and urine production and their compositions should be used with the data on sanitary water quality and consumption to predict the quantity and quality of wastewater. If there are any significant water uses apart from wash basins and toilets/urinals, they should be addressed in the same manner. The utility of the presented methodology was demonstrated in this work, as well as its potential for use with the broader set of water uses.

The modelling of processes in a WWTP using software like BioWin was shown to be of great utility and value. The model was built based on the data obtained from the WWTP functioning, and from all, or most of key parameters regarding the inputs of influents and chemicals solutions. After the calibration by using the results of laboratory testing of the influent and effluent, the model was proved to be a very useful tool for testing several variants of dosing rates of input solutions, recirculation rate and waste activated sludge discharge rate, in order to obtain the best performing set of values in a sense of minimization of TN, P, BOD₅ and COD in the effluent.

The need to check for the compliance with the legislation necessitated additional spreadsheet calculations, which depend on the available parameters from the existing results of laboratory analyses of influent and sanitary water.

The developed approach comprises characterisation of wastewater based on precise knowledge of drinking water uses, modelling software use, and basic spreadsheet calculations to supplement the missing parameters in laboratory results and software output. This methodology, developed on the basis of experimental data and modelling simulations and calculations is beneficial for further extension to other wastewater types and treatment systems.

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Modeliranje sastava sanitarnih otpadnih voda i rada malog membranskog bioreaktorskog postrojenja za prečišćavanje otpadnih voda sa denitrifikacijom i nitrifikacijom

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(Naučni rad)

Izvod

Odnos koncentracija ukupnog azota i petodnevne biohemijske potrošnje kiseonika u sanitarnoj otpadnoj vodi jednog objekta energetske infrastrukture u Srbiji je višestruko veći nego što je uobičajeno za ovaj tip otpadnih voda, zbog čega se u postrojenju za prečišćavanje otpadnih voda (membranski bioreaktor sa anoksičnim i aerobnim reaktorom) denitrifikacijom eliminiše samo polovina ukupnog azota iz otpadne vode. Prvi korak analize je predstavljalo matematičko modelovanje geneze otpadnih voda da bi se ustanovio uzrok neuobičajeno velikog udela organskog i neorganskog azota. Prema projektnom zadatku za postrojenje bio je predviđen skoro deset puta veći broj radnika od sada prisutnih, kao i kuhinja i tuševi za osoblje, kojih nema ili se ne koriste. Na osnovu podataka iz naučne literature o sastavu ljudskih ekskremenata i podataka o sastavu vode koja se koristi za piće, određena je potrošnja vode za piće po čoveku i faktor umanjenja produkcije fecesa tokom radnog vremena u odnosu na srednju dnevnu vrednost uz dobro poklapanje za utvrđenim kvalitetom otpadnih voda. Osim azota, u efluentu je prisutna praktično ista koncentracija ukupnog fosfora kao u influentu. Da bi se ispitalo funkcionisanje postrojenja i isprobali efekti različitih mogućih modifikacija u procesu, napravljen je model u programu BioWin (Envirosim Associates Ltd.). U modelu je i bez značajnije kalibracije postignuto dobro poklapanje sa kvalitetom efluenta određenim laboratorijskim analizama. Ispitano je više varijanti doziranja rastvora acetatne soli u anoksičnom reaktoru, doziranja feri-hlorida u membranskom bioreaktoru radi eliminacije fosfata kao i 50 % rastvora natrijum-hidroksida radi regulacije pH. Rezultati simulacija pokazuju dvadesetostruko smanjenje koncentracije ukupnog azota i tridesetostruko smanjenje koncentracije ukupnog fosfora u efluentu (permeatu)

Ključne reči: softver za simulaciju tretmana otpadnih voda, ekskrement, urin, acetat, azot

