Modeling and Simulating a Novel Biohydrogen Production Technology as an Integrated Part of a Municipal Wastewater Treatment Plant

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A series of mathematical models and simulations was developed and performed using BioWin software suit in order to determine the suitability of implementing a biohydrogen production technology in an existing wastewater treatment plant. The evaluation of the performance of these approach was based on biohydrogen yield and effluent quality. The simulations show high biohydrogen production rates, with picks during the summer months, while most of the effluent environmental parameters remain at the same or even lower levels compared with the currently used technology.

Keywords: biohydrogen, dark fermentation, mathematical modeling and simulation, wastewater treatment.

Our current society increasingly requires more energy to maintain overall ascending economic trends, while the reserves of our primary energy carriers will be depleted within a few decades [1-2]. In addition, our fossil fuel-based economy is dramatically accelerating the process of global warming with severe and permanent consequences for the environment [3]. As a result, novel and safe energy carriers must be introduced. Hydrogen (H_2) satisfies all the requirements for a clean and renewable fuel [4]. It has the highest energy content per unit weight of any known fuel (142 kJ/g or 61000 Btu/lb.) and can be used directly in internal combustion engines or in fuel cells to generate electricity [5-6]. H_2 use in fuel cells is inherently more efficient than the combustion currently required for the conversion of other potential fuels to mechanical energy [7-8].

In the last few years, attention shifted towards novel and less energy-intensive technologies for producing H_2 [9-10]. Among the various hydrogen production processes, the dark fermentation biological methods appear to be the most promising because of the possibility to use various organic wastes as a substrate for fermentative hydrogen production [11]. By doing so, the coupling of organic waste treatment with renewable energy generation can be achieved [4, 12]. This approach may answer the need of reducing the cost of wastewater treatment and finding ways to produce useful products from wastewater [13-15]. One way to address both of these issues is to simultaneously generate bioenergy in the form of hydrogen by utilizing the organic matter present in wastewater [16].

Although a number of studies have been published regarding wastewater treatment coupled with biohydrogen production, most of them refer to lab-scale systems [17-20]. A key aspect in developing and applying such biohydrogen producing systems at an industrial scale is the *in silico* analysis of the integration possibilities of these approaches in the existing wastewater treatment technologies [21]. This approach would considerably decrease the costs of such endeavors. One way to address this issue is by using mathematical models that can accurately predict continuous biohydrogen production at an industrial scale [22-25]. Most of the available anaerobic digestion models were derived for anaerobic digestion of municipal wastewater biosolids [26]. One such model is incorporated in the BioWin software (EnviroSim Associates Ltd., Flamborough, Ontario, Canada), which is widely used for modeling wastewater treatment plants [27-28]. Both steady-state and dynamic modeling of biohydrogen production in the IBRCS using BioWin were successfully evaluated in recent years by a number of research groups [29-31].

In the present study, a process model using BioWin was developed, calibrated, verified and used to dynamically simulate and evaluate the impact of integrating a novel biohydrogen producing technology in an existing wastewater treatment process. In addition, the model was used to define the levels of different process parameters for biohydrogen systems that maximizes process performance and eliminates any methanogenic activity, with a particular focus on effluent quality. The results of this study have the potential to propel us closer to achieving and optimizing an industrial-scale system which will serve the dual purpose of a wastewater pre-treatment coupled with biohydrogen production.

Experimental part

In order to explore the opportunity of developing and implementing a biohydrogen production process in the technological process of an existing wastewater treatment plant, a series of mathematical models and simulations were applied using the BioWin software suit. This is a software package designed to shape and simulate the physical, chemical and biological processes taking place within the wastewater treatment plants. The program comprises 50 variables and 60 aerobic and anaerobic unitary processes. The use of this program for simulating

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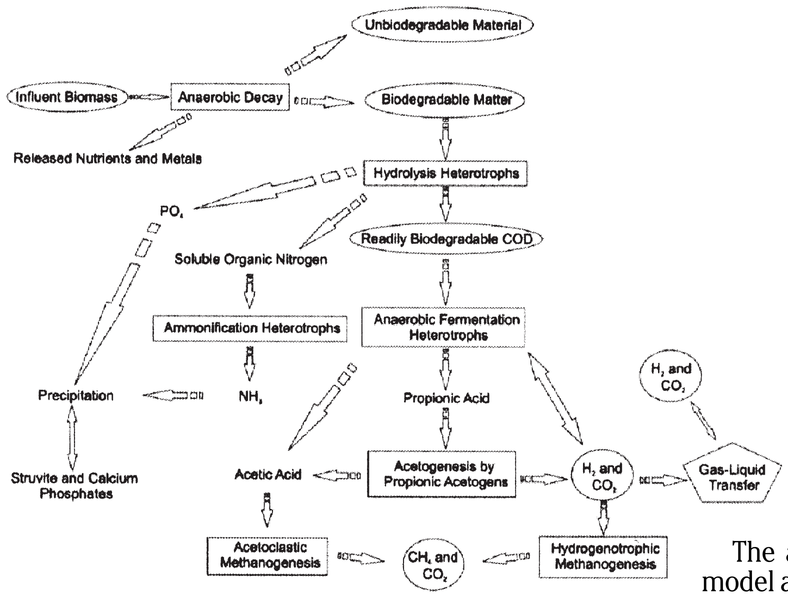


Fig. 1. Graphical representation of the mathematical modeling concept used in BioWin for the dark fermentative biohydrogen production process (adapted from BioWin manual)

technological processes taking place within the wastewater treatment plants implies a series of interconnected successive stages.

Mathematical model formulation

BioWin software suit contains two operational modules which include a steady state module and an interactive dynamic simulator. The steady state module can be used for simulating systems based on constant conditions while the dynamic simulator allows the user to change time varying inputs or changes in operational strategy which reflect real conditions. Thus, dynamic modeling using BioWin was found to be an appropriate tool for simulating the behavior of Timisoara Wastewater Treatment Plant as well as the effects of introducing a novel biohydrogen-producing fermentation technology.

The anaerobic degradation processes in the BioWin model are based on the “four population” model concept (heterotrophs, acetogens, acetoclastic methanogenesis and hydrogenotrophic methanogenesis). A conceptual schematic of the biohydrogen production model is shown in figure 1. The main kinetic parameters for heterotrophs (hydrogen producers) and the methanogens (hydrogen consumers) used in all modeling runs were set to default values (table 1).

Process model setup

The initial stage of our approach consists of mathematically projecting the technological configuration of the wastewater treatment process. In order to accomplish this, the technological diagram of the wastewater treatment plant of the Timisoara City, Romania, was used as a model. Data resulted from an extended monitoring campaign of the operational

Table 1
KINETIC PARAMETERS FOR THE INVOLVED MICROBIAL ORGANISMS

Heterotrophs			Methanogens		
Name	**Default**	**Arrhenius**	**Name**	**Default**	**Arrhenius**
Max. spec. growth rate [1/d]	3.2	1.029	Acetoclastic Mu Max [1/d]	0.3	1.029
Substrate half sat. [mgCOD/L]	5	1	H_2-utilizing Mu Max [1/d]	1.4	1.029
Anaerobic decay [1/d]	0.3	1.029	Acetoclastic Ks [mgCOD/L]	100	1
Anaerobic hydrolysis factor [-]	0.5	1	H_2-utilizing CO2 half sat. [mmol/L]	0.1	1
Adsorption rate of colloids [L/(mgCOD d)]	0.8	1.029	H_2-utilizing Ks [mgCOD/L]	0.1	1
Fermentation rate [1/d]	3.2	1.029	Acetoclastic propionic inhibition [mgCOD/L]	10000	1
Fermentation half sat. [mgCOD/L]	5	1	Acetoclastic decay rate [1/d]	0.13	1.029
Hydrolysis half sat. [mgCOD/L]	0.15	1	H_2-utilizing decay rate [1/d]	0.13	1.029

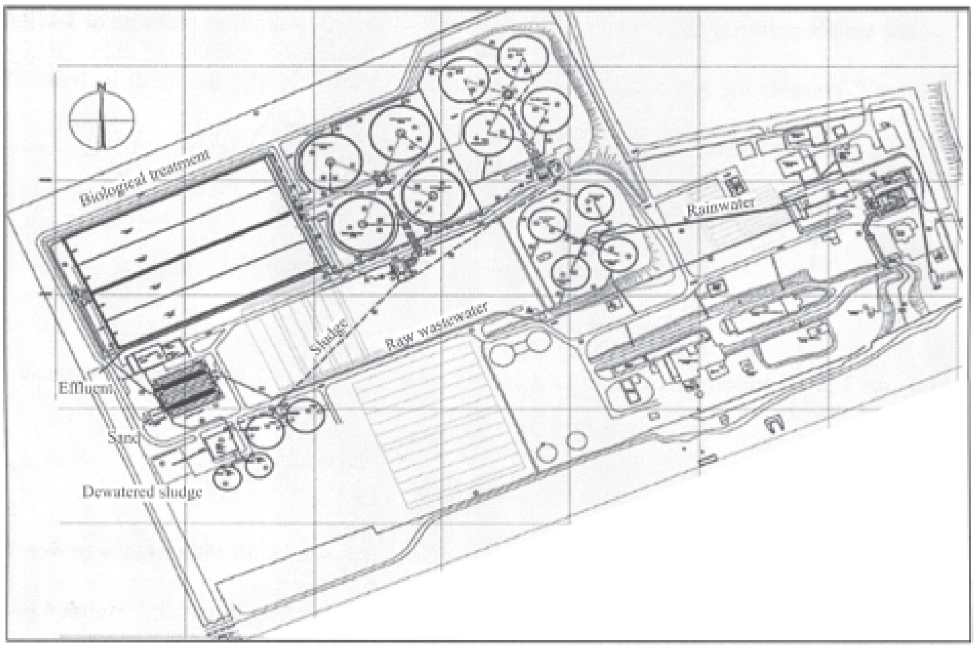


Fig. 2. Technological configuration of the wastewater treatment process currently used in Timisoara Wastewater Treatment Plant

parameters, carried on for one year, was fed into the mathematical model. The present technological configuration lacks the primary clearing tanks. Two of the 4 initial tanks are currently used in carrying out the chemical dephosphorization processes while the other two are used as retention tanks for the meteoric waters (fig. 2). This technological strategy was determined by the diminished organic matter concentration present in the current wastewater. The fact that the sewage system is unitary type further contributes to the dilution of the organic matter in the wastewater by rain water addition. The technological outflow of this wastewater treatment plant consists of two major components, the wastewater processing line and the sludge processing line (fig.2).

The wastewater processing line has two main treatment stages, a mechanical treatment stage followed by a biological treatment stage. The mechanical treatment step consists of a series of successive components, e.g. medium and small grills (4x4), 2 presses x 4 m^3/h, grit and grease removers (4 pieces). The biological treatment step consists of 4 biological tanks (each of them having two components, an anoxic part followed by an aeration part) and secondary clarifiers (8500 m^3 as well as 3650 m^3 volumes).

The sludge processing line (approx.13133 m^3/year) consists of an excess sludge and recycled sludge pumping station, 2 buffer tanks for the excess sludge (2x3509 m^3), mechanical thickeners connected to band-press filter meant to reduce the humidity of the sludge down to a minimum content of 20% dried substance and three sludge thickening and dehydrating lines. The sewage plant of the city of Timisoara is designed to satisfy the following parameters: 440.000 LE; Q day medium = 2.400 l/s; Q day maximum = 3.000 l/s; CBO5 = 22.000 kg/day; solid suspensions (ss) = 28.000 kg/day; ammonium = 5.400 kg/day; phosphates = 1.600 kg/day).

A mathematical representation of the wastewater treatment technological process was developed using the integrated BioWion tools (fig. 3). An intensive sampling campaign during one year (January 2013 - December 2013) was conducted, with a series of key parameters being monitored (table 2). The obtained insights were used to develop the *in silico* model of Timisoara Wastewater Treatment Plant.

Results and discussions

Model calibration

Following the mathematical description of the technological processes taking place in the discussed wastewater treatment plant, a calibration step of the model was developed based on data obtained from different monitoring points sampled during the course of one year. A series of key parameters were investigated both at the entrance and exit of the wastewater treatment plant as well as in different points along the technological steps considered to be important to the accurate and full evaluation of the described processes (table 2).

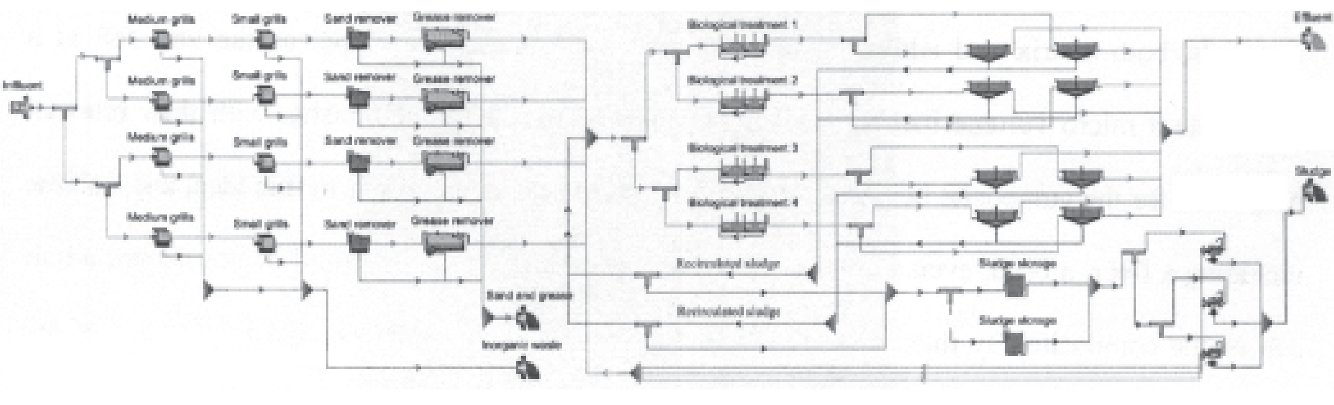


Fig. 3. Modeling the technological configuration of the wastewater treatment process currently used in Timisoara Wastewater Treatment Plant, using BioWin software suite

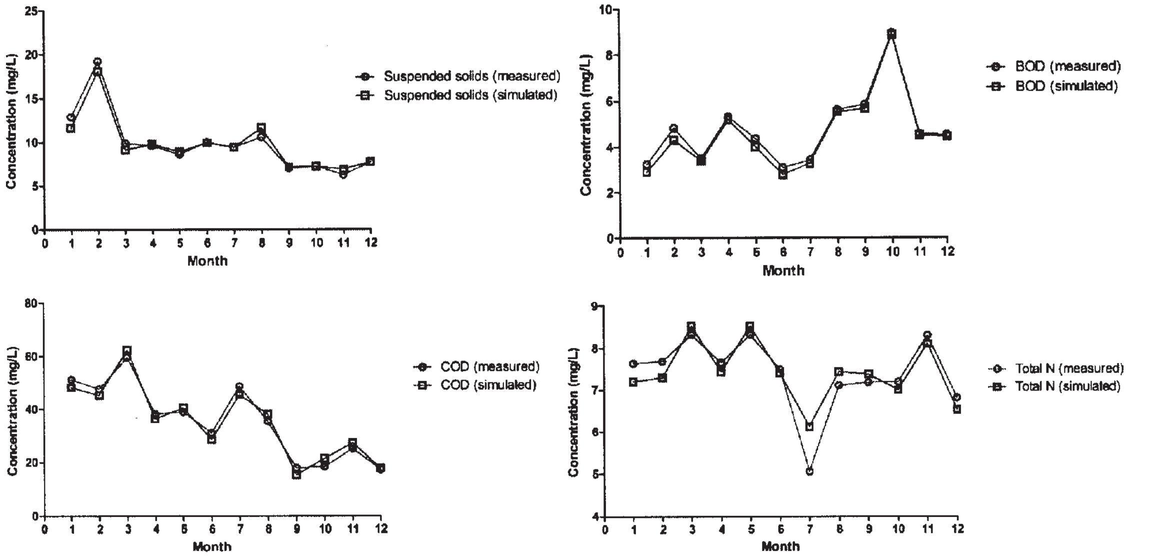
Month	Suspended solids (mg/L)	BOD (mg/L)	COD (mg/L)	Total N (mg/L)	Total P (mg/L)
1.	12.904760	3.238095	51.238090	7.633333	1.182381
2.	19.241380	4.827586	47.637900	7.683214	1.227483
3.	9.909091	3.500000	59.507270	8.316667	0.6959091
4.	9.611111	5.333333	38.333330	7.650000	1.005000
5.	8.625000	4.366667	38.977270	8.313334	1.178182
6.	10.000000	3.100000	31.050000	7.492000	1.099000
7.	9.409091	3.428571	48.590910	5.052500	1.484545
8.	10.590910	5.619048	35.300000	7.105000	1.891818
9.	7.000000	5.850000	17.950000	7.172500	1.979000
10.	7.260000	8.952381	18.347830	7.188334	1.473913
11.	6.238095	4.571429	25.047620	8.295000	1.356667
12.	7.705883	4.529412	17.294120	6.806667	1.251176

Table 2
MEASURED PARAMETERS IN THE WASTEWATER TREATMENT PLANT TECHNOLOGICAL PROCESS, DURING ONE YEAR

Moreover, additional sampling campaigns have been carried out in different points of the wastewater treatment plant in order to complete the existent data. Thus, the acquired information allowed for a calibration of the developed mathematical model to the point where the answers regarding the investigated parameters resulted from the mathematical modeling and simulation were comparable to the observations made *in situ*, at the wastewater treatment plant (fig. 4).

In silico implementation of the novel biohydrogen production system

Once the mathematical model of the technological processes taking place in the investigated wastewater treatment plant was calibrated, the implementation of the novel scenarios containing the biohydrogen producing reactors was investigated in relation to wastewater degradation rates and biohydrogen yields (fig.5). Thus, the major modifications were made to the biological treatment step by replacing the anoxic stage with biohydrogen reactors designed to anaerobically degrade the wastewater while simultaneously generating significant amounts of biohydrogen. The main reasons for which it has been decided upon this strategy are related to the need of developing a cheap alternative to the present technology, capable of wastewater treatment and simultaneous biohydrogen production. The novel biohydrogen reactors are able to anaerobically degrade directly the wastewater



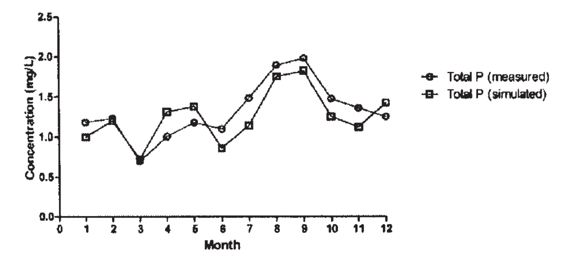


Fig. 4. Calibrating the mathematical model used to describe the technological configuration of the wastewater treatment process currently used in Timisoara Wastewater Treatment Plant, using BioWin software suite

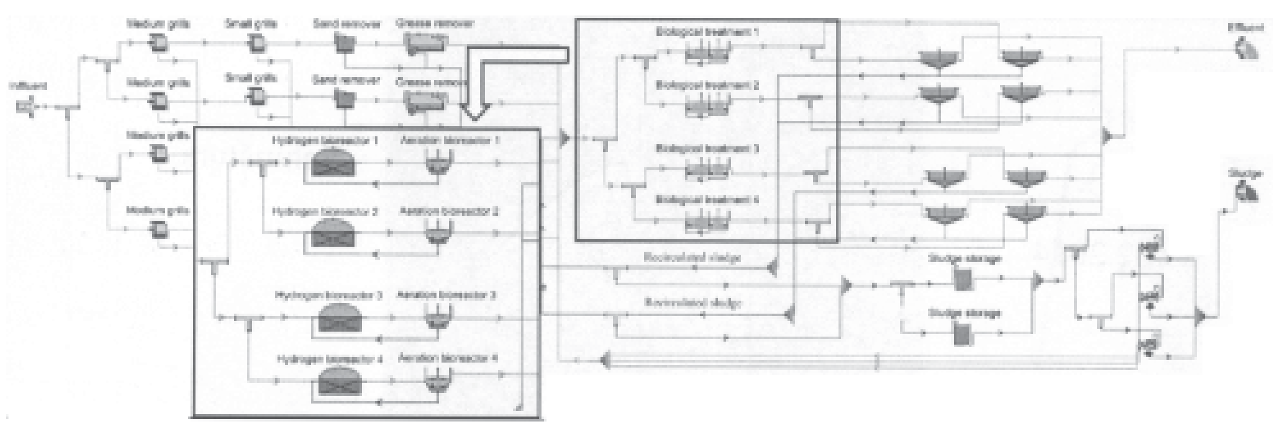


Fig. 5. Simulation scenario containing the novel biohydrogen production technology, to replace the currently used advance anaerobic biological treatment step with a series of anoxic bioreactors, as a integrating part of the wastewater treatment technology.

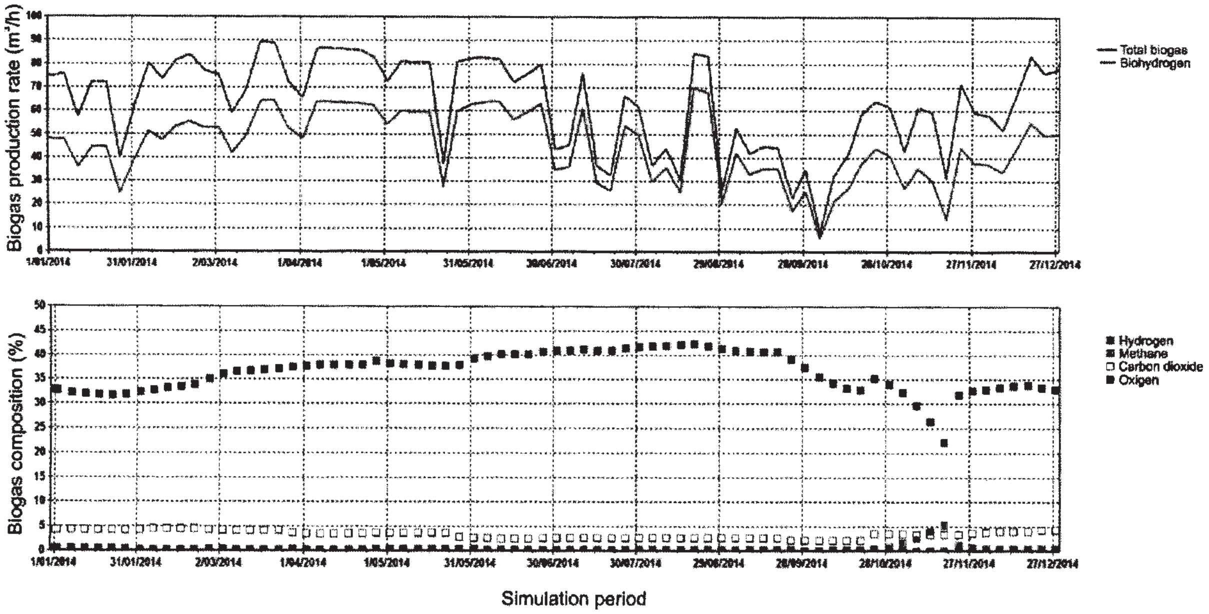


Fig. 6. Biohydrogen production rate (A) and the produced biogas composition (B), over the course of an year, for one of the four biohydrogen fermenters designed to replace the anoxic biological treatment step in the Timisoara's wastewater treatment technology, using BioWin software suite

together with the recalculated sludge, simultaneously producing significant quantities of hydrogen-rich biogas. In addition, these bioreactors can act as denitrification tanks further increasing the biological treatment of the wastewater. By coupling these two components, significant cost reductions can be achieved. Minor modifications were made in the technological process of the wastewater treatment plant, especially regarding the volumes of the recirculated wastewater from the secondary clarifiers to the bioreactors, in order to stabilize the technological process of wastewater treatment and simultaneous biohydrogen production.

In order to monitor the feasibility of introducing such technological modifications into the current wastewater treatment process, dynamic simulations have been carried out while monitoring different operational responses viz. influent fluctuations and climate variations (fig.6). A relatively pronounced seasonal variation in the biogas yields was notice as a result of the simulations carried out using the BioWin software suit. The organic matter availability as well as the atmospheric temperature can be accounted for these variations. The biogas composition is also subject to seasonal variations, especially as far as the hydrogen content is concerned, varying between 25% and 45% of the total biogas produced. As far as the CO_2 concentrations are concerned, the values tend to be relatively constant during the year (between 4% and 4.5% of the total produced biogas). During the *in silico* experiments only traces of O_2 and CH_4 were reported, with the exception of the latest which reached a maximum concentration of 5% of the total produced biogas during the month of November. A mean total daily biohydrogen yield of 180 m^3/h was reported during the simulations, with a minimum value of 40 m^3/h registered during the month of October and a maximum value of 280 m^3/h registered during the month of August.

A series of process parameters were monitored during the biohydrogen production experiments in order to identify the effects of the novel integrated technology on the effluent quality. It has been noticed that in most of the cases the effluent quality is similar or even better regarding some of the investigated parameters. For instance, the total suspended solids concentration within the effluent dropped down considerably from values situated around 9.5 mg/L in the case of the classical wastewater treatment technological approach, to values situated around an average of 6 mg/L in the case of applying the suggested bioenergetic solution. Furthermore, in the case of the final CCOCr concentration, a slight improvement was noticed compared to the classical technology, especially as far as the reduction in seasonal fluctuations is concerned. The final concentrations of total CBO_5 and P registered values close to those measured *in situ*, while the final N concentrations registered slightly higher values as a result of applying the new biotechnological scheme, compared to the values registered *in situ* at the Timisoara Wastewater Treatment Plant.

Conclusions

Certain adequate mathematical models capable of correctly describing the multitude of factors influencing the biohydrogen production process as a result of wastewater degradation have to be developed in order to achieve a more efficient *in silico* industrial scale testing and optimization of these processes in different operational situations. This requires the accurate mathematical description of the main influential factors acting upon the biohydrogen production yield. The approach used during the present study is treating these main groups under different mathematical modules. We used therefore three main mathematical modules describing the wastewater anaerobic fermentation process with simultaneous biohydrogen production, namely: a physical, a chemical and a biological module. This approach allow the mathematical modeling and description of the complex technological processes taking place within the wastewater treatment plant. By developing and validating an accurate mathematical description of the technological processes taking place within a wastewater treatment plant one can design and test different alternative configurations of these processes. Thus, the present study demonstrates that through replacing a big and costly part of the biological treatment step (anoxic tanks) with biohydrogen reactors capable of degrading directly the wastewater together with the recirculated sludge, significant amounts of biohydrogen can be produced. In addition, preserving and even improving in certain cases the quality of the effluent can be achieved through the observed improvement of the denitrification step.

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