Journal of Environmental Science and Engineering A 4 (2015) 559-566
doi:10.17265/2162-5298/2015.11.001

Estimation of GHG Emissions of a Fixed Bed Biofilm Reactor Cascade in Wastewater Treatment

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Abstract: A pilot scale fixed bed biofilm reactor used for treating municipal wastewater was modelled to examine greenhouse gas emissions under different operational parameters. For the calculations, GPS-X 6.3 commercial simulation tool was applied, which coupled the biokinetic modelling with a GHG estimator. Model calibration was based on a twelve-day set of measurements, where the system was operated under near steady-state condition. Simulation results reflected that direct emissions from biological processes are more significant than indirect emissions originating from energy consumption. Optimizing the operational parameters of a wastewater treatment system, a significant amount of GHG emission can be spared (e.g. optimal setup for internal recycle flow and dissolved oxygen levels), whereas, environmental factors such as temperature can also have a remarkable effect on GHG emissions: rising temperature causes faster biological reactions, increasing the production of greenhouse gases, especially methane, from the inner layers of the thick biofilm.

Key words: Biofilm, biokinetic modelling, greenhouse gas emission, wastewater treatment.

1. Introduction

Wastewater treatment causes a significant amount of Greenhouse Gas (GHG) emissions, mainly carbon dioxide, methane, and nitrous oxide. Numerous studies have been published recently about the emissions of existing technologies and their contributions to the greenhouse effect [1-3]. For quantifying the effects, Global Warming Potential (GWP) was introduced, which converts the different gaseous emissions to CO_2 equivalents. CH_4 has a GWP value of 25, while N_2O has a value of 295, based on the Intergovernmental Panel on Climate Change (IPCC) directives [4].

GHG emission in biological wastewater treatment can be divided into two types of sources: (i) direct emissions from the treatment processes and (ii) indirect emissions (energy and chemical consumption) [5].

Biological carbon dioxide emission includes the degradation of organic matter and aerobic respiration of biomass [6]. CH_4 is generally produced simultaneously with CO_2 during anaerobic processes. Its quantity depends on the amount of organic matter in the wastewater—the temperature and the type of the treatment system. In fixed bed reactors, anaerobic conditions generally only occur in the deeper layers of the thick biofilm forming on the carrier mesh [2].

Nitrification requires autotrophic microorganisms (ammonia-oxidizing bacteria), which transform the NH_4^+ ions into an intermediate compound of NH_2OH, followed by NO_2^- ions. The latter step releases NO and N_2O as byproducts. Nitrite oxidizers form NO_2^- ions to NO_3^-. The accumulation of NO_2^- ions could cause higher emissions of N_2O gas. Under conditions with low dissolved oxygen concentrations, ammonia oxidizers can also use NO_2^- as a source of oxygen, which is then reduced into NO, then N_2O, in the process of autotrophic denitrification [7]. Nitrification also consumes CO_2 as an inorganic carbon source [8]. Denitrification is a four step heterotrophic process, during which NO_3^- ions are transformed into NO_2^-

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ions, NO, N_2O and then N_2 gas. Lower C/N ratios of wastewater can be a cause of higher nitrous oxide emissions [7].

GHG emissions of wastewater treatment can be quantified using various approximations from easy-to-use estimators to complex biokinetic-based model approaches. The approximations of the IPCC guidelines drafted in 2001 are based on location specific values, which can alter considerably. Despite the fact that the procedure does not take into account the various technology used in a treatment plant, it is a simple and rapid method for rough estimation of GHG emissions [4].

The Bridle model divides greenhouse gas emission sources as the following: degradation of biomass, oxidation processes, offset by nitrification, and nitrous oxide production expressed as CO_2. It sums up emissions considering the chemical process stoichiometry [8].

An extension of the Benchmark Simulation Model 2 (BSM2) can be also applied for GHG calculations. Since BSM2 adapts the Activated Sludge Model 1 (ASM1) kinetic model for simulations, it estimates biological CO_2 emissions more precisely than the Bridle model [9]. For calculating N_2O emissions more accurately, a more complex model (e.g. ASM2N4DN) is required, which implements two-step nitrification and four-step denitrification, and approaches the diffusion of N_2, NO and N_2O from the water phase [10].

2. Material and Methods

2.1 The GHG Emission Estimating Model—Mantis 3

The Mantis 3 biokinetic model, developed for GPS-X by Hydromantis, was used for estimation of greenhouse gas productions of the reactor cascade, in CO_2 equivalents. The kinetic scheme and Petersen matrix of Mantis 3 is built around ASM2d. It is one of the most advanced models, covering the biological, physical and chemical processes experienced in wastewater treatment, such as hydrolysis, metabolisms involving heterotrophs, autotrophs and phosphorus accumulating. It simulates nitrification and denitrification as two-step processes. It also includes autotrophic denitrification applying NO_2^- as the electron acceptor instead of O_2. An important function in terms of GHG emissions is modelling gas-liquid transfer processes: other than the exchange of oxygen between the gas and liquid phase, it takes into account the absorption and desorption of CO_2, N_2, CH_4, H_2 and N_2O, based on K_La volumetric mass transfer coefficients and saturation concentrations [11].

The most important feature for quantifying GHG emissions in Mantis 3 is the integrated Carbon Footprint (CF) module. It categorizes the emissions into three main types. The sources of these are detailed as follows.

Direct, biology related emissions:

- CO_2 released from anaerobic, anoxic and aerobic biological processes;
- N_2O produced by nitrification and denitrification;
- CH_4 emitted from anaerobic processes.

Indirect, energy consumption related emissions:

- Emissions due to pumping energy requirement;
- Emissions caused by energy demand of aeration;
- Miscellaneous energy use emissions.

Material emissions:

- Chemical use emissions;
- Emissions brought about by material use, such as membranes or media;
- Emissions resulting from transportation.

The CF module also includes offsets of wastewater treatment plants that reduce the net emissions.

Offsets that sequester direct emissions:

- Biogenic capture of CO_2 (e.g. by nitrification);
- Flaring of CH_4;
- Using CH_4 for heating and energy production.

The two other types of emissions virtually cannot be sequestered by any offsets.

Fig. 1 summarizes direct, biological process emissions in the model.

As microorganisms consume organic substrate, part of it is converted into biomass, meanwhile, CO_2 is

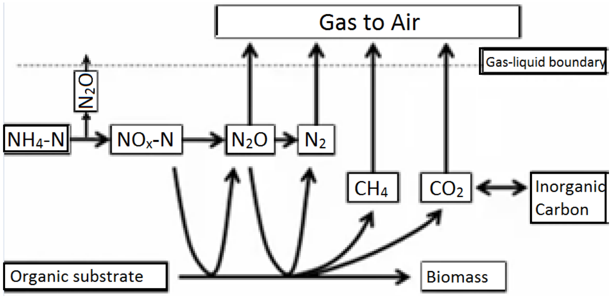

Fig. 1 Brief summary of direct, biological GHG emission pathways included in the CF module of Mantis 3 [12].

released. Depending on the pH of the system, the gas can be either dissolved in the water, increasing inorganic carbon content or be released into the atmosphere. Anaerobic processes also release CH_4, which can be also either dissolved or remain in the gas phase. The sources of N_2O production are simplified on Fig. 1. The CO_2 consumption of nitrifiers is not depicted, however, it is included in the model.

The model estimates direct emissions using Eq. (1) at a given time of t:

$$E_{scope1,i}(t) = K_L a_i(t)\left(C^*_{\infty,i}(t) - C_{L,i}(t)\right)V(t)f_{GWP,i} \quad (1)$$

Where,

$E_{scope1,i}$ (t): direct emissions of gas i in CO_2 equivalent (g/d);

$C_{L,i}$ (t): dissolved gas i concentration in reactor (mg/L);

$K_L a_i$ (t): volumetric mass transfer coefficient of gas i at field conditions (d^{-1});

V (t): reactor volume (m^3);

$C^*_{\infty,i}$ (t): equilibrium concentration of dissolved gas i (mg/L);

$f_{GWP,\,i}$: global warming potential of gas i (-).

Indirect emissions in the model are quantified based on Eq. (2), also at the time of t:

$$E_T(t) = \left(P_{pump}(t) + P_{blower}(t) + P_{mis}(t)\right)\cdot 24 \quad (2)$$

Where,

E_T (t): daily electricity consumption (kWh/d);

P_{pump} (t): pump power (kW);

P_{blower} (t): blower power (kW);

P_{mis} (t): miscellaneous power (kW).

The amount of indirect emissions is determined by substituting the daily energy consumption into Eq. (3):

$$E_{scope2,i}(t) = E_T(t)\cdot f_{elec,i}(t)f_{GWP,i} \quad (3)$$

Where,

$E_{scope2,i}$ (t): indirect emissions of gas i in CO_2 equivalent (g/d);

$f_{elec,i}$: gas i emission factor for electricity generation (-).

The emission factor is a region specific value found in databases. It assumes that the three examined greenhouse gases are generated in a set ratio based on the region’s generalized energy production processes. Certain regions can be selected in GPS-X, of which the US national was selected for the simulations, to generalize GHG calculations [11].

Mantis 3 can also be used to estimate emissions of material use. However, effects of chemical dosing, or replacement of carriers over time was not part of this study.

2.2 The Pilot Scale Reactor Cascade

The GPS-X model was calibrated based on a 12 m^3 volume, pilot scale reactor cascade’s (Fig. 2) effluent wastewater quality measurements. It is a pre-denitrification system, consisting of six reactors. An arranged, stretched out mesh of fabric threads is used as a biofilm carrier. The flat sheet surface of the carriers is 193.5 m^2 in total. The water levels are, in average, approximately 1.9 m. Aeration is supplied through fine bubble diffusers. In the first two anoxic reactors, air is introduced for mixing in order to avoid shearing of the biofilm by mechanical mixing. Treated water flows through weir channels at the outlet. The pilot reactors are primarily used for biological experiments, no phase separation is required after the bioreactors, since in biofilm systems, there is no need for sludge recirculation to sustain the biomass.

2.3 Data Analysis, Preparation of Data for Modelling

During the 12-day time period chosen for adjusting model parameters, operational values were registered

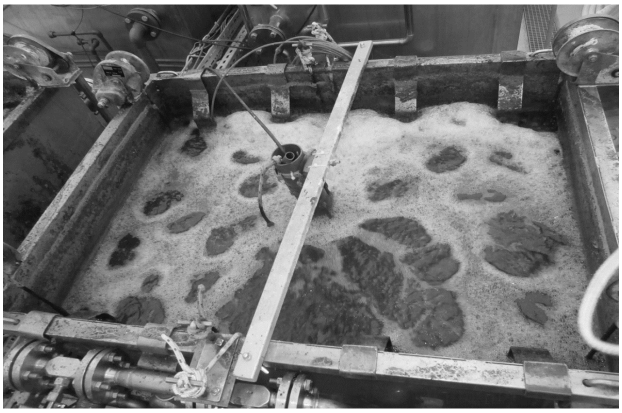

Fig. 2 Photograph of the pilot scale reactor system.

by sensors, and effluent water characteristics were examined in laboratory. All data for modelling were processed as daily average, composite values. Measurements confirm that the operation of the system was stable during this period, the amount of biofilm was suitable based on the suspended solids concentration, and the effluent quality practically also reflects a steady-state condition. The influent load was also considered to be steady-state.

From the laboratory measurements, Chemical Oxygen Demand (COD) was used for examining organic matter removal, and Total Nitrogen (TN), NH_4-N, NO_2-N and NO_3-N values were used for evaluating nitrogen removal processes. For approximation of solids removal, the concentration of Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) were determined. Soluble COD had to be specified by filtration, to separate the particulate fraction of organics, which is an important attribute of the model in terms of biodegradation. Daily values were used dynamically for the model. Table 1 shows their overall average.

Despite the lack of phase separation, the system can remove most of the suspended solids and COD. Nitrification is highly effective, and nitrate-nitrogen can be kept below 20 mg N/L by denitrification. The system is not designed for phosphorus removal, the Total Phosphorus (TP) concentration decreases because of the phosphorus content taken up by the biomass.

Table 1 Average influent and effluent wastewater quality measurements in the chosen 12-day period for calibration.

Parameter average	Influent value	Effluent value
COD (mg/L)	529.1	117.2
Filtered COD (mg/L)	144.2	37.8
NH_4-N (mg N/L)	46.9	0.12
NO_2-N (mg N/L)	0.28	0.12
NO_3-N (mg N/L)	0.31	18.3
TN (mg N/L)	63.4	24.3
PO_4-P (mg P/L)	5.59	6.38
TP (mg P/L)	9.46	8.23
TSS (mg/L)	264.0	81.7
VSS (mg/L)	227.6	68.4

Operational variables were read continuously by probes, then the values collected by a central computer were processed to form daily averages, and be used as model input parameters. Influent water temperature was measured by a thermometer in an equalization tank, volumetric flows were registered by flow meters, and dissolved oxygen levels were measured by DO probes in each reactor. Table 2 shows the average of operational values in whole.

3. Model Calibration

Kinetic parameters of the GPS-X reactor model were adjusted so that it reproduces the measured effluent water quality. The purpose of model calibration is synchronizing mathematical simulations and laboratory measurements in order to describe biological, physicochemical and mechanical processes reliably. Effects of input parameters can be analyzed, and the expected operation of a specific system can be predicted more precisely by the calibrated model. As a preparatory step, an interval needs to be chosen where the biological system reaches a quasi-steady-state condition. The operational parameters, such as the water volumetric flows and aeration should be maintained approximately constant. In fixed film processes, considerable part of the biomass develops on the large specific surface biofilm carriers. The biofilm mass stabilizes with time, as a dynamic equilibrium is formed between the attachment and detachment processes [12].

Table 2 Averaged operational parameter values in the chosen 12-day period for calibration.

Parameter average	Value
Influent water temperature (°C)	16.0
Influent wastewater flow (m^3/h)	0.4
Internal recycle flow (m^3/h)	0.8
Reactor 1 DO (mg/L)	0.4
Reactor 2 DO (mg/L)	0.1
Reactor 3 DO (mg/L)	3.7
Reactor 4 DO (mg/L)	3.7
Reactor 5 DO (mg/L)	5.5
Reactor 6 DO (mg/L)	6.9

The simple GPS-X layout of the bioreactor cascade is shown in Fig. 3.

The influent raw wastewater characteristics and operational parameters from the twelve-day measurement campaign were specified as daily average values. Influent characterization was necessary to specify BOD_5, filtered COD, TSS and VSS concentrations in the model, whereas, the rest of the measured parameters can be set directly in Mantis 3. The influent fractions (Table 3) were determined for each day, with the help of the mathematical formula given in the influent advisor interface of GPS-X. During the calibration process, consecutive simulations ran to adapt the modelled effluent concentrations to the laboratory measurements by adjusting biokinetic parameters, which were necessary for approaching the cascade's individual behavior. The simulations were started in a steady-state condition, but this function was turned off for the twelve-day interval, so the model could adapt to the dynamically changing input parameters. Matching the effluent filtered COD values was important since this parameter represents the organic fraction which cannot be biodegraded further significantly. The effluent TSS reflects the amount of solids removed biologically in the reactor. Effluent TN can represent the efficiency of denitrification and hydrolysis of organic nitrogen. Concentration of NH_4-N provides clear feedback about nitrification.

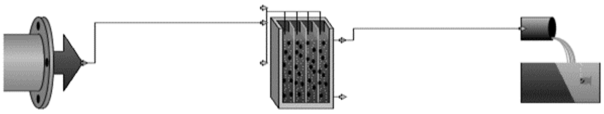

Fig. 3 The GPS-X layout of the pilot scale reactor system.

Table 3 Average results of the influent wastewater characterization.

Influent fraction	Value
Soluble COD to total COD ratio (g COD/g COD)	0.28
Total BOD_5 to total COD ratio (g BOD/g COD)	0.51
Soluble BOD_5 to soluble COD ratio (g BOD/g COD)	0.54
Colloidal substrate (g COD/m^3)	43.4
VSS to TSS ratio (g VSS/g TSS)	0.86
Particulate COD to VSS ratio (g COD/g VSS)	1.67
Ammonium fraction of soluble TKN (-)	0.76

Table 4 Parameters modified during the model calibration.

Modified kinetic parameter	Purpose of calibration	Value
Diffusion constant of total ammonia (cm^2/s)	To adjust nitrification	9.5×10^{-7}
Anoxic heterotrophic yield (g COD/g COD)	To adjust denitrification	0.825
Hydrolysis rate constant of inert residue (d^{-1})	To adjust solids removal	0.045

For calibration, three main kinetic parameters (Table 4) were approximated by trial and error approach and then manually fine-tuned to achieve a close fit between the simulated data shown by continuous lines, and the measurements marked by discrete data points (Fig. 4).

4. Results and Discussion

The effect of four different process variables was examined on the emission of carbon-dioxide, methane and nitrous oxide by running steady-state simulations. The effluent NH_4-N, NO_3-N and soluble COD concentrations were also examined in parallel. The averages of input parameters from the twelve-day measurement set (Tables 1 and 2) were specified as a baseline.

4.1 Effect of Reactor Volume

By increasing the reactor volume and the Hydraulic Residence Time (HRT) of the wastewater, effluent COD and NH_4-N concentrations are lowered, as well as NO_3-N in the anoxic reactor effluent. The simulations show that larger amounts of biodegraded

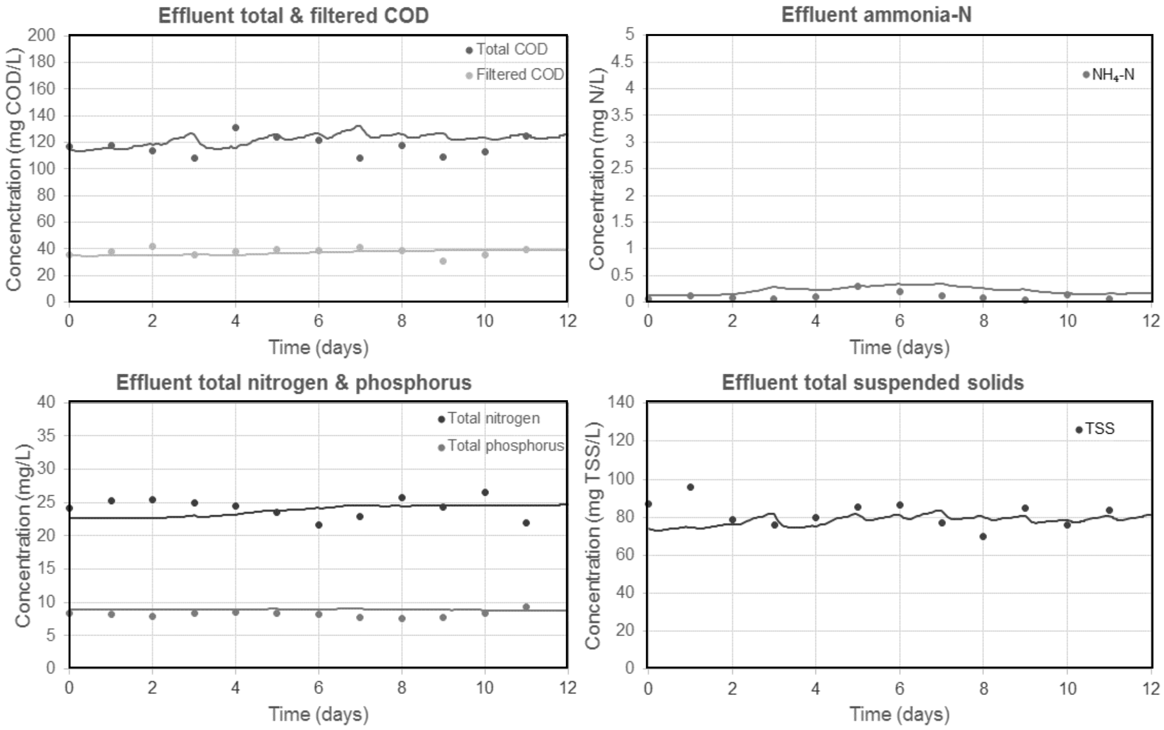

Fig. 4 Results of model calibration, showing the main effluent concentrations relevant to the treatment efficiency.

organics result in higher CO_2 and CH_4 emissions, however, with more efficient nitrification and denitrification—since a higher retention time is available—the N_2O production is lowered (Fig. 5).

Indirect emissions are increased slightly, since the larger liquid volume and faster biological reactions imply higher aeration requirements (Fig. 6).

4.2 Effect of Temperature

Temperature of the raw sewage is an external environmental condition. Considering operational aspects, it affects the biological processes, the treatment efficiency and also GHG emissions accordingly.

Based on the simulation results, at higher temperatures, methane and nitrous oxide emissions are gradually increasing, because of the deeper, anaerobic layers of the thick biofilm, as it is more difficult to ensure the diffusion of oxygen there (Fig. 7). Temperatures lower than 14 °C result in increasing N_2O production, as the metabolism of nitrifying bacteria becomes slower, allowing more byproduct to be released.

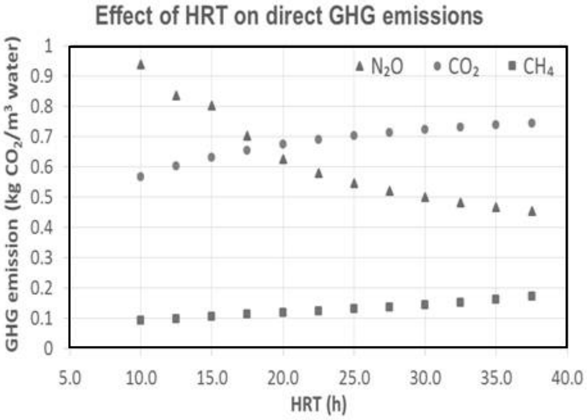

Fig. 5 Direct GHG emissions as a function of HRT.

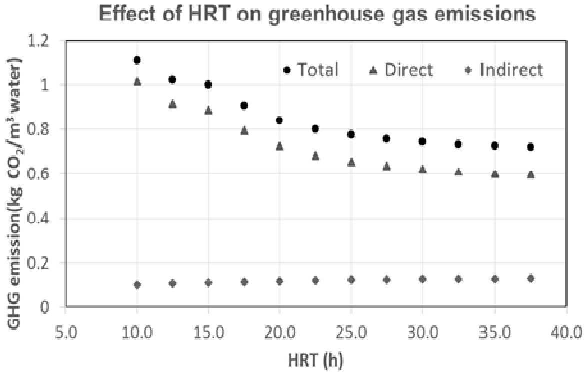

Fig. 6 Summarized GHG emissions as a function of HRT.

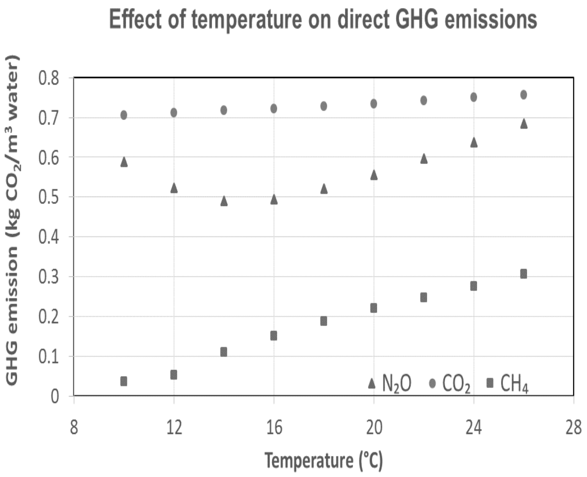

Fig. 7 Direct GHG emissions at different temperatures.

Altogether, direct emissions increase with higher water temperatures, the indirect emissions are only raised very slightly, due to the decreasing solubility of oxygen, which means higher air demand (Fig. 8).

4.3 Effect of Internal Recycle

Increasing the recycle flow improves nitrate-N removal in a diminutive extent, and slows down the rate of denitrification. The water recycled to the anoxic reactors becomes more concentrated in nitrate-N, but contains less carbon than the influent due to COD removal, carbon/NO_3-N ratio decreases. As seen in Fig. 9, simulations show that raising the recycle flow increases N_2O production from denitrification.

To provide higher recycle flows, more pumping energy is required, which raises the indirect emissions slightly (Fig. 10). A practical setting of internal recycle still provides a substantial removal of nitrate-N. In this case study, the optimal internal recycle flow proved to be two times the influent flow.

4.4 Effect of Dissolved Oxygen

The lower the dissolved oxygen levels are in aerobic reactors, the more CH_4 is emitted from anaerobic biofilm layers. Due to the scarcity of oxygen in deeper layers, nitrifying bacteria can instead take up NO_2^- ions, generating more N_2O (Fig. 11).

More aeration also causes higher indirect emissions (Fig. 12). Maintaining DO concentrations of 3 mg/L can mostly reduce GHG emissions in total, and also ensure stable performance of the biological treatment.

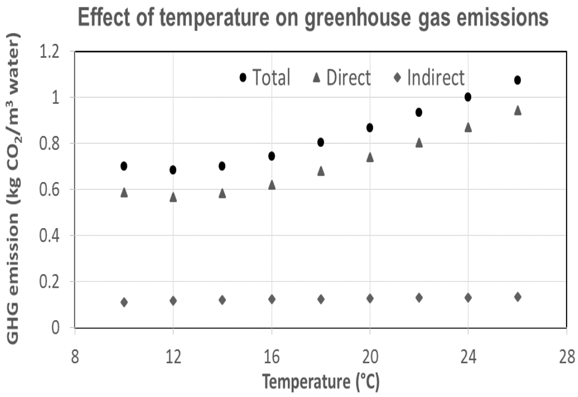

Fig. 8 Summarized GHG emissions at different temperatures.

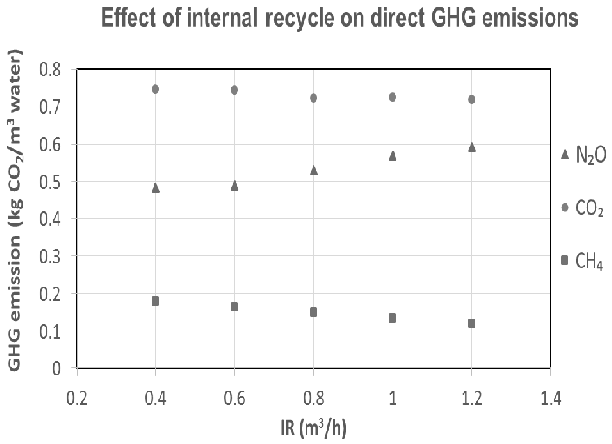

Fig. 9 Direct GHG emissions as a function of IR flow.

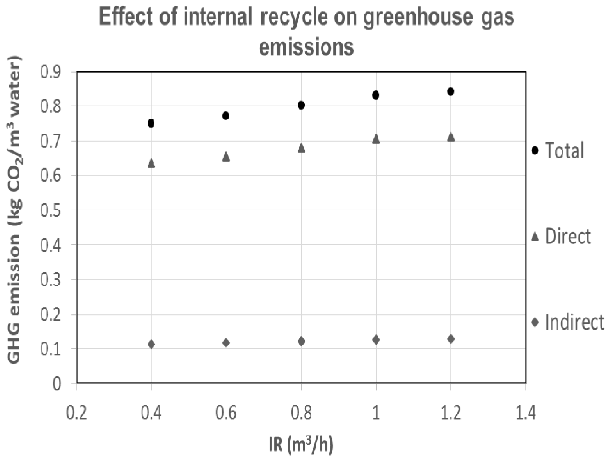

Fig. 10 Summarized GHG emissions as a function of IR.

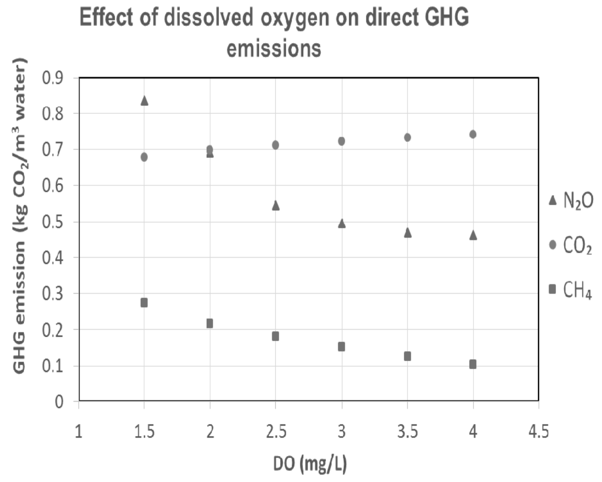

Fig. 11 **Direct GHG emissions at different DO levels.**

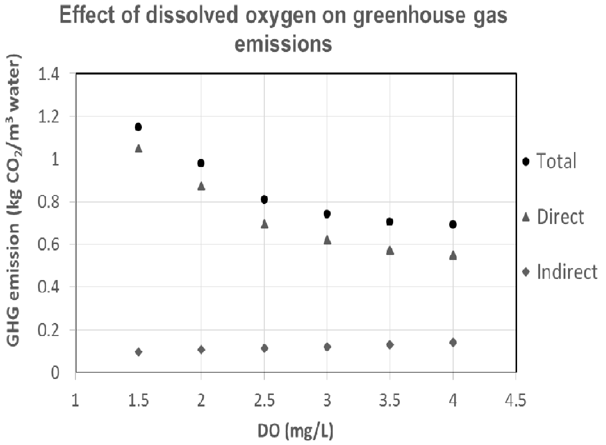

Fig. 12 Summarized GHG emissions as a function of DO.

5. Conclusions

GHG emissions from a pilot fixed biofilm system were evaluated numerically applying a commercial biokinetic simulation tool. As a result, the direct GHG emissions are more substantial than energy use related emissions, applying any operational setting. The examined fixed film process is most sensitive in terms of N_2O production. N_2O emissions can be minimized by adjusting reasonable and sensible values for process variables. Thus, applying a reactor volume that is large enough for complete nitrification, a recycle flow that is essentially required to maintain proper nitrate-N removal, and DO levels that are high enough to provide oxygen for nitrifying bacteria in the biofilm layers—also reducing CH_4 production—are all essential in order to optimize the GHG emissions of wastewater treatment.

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