Model Based Stimulus Experiments to Improve Wastewater Treatment Using Electron Conductive Material

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Abstract

To be sustainable from an ecological, economic and social point of view, municipal wastewater treatment requires a smart technology in which an optimal combination of the ecological and energetic demands is searched for. The integration of electron conductive materials into a traditional constructed wetland (CW) has been demonstrated to be an emerging strategy for wastewater treatment. By exploiting the electron transfer capability of electro-active genus bacteria on electrically conductive materials, the configuration can be used to treat and disinfect urban wastewater from small communities at zero energy operation cost.

At the level of the engineering practice, CWs with and without conductive beds have been implemented using the black-box concept and with a clear focus on experimental rather than theoretical work. However, we believe that in order to accelerate the progress of system design, optimization and practical applications, mathematical models play an important role.

In this contribution, 0D mathematical models were formulated that used the Constructed Wetland Model 1 (CWM1) biokinetics under aerobic conditions. The model equations were implemented and solved numerically using Multiphysics®5.3. With the selected kinetics, parameters and working conditions, the stimulus input signals of O_2, S_{NH}, S_F loadings were proposed to investigate the best scenario for nitrification of the aerobic column. This strategy is especially advantageous for water recycling and the subsequent anaerobic unit where electro-active genus bacteria start to play as a key role for denitrification process.

Keywords: constructed wetland model, electro-active genus bacteria, electron conductive material, nitrification, stimulus experiment

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1. Introduction

Wastewater treatment processes based on biological degradation of sewage through oxidative reactions in presence of electron conductive materials have been demonstrated as a low cost, eco-friendly technology especially for small communities [1-6]. The electron conductive materials are imbedded into the system to enhance the wastewater treatment taking the advantage the electronic property of the materials and the electron acceptor-donor characteristic of electro-active genus bacteria e.g. Geobacter [4-7]. The complex physical, chemical and electro-chemical processes take mainly place in the conductive bed to convert COD to environmentally friendly substances.

The final effluent of treated wastewater is characterized by certain standards e.g. suspended solids removal, redox potential behavior, removal of organic matter, nitrogen removal, and phosphorous removal. Wastewater effluent discharge standards depend much on regional regulatory. In the case of nitrogen removal requirements (e.g. in Denmark), wastewater treatment systems using electron conductive beds, so called microbial electrochemical wetland (MEW), have been proposed as a promising, smart, sustainable and inclusive technology. Similar to a traditional wetland, this system configuration can operate with an air open inlet and can incorporate vegetation [1]. Main processes occur in sequence under aerobic, anoxic and anaerobic conditions. The former ones are met on the upper part of the wetland where O_2 can be dissolved and diffuse from the air and be released from vegetal species whereas the latter conditions correspond typically to the lower part of the wetland.

In urban wastewater from small communities, the main forms of nitrogen are organic nitrogen and ammonia nitrogen, and less nitrites or nitrates. Organic nitrogen is transformed in ammonia nitrogen by ammonification. Part of this ammonia nitrogen is assimilated by the microorganisms. Most of the ammonia nitrogen in MEW is removed by combined processes of nitrification and denitrification [8]. Nitrification is an autotrophic process that transforms the ammonia in nitrate in two stages. The first step of nitrification is carried out by the ammonia-oxidizing bacteria (AOB) that oxidize ammonia to nitrite. Due to the slow growth of these bacteria and their sensitivity to environmental conditions, nitrification has been often considered one of the most unreliable and unpredictable processes in the traditional wastewater treatment or wetland. The anammox (anaerobic ammonium oxidation) model has been proposed as a more energy-efficient alternative to the conventional nitrification and denitrification processes [9]. The anammox process consists of the combination of ammonia and nitrite directly into dinitrogen gas. Compared to other nitrifiers, anammox bacteria coexist with heterotrophic bacteria because heterotrophic consumption of O_2 creates a more anoxic environment beneficial to anammox bacteria but in competition with nitrifiers [10].

Nitrogen removal is historically poorly achieved under anaerobic conditions, showing a bottleneck in the ammonium oxidizing process. In the last years, different research approaches have been proposed to improve the nitrogen removal. The first example is a focus on vertical flow (VF) systems with recirculation to increase the total nitrogen removal efficiency [11-14], because the treated effluent is O_2 limited and has a low availability of carbon source, consequently the removal of total nitrogen is restricted. Additionally, VF systems provide good conditions for nitrification but no denitrification occurs in these systems. Therefore, it has been a growing interest in hybrid systems (incorporated VH and horizontal flow (HF)), where the advantages of both systems can be combined to complement each other in order to achieve higher treatment efficiency, especially for nitrogen. Most of them comprise VF and HF systems arranged in a staged manner [15-20]. The recirculation of a fraction of the effluent of the VF system to the inflow of the HF system was also carried out to improve nitrogen removal.

The utilization of electron conductive materials in wastewater treatment have been proven as an efficient and eco-friendly system not only for carbon based pollutants but also nitrogen removal [7, 1]. A large body of work is dedicated to experiments. The main objective of the current work is to develop a mathematical model which is able to describe the most common processes taking place within the selected wastewater treatment system. At the same time, the model is used to study treatment scenarios of nitrogen removal.

The mathematical model includes ODEs using bio-kinetic model Constructed Wetland Model 1 (CWM1) was built in COMSOL Multiphysics®.

2. Mathematical Model

2.1 Assumptions

- The system is homogenous.
- The reactor volume is constant.
- The contribution of sub-processes like mass transport, charge transport, heat transport, and biofilm growth is neglected.
- The system works under isothermal conditions.

The model adopting these assumptions can only provide qualitative data at the macroscopic level.

2.2 Dynamic modeling of biochemical reaction systems

The dynamics of biochemical reaction networks is described using the ODEs. The internal states $C_\alpha(t, u(t), \theta_x))$, e.g substrate concentration, is determined by the solution of an initial value problem of the form

$$\boldsymbol{\frac{d}{dt} C_\alpha(t) = f(C_\alpha(t), u(t), \theta_x)} \qquad (1)$$

$$f(C_\alpha(t), u(t), \theta_x) = \sum_{j,\alpha} \gamma_{\alpha,j} r_j(C_\alpha(t), u(t), \theta_x) \qquad (2)$$

with initial system states $x(t_0)=x_0$ and the right hand side function $f(x(t), u(t), \theta_x)$ describing biological interaction mechanisms depending on the system states x(t), input $u(t)$ (stimulus) and kinetic parameter set θ_x (Eqs. (1-2)), see also Fig. 1.

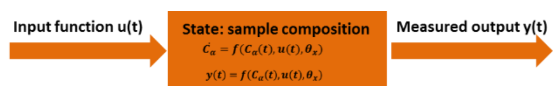

Figure 1: input-output scheme of stimulus design experiment

The control variables O_2, S_{NH}, and S_F are crucial for the nitrification/denitrification processes. In wastewater treatment systems, they can be designed in such a way that the resulting measurement function becomes optimal for the goals of the experiment.

2.3 Reaction mechanism

In the biological wastewater reaction network, the kinetics term in Eq. (1) is quite complicated and composed of many parallel, consecutive and intertwined reactions covering from chemical, biochemical, and electrochemical steps. Developing a detail reaction mechanism of biological wastewater treatment is highly complex as it should include different bacteria groups with multiple biochemical kinetic processes. Therefore, the model development should use information from existing models, previous experimental studies and from the real existing system to be described. There are some widely used kinetic models e.g. Activated Sludge Model (ASM) [21], Constructed Wetland Model 1 (CWM1) [23] and Anaerobic Digestion Model 1 (ADM1) [22] have been used commonly in the literature. The mathematical formulation of these reaction rates is based mainly on the mass action law for chemical reactions, and Monod or Michaelis-Menten equations for related enzymatic and microorganismal steps. The derivation of CWM1 was based on the ASM and ADM and has been widely applied in the last two decades. Convincing results increased the acceptance of CW models in general.

The CWM1 includes 17 processes and 16 components. The stoichiometric matrix of CMW1 and the reaction steps and rates are defined in the original publication [23]. There are three importance transformations in CWM1: the degradation of slowly soluble organic compounds, nitrogen related compounds and sulfur related compounds. They are interlinked by microorganisms. One limitation of CWM1 is that gaseous emissions are ignored.

3. Results and Discussion

3.1 Kinetic behavior

The biokinetic model CWM1 requires a total of 65 input parameters. The component concentrations are initially taken from the experimental data of synthetic wastewater prepared for the typical lab scale experiment. The influent microorganism concentrations are considered to be equal and relatively small (in the range of 10^{-4} mg $COD \cdot L^{-1}$).

Table 1: Influent concentration of species for CWM1

Name	Value	Unit
S_O	5.62	$mgO_2 \cdot L^{-1}$
S_F	533	mg $COD \cdot L^{-1}$
S_A	1e-4	$mgCOD \cdot L^{-1}$
S_I	1e-4	$mgCOD \cdot L^{-1}$
X_S	1e-4	$mgCOD \cdot L^{-1}$
X_I	1e-4	$mgCOD \cdot L^{-1}$
S_{NO}	0.65	$mgN \cdot L^{-1}$
S_{NH}	149	$mgN \cdot L^{-1}$
S_{SO4}	89	$mgS \cdot L^{-1}$
S_{H2S}	1e-3	$mgS \cdot L^{-1}$
X_H	10^{-4}	$mgCOD \cdot L^{-1}$
X_A	10^{-4}	$mgCOD \cdot L^{-1}$
X_{FB}	10^{-4}	$mgCOD \cdot L^{-1}$
X_{AMB}	10^{-4}	$mgCOD \cdot L^{-1}$
X_{ASRB}	10^{-4}	$mgCOD \cdot L^{-1}$
X_{SOB}	10^{-4}	$mgCOD \cdot L^{-1}$

The kinetic parameter set, extracted from the original study, is used in the first step to analyze the kinetic behavior. With the total amount of COD of 533 $mgCOD \cdot L^{-1}$, the incubation time for the biotransformation of wastewater is relatively long for both anaerobic and aerobic conditions (up to 250 days) (Fig. 2).

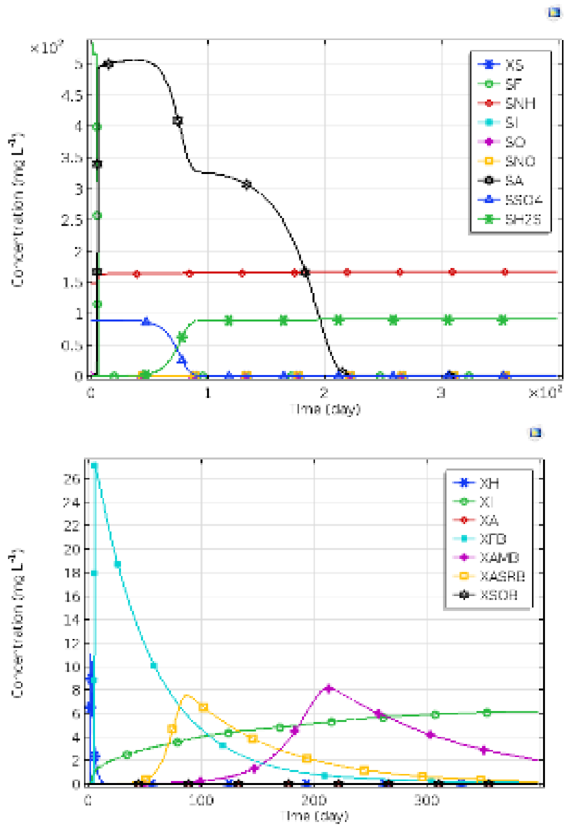

Figure 2: Kinetic behavior of different components in CWM1 under aerobic conditions (top) and anaerobic conditions (bottom). The kinetic parameters are extracted from original publication [23].

The presence of O_2 impacts on the kinetic behavior only for a short time during the incubation, the depletion of O_2 in a batch operating mode system results in an anaerobic operating condition of the system after a certain time (Fig. 2). As can be seen also from Fig. 2, the nitrogen related compounds (S_{NH}) do not transform significantly to other substances during the incubation time, the sulfur related compounds decay considerably after c.a. 50 days on incubation. This behavior, however, does not reflect well the experimental observation of systems in which bio-electrochemical conductive materials are imbedded [1]. The feeding interval for such system is less than 8 hours [1].

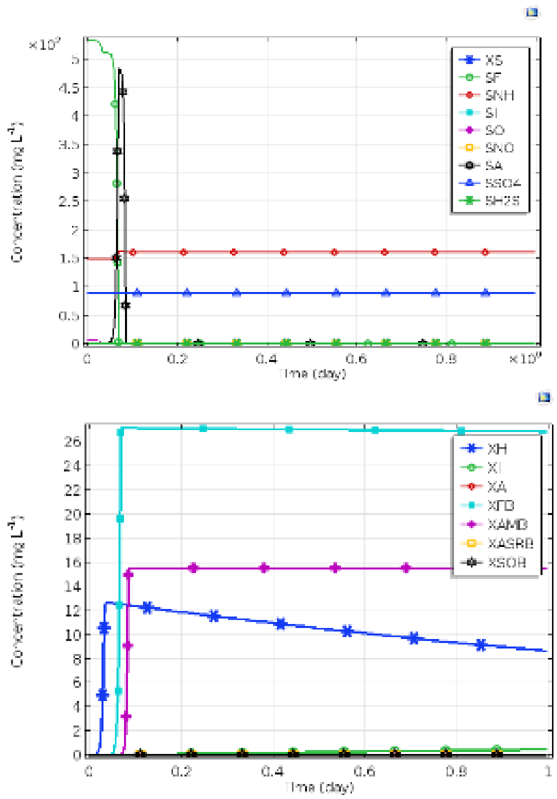

Figure 3: Kinetic behavior of CWM1 using the adjusted parameters presented in Table 2.

An additional simulation was made to qualitatively evaluate the system. The values of K_{NHA}, μ_A, μ_{FB}, μ_{ASRB}, μ_{AMB}, and μ_H in the new set of parameters (Table 2) in the simulation are higher than their original values. These parameters are showing that the working system owns a very fast kinetics which can be ascribed by the outstanding properties of bio-electron conductive materials to microbial communities. A clear evidence of conductive materials which interfere in bacterial growth has not yet been found. But some initial experimental results from bacterial analysis have been shown the predominance and substantial change in the microbial communities of the system using microbial electrochemical technology (MET) in comparison to the traditional microbial system [1].

Table 2: Adjusted kinetic parameters

	Original	Adjusted
μ_{AMB}	0.085	425
μ_{FB}	3	300
μ_H	6	300
μ_A	1	10
μ_{SOB}	5.28	528
μ_{ASRB}	0.18	1.8

3.2 Operating scenarios for the treatment of nitrogen related compounds

As mentioned in the introduction, nitrogen related compounds (S_{NH}) are usually inefficiently removed from the waste water treatment due to the limit of electron acceptor sources (e.g. O_2) in the wastewater. To accelerate the nitrogen removal, O_2 can be chosen as a strategic input signal. Additionally, dosing different substrates (e.g. S_F and S_{NH}) to the operating system can be also suitable to exploit the availability of bacteria inside the conductive bed. Therefore, an effort in simulation was made to realize various operating scenarios i.e O_2, ammonium and ammonia nitrogen (S_{NH}) and fermentation product (S_F, considered to be acetate).

3.2.1 Oxygen supply

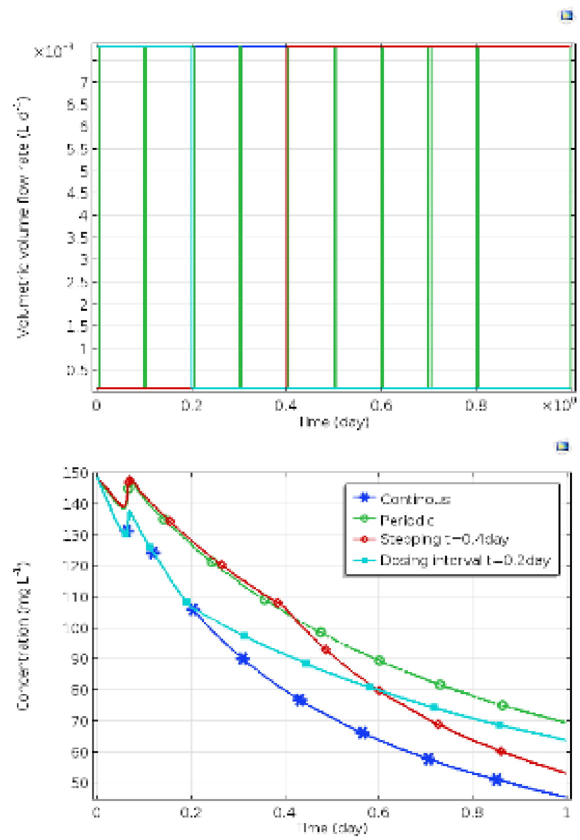

Figure 4: Different O_2 supply scenarios (top) show decay of S_{NH} (bottom).

Different schemes of O_2 supply e.g. ramping, periodic, pulsing, continuous and the conversion of

S_{NH} is presented in Fig. 4. The simulation was done assuming that additional soluble O_2 will not change the reactant volume. In general, c.a. 80% nitrification can be obtained if the continuous supplying scheme of O_2 is applied. Practically, this scheme maximizes O_2 concentration inside the system and can be realized by inserting O_2 gas pipes into the operating system.

3.2.2 S_{NH} and S_F supply

Various recycling schemes of S_{NH} and S_F can be seen in Fig. 5a at the continuous supplying of O_2. This kind of operation can contribute in the decision making of waste water recycling due to the fact that only certain groups of bacteria can consume further substrate. On the other hand, it can potentially improve operating capacity of the system. Due to the intrinsic fast kinetics, supplying additional S_{NH} and S_F are not significantly beneficial for the further removing of S_{NH} which can be seen in Fig. 5b. The improvement is more visible with additional S_{NH} and S_F supply in the case of lacking O_2. This corresponds mostly to the empirical scenario. However, the treatment efficiency in such case is very low as addressed in previous part.

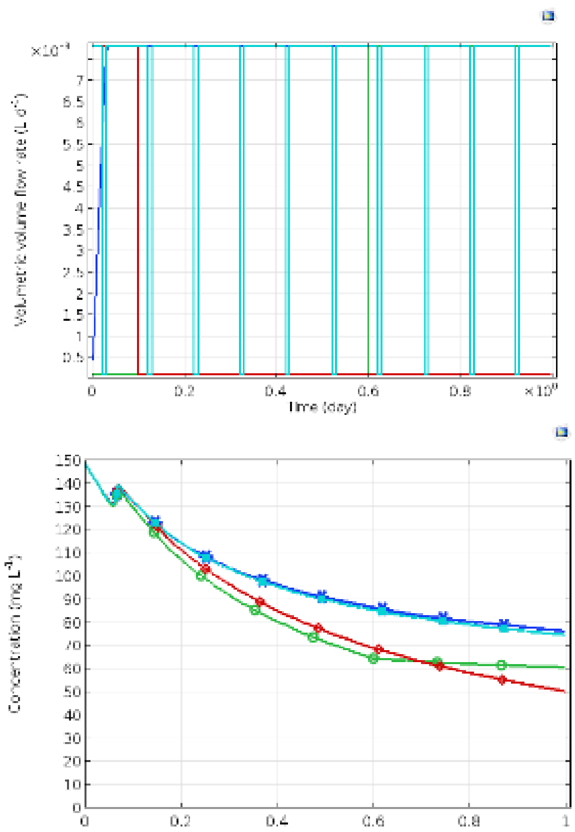

Figure 5: Different recycling scenario of S_F and S_{NH} (top) and decaying of S_{NH} (bottom). Conditions: continuous O_2 supply, simulated parameters in Table 1, Table 2 and in the original publication of CWM1 [23].

4. Conclusions

The combination of conductive materials in waste water treatment systems can significantly improve the pollutant removal efficiency. These materials likely accelerate the bacterial growth and facilitate the electron transfer process inside the treatment systems. The excellence so far is nitrogen related compounds removal through nitrification/denitrification process.

Nitrification, the first step in nitrogen removal cycle, in principle needs to be improved to promote the denitrification step. The contribution focused on finding the input signals which can be designed in the experimental setup improving the nitrification process. The biokinetic model CWM1 had been selected and solved using COMSOL Multiphysics®. Different O_2, S_{NH}, S_F supply scenarios have been proposed to provide the best nitrification process. The best option can be obtained when dosing maximum O_2 into the system. Dosing additionally S_{NH}, S_F in the condition of adequateness of O_2 will not improve the system performance. Further development of 1D model incorporating the electrochemical performance of the system would be very valuable in the studied field.

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