MODELLING THE DEGRADATION OF ORGANIC MATTER IN WASTEWATER

Liana Ioana VUȚĂ[1], Gabriela Elena DUMITRAN[1*], Vlad Florin PÎRĂIANU[1]

Water, soil, sewage and mud are very complex environments in terms of chemical, physical and biological processes. The most complex transformation processes are the ones undertaken by the aquatic biomass. Mathematical modelling represents a useful tool for assessing the success of wastewater treatment processes and remains the most efficient research method. This paper presents a comparison between a simple and a complex mathematical model which allows analyzing the evolution of autotrophic and heterotrophic bacteria, of nitrogen species and the oxygen demand for organic degradation of an urban effluent.

Keywords: biodegradable organic substrate, biodegradation kinetics, mathematical simulation, wastewater treatment.

1. Introduction

It is known that water, soil, sewage and mud are very complex environments in terms of chemical, physical and biological processes. Many species with a wide range of degradative abilities are present. In aquatic environments, the pollutants are processed, more or less rapidly, by physical, chemical or microbiological reactions (absorption, adsorption, volatilization, hydrolyze, photolysis, chemical oxidation or microbiological reactions). Usually, the transformation rates of these reactions depend both on the pollutants concentration and the environmental factors. The transformation of pollutants depends on the sum of speeds of all involved processes. The transformation processes can be particularized through processes which can occur into the water body or at water-atmosphere interface: growth processes and physico-chemical processes. The most complex transformation processes are the ones undertaken by the aquatic biomass.

Mathematical modelling represents a very important tool for assessing the effectiveness of different guiding systems implemented to/in wastewater treatment processes. As in any modelling process, due to a very simplistic approach, abstract models can be attained, which does not describe entirely the structure of these processes [1], [2].

[1] Dept. of Hydraulics, Hydraulic Machinery and Environmental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: gabriela.dumitran@upb.ro

Regarding the evolution of modelling procedure, the literature presents numerous studies. The models have become more advanced, complex and precise, taking into account increased number of components and processes. A detailed literature review in the field of aquatic water quality and ecology has been done by Robson, which assessed 73 distinct models, of which 6 are process-based models of the biological wastewater treatment systems [3].

Specific growth rate of biomass has been studied and modelled by various types of approaches. At this moment, there are four groups of mathematical models designed to forecast the reactor behavior: a) simple basic models, b) un-structured non-segregated model, c) un-structured segregated model and d) structured kinetic model [4]. Therefore, there are numerous descriptive structured models, providing good results and being internationally accepted. For instance, the model developed by Henze [1], e.g. the ASM model, which considers the removal of biological nutrient in activated sludge systems. Also, Mosey developed a model which considers four groups of bacteria and their fate during the degradation of organic matter to carbon dioxide and methane [5]. Kalyuzhnyi proposed a model of the batch anaerobic digestion of glucose [6] and, later on, Knobel & Lewis completed it in order to assess the process of anaerobic digestion in wastewater containing sulfate species [7].

Even if the simple basic model does not consider all the processes involved unlike the other three types of models, they are usually good enough for technical purposes and are accepted as a tool to asses biological wastewater treatment [8]. As a result, the model type Monod has become the most widely used approach, since it provides accurate results in bioreactor engineering [9].

This paper presents a comparison between a simple and a complex mathematical model which allows analyzing the evolution of autotrophic and heterotrophic bacteria, of nitrogen species and the oxygen demand for organic degradation of an urban effluent.

2. Modelling approach

The microbial decomposition of organic matter in aquatic ecosystems has an essential role in energy and mass transformation processes [10]. Discharge of wastewater with organic content into a river leads to uptake of dissolved oxygen, by chemical oxidation of the reducing pollutants or by biodegradation processes. The biodegradation of organic matter is strongly related to bacteria existence, the influence on dissolved oxygen content of water being reflected by biochemical oxygen demand (BOD). BOD includes both heterotrophic and autotrophic microorganism activity. The autotrophic microorganisms are able to synthesize the organic compounds, starting with the inorganic ones. This process uses the energy resulting from the organic matter degradation and the one from the oxygen consumption by protozoa which destroy the nitrification bacteria. Even if the bacteria growth processes are not independent, but more likely consecutively and influenced by many interactions, usually the metabolization of organic matter and the nitrification are individually modelled [11]. Initially, the complex organic matter is decomposed in simple forms, protozoa assimilable, under the catalytic action of the enzymes produced by heterotrophic bacteria. This process of bacteria growth uses oxygen from the water and releases carbon dioxide. When the heterotrophic microflora growth rate equals the extinction rate, the phase of endogenous breathing of heterotrophic bacteria begins. The previously formed biomass is diminished by death and autolysis, and part of the metabolites serve as secondary substrate for still viable germs.

Untreated domestic wastewater contains ammonia. Nitrification represents the process of conversion of ammonia to nitrite, followed by the conversion of nitrite to nitrate. If nitrate must be removed, the denitrification process (i.e. the process of converting nitrate to nitrogen gas) can be used [12]. The nitrification process is due to metabolic processes of two groups of autotrophic nitrifying bacteria. These bacteria are using the energy obtained from inorganic sources (ammonia or nitrite in this case) to build organic molecules. The first phase of nitrification is the oxidation of ammonia to nitrite by ammonia-oxidizing bacteria and the second phase is the oxidation of nitrite to nitrate by nitrite-oxidizing bacteria. Most of the time the first phase is accomplished by nitrosomonas and the second one by nitrobacter [12]. Further on, nitrates are reduced to gaseous nitrogen. This process, named denitrification, is done by facultative anaerobes, like fungi. The bacteria involved in this process are called denitrifiers and they prosper in anoxic conditions, by acquiring the needed oxygen from the compounds which contains it. Generally, these bacteria are heterotrophic and metabolize biodegradable substrate by using nitrate as an electron acceptor. The level of dissolved oxygen must be as low as possible, since denitrification bacteria use it before using the nitrate, in order to have an efficient process of denitrification [12].

The mathematical models used are based on the total concentration of biodegradable organic substance, expressed by the BOD. The paper presents two mathematical models: a simple one, containing just the first three equations (eq. (1) to (3)) (the third equation having in the right side only the first term, i.e. the one corresponding to the action of heterotrophic bacteria) and a complex model, containing eight equations (eq. (1) to (8)). The simple model allows to estimate: the organic content of the effluent (S), the heterotrophic bacteria (Bh), dissolved oxygen (O2), while the complex model includes also ammonia nitrogen (NH3), nitrosomonas bacteria (BNS), nitrites (NO2-), nitrobacter (BNB) and nitrates (NO3-).

The equations describing the two models, encoded in Matlab, are (Popa, 1998):

$$\frac{\mathrm{d}\,\mathrm{B_h}}{\mathrm{dt}}=\left(\mu_{max\,A}\frac{S}{S+K_S}-m_A\right)\cdot B_h \tag{1}$$

$$\frac{\mathrm{d}\,\mathrm{S}}{\mathrm{dt}}=\left(\frac{\mu_{max\,A}}{Y}\frac{S}{S+K_S}-\frac{m_A}{n_S}-q\right)\cdot B_h \tag{2}$$

$$\begin{aligned}\frac{\mathrm{d}\,O_2}{\mathrm{dt}}=&\left(K_A\cdot+\frac{Y_0}{Y}\cdot\mu_{max\,A}\frac{S}{S+K_S}\right).\cdot B_h+\\&+\left[K_B+\frac{Y_{B0}\cdot\mu_{maxB}}{Y_B}\left(e^{\frac{-NH_3}{p_{1i}}}-e^{\frac{-NH_3}{ps}}\right)\right]\cdot B_{NS}+\\&+\left[K_C+\frac{Y_{C0}\cdot\mu_{maxC}}{Y_C}\cdot\frac{NO_2^-}{\left(NO_2^-+p_{2S}\right)\left(1+\frac{NO_2^-}{p2i}\right)}\right]\cdot B_{NB}\end{aligned} \tag{3}$$

$$\frac{\mathrm{d}\,\mathrm{NH_3}}{\mathrm{dt}}=\frac{m_A}{n_B}\cdot B_h-\frac{\mu_{maxB}}{Y_B}\left(e^{\frac{-NH_3}{p_{1i}}}-e^{\frac{-NH_3}{ps}}\right)\cdot B_{NS} \tag{4}$$

$$\frac{\mathrm{d}\,\mathrm{B_{NS}}}{\mathrm{dt}}=\mu_{maxB}\cdot\left(e^{\frac{-NH_3}{p_{1i}}}-e^{\frac{-NH_3}{ps}}\right)\cdot B_{NS}-m_B\cdot B_{NS} \tag{5}$$

$$\begin{aligned}\frac{\mathrm{d}\,\mathrm{NO_2^-}}{\mathrm{dt}}=&\frac{f_B\cdot\mu_{maxB}}{Y_B}\cdot\left(e^{\frac{-NH_3}{p_{1i}}}-e^{\frac{-NH_3}{ps}}\right)\cdot B_{NS}-\\&-\frac{\mu_{maxC}}{Y_C}\cdot\frac{NO_2^-}{\left(NO_2^-+p_{2S}\right)\left(1+\frac{NO_2^-}{p2i}\right)}\cdot B_{NB}\end{aligned} \tag{6}$$

$$\frac{d\,B_{NB}}{dt} = \left(\frac{\mu_{maxC}}{Y_C} \cdot \frac{NO_2^-}{\left(NO_2^- + p_{2S}\right)\left(1 + \frac{NO_2^-}{p2i}\right)} - m_C \right) \cdot B_{NB} \tag{7}$$

$$\frac{d\,NO_3^-}{dt} = \frac{f_C \cdot \mu_{maxC}}{Y_C} \cdot \frac{NO_2^-}{\left(NO_2^- + p_{2S}\right)\left(1 + \frac{NO_2^-}{p2i}\right)} \cdot B_{NB} \tag{8}$$

The values of the coefficients are presented in Table 1.

Equation (3) is giving information of the dissolved oxygen variation and has, for each of the three members on the right side, a term corresponding to own respiration need and another one for growth.

Table 1

The value of the coefficients used in the model

Symbol	Definition	Value
$\mu_{\max A}$	maximum growth rate of heterotrophic bacteria	0.2
$\mu_{\max B}$, $\mu_{\max C}$	maximum growth rate of nitrosomonas/nitrobacter	0.075
m_A	mortality rate of heterotrophic bacteria	0.02
m_B	mortality rate of nitrosomonas bacteria	0.0075
K_S	half-saturation constant	100
Y, Y_0	conversion factor of the substrate to biomass / coefficient of proportionality between oxygen consumption rates and substrate consumption rates	0.5
n_S	feed rate coefficient, covering the metabolic needs of living cells	2
q	substrate consumption rates	
K_A ,K_B, K_C	rate of metabolic consumption of DO	0.01
m_C	mortality rate of nitrobacter	0.001
Y_B	conversion factor of the substrate - biomass for nitrosomonas	0.075
Y_{B0}	coefficient of consumption speed of DO – NH_3 for growth	3.2
Y_C	conversion factor of the substrate in biomass for nitrobacter	0.1
Y_{C0}	coefficient of consumption speed of DO – NO_2^- for growth	1.1
p_{1i}	constant	800
p_{1s}	constant	20
p_{2i}	constant	750
p_{2s}	constant	110
n_B	coefficient of amoniacal nitrogen feed rate by autolysis	50
f_B ,f_C	conversion factor of ammonia to nitrites/nitrates to nitrites	1

Heterotrophic bacteria growth rate is limited by substrate concentration (Monod type kinetics). The values of maximum growth rate and half-saturation constant provides information about the biodegradability capacity, being specific to each type of substrate and bacterial species. Also, they are influenced by the temperature and pH of water [13]. Thus, for substrates with low concentration, if the half-saturation constant is low, the growth rate is high. Also, for values of the half-saturation constant lower than the hydrocarbon substrate, the growth speed does not depend on the concentration of the substrate, but is proportional to the bacterial mass already formed. In exchange, for values of the half-saturation constant higher than the hydrocarbon substrate, the speed of microbial growth substrate is proportional to the concentration of the substrate available in solution [14].

3. Results and discussion

In order to accurately model the processes from wastewater treatment plants (physical, chemical and biological), is necessary to take into consideration all the phenomena [15]. The model was applied to data from a wastewater treatment plant, presented in Table 2.

Table 2

Water quality values from a wastewater treatment plant

Parameter		January	February	March
Turbidity mg/L	Input	248	277	248
	Output	22	22	22
CCO-Cr mg O_2/L	Input	398	345	405
	Output	39	36	37
CBO_5 mg O_2/L	Input	179	145	186
	Output	9	7	8
NH_4 mg /L	Input	6.44	3.35	2.65
TP mg /L	Input	0.86	0.88	0.82

Considering the input variables in a wastewater treatment plant (organic load) and the conditions of the bioreactor (concentration of the reducing microorganisms and nitrogen compounds), the following values were set as baseline of simulation: Bh =10 mg/L, S =150 mg/L, O2 = 0 mg /L, NH3=5 mg /L, BNS = 0.01 mg /L, NO2 = 0.5 mg /L, BNB = 0.01 mg /L, and NO3 = 0 mg /L. For each of the eight state variables, the variation of the concentration during a month was determined.

In terms of water quality, microorganisms play an essential role due to their action in wastewater purification processes. From the different existing electron acceptors, the one that produces the highest quantity of energy are used by microorganism. Consequently, the DO is used first. When the DO is depleted, if nitrate is available, the denitrification process begins, due to the organisms able to use nitrate in the respiration process. When the nitrate is finished, anaerobic conditions occur.

The compounds required for bacterial development (organic matter, oxygen and nutrients) are adsorbed to biofilm's surface. Next, by diffusion mechanism, they are transported and metabolized by microorganisms. The oxygen is consumed when penetrating the biofilm, leading to an external layer with oxygen and an internal one with anaerobic (anoxic) conditions.

These layers are, obviously, influenced by DO, and the nitrate reductions appear in the anaerobic layer [16]. When the heterotrophic microflora growth rate equals the extinction rate, the growth rate cancels and starts the endogenous breathing phase of heterotrophic bacteria [17]. The previously formed biomass is diminished by death and autolysis, and parts of the metabolites serve as secondary substrate for viable germs (Fig. 1).

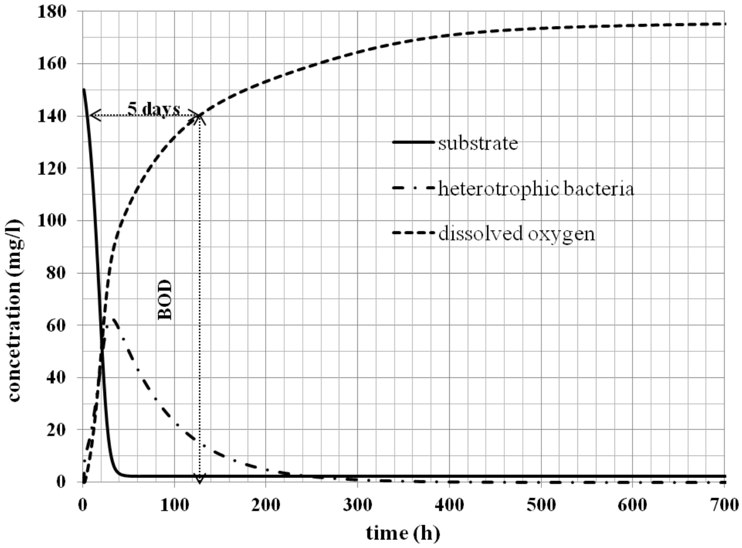

Fig. 1. Constituents variations in a biological reactor over time

In the reactions of degradation of organic matter from the aquatic ecosystems, part of the nitrogen converted to protein nitrogen and incorporated into the cells during the growth phase is now released in form of ammonia nitrogen. Thus, ammonia occurs as a result of the autolysis phenomena during heterotrophic respiration of the endogenous flora and disappears from the environment being used as a nutrient substrate by nitrosomonas bacteria.

When the values of heterotrophic flora growth rate are comparable with the growth rate of autotrophic bacteria (*Nitrosomonas* and *Nitrobacter*) starts the nitrification phase. In this phase *Nitrosomonas* bacteria uses ammonia nitrogen as substrate, and converts it to nitrite. Further, nitrites serve as a substrate for

Nitrobacter and finally, *Nitrobacter* converts nitrite into nitrate (fig. 2).

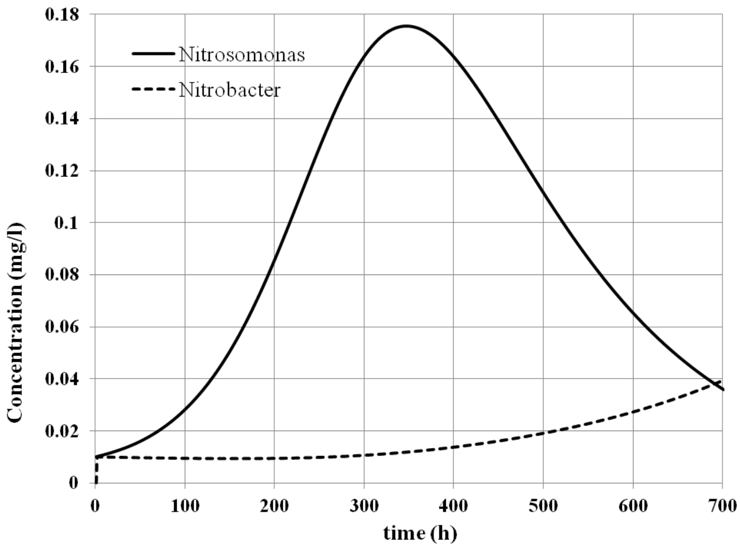

Fig. 2. Biomass variations in a biological reactor over time

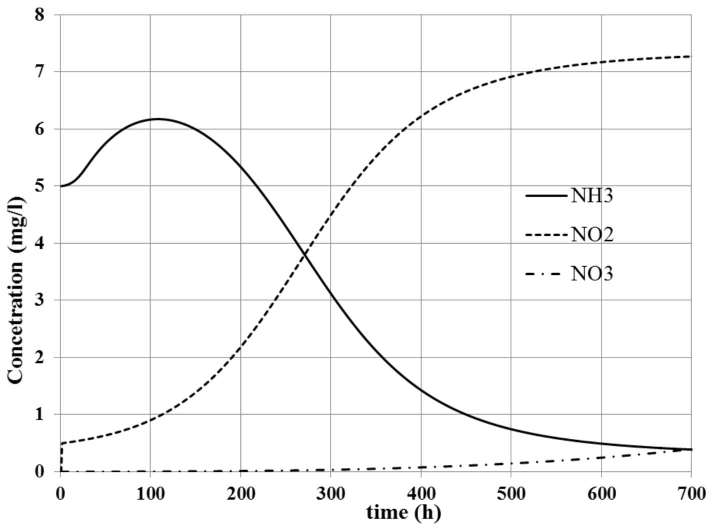

Fig. 3. Nitrogen compounds variations in a biological reactor over time

The concentration of nitrite (NO_{2-}) at a given time is due to the initial concentration and to overall production growth of *Nitrosomonas* and to the consumption necessary to *Nitrobacter* growth.

Nitrites obtained this way serve as a substrate for *Nitrobacter*. Further on, *Nitrobacter* converts nitrite into nitrate. The concentration of the amonical nitrogen is continuously reduced until it is exhausted, resulting in the degeneration of *Nitrobacter* (Fig. 3). Considering the available data, the only parameter which can be used for assessing the performance of the model is the DO. Fig. 4 presents for comparison, the computed DO values and the measured ones.

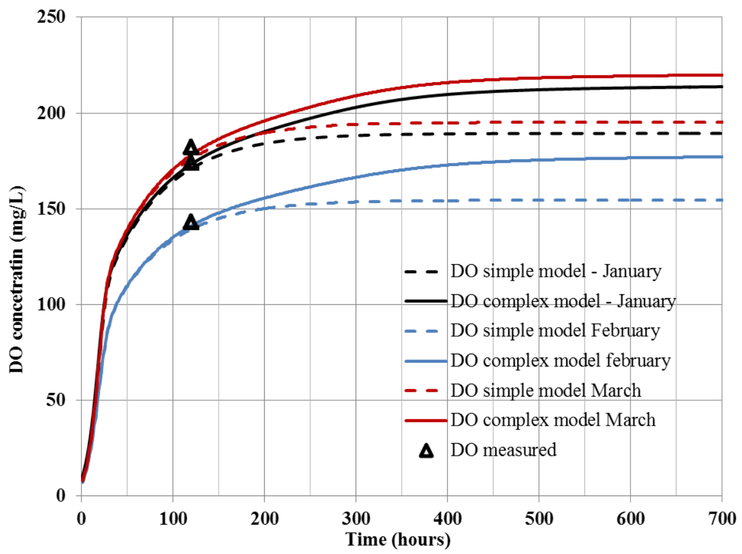

Fig. 4. Comparison of DO for simple and complex models

Also, values have been computed for the root mean square error (RMSE) and the coefficient of determination (CoD). The RMSE value is 2.26 for the complex model and 4.44 for the simple one. The CoD value is 0.982 (complex model) and 0.928 (simple model). These values show a good correlation between the results obtained by calculation and the real values of the investigated variables.

4. Conclusions

The purpose of this study was to investigate two types of models which can be used for assessing the wastewater treatment processes. The simple model presented can be easily developed and applied by any wastewater treatment company. Furthermore, the model can be subsequently improved by adding various equation to describe more processes, and thus becoming increasingly complex. In this study, the complex model developed for simulating the biological process led to the variation curves of the biomass, nitrogen compounds and dissolved oxygen in the water mass.

The results of the two investigated models are not so different. Thus, for a general analysis, when only the substrate, DO and heterotrophic bacteria needs to be assessed, is simpler to use the first model. If the targeted compounds include the autotrophic bacteria or any form of the nitrogen in the aquatic solution, the complex model must be used.

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