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Dynamical Modelling of a Wastewater Treatment Process of the Metallurgical Industry

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Abstract: *In this paper we consider the dynamical modelling and parameter identification of a biological wastewater treatment process from the galvanisation industry used to remove a mixture of organic matter and surface-active agents. In the present study we have considered mainly the measurements of dissolved oxygen and COD (Chemical Oxygen Demand) collected on laboratory and pilot-scale processes. From the identification study, we can conclude that the degradation is characterized by two reactions: one part of the easily biodegradable effluent is degraded with fast kinetics while the remaining part of the effluent is degraded via a slower reaction. This has been modelled by considering two different classes of substrates that indeed correspond to real components of the mixture.*

Keywords: *Dynamical modelling, Parameter identification, Wastewater treatment, Galvanisation.*

Introduction

Wastewater treatment plays a major role in order to remove pollutants from effluents coming both from domestic and industrial uses. The protection of water sources is of major importance to all countries in the world. This is for instance reflected in Europe in the EC directive 91/271 which “aims to protect the environment from any adverse effects due to discharge of such (urban and industrial) waters”. The rapid growth of industry over the last one hundred years has left its mark on our society, in terms of the quality of our drinking water and our water for recreation, and on the environment, in terms of decreasing ecological diversity due to polluted waterways. Biological wastewater treatment is largely used today. Activated sludge processes and anaerobic digesters are the most widely used processes [3, 8], but systems like lagoons (waste stabilisation ponds) [4] or sequential batch reactors (SBR’s) [2] are also well adapted to specific situations and are therefore often considered. Sewers of most major cities in the world today are connected to a network that deliver the effluents from domestic use to municipal wastewater facilities to remove mainly organic matters and nitrogen from the effluent and to deliver clarified water to rivers. Industrial companies have also to comply with environmental regulations and therefore to treat their effluents. In this paper, we report the results of a study performed in cooperation with a metallurgical company involved in the galvanisation of parts used in the automobile industry.

As for any industrial process, the design of industrial wastewater treatment plants requires the knowledge of the process kinetics, more precisely in the present instance, of the biodegradation reaction rate(s). The modelling of the biodegradation kinetics of the effluent under study is therefore of major importance in order to proceed to an optimal design of the plant. The present work has been dedicated to the study of the aerobic biodegradation of a mixture of organic compounds coming from degreasing baths of a galvanisation plant.

Because the process design and control objective of the present study, it was essential to provide a kinetic model simple enough, yet able to explain the main features of the process dynamics by considering a limited number of measurements assumed to represent appropriately the process dynamics.

Process description

Hot temperature galvanisation is the operation in which a thin layer of zinc is put on metallic parts by dipping these parts in a molten zinc bath. However, in order to have an efficient galvanisation, the surfaces to be treated need to be clean without a trace of oxides and grease. That's the reason why the parts that will be galvanised are first stripped and degreased. The stripping consists of putting the metallic part in an acidic bath. In the degreasing section, the part is put in an alkaline bath which for efficiency reasons, contains some quantity of anionic, cationic and non-ionic surface-active agents.

During the process operation, the degreasing bath accumulates organic matters. These organic compounds initially present on the metallic parts are obviously dependent of the treated parts and may therefore change with the type of production. When the quantity of dissolved organic matters in the bath becomes too large, it is necessary to remove it. The removal is performed via the action of an emulsion breaking component. The addition of this component in the galvanisation bath annihilates the action of the surface-active agents and generates a phase separation. Oils and greases concentrate in a lighter phase which can then be separated from the heavier phase which is recycled to the plant.

The upper phase, called organic phase, is indeed a mixture of water, surface-active agents and organic matter which is an effluent that cannot be used as a fuel source. This effluent has therefore to be degraded, the biodegradation of which being modelled with the objective of the design of the industrial plant.

In the following sections, we shall consider the dynamical modelling of the biodegradation process. First the experimental results will show that a single substrate model does not fit in the present instance, since a high oxygen consumption takes place at the beginning of the process operation. In a second step, we shall assume that the degradation can be divided in two distinct reactions degrading two different substrates, giving rise to a model with two reactions for which the reaction rates are different.

Dynamical modelling

We concentrate in this section on the dynamical modelling of the biodegradation of the organic phase coming from the degreasing baths of a galvanisation industrial plant. As we have already pointed out, the composition of this matter is variable. If it contains a mixture of a priori identified surface-active agents, it also contains oils and greases of unknown origin and composition, related to the parts that are degreased. It is therefore not possible to build a reliable deterministic model considering the biodegradation of each component of the

mixture. This explains why models usually consider only one global substance to represent the whole set of biodegradable species.

The first part of this section is dedicated to the development of such a model that involves only one substrate. Then the second part will show that incorporating a second substrate associated to another reaction with a different reaction rate allows to substantially improve the performance and quality of the dynamical model.

Single substrate model

The aerobic biodegradation of one substrate can be modelled by the growth reaction of the biomass *X* by the oxidation of the substrate *S*:

$$y_S\, S + y_{O_2}\, O_2 \rightarrow X + y_{CO_2} CO_2 \tag{1}$$

where y_S, y_{O_2}, y_{CO_2} are the yield coefficients. Reaction (1) represents a macroscopic transformation of the solution and does not correspond to the molecular transformations observed at the cell level. That is why we define yield coefficients and not stoichiometric coefficients as the writing of the reaction equation might suggest [1].

The single substrate growth is characterized by a specific growth rate μ for which the Monod model is most often used to characterize its dependence to the substrate concentration *S*:

$$\mu = \frac{\mu_{\max} S}{K_S + S} \tag{2}$$

where $\mu_{\max}$ and K_S are the maximum specific growth rate and the affinity constant, respectively.

These considerations allow to derive the dynamical model of the process in a CSTR (continuous stirred tank reactor) connected to an appropriate aeration system as follows:

$$\begin{aligned} \frac{dX}{dt} &= -DX + \mu X \\ \frac{dS}{dt} &= D(S_{in} - S) - y_S \mu X \\ \frac{dO_2}{dt} &= k_l a\left(O_2^* - O_2\right) - y_{O_2} \mu X - DO_2 \end{aligned} \tag{3}$$

where X, S, O_2 and V represent the biomass, substrate and dissolved oxygen concentrations, and the volume of the reacting medium.

This model has been the object of several studies and different parameter identification methods can be considered. The yield coefficients can be identified independently of the other model parameters by considering the notion of reaction invariants [1, 3]. The kinetic parameters can subsequently be identified by considering classical parameter calibration methods [8]. These are based on the experimental data of dissolved oxygen, substrate and biomass concentrations gathered from batch experiments. In the present instance, reliable information about the process microbiology and kinetics was clearly lacking, and the selection of the measurements has been mainly based on the following two criteria:

representatives of the measured components as compared to the available knowledge for similar processes, and easiness and low cost of the measuring procedure.

Among the three measured variables, only dissolved oxygen and COD measurements could be used explicitly for the process model identification: it appeared that the biomass measurements were not reliable enough to be considered for more than to give trends in the biomass time evolution. This also motivates, in the following, the writing of the mass balance equations without the biomass balance equation. This does not mean that we do not consider biomass growth, but simply that the modelling and identification will be based exclusively on the dissolved oxygen and substrate(s) dynamics and data.

It is also important to note that in the models considered in this paper, we only consider one biomass. This is clearly an essential assumption that corresponds to a simplification of the process kinetics, yet in line with many other modelling studies, for which evidence (in particular via reliable measurements) of the interaction and activity of different micro-organisms cannot explicitly formalized.

The experimental data gathered from these experiments have shown that the biomass concentration increases significantly during the very first hours of the process operation and then remain constant during the rest of the biodegradation, at values that are close to 10^9/l. It is also worth noting that these experiments have emphasized that after a latency period of a few hours, the COD is decreasing and the dissolved oxygen concentration abruptly drops, as it is illustrated on Fig. 1.

The fact that the biomass concentration remains constant while the COD and the dissolved oxygen concentration are decreasing leads us to conclude that the micro-organisms do not consume substrate for their growth during that phase. We have therefore assumed that the biodegradation was due an enzymatic reaction, catalysed by the biomass but without biomass growth. This leads us to consider not the specific biomass growth rate anymore but a substrate utilization rate r_{SU} instead, this latter rate being classically modelled with Monod kinetics:

$$r_{SU} = \frac{r^0_{SU\,\max} S X}{K_S + S} \tag{4}$$

where $r^0_{SU\,\max}$ and K_S are the maximum specific utilization rate and the affinity constant, respectively. Since the biomass concentration remains constant during this phase, the maximum specific utilization rate can more adequately be expressed as follows:

$$r_{SU\,\max} = r^0_{SU\,\max} X \tag{5}$$

It appeared during the identification of the kinetic parameters that the observed concentrations were too low in order to obtain a reliable value of the affinity constant K_S. Indeed we did not observe for instance initially strict “exponential” growth (which would correspond to a constant value of the specific growth rate and of the specific consumption rates, typical of the situation when μ is close to $\mu_{\max}$). We can therefore assume that the process operation is such that the initial substrate concentration S is low. In such an instance, more specifically when $S << K_S$, the observed kinetics reduces to a pseudo first order kinetics for which the kinetic constant α is the ratio of the maximum specific utilization rate and of the affinity constant:

$$\alpha = \frac{r_{SU\,\max}}{K_S} \tag{6}$$

The process model in a batch reactor then becomes:

$$\begin{aligned} \frac{dS}{dt} &= -r_{SU} \\ \frac{dO_2}{dt} &= k_l a\left(O_2^* - O_2\right) - y r_{SU} \end{aligned} \tag{7}$$

where y is a yield coefficient and the substrate utilization rate is given by the following expression:

$$r_{SU} = \alpha S \tag{8}$$

The biokinetic model (Eqs. (5), (6) and (8)) is indeed also equivalent to the Blackman model for low values of the substrate concentration S and constant values of the biomass concentration X [2].

The identification of the model parameters from the experimental data has given the following values:

α = 0.0066 ± 0.0017 h^{-1}
y = 600 ± 148 mg/g

The simulation results for this model with the numerical values provided in Table 1 and compared to the experimental data are illustrated in Fig. 1. Although the simulation provides globally satisfying results, there exists a noticeable difference between the numerical simulation and the experimental data. The dissolved oxygen at the beginning of the biodegradation indeed drops more rapidly than what is predicted by the model, then rapidly increases up to an intermediate value close to the one provided by the numerical simulation, and finally continues to increase towards its saturation value in agreement with the model predictions.

Table 1. Numerical values used in the numerical simulation of the single substrate model

Variable	Initial value	Unit
O_2	6.5	mg/l
S	3.41	g/l

Parameter	Value	Unit
α	0.0066	1/h
y	0.6	g/g
O_2^*	6.5	mg/l
$k_l a$	4.4	1/h

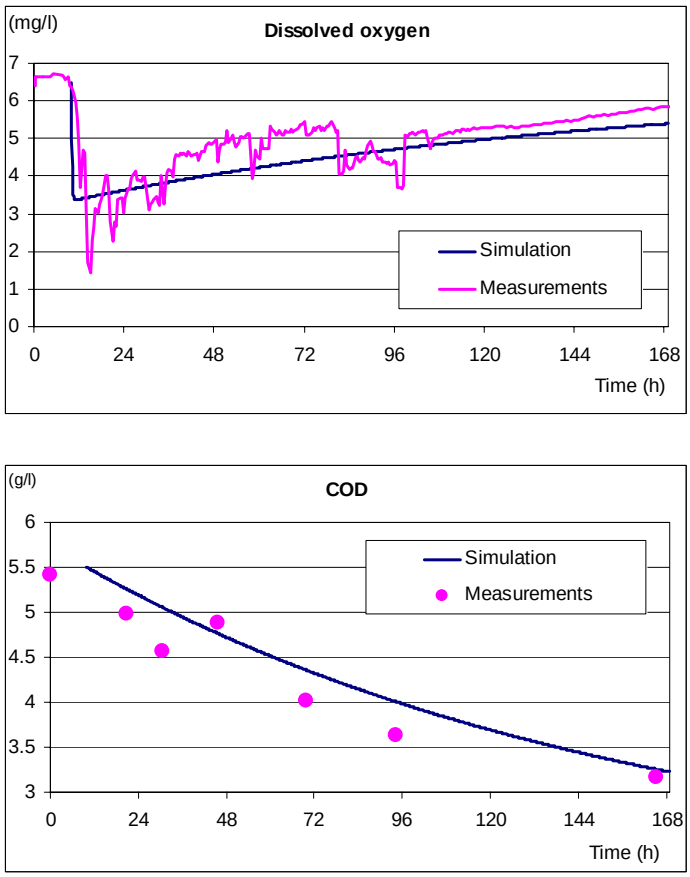

Fig. 1 Identification of the single substrate model

Two substrate model

The discrepancies between the numerical simulation of the single substrate model and the experimental observations have led us to discard the assumption of an unique representative substrate and to consider the simultaneous presence of two types of substrate representing the easily and hardly biodegradable species, respectively [5, 6, 7, 9]. If we assume that both types of substrate are degraded in parallel and without reciprocal influence, the easily biodegradable substrate is completely removed after a relatively short period of time. The dissolved oxygen consumption related to the biodegradation becomes then equal to zero. As a consequence, the dissolved oxygen concentration then moves to an intermediate level that results from the equilibrium between the aeration of the reactive medium and the oxygen consumption related to the degradation of the other substrate. Therefore we can therefore represent the biodegradation by the following reaction scheme:

$$\begin{aligned} S_1 + y_1 O_2 &\rightarrow y_{CO_2 1} CO_2 \\ S_2 + y_2 O_2 &\rightarrow y_{CO_2 2} CO_2 \end{aligned} \tag{9}$$

where S_1 and S_2 represent the concentrations of the easily and hardly biodegradable substrates, respectively, and y_1 and y_2 are the related yield coefficients. We have considered here a kinetic model similar to the one used in the preceding section, i.e. substrate utilization rates associated to each of both reactions:

$$r_{SU1} = \alpha_1 S_1 \tag{10}$$

$$r_{SU2} = \alpha_2 S_2 \tag{11}$$

The biodegradation model in a batch reactor then becomes:

$$\begin{aligned} \frac{dS_1}{dt} &= -r_{SU1} \\ \frac{dS_2}{dt} &= -r_{SU2} \\ \frac{dO_2}{dt} &= k_l a\left(O_2^* - O_2\right) - \left(y_1 r_{SU2} + y_2 r_{SU2}\right) \end{aligned} \tag{12}$$

The limitations of this model are related to the parameter identification. Indeed, since the COD is a measurement of all the oxidable components, it is proportional to the sum of the concentrations of biodegradable and non-biodegradable substrates. Therefore in our case, only the sum $S_1 + S_2$ is available for measurement. The solution to this difficulty is to separate the biodegradation in two phases. In the first phase, both substrates are present while in the second phase, only the hardly biodegradable is assumed to be present, i.e. $S_1 = 0$. The transition between the two phases takes place when the dissolved oxygen increases to reach the intermediate level. During the second phase, the classical identification methods can therefore be used to calibrate the parameters related to the hardly biodegradable substrate. This gives the following results:

$\alpha_2 = 0.0055 \pm 0.0019$ h^{-1}
$y_2 = 514 \pm 100$ mg/g

Once these parameters are identified, the parameters related to the easily biodegradable substrate can then be computed from the experimental data. The values of S_1 considered in the identification procedure are indeed deduced from the difference between the COD measurements and the values of S_2 computed in the first phase by considering the model obtained for the second phase. The following results are then obtained:

$\alpha_1 = 0.0577 \pm 0.0017$ h^{-1}
$y_1 = 316 \pm 25.7$ mg/g

The comparison of the experimental data and of the results of the numerical simulation of the two substrate model with the numerical values given in Table 2 are given in Fig. 2. The figure emphasizes the rapid decrease of the dissolved oxygen to a very low level followed by an increase to an intermediate level, and shows that the model with two biodegradation kinetics fits well to the experimental data.

Besides it is important to note that the separation of the degradable matters in two categories is not simply a theoretical view or an academic exercise and is particularly well adapted to this type of industrial wastewater. More specifically, off-line analyses have been performed at the beginning of the degradation process, when the dissolved oxygen has reached its intermediate level, and at the end of the degradation process. These were performed via GC-MS analyses (Gas Chromatography and Mass Spectroscopy) with the following specifications: 0.4 µl splitless 30s 30m CPsil8MS 0.25mm 0.25µ CF = 1.2 ml/min. These

analyses have shown that the fatty acids initially present have completely disappeared when the dissolved oxygen concentration moves to the intermediate level, while the concentration of polyethylene glycol ethers (surface-active agents) are slowly decreasing from the beginning to the end of the process operation. These observations tend to further validate the assumption of multiple degradation rates.

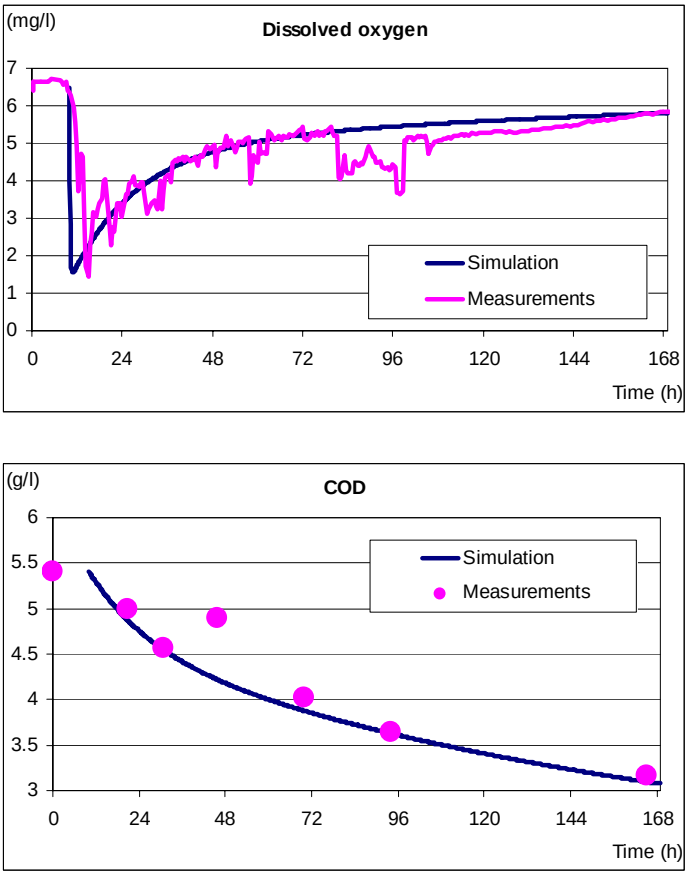

Fig. 2 Identification of the two substrate model

Table 2. Numerical values used in the numerical simulation of the two substrate model

Variable	Initial value	Unit	Parameter	Value	Unit
O_2	6.5	mg/l	α_1	0.0577	1/h
S_1	0.83	g/l	α_2	0.0055	1/h
S_2	2.57	g/l	y_1	316	mg/g
			y_2	514	mg/g
			O_2^*	6.5	mg/l
			$k_l a$	4.4	1/h

Conclusion

The development of a dynamical model of a biodegradation process of wastewater coming from the galvanisation industry has been performed with the objective to design and control an industrial wastewater treatment plant. The study has led to the conclusion that a classical model with one single substrate was not good enough to represent appropriately the process kinetics. Following the observations of the time evolution of the dissolved oxygen concentration during biodegradation batch experiments, we have assumed that the biodegradation takes place with two reaction rates. On one hand, one type of substrate (easily biodegradable) is rapidly degraded and in parallel, another substrate (hardly biodegradable) is degraded more slowly.

Although we have been introducing a higher level of complexity with regard to the classical model, the developed model remains simple and can be used easily in practice. The different parameters of the model can be identified by using classical methods as long as the easily biodegradable species are eliminated before the hardly biodegradable ones.

Complementary off-line analyses performed during the biodegradation have validated the assumption that different molecules are degraded at different rates. More specifically, the fatty acids present in the wastewater are degraded much more rapidly than some surface-active agents. The development of such a model is therefore not simple a theoretical exercise but corresponds to the reality and presents a non negligible industrial interest.

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