Integrated Mathematical Modelling of Advanced Oxidation Processes and Conventional Bio-Processes for Wastewater Treatment

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Abstract

This work proposes the dynamic modelling of systems combining Advanced Oxidation Process (AOP) and biological wastewater treatment processes (WWTP). Mathematical models for WWTP have been widely used, most of them derived from the ASM1 type. Some mathematical models have been developed for AOPs. However, there are no combined reliable models for integration of AOP and WWTP, although AOPs are commonly claimed to be complementary to conventional WWTP in the remediation of wastewaters containing recalcitrant compounds. Thus, most of the partial models (AOP and WWPT) use different approaches and variables that complicates their combination into an integrated process. In this regard, this work addresses a process combining a bio-treatment and a photo-Fenton process, for which develops a combined model that was implemented and solved simultaneously using Simulink. The combined model results in a primary prediction of the outlet concentration of total organic Carbon (TOC). The work discusses the simulation approach and its limitations, and the next steps towards an accurate combined model that could be used for the design and operation of such combined processes.

Keywords: Mathematical Modelling, AOP, Fenton Process, Biotreatment, Wastewater

1. Introduction

Biological processes are known to be 5 to 20 times less expensive than chemical processes (Marco, et al., 1997). However, non-biodegradable contaminants require chemical oxidation. Several researchers have reviewed experimental examples of combinations of AOPs and biological treatments (Ballesteros Martín et al. 2008, Huang et al. 2017). Although mathematical modeling is crucial for efficient design and operation of wastewater treatment processes, no accurate kinetic models have been used for the combined system. A widely accepted kinetic modeling approaches are available for biological treatment (Vlad et al. 2011, Kuriqi 2014) as well as photo Fenton process (Cabrera Reina et al., 2012). However as a result of the complexity of the processes and implementation of different approaches and variables in the developed models, combining the models being a complicate procedure while reliable result is required. In this study, based on the previous empirical studies (Huang et al., 2017) and the nature of the contaminant degradation through the processes, corresponding variables were selected and linked in order to develop coupled ordinary differential equations (ODEs) that were solved simultaneously by Simulink.

2. Modeling approach

This work focuses on the combination of the photo Fenton process and activated sludge biodegradation. Reported models were first selected and adapted, and later on, the models were coupled by a convenient matching of the related variables.

2.1. Kinetic model for bioreactor

The Activated Sludge Model No.1, ASM1, (Vlad et al. 2011, Kuriqi 2014) based on four fundamental mass balance equations was adopted for modelling the biological wastewater treatment process. The equations linked to the balance of the active sludge at the level of the aeration tank, the mass balance of the substrate, the mass balance of the oxygen in the water mass, and the balance of the active sludge at the level of the settling tank are given in Eqs. (1-5).

$$\frac{dX(t)}{dt} = \mu(t)X(t) - D(t)(1+r)X(t) + rD(t)X_r(t) \quad (1)$$

$$\frac{dX_r(t)}{dt} = D(t)(1+r)X(t) - D(t)(\beta + r)X_r(t) \quad (2)$$

$$\frac{dS(t)}{dt} = -\frac{\mu(t)}{Y}X(t) - D(t)(1+r)S(t) + D(t)S_{in} \quad (3)$$

$$\mu = \mu_{max}\frac{S(t)}{K_s + S(t)} + \frac{DO(t)}{K_{DO} + DO(t)} \quad (4)$$

$$\frac{dDO(t)}{dt} = -K_0\frac{\mu(t)}{Y}X(t) - D(t)(1+r)DO(t) + D(t)DO_{in} + \alpha W[DO_{max} - DO_t] \quad (5)$$

The biomass growth rate (μ), was modelled by the Monod law. The model equations include: X(t), biomass; S(t), substrate; DO(t), dissolved oxygen; DO_{max}, maximum amount of dissolved oxygen; X_r(t), recycled biomass; D(t), dilution rate (the ratio between the flow rate of the influent and the volume of the aeration tank); S_{in} and DO_{in}, concentrations of dissolved oxygen and of substrate in the mass of the influent; Y, biomass yield factor; α, oxygen transfer rate; W, aeration rate; K_0, model constant; r, the ratio between the re-circulated flow rate and the influent flow rate; β, the ratio between the waste flow rate and the influent flow rate; K_{DO}, saturation constants; and K_s, affinity constant.

2.2. Formulation and modelling of Fenton process

The photo-Fenton process model proposed and validated by Cabrera Reina et al. (2012) was re-written by Audino et al. (2019) to describe the continuous operation instead of the original batch mode. The proposed model assumes nine processes and eight states—these being the two ferric species ($Fe^{2+}$and Fe^{3+}); hydrogen peroxide, H_2O_2; the radicals formed from peroxide (whatever their form), R; the dissolved oxygen, O_2; three states accounting for the organic matter – two kinds of partially oxidized organics plus the parent compound present at the beginning of the reaction – named as MX_1, MX_2, and M, respectively, which are responsible for the lumped parameter measured (TOC). Also, the subscript "in" refers to inlet and dilution rate (F/V) is represented by inlet flow-rate of wastewater, F and total reactor volume, V. This model is given by the following equations:

$r_1 = k_1.[Fe^{2+}][H_2O_2]$ (6) $d[H_2O_2]/dt = (F/V)\cdot([H_2O_2]_{in} - [H_2O_2]) - r_1 - r_3$ (15)

$r_2 = k_2.[Fe^{3+}][I]$ (7) $d[Fe^{2+}]/dt = (F/V)\cdot([Fe^{2+}]_{in} - [Fe^{2+}]) - r_1 + r_2$ (16)

$r_3 = k_3.[R][H_2O_2]$ (8) $d[Fe^{3+}]/dt = (F/V)\cdot([Fe^{3+}]_{in} - [Fe^{3+}]) + r_1 - r_2$ (17)

$r_4 = k_4.[R][R]$ (9) $d[R]/dt = (F/V)\cdot([R]_{in} - [R]) + r_1 + r_2 - r_3 - (2\times r_4) - r_5 - r_6 - r_7 - r_8 - r_9$ (18)

$r_5 = k_5.[M][R][O_2]$ (10) $d[M]/dt = (F/V)\cdot([M]_{in} - [M]) - r_5 - r_6$ (19)

$r_6 = k_6.[M][R]$ (11) $d[MX_1]/dt = (F/V)\cdot([MX_1]_{in} - [MX_1]) + r_5 + r_6 - r_7 - r_8$ (20)

$r_7 = k_7.[MX_1][R]$ (12) $d[MX_2]/dt = (F/V)\cdot([MX_2]_{in} - [MX_2]) + r_7 - r_9$ (21)

$r_8 = k_8.[MX_1][R]$ (13) $d[O_2] / dt = (F/V)\cdot([O_2]_{in} - [O_2]) + (g_{1DO}\times r_3) + (g_{2DO}\times r_4) - (c_{1DO}\times r_5) + (K_La([O_2]_{in}{}^{*} - [O_2]))$ (22)

$r_9 = k_9.[MX_2][R]$ (14) $TOC = M + MX_1 + MX_2$ (23)

3. Hybrid combined model and simulation results

In order to couple the photo-Fenton and biotreatment models, the lumped parameter TOC is considered equal to the outlet substrate in biotreatment for the integration of the processes instead of monitoring some specific pollutants presented in the raw wastewater. Additionally, dissolved oxygen DO is directly linked to O_2 concentration in the photo Fenton process. The structure of this coupled process is illustrated in Figure 1. The following conditions, Eq. (24), are the ones that link the bio model and photo Fenton process:

$$F/V = D(1-\beta)\ ; \quad [M]_{in} = [S(t)_{out}]\ ; \quad [MX_1]_{in} = 0\ ; \quad [MX_2]_{in} = 0\ ; \quad [O_2]_{in} = [DO(t)_{out}] \quad (24)$$

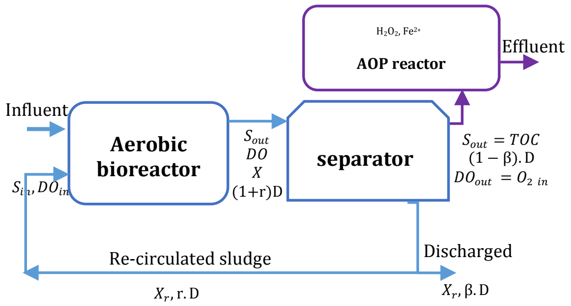

Figure 1: Block diagram of the integrated process.

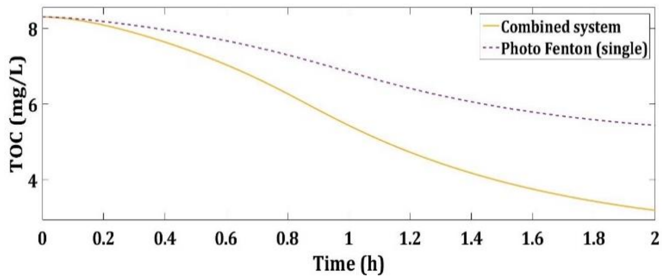

Figure 2: Simulated TOC profiles.

The simulation was performed by using the SIMULINK toolbox. The data of the kinetic constants given by Cabrera Reina et al. (2012) and Vlad et al. (2011) were used for the simulation. Initial concentration ranges were selected corresponding to the reported values. Hence, Figure 2 shows a primary prediction given by the combined model of TOC profiles at the given conditions. The simulation of model for the photo Fenton process as a unique reactor and the integrated process (photo Fenton plus biotreatment) reproduced the TOC profile in the combined system and as expected, more TOC reduction was indicated in the coupled process.

4. Conclusions

In this contribution, a hybrid model was developed and implemented in Simulink combining photo Fenton process (AOP) and activated sludge biodegradation (WWTP). The simulation model is based on the mass balance approach to model. The development of the model and the results obtained have provided insight into the study the combined use of these treatments, which are proposed in the literature but lack of convenient simulation models. Future research will exploit these models for addressing design and operation problems in complex wastewater treatment processes combining both technologies.

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