Kinetics and Effects of Hydraulic Residence Time and Biomass Concentration on Removal of Organic Pollutants in a Continuous Unsteady State Activated Sludge Process

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Activated sludge processes are generally affected by the variation of influent flow leading to a modification in biomass concentration and COD removal efficiency. This unsteady state situation can be mathematically explained by a Monod–type kinetics transformed using γ_{So} / γ_X (influent substrate to reactor biomass ratio) as a control parameter. The kinetic equation has been applied to experimental data obtained in an activated sludge lab plant (5.5 L) using synthetic wastewater (γ_{COD} = 2200 ± 300 mg L^{-1}). Organic load has been modified by increasing gradually influent flow in order to attain different hydraulic residence times (t = 10 to 45 h), leading to optimum values of biomass concentration (γ_X = 450 to 3200 mg L^{-1}) for maximum COD removal. The application of this type of kinetics that explains experimental results on substrate utilization rate under unsteady state conditions is discussed.

Key words:
Wastewater treatment, activated sludge, unsteady state, γ_{So}/γ_X ratio

Introduction

In chemical engineering literature lots of useful models have been formulated for the description of activated sludge processes under steady state conditions. Some of them are general kinetic models of bacterial growth (Tessier, Monod, Moser, Contois),[1] others are mathematical models formulated specifically for activated sludge processes,[2–7] and the last ones are dynamics multivariable models.[8–10] All these models use kinetic expressions dependent on effluent substrate mass concentration (γ_{Se}): this variable reflects COD concentration to which microorganisms are exposed in the completely mixed reactor.

However, steady state conditions are not often reached in activated sludge processes because most plants are subjected to disturbances working under unsteady state conditions. In these circumstances, an inadequate kinetic model, based on γ_{Se} (steady state conditions), would not accurately reflect the effects of process disturbances and would be useless for simulation studies of plant dynamics and control systems.

Some conditions can lead to an unsteady state situation in an activated sludge process, specially variation of influent COD concentration (γ_{So}) and volumetric flow. Biomass concentration (γ_X) can be also modified by these two variables: the optimal population of microorganisms in a bioreactor is dependent on the available substrate. For kinetic treatment, the situation of an unsteady state activated sludge reactor, where influent substrate concentration and biomass concentration are frequently modified, could be considered more similar to a batch reactor than a continuous-flow-reactor.

Liu et al.[11,12] used the ratio initial substrate mass concentration to initial biomass concentration (γ_{So}/γ_{Xo}) as a control parameter describing the metabolic behaviour of microorganisms in batch cultures.[13–15] Their kinetic model explains the dependence of the growth yield on the γ_{So}/γ_{Xo} ratio, decreasing the former by increasing γ_{So}/γ_{Xo} ratio, as a result of an unbalance between anabolism and catabolism, leading to energy spilling.

Nevertheless, this kinetics with a constant γ_{Xo} value cannot be applied in an unsteady state continuous activated sludge reactor where biomass concentration is continuously changing. To solve this situation, we propose the change of the γ_{So}/γ_{Xo} ratio used in batch reactors, by the γ_{So}/γ_X ratio for describing kinetics of substrate removal in an unsteady state continuous activated sludge reactor, where γ_{So} is the influent COD and γ_X is the biomass concentration in the bioreactor.

In this work, a kinetic model for a continuous unsteady state activated sludge plant has been applied, using a Monod-type equation in which efflu-

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ent substrate mass concentration (γ_{Se}) is replaced by γ_{So}/γ_X ratio, in order to study variations of influent substrate concentration and biomass concentration affecting substrate removal rate. An activated sludge lab plant was used for the experimental assays, increasing continuously organic load for performing unsteady state conditions.

Experimental

Activated sludge lab plant

Experiments were carried out in an activated sludge lab plant (Fig. 1) with a total volume of 5.5 L, consisting of a reactor with sludge drain (3.0 L) and a cylindrical settler (1.75 L) with distribution and recirculation tubes (0.75 L) made of methacrylate.[16] Total volume of completely mixed zone occupied by microorganisms was 3.75 L coming from reactor, distribution and recirculation tubes.

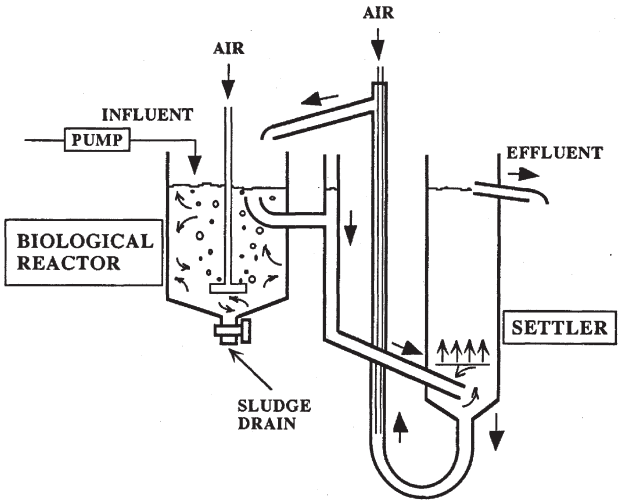


Fig. 1 – *Activated sludge lab plant*

Heterogeneous microbial populations were developed in reactor working in batch operation (closed system). When sufficient cells have been accumulated, the feed solution was pumped to the aeration tank continuously at the desired flow rate. Settled sludge was recirculated from the clarifier to the aeration tank by airlift and excess sludge was drained from reactor to attain the desired biomass concentration.

Temperature in the reactor was set at 20 ± 3 °C and pH was 8.5 ± 0.3 during the experiments. Oxygen in the reactor was supplied by air flow through a submerged aerator working in the oxygen concentration range of 5.8 – 8.8 mg L^{-1} to prevent low D.O. bulking.[4,17]

Synthetic wastewater

Synthetic wastewater was prepared with a mixture of peptone and meat extract as carbon source, urea, K_2HPO_4, NaCl, $CaCl_2$ and $MgSO_4$ (table 1) with COD = 2200 ± 300 mg L^{-1}, $P–PO_4^{3-}$ = 15 ± 3 mg L^{-1}, and $N–NH_4^+$ = 18 ± 3 mg L^{-1}. This synthetic wastewater was a culture medium with enough amounts of ammonium and orthophosphate to avoid any limitation for biomass growth due to nitrogen or phosphorus concentration.

Table 1 – *Composition of synthetic wastewater*

Component	Mass concentration mg L^{-1}
peptone	1900
meat extract	110
urea	30
K_2HPO_4	28
NaCl	7
$CaCl_2 \cdot 2H_2O$	4
$MgSO_4 \cdot 7H_2O$	2

Analytical methods

Total COD, phosphorous and ammonia mass concentration were analysed by the standard methods.[18]

Biomass concentration was determined by filtering 100 mL sample on a 0.45 μm Millipore membrane, drying (24 h at 105 °C), and weighing the dried filter.[19] This method is considered more accurate than the standard determination of volatile solids[18] avoiding the measurement of dissolved organics.

pH and temperature were measured with a calibrated electrode (CRISON micro pH 2000) and a thermometer, respectively. Oxygen concentration in the reactor was analysed by a selective electrode (CRISON OXI 92).

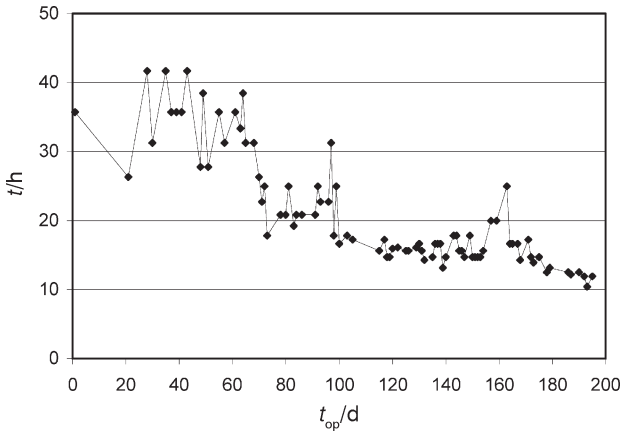
All measurements were carried out in triplicate, three times a week, except influent flow, pH and temperature in the reactor that were daily analysed. Experimental error was always below 5 %.

Results and discussion

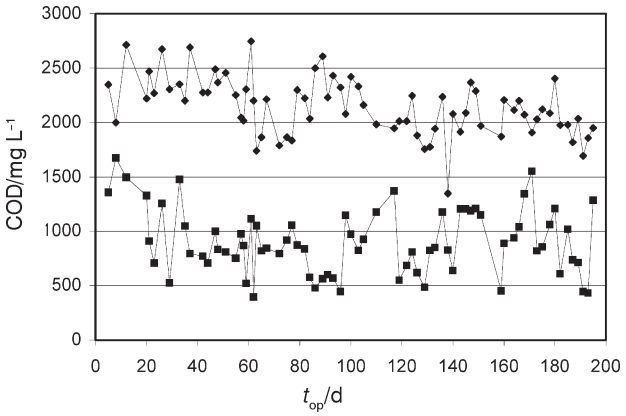
Experimental strategy

Experimental strategy was based on the gradual increase of the organic load in the system: 1–4 kg m^{-3} d^{-1} COD.

According to experimental strategy, a series of continuous experiments was carried out at different hydraulic residence times ranging from 10 to 45 h (average values: 12.4, 16.4, 20.4 and 34.2 h). Each residence time was maintained only a few days in order to avoid the establishment of steady state conditions (figure 2). The response of the system with regard to COD is shown in figure 3, where the difference between the influent substrate concentration γ_{So} and the effluent substrate concentration γ_{Se} (both expressed as COD) can be seen for the operating time. The organic loads obtained from experimental values of hydraulic residence time and influent COD appear in figure 4. It proves the gradual increase of the organic load previously cited.



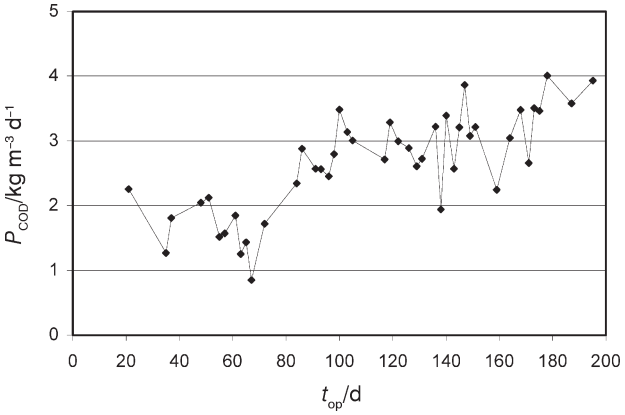
F i g . 2 – *Hydraulic residence time in lab plant during the experiments*



F i g . 3 – *Influent substrate concentration* γ_{S_0} (♦) *and effluent substrate concentration* γ_{S_e} (■) *(expressed as COD) during the experiments*

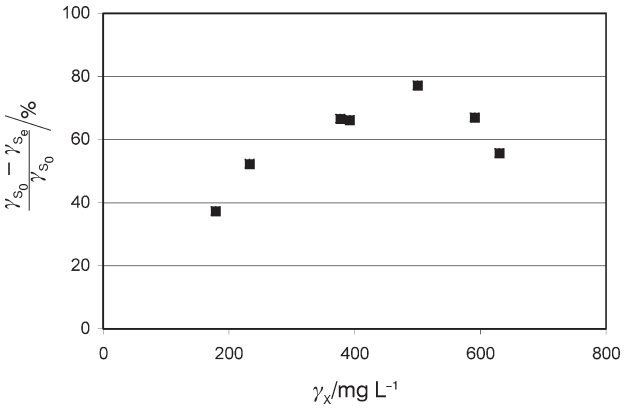
Biomass concentration and hydraulic retention time on removal of organic pollutants

Biomass concentration effect on removal of organic pollutants was studied for the average hydraulic residence times selected. The values of biomass concentration were in the range of 100–4000 mg L^{-1}.



F i g . 4 – *Organic load in reactor* ($P_{COD} = \gamma_{S_0} \cdot t$).

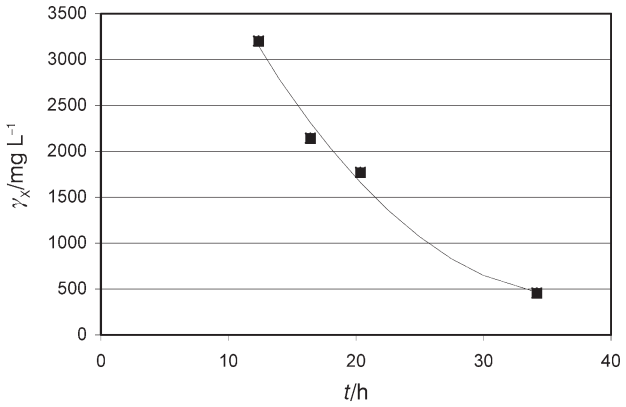
For each average hydraulic residence time, COD removal versus biomass concentration was analysed. Figure 5 shows results for t = 34.2 h and it serves by way of example for the shape of figures obtained for the other hydraulic residence times studied. In all cases, COD removal presented a maximum value dependent on the biomass concentration for each hydraulic residence time. This seems to indicate the existence of an optimum value in biomass concentration for each hydraulic residence time.



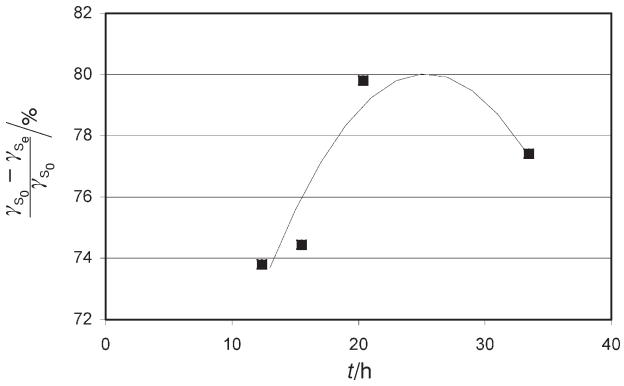
F i g . 5 – *Biomass concentration effect on COD removal (t = 34.2 h)*

From figure 5, optimum value of biomass concentration for the maximum COD removal, when t = 34.2 h, was determined by non–linear regression analysis: γ_X = 458 mg L^{-1}. As we said previously, other operating conditions (t = 12.4, 16.4 and 20.4 h) led to optimum values of biomass concentration at the different hydraulic residence times by similar relationships to Fig. 5.

The optimum values of biomass concentration for the maximum COD removal obtained from these relationships, are plotted versus the average hydraulic residence time in Fig. 6, where the effect of endogenous respiration can be observed as a re-



F i g . 6 – *Biomass concentration effect on COD renoval (t = 34.2 h)*



F i g . 7 – *Hydraulic retention time effect on COD removal for optimum biomass concentration*

sult of the decrease of the optimum value of biomass concentration when hydraulic residence time is increased.[20] Values of hydraulic residence time higher than $t = 20$ h (activated sludge extended aeration process) lead to an optimal value of biomass concentration much lower, $\gamma_X = 450$ mg L^{-1}, compared with data for $t = 12$ h (activated sludge conventional process), $\gamma_X = 3200$ mg L^{-1}. These results show as the optimum value of biomass concentration for the maximum removal of COD is not unique but it depends on the hydraulic residence time.

Why biomass concentration has an optimum value dependent on organic loading is something reported by some authors.[20] The main reason is explained by a decrease in the activity of microorganisms with an increase in their concentration.[5] Other reasons can be argued like the increase in the inactive fraction of biomass (floc) with the increase in biomass concentration, resulting in big flocs with a low internal mass transfer rate inside for substrate and oxygen.[6]

Hydraulic retention time effect on the removal of organic pollutants was also analysed for the optimum values of biomass concentration previously obtained. An optimum value of hydraulic retention time for the maximum COD removal, when plant works with optimum biomass concentration, can be observed in figure 7. From non–linear regression analysis, an optimum value of 25.4 h was determined for the hydraulic retention time. According to data in figure 6, the optimum value of biomass concentration for this time should be 1027 mg L^{-1}.

The existence of an optimum value for hydraulic retention time in aerobic sludge processes is something also reported by some authors.[21] It can be explained by the strongly dependence of the hydraulic residence time on wastewater characteristics: COD value, fast biodegradable fraction, solids concentration. At the shortest times of 12.4 and 16.4 h, there is not time enough for degrading COD. At the longest time of 34.2 h, an extended aeration process can be assumed (hydraulic retention time of 34.2 h is close to the highest value in the range of this process[20]) with the subsequent increase of the effluent COD as a result of increasing effluent solids concentration, because of the amount of rests of dead cells.

Kinetics of unsteady state process

Substrate utilization rate (r) is supposed to follow a Monod kinetics, in which effluent substrate mass concentration (γ_{Se}) is replaced by influent substrate mass concentration to biomass concentration ratio (γ_{So}/γ_X):

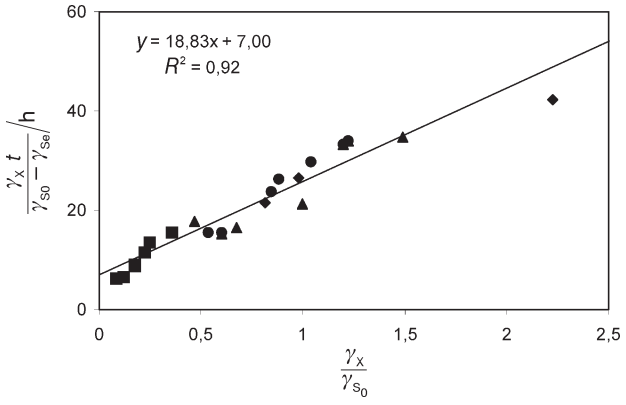
$$r = r_{max} \frac{\dfrac{\gamma_{S_0}}{\gamma_X}}{K_{S/X} + \dfrac{\gamma_{S_0}}{\gamma_X}} \tag{1}$$

where $K_{S/X}$ is the γ_{So}/γ_X ratio–related saturation constant and r_{max} the maximum substrate utilization rate. Substrate utilization rate can be written as the substrate removed for the biomass concentration and residence time in the reactor:

$$r = \frac{\gamma_{S_0} - \gamma_{S_e}}{\gamma_X \, t} \tag{2}$$

For determining the kinetic parameters r_{max} and $K_{S/X}$, equation (1) is rearranged to the following form:

$$\frac{1}{r} = \frac{K_{S/X}\gamma_X}{r_{max}\gamma_{S_0}} + \frac{1}{r_{max}} \tag{3}$$



F i g . 8 – *Determination of kinetic parameters for the proposed model (* ■ *t = 34.2 h,* ● *t = 20.4 h,* ▲ *t = 16.4 h,* ♦ *t = 12.4 h)*

In Fig. 8, $1/r$ *versus* γ_X/γ_{So} is presented for the different hydraulic retention times used (ranged from 10 to 45 h). A good agreement between experimental data and the kinetic model proposed was obtained and the parameters determined for the model were $r_{max} = 0.14$ h^{-1} and $K_{S/X} = 2.68$ mg mg^{-1} COD per unit of biomass. Maximum specific substrate utilization rate value ($r_{max} = 0.14$ h^{-1}) is generally higher in the kinetic model proposed related to steady state models ($r_{max} = 0.086$ h^{-1} and 0.096 h^{-1}).[5] We assume that it is due to the high value of influent COD which is known that can increase substrate utilization rate of the cells. γ_{So}/γ_X ratio–related saturation constant value ($K_{S/X} = 2.68$ mg mg^{-1} COD per unit of biomass) reflects the average value between influent COD and biomass concentration in the reactor (about 2 – 3 times). This value is much higher for a batch system ($K_{S/X} = 20$–80 mg mg^{-1} COD per unit of biomass)[11] due to the lower initial biomass concentration in a batch culture.[22,23] The high value of the ratio–related saturation constant in a batch system is also related to high γ_{So}/γ_{Xo} ratios, which is the main reason for considering not applicable experimental assays in batch systems to evaluate the kinetic coefficients of microbial growth and substrate utilization in activated sludge plants.[11] The high value of γ_{So}/γ_{Xo} ratio can cause an unbalance between anabolism and catabolism due to the excess of the potential energy source with respect to the catabolic enzymes of the cells.[24] In this case the substrate will not be completely oxidized and, therefore, more substrate is required to obtain the same amount of energy production for growth.[25] The final result is the decrease in the growth yield of the cells and, in this situation, batch experiments are not reflecting the behaviour of the cells in an activated sludge system.

Conclusions

The use of the parameter γ_{So}/γ_X in a Monod–type equation takes into account variations of influent flow and biomass concentration in an activated sludge plant, for describing kinetics of substrate removal in an unsteady state system. The application of the kinetic model for the system, in which biomass concentration changes as a result of the modification of influent flow, leads to the determination of the kinetic parameters. $K_{S/X}$ represents the average ratio *influent substrate to biomass*, much lower in a continuous system due to the high value of biomass concentration. If experimental assays are done in a batch system, this kinetic parameter will be much higher, because of the low concentration of the cells. r_{max} is strongly dependent on $K_{S/X}$ (in accordance to a Monod type kinetics), so it is expected different behaviour in continuous and batch systems. The results obtained for kinetic parameters show why they have to be measured in a continuous system.

The most significant contribution of this study is the application of a kinetic model in which a Monod–type equation is modified for an unsteady state activated sludge system, which describes properly the behaviour of the experimental data.

This kind of kinetics is able to explain the modification of substrate utilization rate in a system in which retention time and biomass concentration is changing continuously.

Nomenclature

m – mass, mg
COD – Chemical Oxygen Demand, mg L^{-1}
D.O. – Dissolved Oxygen, mg L^{-1}
$K_{S/X} = \gamma_{S_0}/\gamma_X$ – ratio related saturation constant, mg mg^{-1}
P_{COD} – organic load, kg m^{-3} d^{-1}
r – substrate utilization rate, mg L^{-1} h^{-1}
r_{max} – maximum substrate utilization rate, mg L^{-1} h^{-1}
γ_{Se} – effluent substrate mass concentration, mg L^{-1}
γ_{So} – influent substrate mass concentration, mg L^{-1}
t – hydraulic residence time, h
γ_X – biomass concentration in the biological reactor, mg L^{-1}
γ_{Xo} – initial biomass concentration in batch system, mg L^{-1}
t_{op} – operating time, d

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