Calibration and simulation of ASM2d at different temperatures in a phosphorous removal pilot plant.

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Abstract
In this work an organic and nutrient removal pilot plant was used to study the temperature influence on phosphorous accumulating organisms. Three experiments were carried out at 13, 20 and 24.5ºC achieving a high phosphorous removal percentage in all cases. ASM2d model was calibrated at 13 and 20ºC and the Arrhenius equation constant was obtained for phosphorous removal processes showing that the temperature influences on the biological phosphorus removal sub-processes in a different degree. The 24.5ºC experiment was simulated using the model parameters obtained by means of the Arrhenius equation. The simulation results for the three experiments showed a good correspondence with the experimental data demonstrating that the model and the calibrated parameters were able to predict the pilot plant behaviour.
Keywords
Activated sludge plants; ASM2d; biological nutrient removal; calibration; temperature.

INTRODUCTION

The number of wastewater treatment plants (WWTPs) equipped with biological nutrient removal is increasing worldwide. Several studies have been carried out to establish the influence of the main parameters affecting the biological phosphorus removal (BPR). The sludge retention time (SRT) variation has an important influence on the BPR. It has been stated that the SRT affects the phosphorus-glycogen accumulating organisms ratio. Many authors have reported that the population of glycogen accumulating organisms (GAOs) increases with SRT (Satoh *et al*., 1994; Rodrigo *et al*., 1996; García-Usach, 2002). The temperature influence on BPR has also been investigated in numerous studies showing different results. While some authors have reported better phosphorus removal efficiencies at high temperatures (20-37ºC) (Mamais and Jenkins, 1992; Converti *et al*., 1995; Brdjanovic *et al*., 1997) others have reported better efficiencies at low temperatures (5-15ºC) (Barnard *et al*., 1985, Erdal *et al*., 2003). Moreover, the BPR requires the presence of volatile fatty acids (VFA), so the influence of different VFA composition on the BPR process has also been studied (Moser-Engeler *et al*., 1998; Schuler and Jenkins, 2003; Oehmen *et al*., 2004).

The study of biological nutrient removal processes involves a large number of interacting processes which require a deep analysis. Mathematical models have been found as very successful tools for research, development and optimization of biological nutrient removal processes since they include all the information related to the processes. Several models have been developed as the Activated Sludge Models proposed by the IWA (ASM1, ASM2, ASM2d, ASM3) or the TUDP model (Murnleitner *et al*., 1997). Among then, the ASM2d (Henze *et al*., 1999) is one of the most accepted for describing the behaviour of activated sludge processes for nutrient and organic matter (COD) removal.

The verification of a mathematical model provides an important tool for the investigation of advanced control strategies that may assist in the operation or control of WWTPs. Once the model has been calibrated, it can be used to optimize a non optimal performance, proposing modifications

focused on the plant layout and the operation strategies, or to predict the plant performance when the influent conditions change (organic load increase, temperature variations, etc.).

The temperature influence on phosphorus accumulating organisms has been studied in this work using an organic matter and nutrient removal pilot plant. Two stationary-states, at different temperatures, have been calibrated and simulated using the ASM2d model. The Arrhenius equation constant has been obtained for phosphorous accumulating organisms (PAOs) processes. By means of the calibrated parameters and the Arrhenius relationship it has been simulated a third stationary-state at a new temperature.

METHODS

Pilot plant

The experiments were carried out in a pilot plant according to a variant of the modified UCT process. The pilot plant was located in a large WWTP of Valencia (Spain) and received 40 l h^{-1} of municipal raw wastewater. Major operation conditions and the layout of the pilot plant are shown in Figure 1. The pilot plant was operated at three different temperatures (13, 20 and 24.5ºC), reproducing the temperature variations of the region during the year. The sludge retention time was maintained in 10 days for all the experiments.
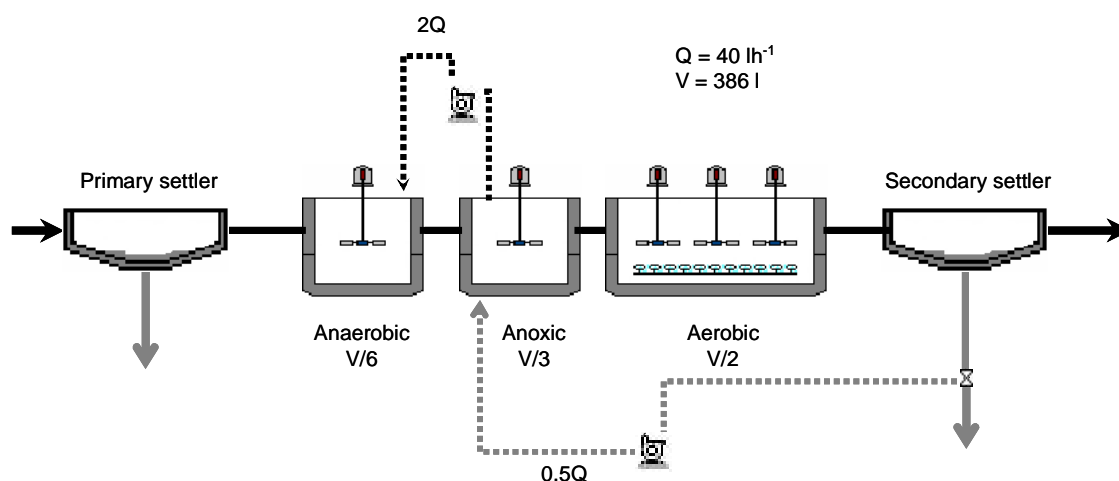

Figure 1 Pilot plant layout

Measurements

Application of the ASM2d model to full scale WWTPs requires experimental data on activated sludge and wastewater characteristics. Integrated samples were collected on a daily basis from influent, effluent and anaerobic, anoxic and aerobic reactors. The influent and effluent characterization consisted in analysing total suspended solids (TSS), volatile suspended solids (VSS), COD_{total}, $COD_{filtered}$, $BOD_{l\ total}$, $BOD_{l\ filtered}$, VFA, NO_3-N, NH_4-N, total nitrogen (N_{tot}), total phosphorus (P_{tot}), PO_4-P and alkalinity (Alk). The average measurements results obtained in the three experiments are presented in Table 1. Mixed liquor suspended solids (MLSS), COD_{total}, NO_3-N, NH_4-N and PO_4-P were determined for activated sludge characterization.

Most of the analytical techniques used in this work were in accordance with Standard Methods (1998) (TSS, VSS, COD, NH_4-N, P_{tot}, PO_4-P). COD (10-125 mg l^{-1}), NO_3-N and Total N were determined with specific MERK kits. VFA were determined by titration using the method proposed by WRC (1992). BOD was determined by pressure measurements using a WTW OXITOP CONTROL system.

Table 1 Influent and effluent wastewater characteristics

Parameter	Unit	Influent			Effluent		
		13ºC	20ºC	24.5ºC	13ºC	20ºC	24.5ºC
TSS	mg l^{-1}	76	57	50	7	6	7
VSS	mg l^{-1}	72	41	39	6	5	6
COD$_{total}$	mgCOD l^{-1}	286	265	222	36	23	33
COD$_{filtered}$	mgCOD l^{-1}	169	157	139	28	22	30
BOD$_{l\ total}$	mgCOD l^{-1}	213	216	190	10	13	15
BOD$_{l\ filtered}$	mgCOD l^{-1}	145	150	119	4	7	10
VFA	mgCOD l^{-1}	78	83	81	0	0	0
NO$_3$-N	mgN l^{-1}	<0.2	<0.2	<0.2	1.7	12.7	11.2
NH$_4$-N	mgN l^{-1}	26.3	26.2	17.6	16.8	0.5	0
N$_{tot}$	mgN l^{-1}	36.4	33.9	25.8	26.9	14.7	11.9
N$_{tot\ filtered}$	mgN l^{-1}	31.6	29.5	21.0	26.4	14.6	11.6
P$_{tot}$	mgP l^{-1}	8.9	8.7	8.7	0.5	2.1	1.4
PO$_4$-P	mgP l^{-1}	7.4	6.8	6.8	0.3	0.3	0.7
Alk	mgCaCO$_3$ l^{-1}	390	353	353	375	320	335

The experimental results indicated that the phosphorous removal process was efficiently performed in the three experiments showing a maximum phosphorous removal percentage at 13ºC (≈94%). The nitrification process was achieved at 20ºC and 24.5ºC as indicates the low ammonia concentration in the effluent flow. Nevertheless, the nitrification was minimal at 13ºC, as was expected at this low temperature value.

RESULTS AND DISCUSSION
Wastewater characterization
A previous step to the ASM2d calibration consists in determining the different wastewater organic components: inert soluble COD (S$_I$), readily biodegradable COD (S$_F$), volatile fatty acids (S$_A$), heterotrophic biomass (X$_H$), nitrifying biomass (X$_{AUT}$), phosphorus accumulating biomass (X$_{PAO}$), storage products of PAOs (X$_{PHA}$), inert particulate (X$_I$) and slowly biodegradable organic matter (X$_S$). The wastewater characterization was carried out following a physico-chemical separation technique as described in Penya-Roja et al. (2002). The obtained results are summarised in Table 2.

Table 2 Wastewater characterization

Parameter	Unit	13ºC	20ºC	24.5ºC
S$_I$	mgCOD l^{-1}	24	15	20
S$_F$	mgCOD l^{-1}	67	59	38
S$_A$	mgCOD l^{-1}	78	83	81
X$_I$	mgCOD l^{-1}	49	34	12
X$_S$	mgCOD l^{-1}	68	74	71
S$_{NO3}$	mgN l^{-1}	0	0	0
S$_{NH4}$	mgN l^{-1}	26.3	26.2	17.6
S$_{PO4}$	mgP l^{-1}	7.4	6.8	6.8

Calibration
Given the high number of parameters included in the ASM2d, a selective calibration was done. High influence kinetic and stoichiometric parameters were determined using off-line calibration

techniques according to Penya-roja *et al.* (2002). Off-line calibration comprises respirometric techniques and individualized analysis of the different processes carried out by heterotrophic, nitrifying and phosphorus accumulating microorganisms. The calibration was performed for the 13 and 20°C experiments once the stationary-state was reached (at least after three times the sludge retention time). Table 3 shows the kinetic and stoichiometric parameters obtained for heterotrophic, nitrifying and phosphorous accumulating organisms.

Table 3 Heterotrophic, nitrifying and PAO parameter values

Parameter	Unit	13°C	20°C	24.5°C
Y_H	mgCOD mgCOD^{-1}	0.54	0.58	0.58
μ_H	d^{-1}	1.22	1.38	2.66
K_F	mgCOD l^{-1}	8.69	0.84	8.69
b_H	d^{-1}	0.19	0.39	0.41
η_{NO3}		0.56	0.26	0.56
μ_A	d^{-1}	---	1.14	1.90
K_{NH4}	mgN l^{-1}	---	0.23	0.23
b_A	d^{-1}	---	0.20	0.33
Y_{PO4}	mgP mgCOD^{-1}	0.46	0.42	0.40
q_{PHA}	d^{-1}	3.14	4.00	4.67
K_A	mgCOD l^{-1}	1.00	1.00	1.00
Y_{PAO}	mgCOD mgCOD^{-1}	0.67	0.65	0.64
μ_{PAO}	d^{-1}	1.56	2.31	2.97
q_{PP}	mgP mgCOD^{-1} d^{-1}	2.28	3.27	4.12
b_{PAO}	d^{-1}	0.12	0.20	0.27
K_{PHA}	mgCOD mgCOD^{-1}	0.076	0.071	0.068
K_{IPP}	mgP mgCOD^{-1}	0.007	0.007	0.007
K_{MAX}	mgP mgCOD^{-1}	0.34	0.34	0.34
η_{NO3}		0.56	0.44	0.56

The calibration procedure, as well as, the experimental values showed that no significant nitrification took place at 13°C and 10 days of sludge retention time.

The heterotrophic kinetic parameters obtained at 20°C indicated inhibition problems reflected in a low maximum growth rate and in a low reduction factor for denitrification. Nevertheless, the nitrifying and PAOs organisms were not affected by this inhibition. This fact can be explained considering that the inhibition was a consequence of leached liquor discharges, with a high content in heavy metals, received in the WWTP during this operational period. Heavy metals use to be combined with organic matter forming complex compounds which have greater effects on the heterotrophic organisms than on the nitrifying and PAOs organisms (Braam and Klapqijk, 1981; Kong *et al.*, 1996).

The PAOs parameter values Y_{PO4}, Y_{PAO} and K_{MAX} can be used to indicate the presence of GAOs (Penya-roja *et al.*, 2002; Ferrer *et al.*, 2004). As GAOs are not included in the ASM2d model, its presence can be detected in the PAOs parameters values. The values obtained for these parameters in the two stationary-states calibrated are quite similar to the ASM2d values, so it can be assumed the absence of GAOs in the process.

As it has been said before, the 24.5°C stationary-state was not calibrated. The ASM2d parameters, needed for the simulation, were calculated using the Arrhenius relationship (Eq. 1). The use of this

equation requires a set of calibrated parameters and the values of the Arrhenius constant for each model parameter. In the case of PAOs, the *a* constant values of the Arrhenius equation were calculated using the ASM2d calibrated parameters obtained at 13ºC and 20ºC experiments (Table 4). Afterwards, the 24.5ºC model parameters for PAOs were determined using the obtained constants and the calibrated parameters at 20ºC. However, due to the presence of inhibitory effects at 20ºC for the heterotrophic organisms and the absence of nitrification at 13ºC, the use of ASM2d Arrhenius constants was required. The heterotrophic parameters at 24.5ºC were calculated using the 13ºC calibrated values and the ASM2d Arrhenius constant (1.07). In that way, the nitrifying parameters at 24.5ºC were calculated using the 20ºC calibrated values and the respective ASM2d Arrhenius constant (1.12).

$$k1 = k2 * a^{(T1 - T2)} \tag{1}$$

Table 4 Arrhenius constant value for PAOs model parameters

Parameter	a		
Y_{PO4}	0.987	q_{PP}	1.053
q_{PHA}	1.035	b_{PAO}	1.071
K_A	1.000	K_{PHA}	0.990
Y_{PAO}	0.996	K_{IPP}	1.000
μ_{PAO}	1.058	K_{MAX}	1.000

Attending to the Arrhenius constant values summarised in Table 4, the PAOs model parameters can be classified into two groups: on the one hand the non temperature dependent parameters ($a \approx 1$) where the saturation, the inhibition and the stoichiometric coefficients, excepting Y_{PO4} are included; and on the other hand the temperature dependent parameters ($a \neq 1$) where the kinetic parameters q_{PHA}, q_{PP}, μ_{PAO} and b_{PAO} are included.

In the ASM2d, the PAOs processes, excepting the lysis process, are considered to have the same temperature dependency value ($a = 1.041$). The mean value of the Arrhenius constant obtained for the q_{PHA}, q_{PP}, μ_{PAO} parameters ($a = 1.048$) is quite closer to the ASM2d value. The Arrhenius constant value obtained for the b_{PAO} parameter ($a = 1.071$) agrees with the ASM2d value.

Unlike ASM2d, many authors use to set different Arrhenius constant values depending on the PAOs process considered. The reason for that is based on the idea that the temperature affects the biological phosphorus removal sub-processes in a different way. The experimental and the literature Arrhenius constant values found for each process carried out by PAOs are summarised in Table 5.

In anaerobic conditions, the *a* values obtained for the rate constant for storage of polyhydroxialkanoates (q_{PHA}) and the maximum rate for phosphorous release (estimated as the product $Y_{PO4} \cdot q_{PHA}$) were 1.035 and 1.022 respectively. As it can be observed, the temperature influence on the maximum rate for polyhydroxialkanoates storage is greater than the influence on the maximum rate for phosphorous release. This tendency, showed in the PAOs anaerobic processes, agrees with the literature data showed in Table 5.

In aerobic conditions, the *a* values obtained for the rate constant for storage of polyphosphate (q_{PP}) and for the maximum growth rate (μ_{PAO}) were 1.053 and 1.058 respectively. These values are closer to those proposed by Mamais and Jenkins (1992) but differ considerably from those obtained by Brdjanovic *et al*. (1998). The experimental conditions used by Mamais and Jenkins (1992) were very similar to those used in this work, where the activated sludge was acclimatized to the studied

temperature and the sludge retention time was kept constant and low enough to avoid the GAOs presence. On the contrary, Brdjanovic *et al*. (1998) used a different methodology where not only the temperature was changed during the study but also the sludge retention time.

Table 5 Literature Arrhenius constant values for PAOs processes

Author	PHA Storage	P release	PP Storage	Growth
Experimental values	1.035	1.022	1.053	1.058
Mamais and Jenkins (1992)	1.048	1.043	1.055	1.053
ASM2d (1999)	1.041	1.041	1.041	1.041
Brdjanovic *et al*. (1997)	1.080 ± 0.011	1.055 ± 0.019	1.048 ± 0.012	-
Brdjanovic *et al*. (1998)	1.095 ± 0.013	1.075 ± 0.012	1.031 ± 0.017	>1.110
Helmer and Kunst (1998)	-	1.018	1.025	-
Baetens *et al*. (1999)	1.079 ± 0.024	1.071 ± 0.032	1.067 ± 0.006	-

Simulation

Once the kinetic and stoichiometric parameters were determined, the plant behaviour was simulated in order to reproduce the experimental data obtained at the three studied temperatures. The simulation task was performed using the software DESASS (DEsign and Simulation of Activated Sludge Systems) (Seco et al., 2004). The simulation results for the two experiments calibrated (13ºC and 20ºC) are summarised in Table 6 and Table 7 showing a good correspondence with the experimental data.

The 24.5ºC experiment simulation was carried out using the model parameters obtained by means of the Arrhenius equation. The simulated results also showed a good correspondence with the experimental data (Table 8).

Table 6 Experimental and simulated values at 13ºC

Parameter	Unit	Anaerobic		Anoxic		Aerobic		Effluent	
		Exp	Sim	Exp	Sim	Exp	Sim	Exp	Sim
TSS	mg l^{-1}	2356	2428	3271	3232	3376	3327	7	7
COD$_{total}$	mgCOD l^{-1}	3050	2798	3886	3875	3829	3798	36	40
NO$_3$-N	mgN l^{-1}	<0.2	0.0	<0.2	0.0	0.8	1.0	1.7	1.0
NH$_4$-N	mgN l^{-1}	23.4	25.9	23.2	25.5	21.0	19.6	16.8	20.0
PO$_4$-P	mgP l^{-1}	33.6	34.5	33.7	33.6	0.4	1.0	0.3	1.1

Table 7 Experimental and simulated values at 20ºC

Parameter	Unit	Anaerobic		Anoxic		Aerobic		Effluent	
		Exp	Sim	Exp	Sim	Exp	Sim	Exp	Sim
TSS	mg l^{-1}	1701	1779	2546	2568	2704	2658	6	7
COD$_{total}$	mgCOD l^{-1}	2170	2121	2978	2946	2762	2860	23	24
NO$_3$-N	mgN l^{-1}	0.7	0.0	<0.2	0.2	16.9	17.6	12.7	15.5
NH$_4$-N	mgN l^{-1}	18.9	21.1	18.1	18.7	0.6	0.5	0.5	0.5
PO$_4$-P	mgP l^{-1}	28.6	29.9	26.4	28.8	0.6	1.0	0.3	0.7

Table 8 Experimental and simulated values at 24.5ºC

Parameter	Unit	Anaerobic		Anoxic		Aerobic		Effluent	
		Exp	Sim	Exp	Sim	Exp	Sim	Exp	Sim
TSS	mg l^{-1}	1418	1360	1988	1961	2057	2027	7	7
COD$_{total}$	mgCOD l^{-1}	1502	1506	2088	2079	2073	2009	33	32
NO$_3$-N	mgN l^{-1}	0.8	0.0	0.7	0.1	11.2	11.3	11.2	11.0
NH$_4$-N	mgN l^{-1}	14.0	14.0	10.2	12.3	0.0	0.3	0.0	0.3
PO$_4$-P	mgP l^{-1}	26.0	26.1	22.4	25.2	1.0	1.0	0.7	0.9

CONCLUSIONS

The phosphorous removal process was efficiently performed in the three experiments carried out showing a maximum value at 13ºC. The PAOs calibrated parameters indicated the absence of GAOs in the process.

The Arrhenius constant values obtained for the PAOs reflected that the temperature influences on the biological phosphorus removal sub-processes in a different way. The maximum rate for polyhydroxialkanoates storage is more influenced by the temperature than the maximum rate for phosphorous release.

No calibration step was necessary for the 24.5ºC experiment. The model parameters for this temperature were calculated by means of the Arrhenius equation and the calibrated parameters at 13ºC and 20ºC. The simulation results accurately reproduced the experimental data.

On balance, the good simulation results point out the advantage of using calibrated models and simulation tools in order to predict changes in wastewater process performance.

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