Optimal operation for timely adaptation of activated sludge plants to changes in the surfactant composition of wastewater

G. Carvalho*, J.M. Novais*, P.A. Vanrolleghem and H.M. Pinheiro***

* Centro de Engenharia Biológica e Química, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

** BIOMATH, Ghent University, Coupure Links 653, B-9000 Gent, Belgium

Water Science and Technology **Vol 45 No 4–5 pp 345–353** © IWA Publishing 2002

Abstract The composition of a textile industry wastewater is highly variable, as the industrial process has to follow fashion and season trends. Surfactants represent one of the largest COD fractions in a typical textile wastewater. Therefore, it was the aim of this paper to model the acclimatisation behaviour of an activated sludge system when subjected to composition variations in the surfactant containing feed. The model was based on data obtained in SBR experiments in which a linear alkyl ethoxylate as sole carbon source in the feed was replaced by another with a longer ethoxylate chain. A previously developed model (Fractionated Degradation Model) was applied to each of the 21 SBR cycles carried out in this study. The resulting best-fit parameters were investigated and sub-models were further developed, to create an acclimatisation model, able to predict the sludge acclimatisation level. Using the information given by this model, it was possible to propose an optimal operation scheme to pre-acclimatise the sludge before a surfactant replacement is made in the textile process. A cost analysis was carried out to compare different scenarios, with and without the application of this operation scheme. It was concluded that the proposed pre-acclimatisation process may be cost effective as compared to other scenarios if a cheap surfactant-containing product was employed.

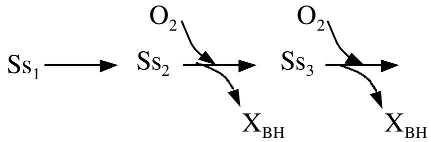
Keywords Acclimatisation model; activated sludge; cost analysis; optimal operation; sequencing batch reactor; surfactants

Introduction

Textile industry effluents are characterised by a wide variability in flow and composition. These oscillations may affect the performance of biological wastewater treatment units such as activated sludge reactors. Surfactants often constitute a major fraction of the organic load in textile effluents. Thus, adaptation to different surfactants seems to be an important feature for textile wastewater treatment plant operation. For that, it is important to develop the ability to predict the response of activated sludge systems when subjected to variations in the surfactant composition of the feed. Non-ionic surfactants are the most commonly used in textile industries, linear alkyl ethoxylates representing an increasingly widespread subclass. Alkyl ethoxylates with longer ethoxylate (EO) chains are known to be more resistant to biodegradation (Swisher, 1987). Thus, it would be useful to have some knowledge of the sludge response when, in the bioreactor feed, a surfactant with short EO content is replaced with a long EO content counterpart. A mathematical model of the activated sludge response to such variations can be helpful to study and control the biodegradation efficiency when a replacement in the textile process chemicals is expected. A good control system keeps the effluent quality more consistent, allowing the operational margins to be smaller, thus reducing the costs. Many plants have been overdesigned to take varying loads into account (Olsson, 1998).

The objective of this study was to find an optimal operation scheme to induce acclimatisation in an activated sludge system under varying influent composition. Hence, the biological system could be operated steadily, with no adaptation times and over-designed tanks being needed.

A dynamic model (Fractionated Degradation Model or FDM) was previously developed to describe activated sludge degradation of non-ionic surfactants (Carvalho *et al.*, 2001). This model was based on the assumption of three sequentially degraded COD fractions, where the second fraction is a metabolite of the original molecule and the third fraction is a more slowly biodegradable metabolite resulting from the secondary degradation. This is presented in the following scheme:



In this work, the FDM was used as a basis for an acclimatisation model applied to predict the sludge performance and degradation capacity as sludge adapts to a different non-ionic surfactant.

Materials and methods

Materials

The experimental data was obtained in a 4.8 l laboratory-scale Sequencing Batch Reactor (SBR) with a 24 hour computer-controlled cycle, consisting of 18 min filling, 21 h 45 min aeration, 60 min settling, 28 min drawing off the exhausted supernatant and 29 min idle. A hydraulic retention time of 27 h and a sludge retention time of 15 days were imposed. Other details concerning the SBR inoculum, feed composition and maintenance are described elsewhere (Carvalho *et al.*, 2000). Biodegradation was monitored by Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) measurements, specific titrimetric analysis of the non-ionic surfactant concentration (NIO) and sequential closed respirometry. About one hour of aeration at the beginning of the experiment was needed to achieve a stable endogenous respiration rate before the injection of the carbon source, giving a working aeration time of 20.8 h. Polyoxyethylene 4 and 10 lauryl ethers (referred to as Brij 30 and POE-10-LE, respectively) were consecutively fed to the SBR as sole carbon source (laboratory-grade products from Sigma, USA). A food to microrganism ratio of 0.4 gCOD/gCOD was imposed. Sludge adapted to Brij 30 was fed with POE-10-LE and the acclimatisation process was followed for 21 days.

Mathematical data treatment

The FDM was fitted to the respirometric and titrimetric data from the 21 SBR cycles fed with POE-10-LE, using the WEST® modelling and simulation software environment (Hemmis NV, Kortrijk, Belgium), through a Simplex optimisation routine. The model consists of nine equations and eleven parameters, which were fitted to each batch experiment data by the aid of a weighted sum of squared errors cost function (the weights were 1,000 and 0.0001 for respirometric and NIO data, respectively). In addition, two degradation capacity indicators (k_1 and k_2, Carvalho *et al.*, 2000) were calculated by plotting the logarithm of the NIO data (k_1) and TOC data (k_2) against time, corresponding to apparent first order kinetic constants for the studied surfactants. The NIO data reflect the decrease in surfactant properties (fraction Ss_1) or primary degradation, whereas the TOC data reflect the secondary or ultimate degradation (all fractions).

Results and discussion

Calibration of the fractionated degradation model to POE-10-LE acclimatisation data

The FDM parameters were optimised to the data from the sludge acclimatisation study to POE-10-LE and good fits were obtained, as exemplified in Figure 1 for cycles 1, 9 and 19.

The time evolution of the eleven FDM parameters as the acclimatisation proceeds is shown in Figure 2. Table 1 summarises the average values and corresponding standard deviations.

An attempt to prove the structural identifiability of the model (results not shown; Dochain *et al.*, 1995) failed due to the high complexity of the resulting differential equations. Therefore, the parameters that should be submitted to estimation were identified by performing a sensitivity analysis. It was found that the model was not sensitive to variations of b_H, which was fixed to a typical value (Table 1). K_{S1} had also little influence on the cost function during the initial assays. Therefore, the value determined by trial and error was kept constant during the first 5 SBR cycles. Finally, this analysis revealed low model sensitivity towards variations of the parameter K_I.

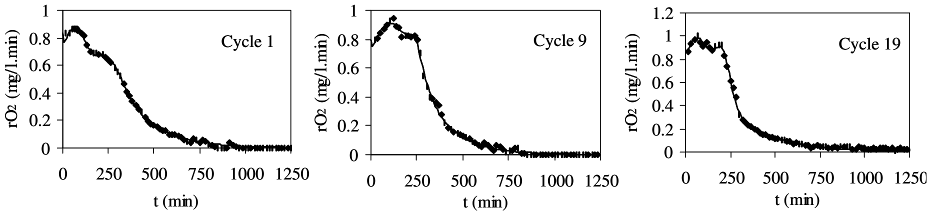


Figure 1 Respirometric experimental data and results given by the FDM for cycles 1, 9 and 19 of sludge acclimatisation to POE-10-LE. Experimental data (●), model (—)

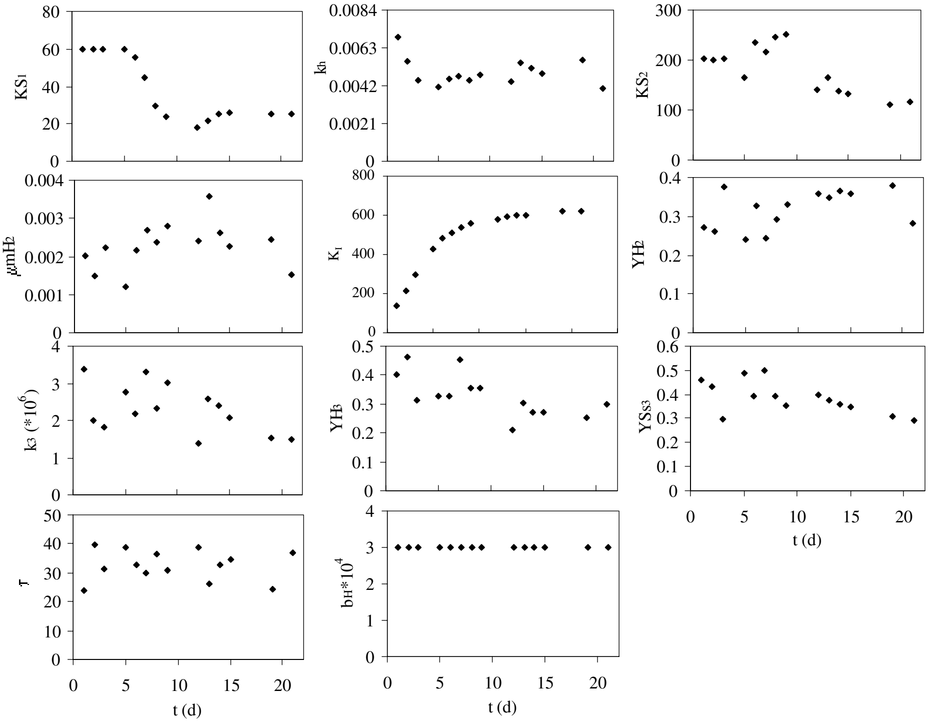


Figure 2 Variation of the FDM parameters along the 21 days of the acclimatisation study to POE-10-LE. See Table 1 for nomenclature and units

Table 1 Average values and corresponding standard deviations of the FDM parameters during sludge acclimatisation to POE-10-LE

Parameter	Meaning	Average	St. dev. (%)
K_{S1} (mg/l)	Affinity constant for Ss_1	38	45
k_h (min^{-1})	Hydrolysis rate constant of Ss_1	0.0049	15
K_{S2} (mg/l)	Affinity constant for Ss_2	180	27
μmH_2 (min^{-1})	Maximum specific growth rate for Ss_2	0.0023	27
K_I (mg/l)	Inhibition constant for Ss_2	485	33
k_3 (min.mg/l)$^{-1}$	First order kinetic constant for Ss_3	$2.3*10^{-6}$	28
b_H (min^{-1})	Decay rate for heterotrophic biomass	0.0003	0
t (min)	Transition time constant	33	16
YH_2 (mgCOD/mgCOD)	Yield of heterotrophic biomass from Ss_2	0.32	16
YH_3 (mgCOD/mgCOD)	Yield of heterotrophic biomass from Ss_3	0.33	22
YSs_3 (mgCOD/mgCOD)	Yield of conversion of Ss_2 into Ss_3	0.39	17

Acclimatisation model

The profiles displayed in Figure 2 and the standard deviations presented in Table 1 seem to indicate that the acclimatisation observed on the sludge performance was mainly due to evolution of parameters K_{S1} and K_I. Although the K_I values were poorly identifiable from a single batch experiment, it was found that fitting the whole series with the least parameters being changed was best achieved by varying K_I in addition to K_{S1}. In other words, K_I was poorly identifiable from the single batch tests but its time evolution could be identified well from the complete set of batch experiments. The parameters K_{S1} and K_I were thus selected to quantify sludge acclimatisation. By observation of the respective profiles along the consecutive batch assays, the following secondary model structures of FDM parameter evolution could be proposed:

$$\frac{dK_{S1}^{acc}}{dt} = a * \frac{Ss_1}{b + Ss_1} * (K_{S1m}^{acc} - K_{S1}^{acc}) * K_{S1}^{acc} \tag{1a}$$

$$K_{S_1} = K_{S1}^{0} - K_{S1}^{acc} \tag{1b}$$

$$\frac{dK_I^{acc}}{dt} = c * \frac{Ss_2}{d + Ss_2} * \left(K_{I_m}^{acc} - K_I^{acc}\right) \tag{2a}$$

$$K_I = K_I^0 + K_I^{acc} \tag{2b}$$

with: K_{S1}^0, K_I^0 = constitutive affinity and inhibition constants, exhibited by non-acclimatised sludge;

K_{S1}^{acc}, K_I^{acc} = affinity constant reduction and inhibition constant increment, resulting from acclimatisation;

a, c = acclimatisation rate constants for K_{S1}^{acc} and K_I^{acc};

b, d = affinity constants for K_{S1}^{acc} and K_I^{acc};

K_{S1m}^{acc}, K_{Im}^{acc} = maximum values for K_{S1}^{acc} and K_I^{acc}.

The proposed acclimatisation model consisted, thus, of the same equations as the FDM, where the parameters K_{S1} and K_I were transformed into state variables given by Eqs (1) and (2). The other nine parameters were kept constant and equal to the average values presented in Table 1. With this model, it is possible to predict the acclimatisation state of an activated sludge system at a given time after the start of the new substrate feed to the

Table 2 Optimal values obtained for the acclimatisation parameters of the secondary models

K_{S1}^0 (mg/l)	60	K_I^0 (mg/l)	63.4
$K_{S1}^{acc}m$ (mg/l)	36.5	$K_I^{acc}m$ (mg/l)	570
a (min.mg/l)$^{-1}$	0.0002	c (min^{-1})	0.0035
b (mg/l)	20	d (mg/l)	150
K_{S1}^{acc} (0) (mg/l)	0.0001	K_I^{acc} (0) (mg/l)	0.0001

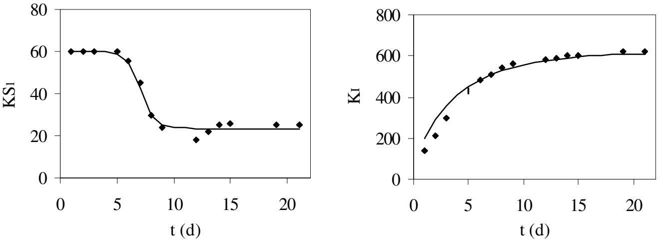


Figure 3 K_{S1} and K_I data (●) and values given by the respective models (—). Units of Table 1

reactor. This acclimatisation process can be followed in time through the evolution of the acclimatisation factors K_{S1}^{acc} and K_I^{acc}. The best fits corresponding to the calibration of these secondary models (Eqs (1) and (2)) are presented in Figure 3 and the respective parameter values are listed in Table 2.

Acclimatisation indicators

In order to verify the acclimatisation model, the apparent first order kinetic constants k_1 and k_2 were used as acclimatisation indicators. k_2 was obtained from TOC data, which were not used for the development of the FDM, and k_1 was determined from NIO data, which were taken into account in the multivarible fitting of the FDM but with a very low weight. Based on the profiles of these two factors (Figure 4), two models were developed:

$$\frac{d\,k_1^{acc}}{d\,t} = \alpha_1 * \frac{Ss_1}{\beta_1 + Ss_1} * (k_{\max_1}^{acc} - k_1^{acc}) * k_1^{acc} \tag{3a}$$

$$k_1 = k_1^0 + k_1^{acc} \tag{3b}$$

$$\frac{d\,k_2^{acc}}{d\,t} = \alpha_2 * \frac{Ss_{tot}}{\beta_2 + Ss_{tot}} * (k_{\max_2}^{acc} - k_2^{acc}) \tag{4a}$$

$$k_2 = k_2^0 + k_2^{acc} \tag{4b}$$

where the indices 1 and 2 stand for primary and secondary degradation, respectively, and:
$k_{1,2}^0$ = constitutive degradation rates, exhibited by non-acclimatised sludge;
$k_{1,2}^{acc}$ = degradation rate increments resulting from acclimatisation;
$\alpha_{1,2}$ = acclimatisation rate constants;
$\beta_{1,2}$ = affinity constants for the degradation rate increments;
$k_{\max_2}^{acc}$ = maximum degradation rate increments;
Ss_1 = surfactant concentration (NIO data);
Ss_{tot} = total substrate concentration (original surfactant molecule and metabolites).

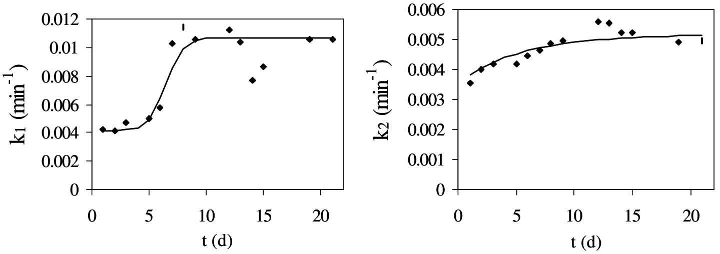


Figure 4 Acclimatisation indicators (k_1 and k_2) data (●) and values given by the respective models (—). Units of Table 1

The optimal fits for the models developed to describe the k_1 and k_2 acclimatisation indicators (Eqs (3) and (4)) are shown in Figure 4, and Table 3 contains the respective parameter values.

Acclimatisation model verification

The acclimatisation indicators k_1 and k_2 give the same information on the sludge acclimatisation state as the models developed for K_{S1} and K_I and can thus be used as a tool to verify the model independently from the original FDM. However, they cannot be used as acclimatisation models as they do not affect the model output. Only the K_{S1} and K_I submodels are used to generate the global acclimatisation model results, affecting the model output variables rO_2 (respiration rate) and Ss (substrate concentrations).

K_{S1} and k_1 are both related to the surfactant primary biodegradation (breakdown of the original molecule Ss_1), while K_I and k_2 reflect the secondary biodegradation process. Therefore, the partial acclimatisation model developed for K_{S1} (Eqs (1a–b)) can be confirmed by comparison to the k_1 model (Eqs (3a–b)), which presents the same form, although inverted. The model structure for the K_I partial acclimatisation model (Eqs (2a–b)) was inspired on the model for k_2 (Equations (4a–b)), since the lack of sensitivity of the FDM towards this parameter hampered the precise estimation of the corresponding values. Running simulations for the studied conditions, these four models all indicate that the sludge can be considered acclimatised (further value changes lower than 10%) after around 9 days. This shows that the modelled parameters K_{S1} and K_I are consistent with the first order kinetic constants k_1 and k_2, calculated independently from the FDM, which verifies the model structure and the parameter values.

Optimal operation scheme

When a surfactant is replaced in the textile process, a temporary loss in degradation efficiency takes place in the activated sludge system. The solution proposed in this paper involves the sludge pre-acclimatisation in order for it to be able to efficiently remove the new surfactant from the first day it is discharged. This pre-acclimatisation process consists of feeding scheduled amounts of the new surfactant to the bioreactor together with the normal discharged process wastewater. The two situations can be schematised on a one-year basis as shown in Figure 5, for a textile process where a surfactant replacement occurs at the transitions between the two seasons.

Table 3 Optimal values obtained for the acclimatisation indicator model parameters

k_1^0 (min–1)	0.00416	k_2^0 (min^{-1})	0.00354
$k_{max\,1}^{acc}$ (min^{-1})	0.00654	$k_{max\,2}^{acc}$ (min^{-1})	0.0017
α_1 (–)	0.8	α_2 (min^{-1})	0.0006
β_1 (mg/l)	10	β_2 (mg/l)	200
$k_1^{acc}(0)$ (min^{-1})	10^{-6}	$k_2^{acc}(0)$ (min^{-1})	10^{-8}

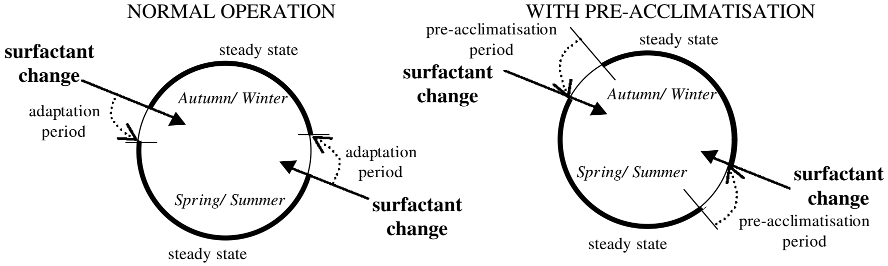


Figure 5 Normal and pre-acclimatisation operational schemes on a one-year basis

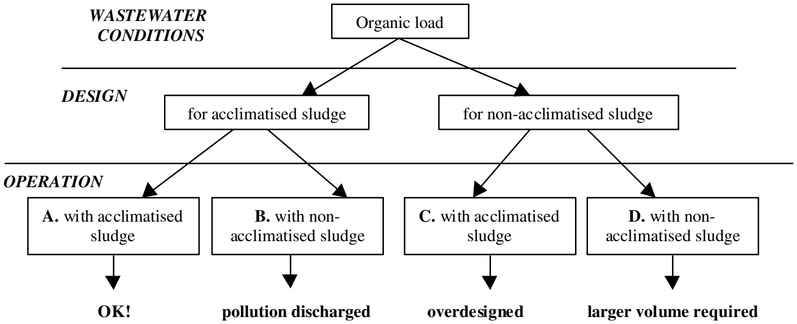


Figure 6 Four conjectured scenarios for the economic analysis of pre-acclimatisation

Running simulations of the acclimatisation model developed above, an optimal operation scheme for the studied situation was determined. The proposed pre-acclimatisation process would take 41 days, where the POE-10-LE should be fed by repeating the following organic load sequence: 1 day with 0.6 kg COD/kg SS, followed by three days with 0.05 kg COD/kg SS.

Economic analysis

The cost analysis is generally divided in investment and operational costs. Within the former, the set up of the oxidation tank and the aeration system were considered. The operational costs included costs associated to the power supplied for aeration, the surfactant needed for pre-acclimatisation, sludge disposal and fines related to poor effluent quality. Four scenarios were conjectured in this analysis (Figure 6). The wastewater treatment plant can be designed considering pre-acclimatisation (scenarios A and B) or not (C and D). The plant can be operated according to (A and D) or regardless (B and C) the plans of construction.

The degradation capacity of the SBR activated sludge system was defined as the maximum load that can be degraded down to 80 mgCOD/l during the cycle working time. The degradation capacity of acclimatised and non-acclimatised sludge were determined by model simulations. Dividing these values by the aeration time of the SBR cycle, a net degradation capacity was calculated. The required tank volume was obtained by dividing the estimated organic load (515 kgCOD/d) by the net degradation capacity of the sludge. As expected, the acclimatised sludge presented a higher degradation capacity, thus requiring a smaller tank volume (206 m^3 instead of 312 m^3 for non-acclimatised sludge). The aeration system was designed in order to supply air at the maximum required respiration rate. In spite of the differences between acclimatised and non-acclimatised sludge respirometric response, the air flow requirements were about the same (45 kgO_2/h), as both systems had to degrade the same organic load. Two power laws compiled by Gillot *et al.* (1999) were used to calculate the costs associated to the oxidation tank and the aeration system. These investment costs were assumed to be depreciated in 10 years.

The energy supplied for aeration was calculated considering that aeration is controlled using the respirometric information given by the model simulations and a variable flow compressor. The costs associated to the surfactant needed for pre-acclimatisation (2.93 €/Kg), sludge disposal (375 €/tonSS) and effluent quality were determined based on the model simulation results for the four hypothetical scenarios. The fines related to poor effluent quality were calculated by applying the cost formulas given in Vanrolleghem *et al.*, (1996). The study was done for a working interval of one year, considering the periods of adaptation or pre-acclimatisation to a new surfactant between two periods of steady state operation. A total cost balance is summarised in Table 4.

From Table 4, the most cost-effective situation is given by scenario B, but it involves higher pollution discharges. This problem is not obvious from the values presented in Table 4, calculated for a basic effluent load, giving similar fines for effluent quality for all scenarios. However, when one focuses at periods where the estimated maximum load is fed (about 5 times the one used in the basic scenarios), these costs suffer an increase of about 70% for case B, whereas this increase is less than 5% for the other situations. This means that scenario B is not only inefficient but also results in higher costs.

Among the considered hypotheses, scenario A, although resulting in higher operational costs, allows the achievement of the same effluent quality performance in a smaller system, thus reducing the investment costs as compared to D. In addition, the pre-acclimatisation could eventually be carried out using a less purified product containing the same surfactant, resulting in lower operational costs for scenario A (e.g., using a product 30% cheaper would make scenario A the most cost effective).

Conclusions

A previously developed model was successfully applied to an activated sludge acclimatisation study to a non-ionic surfactant. Based on the parameter values obtained from model calibrations on a series of batch experiments, an acclimatisation model was developed. Secondary models were proposed for two parameters (K_{S1} and K_I), as these were found to vary more significantly with acclimatisation than the other parameters of the model, which were set constant in the acclimatisation model. Two independent factors, first order kinetic constants for primary and secondary biodegradation, were used as acclimatisation indicators for model verification. The acclimatisation model was applied to simulate the sludge acclimatisation evolution given different operational strategies. An operation scheme was proposed to pre-acclimatise the sludge when a change in the surfactant composition of the influent is predicted. A cost analysis was carried out, comparing four scenarios of acclimatisation design and performance. The lowest costs apparently result from a scenario

Table 4 Total cost balance for the four hypothetical scenarios

Scenario	**A**	**B**	**C**	**D**
Oxidation tank (€)	134,220	134,220	163,560	163,560
Aeration system (€)	45,920	45,920	45,900	45,900
Total investment (€)	180,140	180,140	209,460	209,460
Depreciation of investment (€/yr)	18,140	18,140	20,950	20,950
Energy for aeration (€/yr)	11,290	11,290	11,090	11,120
Surfactant for pre-acclimatisation (€/yr)	6,900	–	6,900	–
Sludge disposal (€/yr)	11,550	11,470	11,530	11,460
Effluent quality (€/yr)	880	880	900	900
Total operational costs (€/yr)	30,620	23,640	30,420	23,480
TOTAL (€/yr)	48,630	41,780	51,370	44,430

which assumes that the plant is designed to apply the pre-acclimatisation scheme but in which the operation does not take it into account, with more pollution being discharged. However, this results in much higher costs when there is an increase in the fed organic load. Among the more sustainable scenarios, the pre-acclimatisation seemed to lead to higher operation costs, but lower investment costs. Moreover, this operation strategy may be cost effective when compared to other scenarios if a cheap surfactant-containing product is employed for the pre-acclimatisation process.

References

Carvalho, G., Paul, E., Novais, J.M. and Pinheiro, H.M. (2000). Studies on activated sludge response to variations in the composition of a synthetic surfactant-containing feed effluent. *Wat. Sci. Tech.*, **42**(5–6), 135–143.

Carvalho, G., Nopens, I., Novais, J.M., Vanrolleghem, P.A. and Pinheiro, H.M. (2001). Modelling of activated sludge acclimatisation to a non-ionic surfactant. *Wat. Sci. Tech.,* **43**(7), 9–17.

Dochain, D., Vanrolleghem, P.A. and Van Daele, M. (1995). Structural identifiability of biokinetic models of activated sludge respiration, *Wat. Res.*, **29**(11), 2571–2578.

Gillot, S., de Clercq, B., Defour, D., Simoens, F., Garnaey, K. and Vanrolleghem, P.A. (1999). Optimisation of wastewater treatment plant design and operation using simulation and cost analysis, in Proceedings of the 72nd Annual WEF Conference and Exposition, New Orleans, USA.

Swisher, R.D. (1987). *Surfactant Biodegradation*, 2nd ed., Marcel Dekker, New York.

Olsson, G. (1998). Process control in biological wastewater treatment. In: *Dynamics and control of wastewater systems*, ed. Barnett, M., Stenstrom, M. and Andrews, J., Technomic Publishing Co. Inc., USA.

Vanrolleghem, P.A., Jeppsson, U., Carstensen, J., Carlsson, B. and Olsson, G. (1996). Integration of WWT plant design and operation – a systematic approach using cost functions, *Wat. Sci. Tech.*, **34**(3–4), 159–171.