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Development and application of kinetic models for the primary biodegradation of non-ionic surfactants

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ABSTRACT

The growing concern for the environment is promoting the use of surfactant products from renewable sources such as fatty alcohol ethoxylates. The high production and use of these products implies the need to develop models that enable predictions of their behaviour in biodegradation processes. The biodegradation tests were carried out according to the OECD 301 E test for ready biodegradability. In this work, kinetic models of general application to surfactant biodegradation are developed, both for substrates that do not support growth and for those that do, considering a residual substrate concentration as not being biodegraded. The models were applied to three commercial non-ionic surfactants, fatty alcohol ethoxylates with different carbon-chain lengths and degrees of ethoxylation, also analysing the initial surfactant concentration.

1. Introduction

The need to formulate expressions that describe the biodegradation rate in an aquatic environment has given rise to models that predict the behaviour of products that are difficult to biodegrade under different environmental conditions. The standard methods used in the study of surfactant biodegradability [1] are useful to indicate whether a product is biodegradable or not but are not useful to predict the rate at which a given product biodegrades in the environment.

In the literature, mathematical models applied to the biodegradation of the most widely used anionic surfactants (linear alkylbenzene sulfonate, LAS) are more common, being fitted on occasions to a zero-order kinetics [2] as well as to the models proposed by Schmidt et al. [3] and by Quiroga and Sales [4]. Information on the biodegradation of non-ionic surfactants remains scant.

Carvalho et al. [5] studied the respirometric profiles in biodegradation processes of non-ionic surfactants, suggesting that saturation and inhibition effects were involved in this surfactant-biodegradation system. However, simple Monod and Haldane models based on a single carbon source were not able to predict the wide variety of respirometric profiles. Indeed, the original surfactant molecule and its successive metabolites can be regarded as different substrates which are degraded by different enzymes or bacterial consortia with different kinetic character. In view of this, they developed a dynamic model in which primary degradation of the intact surfactant molecule was considered to be an enzymatic conversion, with no growth associated with it (Michaelis–Menten kinetic equation). The apparent inhibition effect was admitted to be associated to the degradation of one of the metabolites and not to the initial molecule (Haldane kinetic equation).

The fact that in the near future the use of surfactant products from renewable resources such as fatty alcohol ethoxylates (FAEs) could have far more significant use raises the necessity of studying and analysing the development of models that predict their behaviour in the biodegradation process.

The present work develops models for general application to the biodegradation of surfactants and are applied to three fatty alcohol ethoxylate non-ionic surfactants having different carbon-chain lengths and degrees of ethoxylation.

2. Experimental

2.1. Reagents

The surfactants used in this study were fatty alcohol ethoxylates with the general formula $R(-O-CH_2-CH_2)_n-OH$, and commercial name FINDET 1214N/23 (R: 12–14, *n*: 11), FINDET 1214N/16 (R: 12–14, *n*: 4) and FINDET 1618A/18 (R: 16–18, *n*: 6) supplied by Kao Corporation, S.A. (Tokyo, Japan). The surfactants were used directly without purification. They are polydispersal mixtures and properties indicated in Table 1 are mean values. The rest of the reagents used were PA quality and purchased by Panreac.

2.2. Standard biodegradation assay

The biodegradation tests were carried out according to the OECD 301 E test for ready biodegradability [1]. A solution of the surfac-

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Nomenclature

k	maximum specific growth rate on a substrate other than the surfactant (h^{-1})
K_M	half-saturation constant (mg/L)
K_S	half-saturation constant (mg/L)
r_{max}	maximum specific reaction rate (h^{-1})
S	substrate concentration (mg/L)
S_0	Initial substrate concentration (mg/L)
S_R	non-biodegradable substrate concentration (mg/L)
t	time (h)
t_i	time of inflexion point for logistic model (h)
X	biomass concentration (CFU/mL)
x	substrate conversion
X_{max}	maximun biomass concentration (CFU/mL)
X_0	initial biomass concentration (CFU/mL)
X_i	biomass concentration of inflexion point for logistic model (CFU/mL)
Y_{ap}	apparent yield (g biomass/g substrate)
μ_m	maximum specific growth rate (h^{-1})
x_m	maximum conversion

tant, representing the sole carbon source for the microorganisms, was tested in a mineral medium, inoculated and incubated under aerobic conditions in the dark. The procedure consists of introducing 1.2 L of surfactant solution (for which the biodegradability is to be determined) into a 2-L Erlenmeyer flask and inoculating the solution with 0.5 mL of water from a secondary treatment of a sewage-treatment plant (STP) that operates with activated sludges. The Erlenmeyer flask is plugged with a cotton stopper and left in darkness in a thermostatically controlled chamber at 25 °C. The constant rotary speed of the orbital shaker (125 sweep/min) provides the necessary aeration. The surfactant solution is prepared by dissolving the desired quantity of surfactant in the nutrient solution.

Reference assays were made with an easily biodegradable surfactant (LAS) in order to determine the activity of the microbial population present in the test medium. The initial concentration of the reference assay was 5 mg/L in all cases, and the mean biodegradability at 5 days was 97.3% ± 1.5. According to the OECD [1], for the validity of the assay to be accepted, the percentage of the biodegradation of the soft standard after 5 days should be greater than 90%. It is known that sorption may significantly influence the resulting environmental effects of surfactants [9] and it has been studied by some authors [10] who have proposed expressions to predict the sorption onto activated sludge particles for alcohol ethoxylates. In the biodegradation assays presented here, the sorption can be considered negligible, given the scant biomass formation. As a means of confirming this fact, abiotic assays were made in the presence of $HgCl_2$, observing that the values of the residual surfactant remained around 100% over the biodegradation period. These results indicate that the contribution of abiotic processes in the degradation of the FAEs in the biodegradation tests can be dismissed.

The biodegradation was studied at different initial concentrations ranging from 5 to 25 mg/L.

2.3. Surfactant analysis

The biodegradation process was monitored by measuring the residual surfactant concentration over time. The FAEs were determined by the iodine–iodide colorimetric method [11]. For the absorbance measurements, a double-beam spectrophotometer Spectronic Unicam UV-V was used. The absorbance was directly proportional to the surfactant concentration.

2.4. Biomass growth during the biodegradation process

During the biodegradation assays, the number of viable microorganisms was measured by counting of heterotrophic microbes in a dish, expressing the result as colony-forming units (CFU) per mL. The culture medium, nutrient agar, enabled the detection of a broad variety of microorganisms. With a sterile pipette, 1 mL of sample was taken from the culture, and a series of 1:10 dilutions made in ClNa at 0.9% until reaching a suspension of microorganisms containing between 30 and 80 viable cells per mL of test solution.

Each dilution was analysed in duplicate: 1 mL of sample to be analysed was placed on a 10 cm dish. Then 20 mL of previously sterilized culture medium was poured onto the dish, tempered at 60 °C, and gently stirred to complete the homogenization. The mixture was left to cool until complete solidification and then incubated at 25 °C for 72 h in darkness. The total number of microorganisms was determined by multiplying the number of CFU by the corresponding dilution factor. The count was made in an automatic colony counter (Countermat Flash IUL Instruments).

3. Results and discussion

Fig. 1 shows the biodegradation profiles for the surfactants tested, $C_{12-14}E_4$, $C_{12-14}E_{11}$, and $C_{16-18}E_6$. The percentage of biodegradation at 50 h of assay in all cases surpassed 90% at low concentrations. This percentage declined when the initial surfactant concentration increased, being especially low for surfactant $C_{12-14}E_4$, which at 25 mg/L did not exceed 60% biodegradation.

Fig. 2 presents the growth curves for the microorganisms together with the variation in the surfactant concentration during the biodegradation process for the surfactants $C_{12-14}E_4$, $C_{12-14}E_{11}$, and $C_{16-18}E_6$. It was found for all the surfactants that at low initial assay concentrations (lower than 25 mg/L), the percentage of residual surfactant rapidly declined over time, reaching a constant residual surfactant concentration. For higher concentrations, after an initial period of acclimation of the microorganisms, the biodegradation process was slower, also reaching a constant residual surfactant concentration in all cases. Also, it was found that during the exponential growth phase, the residual surfactant concentration underwent a linear decline. In experiments with 5 mg/L of initial concentration, when the surfactant concentration remained constant at its lowest values, there appeared to be no growth of the microorganisms. With higher initial surfactant

Table 1
Description and properties of the surfactants employed in the biodegradation tests.

Comercial name	Symbol	Structure[a]	HLB [6]	MW [7] (g/mol)	CMC [8] (mg/L)
FINDET 1214N/16	$C_{12-14}E_4$	R: 12(70%)–14(30%), EO: 4	9.5	370	20.35
FINDET 1214N/23	$C_{12-14}E_{11}$	R: 12(70%)–14(30%), EO: 11	14.4	630	88.20
FINDET 1618A/18	$C_{16-18}E_6$	R: 16–18, EO: 6	10.2	603	0.81

R: size of the hydrocarbon chain; EO: number of ethylene oxide units; HLB: hydrophilic/lipophilic balance calculated according to Griffin [6]; MW: molecular weight; CMC: critical micelle concentration.

[a] Indicated by the manufacturer.

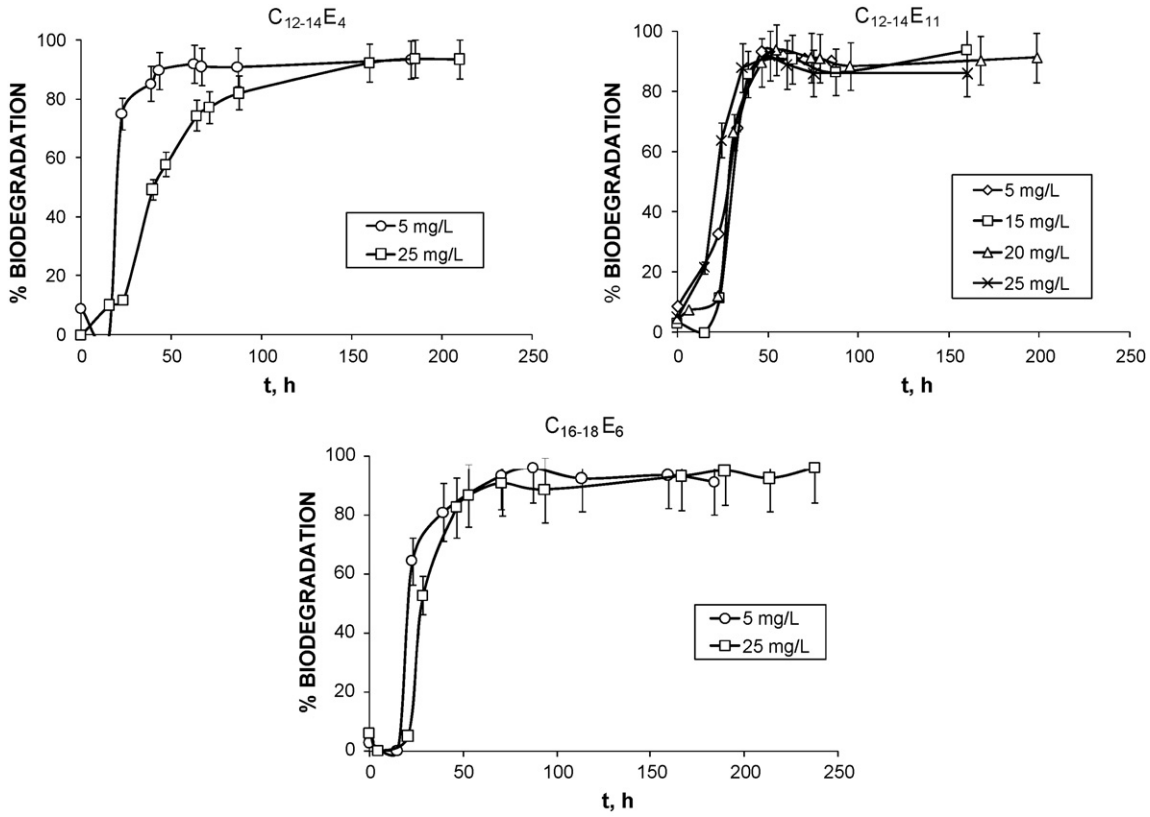

Fig. 1. Primary biodegradation profiles for non-ionic surfactant FAE representing the disappearance of the surfactant in relation to the initial concentration. Error bars represent the precision of the analytical method [11].

concentration biphasic curves appeared at long reaction times, suggesting the inhibition of the microorganisms existing at the beginning of the assay and the growth of new populations due to the biodegradation of the metabolites. This fact may be due to the necessity of a level of metabolites in the medium that provides only upper surfactant concentration.

4. Kinetic models

The biodegradation kinetics of an organic compound by a microorganism population or mixed populations depends on whether this compound supports microorganism growth. That is, it is the main source of carbon and energy; if not, different kinetic models can be proposed, models for substrate biodegradation that do not support microorganism growth.

4.1. Models for the kinetics of degradation of substrates which do not support microorganism growth

To model the degradation of compounds that do not contribute appreciably to the growth of the organisms responsible for their metabolism, expressions for growth of the active organisms are needed, since growth is independent of the transformation rate per cell of the test substrate. Schmidt et al. [3] expressed the transformation rate of the substrate by a saturation kinetics using the Michaelis–Menten equation:

$$\frac{dS}{dt} = -\frac{r_{\max} S}{K_M + S} X \tag{1}$$

and growth using the logistic model:

$$\frac{dX}{dt} = kX\left(1 - \frac{X}{X_{\max}}\right) \tag{2}$$

where X represents the concentration of biomass and S the concentration of the biodegraded organic compound (see supporting information, SI).

Integrating Eq. (2), replacing it in Eq. (1), introducing the conversion (x) and maximum conversion (x_m) in accordance with

$$x_m = \frac{S_0 - S_R}{S_0} \qquad S_R = S_0(1 - x_m) \tag{3}$$

as the substrate has a non-biodegradable fraction, S_R, we get

$$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) + x = \beta_X \ln(\alpha_X(\exp(kt) - 1) + 1) \tag{4}$$

If instead of logistic growth we use exponential biomass growth, linear biomass growth, or growth at the maximum biomass concentration permitted, combined with the two limit cases of the Michaelis–Menten equation, lead to 12 models that correspond to those proposed by Schmidt et al. [3] but which have been corrected to include the existence of a non-biodegradable fraction of the substrate, as presented in Table 2.

With the application of the equations presented above, the models that consider a logistic equation for biomass and Michaelis–Menten and first order for the substrate (models A and B, respectively), and those that consider the same equations for the substrate with exponential growth for the biomass (models D and E) predict an evolution of the conversion as a function of time similar to the experimental results at low substrate concentrations, but the β_M values found do not follow the evolution with the substrate concentration predicted by Eq. (S12) (see SI).

On the other hand, Fig. 2 indicates that the reduction in the surfactant present in the medium is closely related to the growth of the microorganisms in the medium and therefore the kinetic models that support microorganism growth are proposed.

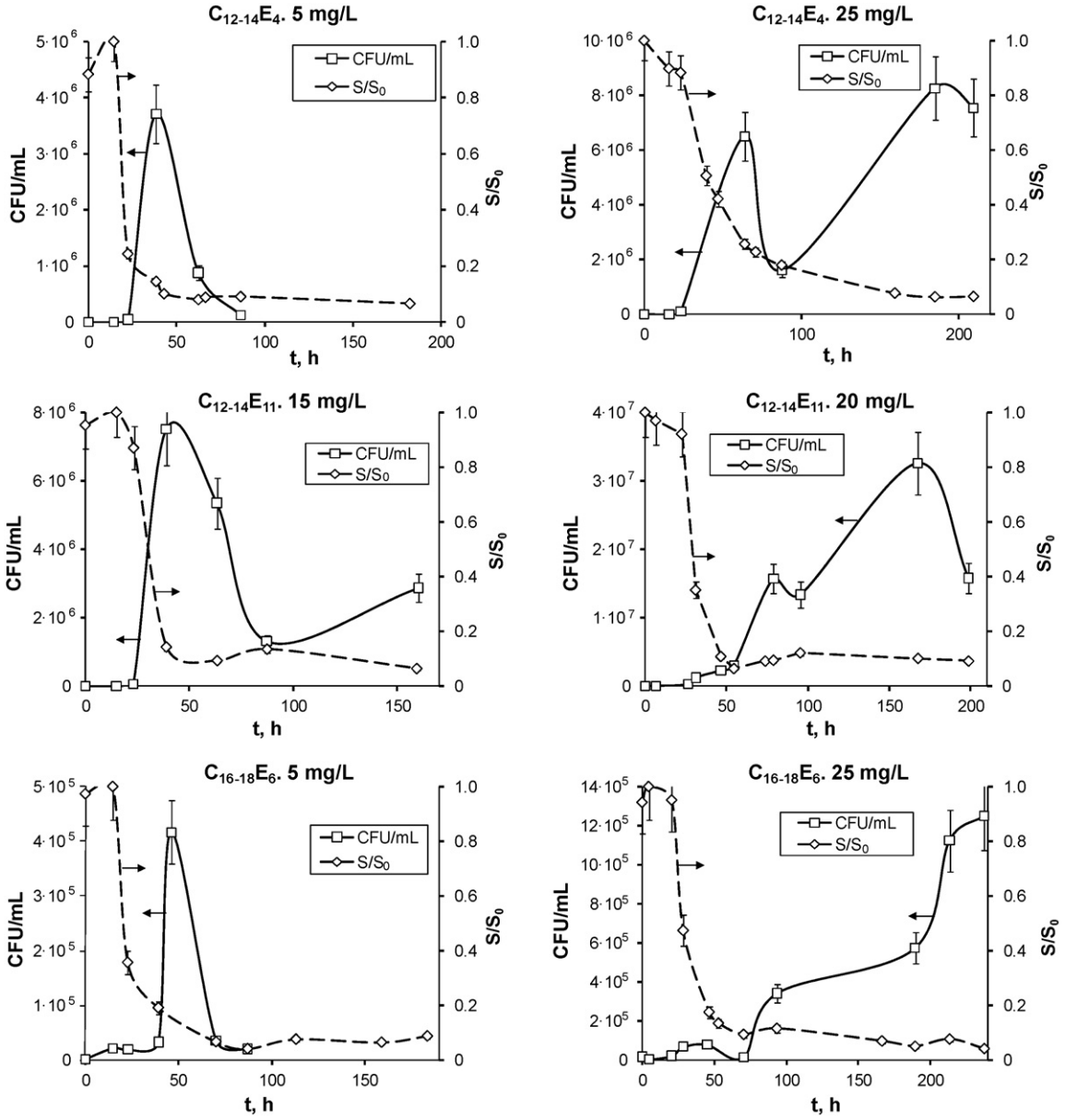

Fig. 2. Growth curves of microorganisms and variation of the surfactant concentration over time at different concentrations. Error bars represent the precision of the analytical method [11].

Table 2
Kinetic models for the biodegradation of substrates that do not support the growth of microorganisms and that take into account a residual concentration.

Conditions	Integrated kinetic equation
(A) Logistic equation for biomass, Michaelis–Menten for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) + x = \beta_X \ln(\alpha_X(\exp(kt) - 1) + 1)$
(B) Logistic equation for biomass, first order for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) = \beta_X \ln(\alpha_X(\exp(kt) - 1) + 1)$
(C) Logistic equation for biomass, zero order for substrate	$x = \beta_X \ln(\alpha_X(\exp(kt) - 1) + 1)$
(D) Exponential growth for biomass, Michaelis–Menten for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) + x = \beta'_X(\exp(kt) - 1)$
(E) Exponential growth for biomass, first order for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) = \beta'_X(\exp(kt) - 1)$
(F) Exponential growth for biomass, zero order for substrate	$x = \beta'_X(\exp(kt) - 1)$
(G) Linear growth for biomass, Michaelis–Menten for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) + x = \beta_{X1} t + \beta_{X2} t^2$
(H) Linear growth for biomass, first order for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) = \beta_{X1} t + \beta_{X2} t^2$
(I) Linear growth for biomass, zero order for substrate	$x = \beta_{X1} t + \beta_{X2} t^2$
(J) Maximum biomass concentration, Michaelis–Menten for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) + x = \beta_{X3} t$
(K) Maximum biomass concentration, first order for substrate	$\beta_M \ln\left(\frac{x_m}{x_m - x}\right) = \beta_{X3} t$
(L) Maximum biomass concentration, zero order for substrate	$x = \beta_{X3} t$

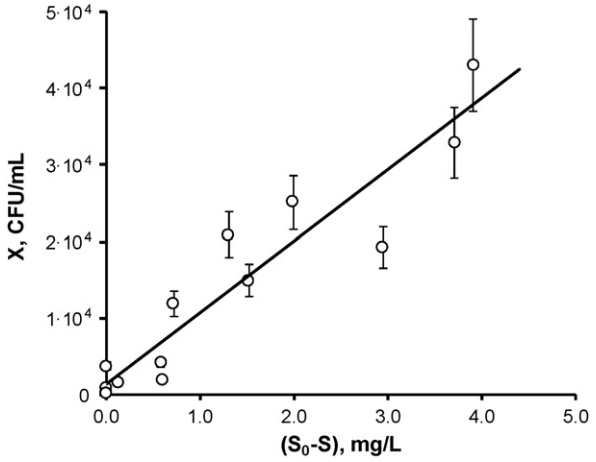

Fig. 3. Application of Gaden equation for the surfactants $C_{12-14}E_{11}$ (15 and 20 mg/L), $C_{12-14}E_6$ (5 and 25 mg/L) and $C_{16-18}E_6$ (5 and 25 mg/L). Error bars represent the precision of the analytical method.

4.2. Models for the kinetics of biodegradation of substrates which do support microorganism growth

In general, when the substance considered supports microorganism growth, the growth rate and the disappearance of the organic compound are linked, this implying that the equation of Gaden [13] is approximately fulfilled, neglecting the maintenance term:

$$\frac{dX}{dt} = -Y_{ap}\frac{dS}{dt} \tag{5}$$

which by integration enables the biomass concentration (X) to be related to the concentration of the organic compound (S):

$$X = X_0 + Y_{ap}(S_0 - S) \tag{6}$$

If we plot the biomass concentration against $(S_0 - S)$, getting the values from the biodegradation and biomass-growth experiments, there is a linear relationship in all cases. Fig. 3 shows the results for experiments $C_{12-14}E_{11}$ 15 and 20 mg/L, $C_{12-14}E_6$ 5 and 25 mg/L and $C_{16-18}E_6$ 5 and 25 mg/L. The time range represented is up to 30 h.

Under these conditions, to develop models for the biodegradation of a substrate, it is equivalent to propose a kinetic model for microorganism growth or for substrate consumption.

The Monod model [14] is used for the growth:

$$\frac{1}{X}\frac{dX}{dt} = \mu = \frac{\mu_m S}{K_S + S} \tag{7}$$

the biodegradation rate of the substrate is

$$\frac{dS}{dt} = -\frac{1}{Y_{ap}}\frac{\mu_m S}{K_S + S}X = -\frac{\mu_m S}{K_S + S}\left(\frac{X_0}{Y_{ap}} + S_0 - S\right) \tag{8}$$

with its two limit cases, depending on the relative values of K_S and S:

(a) For $K_S \gg S$:

$$\frac{dS}{dt} = -\frac{\mu_m}{K_S}S\left(\frac{X_0}{Y_{ap}} + S_0 - S\right) \tag{9}$$

(b) For $K_S \ll S$:

$$\frac{dS}{dt} = -\mu_m\left(\frac{X_0}{Y_{ap}} + S_0 - S\right) \tag{10}$$

Introducing the substrate conversion (x) into Eq. (8), separating variables, and integrating, we get:

$$\frac{\beta_S}{1+\alpha_0}\ln\left(\frac{\alpha_0 + x}{\alpha_0(1-x)}\right) + \ln\left(\frac{\alpha_0 + x}{x}\right) = \mu_m t \tag{11}$$

where

$$\beta_S = \frac{K_S}{S_0} \quad \alpha_0 = \frac{X_0}{Y_{ap}S_0} \tag{12}$$

In some cases, the substrates considered are complex substances that can contain non-biodegradable components, or the biodegradation can end before reaching complete mineralization of the substrate, and therefore a fraction of the substrate must be considered non-biodegradable (S_R). This case would correspond to the surfactant assays, as in previous studies [15].

The limit simplifications of the Monod equation, with a fraction of the non-biodegradable substrate, lead to:

(a) For $K_S \gg S$:

$$-\frac{dS}{dt} = \frac{\mu_m}{K_S}(S - S_R)\left(\frac{X_0}{Y_{ap}} + S_0 - S\right) = -\frac{\mu_m}{K_S}S^2 + \frac{\mu_m}{K_S}\left(\frac{X_0}{Y_{ap}} + S_0 + S_R\right)S - \frac{\mu_m}{K_S}S_R\left(\frac{X_0}{Y_{ap}} + S_0\right) \tag{13}$$

this expression being similar to that proposed by Quiroga and Sales [4]:

$$-\frac{dS}{dt} = K_2 \cdot S^2 + K_1 \cdot S + K_0 \tag{14}$$

so that the primary parameters of the initial kinetic equation are

$$K_2 = -\frac{\mu_m}{K_S} \quad K_1 = \frac{\mu_m}{K_S}\left(\frac{X_0}{Y_{ap}} + S_0 + S_R\right)$$

$$K_0 = -\frac{\mu_m}{K_S}S_R\left(\frac{X_0}{Y_{ap}} + S_0\right) \tag{15}$$

If we take into account the definition of conversion, when there is a residual concentration S_R (Eq. (3)), the expression as a function of the conversion would be

$$\frac{dx}{dt} = \frac{\mu_m}{\beta_S}(x_m - x)(\alpha_0 + x) \quad t = 0 \quad x = 0 \tag{16}$$

When the variables are separated and integrated, it can be expressed in an explicit way for x as follows:

$$x = \frac{\alpha_0 x_m(1 - \exp(-(\mu_m/\beta_S)(x_m + \alpha_0)t))}{x_m \exp(-(\mu_m/\beta_S)(x_m + \alpha_0)t) + \alpha_0} \tag{17}$$

(b) For $K_S \ll S$:

$$\frac{dx}{dt} = \mu_m(\alpha_0 + x) \quad t = 0 \quad x = 0 \tag{18}$$

Integrated, it would be

$$x = \alpha_0(\exp(\mu_m t) - 1) \tag{19}$$

Table 3 summarizes the equations proposed for the application of the Monod model under the different conditions presented above as a function of the conversion.

As an example, Fig. 4 shows the results found on applying the different equations (Table 3) to the surfactant $C_{12-14}E_{11}$. It is applicable only to the Monod model that considers $K_S \gg S$, and a residual non-biodegradable substrate concentration (Eq. (17)), since the general

Table 3
Kinetic models for substrates that support microorganism growth.

Conditions	Kinetic equation
General Monod model without considering a fraction of the non-biodegradable substrate	$\frac{\beta_S}{1+\alpha_0}\ln\left(\frac{\alpha_0+x}{\alpha_0(1-x)}\right)+\ln\left(\frac{\alpha_0+x}{x}\right)=\mu_m t$
Monod model for $K_S \gg S$ and a residual concentration of non-biodegradable substrate (S_R)	$x=\frac{\alpha_0 x_m(1-\exp(-(\mu_m/\beta_S)(x_m+\alpha_0)t))}{x_m\exp(-(\mu_m/\beta_S)(x_m+\alpha_0)t)+\alpha_0}$
Monod model for $K_S \ll S$ and a residual concentration of non-biodegradable substrate (S_R)	$x=\alpha_0(\exp(\mu_m t)-1)$

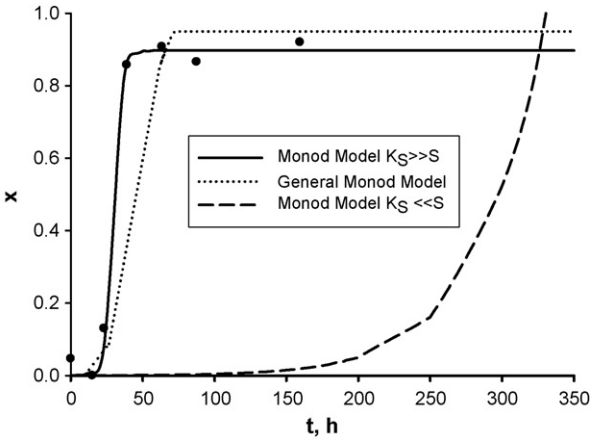

Fig. 4. Application of the different equations of the Monod model for the surfactant $C_{12-14}E_{11}$.

model tends to conversion values equal to 1 when the biodegradation time lengthens, while the simplification of the general model for values of $K_S \ll S$ would provide an exponential curve, without tending to reach a constant maximum value.

Table 4
Kinetic parameters of the model proposed (Eq. (20)) for the surfactant $C_{12-14}E_{11}$.

FINDET 1214N/23 ($C_{12-14}E_{11}$)			
S_0 (mg/L)	X_0/Y_{ap}	μ_m/K_S	r^2
4.57	0.0251	0.0452	0.997
15.3	0.00205	0.0218	0.996
19.1	0.000951	0.0199	0.998
23.8	0.159	0.0109	0.993

The fitting of the experimental data to the model proposed, Eq. (17), is a function of the initial concentration (S_0). Experimental quotient X_0/Y_{ap} that we have calculated are negligible versus $x_m S_0$. So, having into account Eq. (12), Eq. (17) may be simplified to

$$x=\frac{(X_0/Y_{ap})x_m(1-\exp(-(\mu_m/K_S)x_m S_0 t))}{x_m S_0\exp(-(\mu_m/K_S)x_m S_0 t)+(X_0/Y_{ap})} \quad (20)$$

In any case, this model just enables us to calculate the quotient μ_m/K_S, because we are using the pseudo-first-order Monod simplification.

Table 4 shows the kinetic parameters found by non-linear regression on applying the model to the surfactant $C_{12-14}E_{11}$, for which a greater number of initial concentrations of the surfactant were assayed. The maximum conversion was enforced to 0.905, the average experimental value.

Although inoculum conditions are maintained for each experiment performed, parameter X_0/Y_{ap} depends on the number of viable cells. Seeking to adjust all the experiments to the same value of the μ_m/K_S parameter, we found that the experiment made at 5 mg/L was not capable of being fit altogether. The smallest initial concentration presented a faster growth rate and biodegradation rate. Fig. 5 summarizes the results of fitting together with experimental data, showing the parameters obtained.

These results indicate that the model proposed successfully fits the experimental data. However the decrease in parameter μ_m/K_S when the initial concentration increases, indicates a certain substrate inhibition.

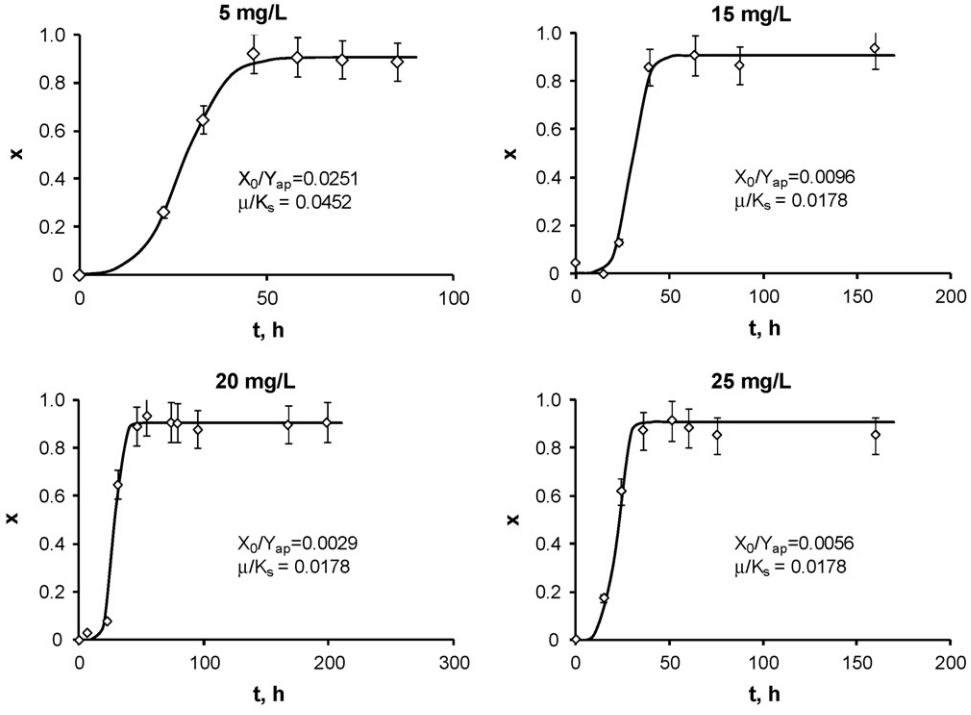

Fig. 5. Fitting of experimental data to Eq. (20) and parameters obtained for surfactant $C_{12-14}E_{11}$. Error bars represent the precision of the analytical method [11].

Table 5
Kinetic parameters for the fatty alcohols ethoxylates from the application of Eq. (17).

Surfactant	S_0 (mg/L)	X_0/Y_{ap}	μ_m/K_S	x_m	r^2
$C_{12-14}E_4$	5.16	0.00228	0.0823	0.926	0.968
	28.3	0.488	0.00360	0.926	0.972
$C_{12-14}E_{11}$	4.57	0.0251	0.0452	0.905	0.997
	15.3	0.00962	0.0178	0.905	0.994
	19.1	0.00295	0.0178	0.905	0.997
	23. 8	0.00564	0.0178	0.905	0.978
$C_{16-18}E_6$	4.58	0.178	0.0331	0.942	0.920
	26.2	0.240	0.00639	0.942	0.973

The rest of surfactants assayed were also fitted to this model, although it has not been possible to apply the simplification explained above. That is, because the parameter X_0/Y_{ap} was not negligible. Thus, it was necessary to use Eq. (17). The resulting parameters are summarized in Table 5.

It was found that on increasing the surfactant concentration, the quotient μ_m/K_S decreased, implying a slowing down of the biodegradation process and of microorganism growth.

5. Conclusions

The present work develops general kinetic models that can be applied to the biodegradation of surfactants, considering a residual non-biodegraded substrate concentration. The models were applied at three non-ionic surfactants, fatty alcohol ethoxylates with different carbon-chain lengths and degrees of ethoxylation, and for different initial surfactant concentrations.

It was found that the kinetic models for the biodegradation of a substrate that does not support growth were not applicable in our case.

The analysis of the results indicates that the decrease in surfactant concentration in the medium is closely related to the growth of the microorganisms present. The experimental results can be explained with kinetic models for the biodegradation of a substrate that supports the growth of microorganisms. The Monod model that considers $K_S \gg S$ (Eq. (17)), was applied together with its simplification for $X_0/Y_{ap} \ll x_m S_0$ (Eq. (20)), and a residual concentration of non-biodegradable substrate in both cases. The kinetic parameters reproduce the experimental results. On increasing the initial substrate concentration the biodegradation process became slower, reducing the parameter μ_m/K_S. In the case of the surfactant $C_{12-14}E_{11}$, the same value of this parameter was found for the initial concentrations of 15, 20, and 25 mg/L. The parameter X_0/Y_{ap}, however, did not follow any trend, since it depended on the number of viable cells in the inoculum.

Some authors [12] indicate that the increase of surfactant concentrations from sub- to supra-CMCs significantly decreased primary biodegradation, ultimate biodegradation, and foam degradation. This decrease may be attributed to the limited bioavailability of the surfactants in the micellar phase as compared to the monomeric surfactants. Table 1 shows values of CMCs for the surfactants assayed. These values indicate great variability. Thus, all experiments with FAE $C_{12-14}E_{11}$ have been performed to sub-CMC, these giving similar parameter values. FAE $C_{16-18}E_6$ has been assayed to supra-CMC. However, FAE $C_{12-14}E_4$ is assayed from sub- to supra-CMC. This latter surfactant is the only one that clearly decreases the biodegradation rate as the initial concentration grows. The high values of parameter X_0/Y_{ap} found when experiments were performed to supra-CMC ($C_{12-14}E_4$ 25 mg/L and $C_{16-18}E_6$ 5 and 25 mg/L) indicates that microorganisms grow better when the surfactant is forming micelles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.01.030.

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