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Surfactants Elimination by biological pathway

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ABSTRACT/RESUME

Abstract: *Surfactants are major components of detergents and cosmetics; they are among the most undesirable pollutants in the environment because of their toxic effects on aquatic organisms.*

The main objective of this work is to define the elimination limits of the three different types of surfactants (anionic, cationic and amphoteric) by activated sludge.
The results obtained were modeled by the model ASM1 (Activated Sludge Model N°1) in order to establish a better representation of the kinetic parameters such as the rate of disappearance of surfactant rs and the growth rate of the biomass rc. According to the classification based on biodegradation surfactants, the results obtained suggest that the AES is more degraded than the other surfactants with $r_{s\ AES}$ *= 17.01 mg / lh at (*c_{AES} *= 40 mg / l, T = 35 ° C) and* $r_{c\ AES}$ *= 1.42. mg / lh under the same conditions.*

I. Introduction

Domestic wastewater contains various pollutants difficult to eliminate such as cosmetics (1). Surfactants are one of the main components of these products, considered the major and most undesirable pollutants detected in the aquatic environment and terrestrial (2, 3, 4, 5). The potential for the toxic effect of surfactant releases and their ecological risk in the environment is attracting more attention (6, 7). Indeed their student application explains their presence at high concentrations in the rejections (8, 9).
The use of surfactants is extremely common and has recently increased from 15.93 million tones used in 2014 to 24.19 million tones planned in 2022 (40).In the United States, all surfactants that bypass wastewater treatment must meet specific criteria (41). Despite the evolution of regulations, the disposal of surficial wastewater agents remains an important issue to consider in terms of their presence in discharges and their toxic effects. This results in an increase in the number of publications dealing with both surfactants and their treatment in wastewater (42).

Generally, the surfactants present in urban wastewater are essentially treated biologically in the treatment plants, but their foaming character causes problems of oxygenation in the aeration basins. Indeed, these compounds are hardly biodegradable. However, researchers have assumed that biological or physicochemical treatment treatments are unable to completely eliminate these surfactants (10, 11, 12, 13). The main objective of this work is to look for the limits of surfactant removal by activated sludge taking into account the operating conditions. The search for the boundary conditions of an activated sludge surfactant removal is important; it is conditioned by the determination of the maximum and acceptable surfactant mass load to be removed by the activated sludge.
For this, an experimental study of biodegradation of surfactants was carried out for a short time. The results obtained were modeled according to the model

Activated Sludge Model No. 1 (ASM1) allowing a better representation of the kinetic parameters of the biodegradation reaction (T °, μmax, ki, rc, rs ...).

II. Materials and methods

In order to demonstrate the biodegradability of the surfactants, a bioreactor has been implemented to ensure the control of the operating conditions of the biodegradation.

II.1. **Experimental description**

The typical bioreactor used to replicate the conditions of aeration tank. It has a capacity of 2 liters, it is agitated by two turbines which turn at 150 rpm and aerated by a perforated crown. Several probes are associated to control various parameters: pH, dissolved oxygen and temperature.

In order to ensure the availability of minerals for the biomass during the biodegradation test, a nutrient solution was added at the beginning of the experiments. The composition of the nutrient solution was: $(NH_4)_2SO_4$ (741.5 mg / l), KH_2PO_4 (445.7 mg / l), $NaHCO_3$ (1152 mg / l), $MgSO_4$.$7H_2O$ (502.9 mg / l), $CaCl_2$ (300.4 mg / l). 1) and $(NH_4)_2Fe\ (SO_4)_2$ (31.3 mg / l) (14).

The biodegradation tests were carried out on several surfactant solutions at different concentrations (from 20 to 100 mg / l) for five days.

II.2. Surfactant molecules

The selected surfactants are used mainly in cosmetics. Such as; Anionics (alkyl ether sulfate), cationic (hexadecyl trimethyl ammonium bromide) and amphoteric (lauramidopropyl betaine) are shown in Table 1.

Table 1: Surfactants

Name of surfactant	Symbol	Type of surfactants	Formula	N° case
Alcohol ether sulfate	AES	Anionic	$C_{12+2n}H_{23}$+4nNaO_4+nS	3088-31-1
hexadecyl trimethyl ammonium bromide	CTAB	Cationic	$[CH_3\ (CH_2)_{15}N(C\ H_3)_3]Br$	9002-93-1
lauramidopropyleBétaïne	BLP	Amphotric	$C_{19}H_{38}N_2O_3$	61789-40-0

II.3. Activated sludge

The activated sludge selected for the experiments was collected from the urban effluent treatment plant in the city of Boumerdes, located about fifty kilometers east of Algiers at the edge of the Mediterranean Sea.

Activated sludge is a complex matrix in which different interfering are present [1 to 5 × 10 5 individuals / l of metazoans (rotifers, nematodes), 107 of protozoa (flagellates, sarcodines, ciliates) and 1012 of bacteria).

To get rid of these during the assays, an experimental protocol was set up. At first, the sludge is washed with water. After decanting, the supernatant is removed, and the pellet (sludge) is again washed with water and mixed well. The mixture is centrifuged for 15 minutes and the supernatant discarded. This operation is referred to 5 times. After washing the sludge, the amount of dry matter is determined (6.12 g / l) in order to know the initial concentration of sludge in the reactor. From this concentration, the volume of sludge to be introduced into the bioreactor can be determined to have a concentration of 5 g / l.

II.4. Modelization

II.4.1.The ASM dynamic model

The Activated Sludge Model (ASM) model is a semi-deterministic model whose equations express the course of chemical and biological transformations that take place within treatment systems (15). It implements the course of reactions with simplifications less than those required for the steady state and provides the impact of dynamic operating conditions given at the output of the installation (16).

The equations of the ASM model appeared at the end of the 80's. Associating simplicity of description of the biological phenomena and conformal representation of the reality, they express the rates of degradation of the substrates according to the state of pollution (variables) and characteristics biomasses that provides the treatment.

II.4.2. Variables of the reaction medium

The organic matter is divided into different fractions whose definitions are distinguished according to their role in the growth of biomass. They intervene in the model in the form of variables and characterize the state of pollution of the raw effluent, the mud of the basins and the treated effluent.

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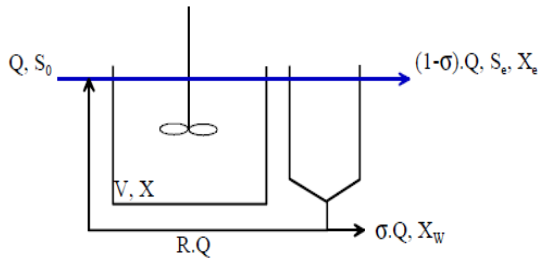
We distinguish between degradable pollution, contributing to the growth of biomass, and pollution that is refractory to treatment. Each of them has two compartments composed of a soluble part, quickly degradable, and a particulate part, requiring to be hydrolyzed before the bacteria reach it. Biomass is represented in three organic forms (COD): living biomass (heterotrophic and autotrophic) and inert (resulting from the mortality of living biomass). Overall, there are finally seven fractions: X_i (inert particulate), X_s (slowly degradable), S_i (inert soluble), Ss (rapidly degradable), Xbh (heterotrophic biomass), X_{ba} (autorotropic biomass), X_p (17).

r_X : the growth rate of biomass (mg MVS L^{-1} d^{-1}),
b_X : the kinetics of biomass death (mg MVS L^{-1} d^{-1}),
μ_{max}: the maximum growth rate of biomass (d^{-1}),
X: the concentration of active biomass (mg MVS L^{-1}),
S1 and S2: concentrations of substrates 1 and 2 (mg L^{-1}),
K_{S1} and K_{S2}: the half-saturation constants for the substrates (mg L^{-1}),
b : the death rate of the considered biomass (d^{-1}),
MVS: Volatile Suspended Substances.



Q: Incoming flow (m3 / d)
V: Volume of the reactor (m3)
X: Sludge concentration in the reactor (g / l)
Xw: Mud concentration at the bottom of the decanter (g / l)
X e: Concentration in MES at the output (mg / l)
R: Recycling rate (%)
σ: Sludge extraction rate (%)
S: Concentration in carbon pollution of the input (mg / l)
Se: Concentration in carbon pollution at the outlet (mg / l)
Y: Cell yield (g COD / g COD)
b: Death rate of biomass (1 / d)

Figure 1 . *Diagram of an activated sludge treatment plant*

II.4.3. Model of biomass growth and substrate consumption

The effectiveness of biological treatment is governed by microbial growth. The latter is expressed as the difference (Equation 1) between production kinetics (Equation 2) and biomass death (Equation 3). Several mathematical models have been proposed to account for the kinetics of bacterial production. The Monod model is the oldest and the most used.

$$\boldsymbol{Rp = rx - bx}$$ Equation 1

$$\boldsymbol{rx = \mu max . X . \frac{S1}{S1 + Ks2} . \frac{S2}{S2 + Ks2}}$$ Equation 2

Or

r_P: the rate of biomass production (mg MVS L^{-1} d^{-1}),

The substrate consumption kinetics (mg L^{-1} d^{-1}) is the ratio between the biomass growth rate and the conversion efficiency of the substrate to biomass (Equation 3).

$$\boldsymbol{rs = \frac{rX}{Y}}$$ Equation 3

Y is the conversion efficiency of the substrate into biomass (mg MVS mg-1)

These parameters are very important for the design of treatment processes (18). There are many models to describe the biological sludge treatment process.
In Table 2, the models applied to the activated sludge process have been assembled (19). All these equations establish a relationship between the specific growth rate (μ) and the limiting substrate concentration (S). Today, Monod's model is still widely used to describe

microbial growth in biotechnological processes. Nevertheless, this equation has often been questioned, which is why several alternative models have been proposed. The problem inherent in most of these models remains the precise evaluation of the experimental data for the validation of the different models of growth. Each model has a form similar to the Monod model but those that are drifting, are more complex than this one.

Table 2: models to the kinetics of activated sludge (19).

Model	Equation	Constants
HALDANE (1930)	$\mu=\mu max.\frac{S}{S+Ks+\frac{s^2}{Ki}}$	K_i : inhibition constant in the Haldane model
MONOD (1942)	$\mu=\mu max.\frac{S}{Ks+S}$	K_s : threshold concentration -value of S for which P=Pm/2
MOSER (1958)	$\mu=\mu max.\frac{1}{1+Ks^x.s^x}$	X: constant determined experimentally in the Moser model
TEISSIER, GAUDDY et Al (1967)	$\mu=\mu max.(1-exp^{(-\frac{S}{T})})$	T : saturation constant in Teissier's model
HERBET , LENDENMAN et Al (2000) .	$\mu=(\mu max+m)\frac{S}{Ks+S}-m$	m : maintenance

Several authors have compared these models with each other, concluding that the Monod model is the most appropriate model to describe the microbial growth of a monoculture. It turns out, however, that this model is also the most used to describe activated sludge processes. This is the most widely used model for calculating the biological constants of activated sludge (20).

III. Results and discussion

III.1. Study of the biodegradation of surfactants

III.1.1. Evolution of COD

The chemical oxygen demand is quantified according to the HACH-Lange micro method and approved by the USEPA.

The surfactant solutions in a low COD (less than or equal to 100 mg / l). This parameter allows us to monitor the purification of surfactants. The reduction in the COD removal rate is related to the degradation phase of the surfactants (<80 mg / l). And from this concentration the elimination rate of the COD becomes stable that can come from a lysis of the microorganisms or a stress which modifies their metabolism.

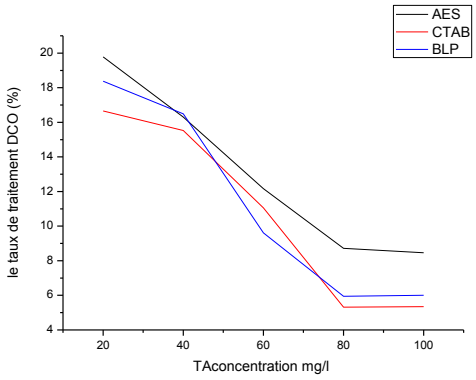


Figure 2. *Evolution of Chemical Oxygen Demand (COD) during activated sludge treatment at room*

III.1.2. pH evolution

In the initial mixtures and when adding a surfactant, the pH maintains between 6.9 and 5.7 for AES concentrations between 20 and 100 mg /l, for the same concentrations of CTAB and BLP the pH varies from 6.98 to 3.00 and 6.97 to 3.45 respectively.

After the biological treatment, a slight increase in pH is observed after the tests of treatment of the AES and CTAB for the different concentrations. On the other hand, the pH changes in another way after the BLP treatment tests. The pH underwent a decrease above 40 mg / l of BLP and beyond this concentration the pH increases. This may be the composition of lauramidopropyl betaine (BLP) which contains several oppositely charged functional groups (21).

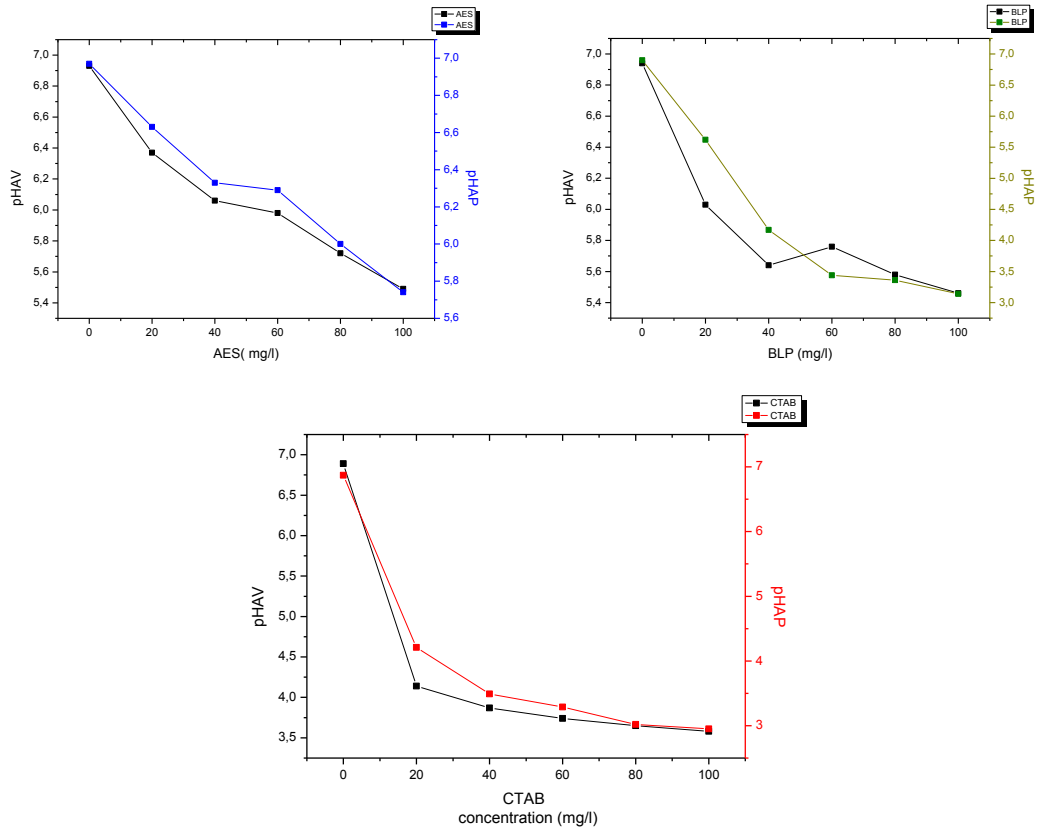


***Figure 3**. Evolution of pH as a function of TA concentrations, during treatment at room temperature.*

III.2. Behavior of sludge

III.2.1. Evolution of suspended matter (SM)

There is an increase in SM during the surfactant release treatment experiment. This increase is due to the deflocculation of the sludge caused by the surfactants. These MES values are correlated with microscopic observations that reveal the significant presence of free bacteria.
Strong deflocculation is observed in CTAB releases (with SM values of 3.32 and 6. 20 mg / l). AES at least sludge deflocculation effect (MES = 4.09 at a concentration of A 100mg / l.

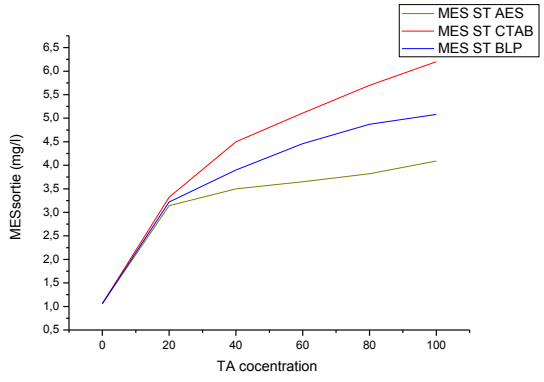


***Figure 4.** Evolution of SM as a function of TA concentrations after treatment at room temperature.*

III.2.2. Evolution of biomass

The evolution of the biomass is carried out by measuring the turbidity (optical density) of a bacterial culture using a spectrophotometer at λ = 600 nm. This is the most used technique because it is simple, fast and the least expensive.

At the beginning of the treatment, the optical density of the biomass increase, it is relatively high between (20 and 40mg / l) for the three surfactants then it gradually decrease to 40mg / l.

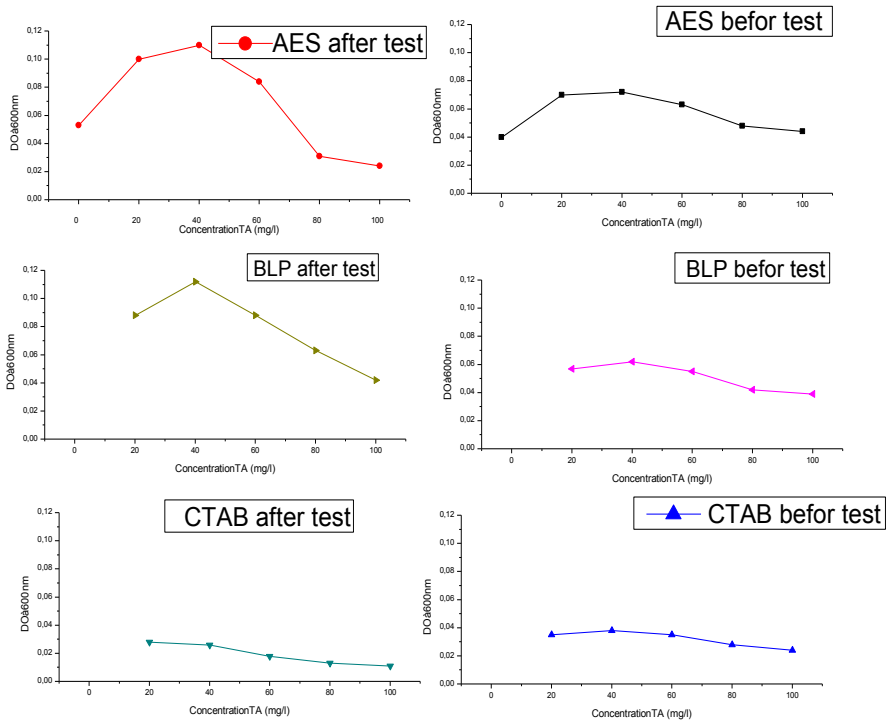


***Figure5**. Evolution of the biomass by measuring OD at 600 nm for each test after treatment at room temperature*

III.2.3. Evolution of microorganisms

Microscopic observation indicates that the evolution of microorganisms is similar. Indeed, the surfactant releases contain the same families of protozoa and metazoans. The presence of free bacteria did not change during treatment.

Many protozoa at the beginning and during treatment are not present at the end of the test. The protozoa of the flagellate family have disappeared.

The development of this family of protozoa is related to the stability of the system resulting in a good quality of treated water. In parallel, the development of metazoan rotifers also indicates a good operation of the installation (22).

Several studies have shown the ability of different bacterial species to degrade surfactants, for example, Pseudomonas, Aeromonas, Achromobacter, Xanthomonas and Stenotrophomonas have the ability to degrade cationic surfactants (45,46,47,48,49,50).

Consequently, Bergero et al confirmed that degradation of the tetradecyltrimethylammonium cationic surfactants of bromide (QACs) by immobilized bacteria with an adsorption rate of 81 to 98% for an initial concentration of 200 mg / l after 2 hours of treatment (51).

Table 3: Evolution of the sludge microorganisms before and after the biological treatment

Microorganisms		Density of observation	
		After treatment	Before treatment
Métazoa	Rotiferes	X	-
	Nematods	X	-
Protozoa	Cilies	XX	X
	Sarcodines	X	-
	Flagella	X	XX
Bacteries	Flocculates	XXX	X
	Filamentous	XXX	XXX
	Free	X	XXX

XXX : Strong Density (Not Quantifiable)
XX : Average Density
X : Low Density (<5 organisms / blade)
- : Absence

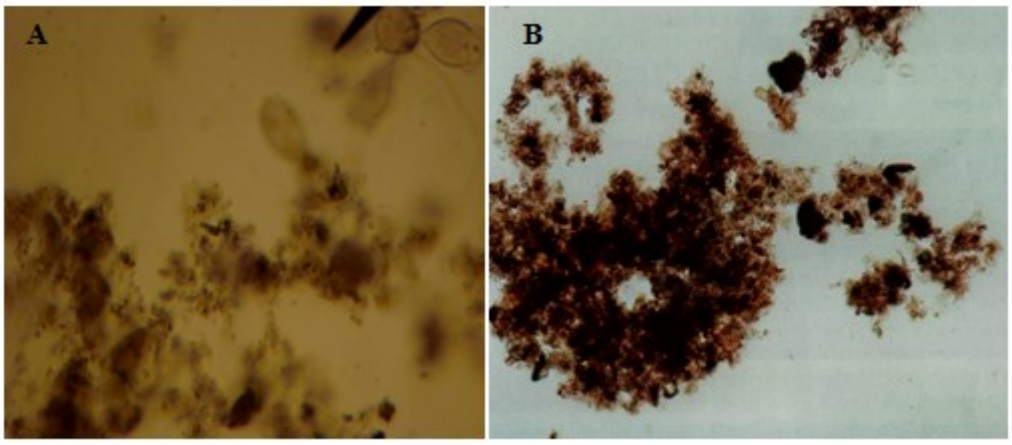


***Figure 6**. Observation of activated sludge microorganisms before (B) and after (A) test.*

III.2.4. Evolution of the surfactant content in sludge after biological treatment

A measurement of the surfactant content in the sludge was carried out after the biological treatment, this measurement is carried out by SHIMADZU LC-10 ATVP High-Performance Liquid Chromatography (HPLC) with a Nucleosil C18 separation column, Machrey-Nagal AG and a detector SHIMADZU UV-VIS. The method of extraction of surfactants in sludge has been developed in the laboratory and described in Figure 7.

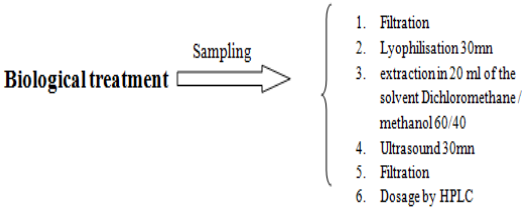


***Figure** 7.Method of extracting surfactants from activated sludge.*

The results demonstrate the low surfactant content in the sludge after treatment and this varies depending on the initial concentration and the nature of the surfactants. The highest concentrations of surfactant found in the sludge are Alcohol Ether Sulfate (AES). On the other hand, the very low levels are for the cationic surfactant Hexadecyl Trimethyl Ammonium Bromide (CTAB). In the same axis, Matthew J shows that the activated sludge resulting from wastewater treatment generally contains from 0 to 3 mg kg -1 cationic surfactant (23).

Table 4: Levels of TA in sludge after biological treatment (µg / g of Ms).

Concentrations	**TA concentrations in the sludge after biological treatment (µg / g of SM)**		
Initial Concentration (mg/l)	AES	CTAB	BLP
20	14.85	11.43	12.41
40	14.04	4.47	11.69
60	13.77	3.58	11.50
80	12.96	1.93	10.81
100	10.53	1.54	8.28

The contents of the three surfactants in the sludge after treatment are generally low, these contents will allow us to determine the capacity of accumulation of the surfactants by the biomass, and this process of contamination is the bioconcentration. The bioconcentration potential (BCF) is defined by the ratio calculated between the coefficient of the absorption rate and the depuration coefficient:

(BCF = Ku / Kd) (ml g-1). (24).

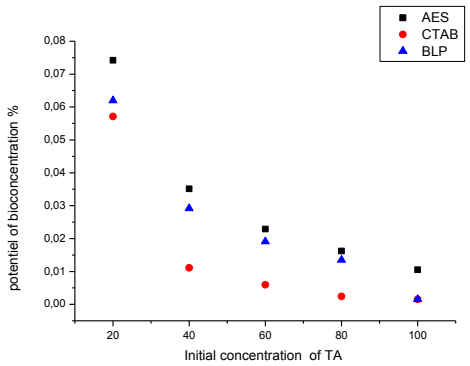


***Figure 8**. Bioconcentration potential of each surfactant at different concentrations after biological treatment*

III.3. Comparison of kinetic parameters

To evaluate the different kinetic parameters of surfactant degradation and microorganism growth, it is important to accurately determine the model parameters of the biodegradation process (18,25). We used the ASM1 model based on the Monod relationship to describe this process. For this, the following parameters have been determined such as:

- A growth rate of biomass;
- The coefficient of inhibition;
- The growth rate of biomass;
- The rate of disappearance of the surfactants;

III.3.1. Determination of growth rate of biomass (µmax)

Table 5 Biomass growth rate as a function of concentration and nature of TA.

	growth rate µmax (h-1)				
Concentration of TA (mg/l)	**20**	**40**	**60**	**80**	**100**
AES	1.30	1.20	1.02	0.93	0.85
CTAB	0.11	0.097	0.088	0.075	0.069
BLP	0.90	0.82	0.68	0.65	0.54

The growth rates decrease with the increase of the concentration of surfactant, in the three surfactants tested. Figure 10 allows us to more easily assess trends in the growth rate as a function of the substrate used. It appears that the growth rates are globally greater for the AES test with a µmax of 1.3 and 0.85h-1.

For concentrations of 20 and 100 mg / l. The lowest growth rates range from 0.11 to 0.069 h-1 back to the CTAB test for 20 and 100 mg / l.

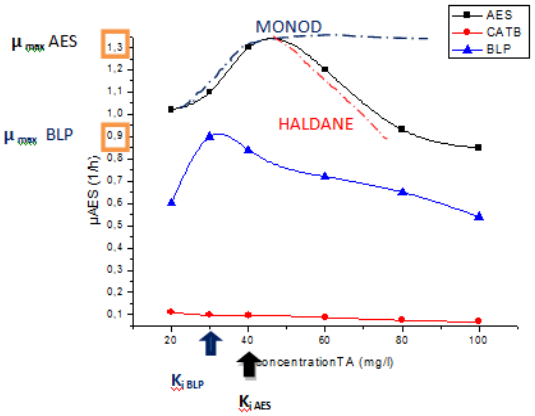


***Figure 9**.Evolution of growth rate of biomass μ_{max} as a function of the concentration of surfactants*

The inhibition coefficient Ki for the effluent AES (K_i AES ≈ 40 mg L^{-1}, $\mu_{max\ AES} \approx 1.3\ h^{-1}$) and for the effluent BLP $K_{i\ BLP} \approx 30$ mg. L^{-1}; $\mu_{max\ BLP} \approx 0.90\ h^{-1}$).

The curve shapes observed for AES and BLP in FIG. 9 follow the equations of the two MONOD and HALDANE models and also correspond to these theoretical curves which are shown in this figure.
These two (AES and BLP) curves allow us to determine the maximum growth rate without inhibitor at a concentration below 40mg / l. And when the concentration of TA increases the growth rate for the curves of the AES and BLP with an appearance of inhibition rate.
According to the CTAB curve, it is impossible to determine the maximum growth rate because the cationic surfactant appears as an inhibitor of the growth of biomass that due to their antimicrobial properties (26, 27, 28, 29,30). And they are not biodegradable and toxic to aquatic organisms (31).
Ranges, L.M. et al. Suggest that the addition of 20 mg / l CTAB has no effect on the degradation of organic compounds in synthetic wastewaters (32). In the same concept, Zhang et al. found that blood alcohol level (C12 - C16) causes inhibition of respiratory enzymes in an activated sludge system with EC50 values between 0.12 and 3.60 mg / l (43). Another study showed that 10 to 15 mg / l of blood alcohol level was an inhibitor of nitrifying activated sludge (44).

III.3.2. Determination of the growth rate of biomass (rc)

The table below represents the rc values obtained from the biological treatment tests of the three surfactants at room temperature (20 ° C) by varying their concentrations.

Table 6: The rate of growth of rc biomass as a function of the nature and concentration of surfactant

Concentration of TA (mg/l)	rc (mg/l.h)		
	AES	CTAB	BLP
20	0.96	0.05	0.56
40	1.01	0.04	0.52
60	0.81	0.03	0.29
80	0.50	0.02	0.20
100	0.36	0.02	0.18

It is observed that the growth rate of the biomass in contact with AES is faster than the other surfactants (between 0.96 and 0.36 mg /lh). However, the rc in contact with CTAB is negligible (0.05 mg /lh) this low value. Returns to the inhibitory effect of this type of surfactant due to their antimicrobial properties (33).

The concentration of the surfactants influences the growth rate of the biomass, rc decreases with the increase of surfactant concentrations. This decrease is explained by the inhibitory effect of surfactant on the biomass. To study the effect of temperature on the treatment process of surfactants activated sludge was carried out the previous tests appropriate to these temperatures (15, 20, 25.30 and 35 ° C). The evolutions of rc observed are shown in Fig10.

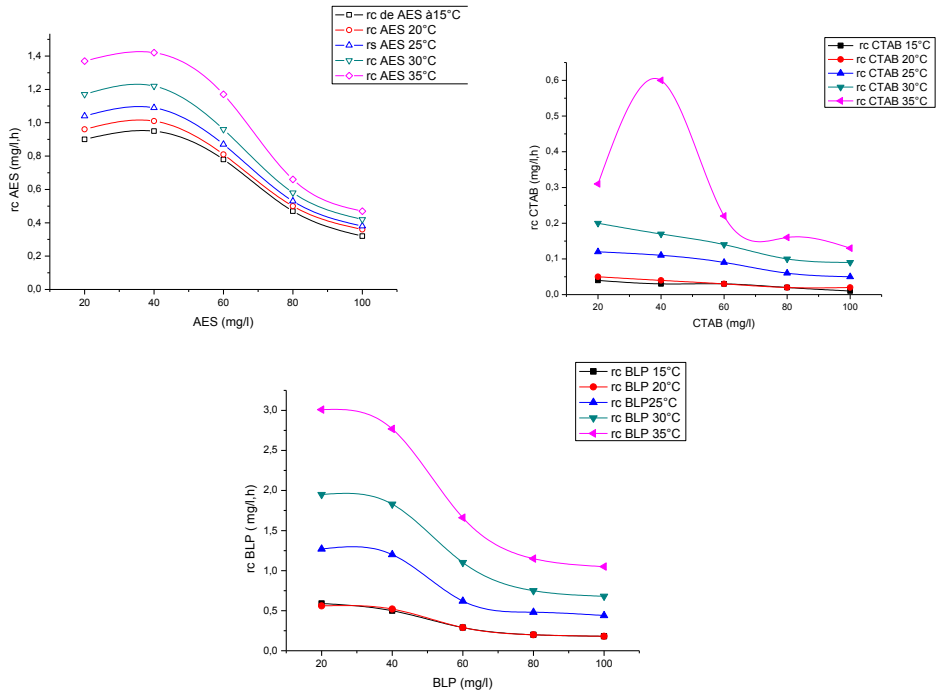


Figure 10. *The growth rate of biomass (rc) as a function of temperature*

In Figure 10, we note that the shape of the curves of rc are identical for the different concentrations of AES, whose growth rate of the biomass exceeds 1.40mg/ lh at (C_{AES} = 40mg/l and T ° = 35 ° C) and which decreases with increasing concentration, keeping these maximum values at C_{AES} = 40mg / l for the different temperatures.

The same remarks are observed for the BLP curves, having maximum values of r_c at C_{BLP} = 20mg / l, rc = 3.01mg/ lh at T = 35 ° C, with these values the rc is faster in BLP compared to AES.

While the rc of CTAB is of the order of 0.05 mg /lh at room temperature (T ° = 20 ° C), the rc decreases with increasing C_{CTAB}, with a peak at 35 ° C at C_{CTAB} = 40mg / l.

García et al. studied the degradation of quaternary ammonium surfactants by sludge. A positively charged nitrogen atom exists in a quaternary ammonium surfactant molecule. A strong electrostatic attraction develops between the molecules and the surfactant where all types of solids are negatively charged. Therefore, cationic surfactants adsorb by sludge causes dehydration (37).

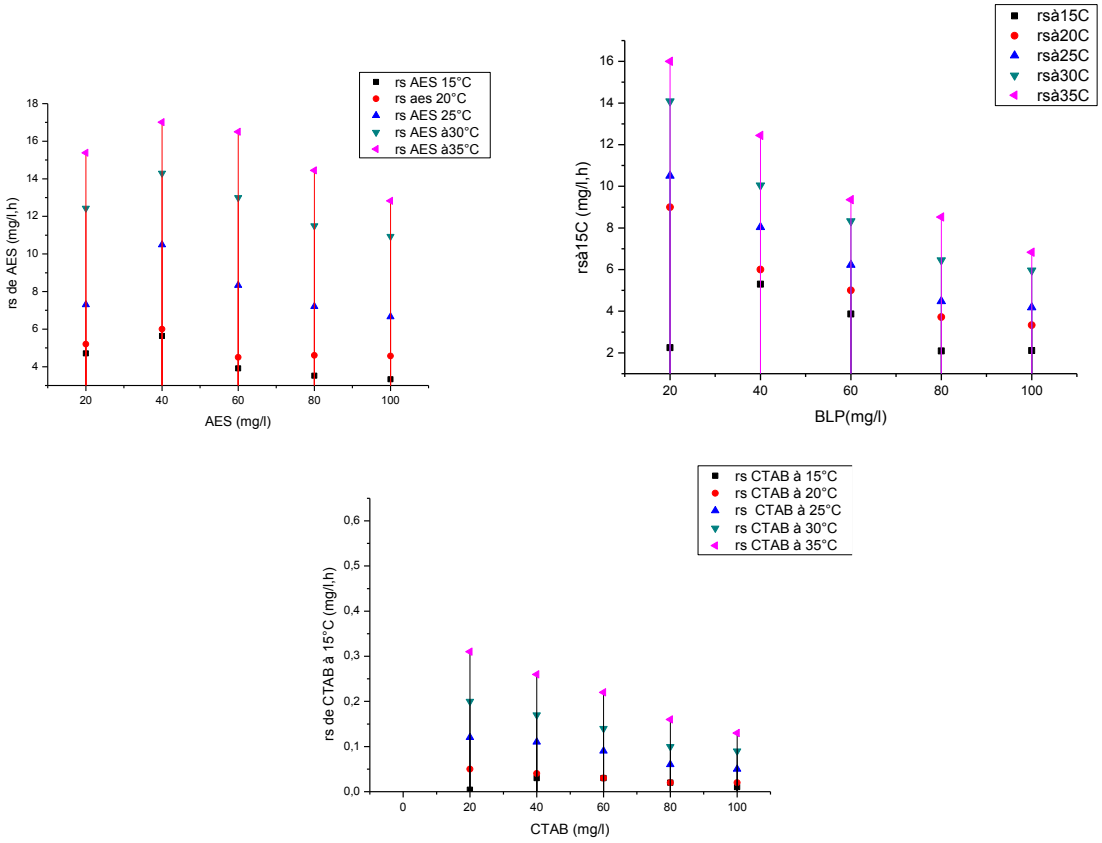


***Figure 11**. The rate of disappearance of the surfactants (r_S) by the sludge as a function of the temperature variation.*

The three curves show that high temperatures accelerate the rate of disappearance of TA (r_s). And each time one increases the TA concentrations the rs decreases.

Finally conclude that the degradation of these surfactants by activated sludge is low, expressed by the kinetic parameters (r_s and r_c), the variation of the operating parameters resulting in that the raised temperatures accelerate the degradation of the surfactants (r_s) and the speed of growth. biomass (r_c) and increase the growth rate of biomass (μ).

However, Quiroba has shown that the rate of biodegradation of surfactants varies depending on the temperature when T ° is between 20 and 25 ° C the rate of biodegradation of the surfactants exceeds 90% in 10 days but less than 10 ° C it does not exceed 5% in 21 days (34).

According to the researchers, the length of the alkyl chain of surfactant influences its degradation rate plus the alkyl chain is slow plus it is difficult to degrade (39). Among the physicochemical parameters influencing the degradation of surfactants is the water hardness, the latter reducing the critical value of the micelle concentration of the alkylbenzyl dimethyl ammonium homologs (37, 38).

It is noted that AES degrades by a more or less high speed compared to other surfactants but its degradation rate remains low under aerobic conditions, compared to the degradation rate under anaerobic conditions reported by Scho berl et al that is 96% in 30 days (closed bottle test) (35). Zhou et al add that the sludge hydrolysis rate is improved when the surfactants are present in the anaerobic digestion because the surfactants accelerate the degradation of the MO. In addition, the enzymes trapped in the sludge flocs can be released (36).

IV. Conclusion

The overall objective of this work was to define the limits of implementation of activated sludge activated surfactant removal; first, we studied the biodegradation of surfactants by the evolution of physicochemical parameters, then followed the behavior of mud and determine their bioconcentration factors (BCF) in surfactants.

In conclusion, this study confirms to a large extent that the activated sludge process has a very low degradation of surfactants. This slight degradation is explained by the kinetic parameters obtained by

the model adaptation of Monod, r_c <1 mg/ lh for AES and BLP.
The CTAB r_c is ten times lower than the rc AES and r_c BLP. The values of the growth rate of the biomass are approximate to that of the rate of disappearance of the surfactants r_s.

V. References

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