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Toxic effect of surfactants on marine species Mediterranean mussel: *Mytilus gallprovinciallis* and evaluation of their aquatic toxicology impact by LCA methodology

M. Belkhir. S. Boughrara. H. Boutiche

Food Technology Research Laboratory, University of Boumerdes, 35000 - Boumerdes, ALGERIA

*Corresponding author: belkhirmeriem4@gmail.com

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ABSTRACT / RESUME

The increase of over 500% in ten years, the use of synthetic detergents explains the high concentrations explain the high concentrations in liquid effluents. Part of these discharges flow without purification in rivers. Which it is interesting to assess the impacts thus generated by such a detergent manufacturing process. In our study we used the tool life cycle assessment (LCA) methodology to assess the aquatic toxicology impact of liquid detergent intended multi user. This study needs the use of SimaPro7.1 software and EDIP 2003method.In order to explain aquatic toxicology impact was chosen by selecting a type of marine species Mediterranean mussel ***Mytilus gallprovinciallis.*** *In our study we determined the toxic effect of anionic surfactants (LAS, AES) characterization of liquid effluents generated by one of the leading Algerian companies in detergents. Comparing the toxicology of two anionic surfactants is obtained after determining the lethal concentrations of fifty percent (LC50) of the individuated simmering with forty-eight hours (48h), Ensuring living conditions (temperature, O2, pH, TH, TA, TAC). In an aquarium. Any and controlling various pollution parameters (BOD5, COD, Nitrate, Nitrite, Phosphate, Sulfate, Dissolved Oxygen.*

I. Introduction

With the growing awareness of environmental issues, the integration of sound environmental management practices in our industry is growing in importance. In response to this reality, various environmental assessment tools have been developed, such as environmental risk analysis, analysis of material flow, the ecological footprint. According to the article Finnveden, G., Hauschild, MZ, Ekvall, "Recent developments in Life Cycle Assessment" pull Journal of Environmental Management, these players end up saying that environmental tools provide some answers for decision informed decisions, both for those in the public and private sectors **[1].** LCA appears as an appropriate tool to measure and certify the improvement of its production cycle or ease of waste treatment. In fact, some organizations rank companies based on their impact on the environment **[2]**. This methodology has taken place within ISO 14040 series [3-6]. The control of the environmental impact of activities in the detergents manufacturing industries is now essential for their durability, as well as the reduction of production costs or improving product quality. It also affects the image of the products from the consumer and also intervenes in their "quality"[7]. Surfactants are an important part of the composition of detergents in 1995, the Health Research Institute and safety at work of Québec, Montreal shows that global production is about 3106 tons or increased in the past ten years is over 500%, this increase explains their high concentrations in industrial effluents and sewage, or they flow without purification in rivers. In our study we determined the toxic effect of three kinds of surfactants (LAS, AES and NI07) that fall within the composition of a multi user detergence.

LAS: *Linear Alkyl benzene sulphonate (anionic)*
AES: *Alkyl Ether Sulfate (sulphonate) (anionic)*
NI 07: *Fatty Alcohol Ethoxylate (nonionic)*

And for the purpose of an environmental assessment of their impacts aquatic toxicology, we applied the approach Life Cycle Assessment to justify of results obtained by their ecotoxicity tests.

II. Materiels and methods

The methods used in our study are:

The determination of the lethal concentrations of fifty percent (LC50) of three surfactants on mussels

The potential ecotoxicity was addressed by performing a toxicity test (acute effects) assets tensions LAS, AES and NI07 on an aquatic organism Mediterranean mussel ***Mytilus galloprovincialis*** causing mortality 50% of the population exposed to a fixed concentration of a 24H and 48H surfactant with mid renewal.

Experimental Protocol

More than 200 species of mussel ***Mytilus galloprovincialis*** were collected in July 2013, in a Sghirate site, it is located 5km from the center wilaya of Boumerdes (east of Algiers). The molds were kept in seawater and transported to the laboratory in coolers. Before moving to the toxicological test should be allowed mussels an adjustment period in aquariums, with a dozen mussels in 10L water ensuring ventilation the one hand and avoiding their toxicity nitrate comes from their nitrogenous waste.

Preparing the aquarium

The main difficulty in setting up an aquarium is to recreate the best conditions for living environment mussels (sea water), either the temperature, the hardness of the water, the nitrate problem etc. The molds are placed in the tank (food plastic basin) at a temperature entre14 ° C and 16 ° C (temperature of sea water).

The Life cycle assessment

LCA is a method for environmental analysis identifies the major sources of environmental impacts and avoiding further transfer of pollution from one phase of the life cycle to another. It is therefore essential to cover the entire life cycle so that improving the overall rendering is not reflected on another scale.[8]. These steps are more commonly referred to as "cradle to grave". During each of these steps, products and processes interact with the environment.

Goal and scope of the study

The goal of the present study is to assess the environmental performance of detergent. The model focuses on production of detergent liquid form that is: multi user liquid, the production processes include the mixture of all compounds in aqueous solution. The functional. Unit of analysis in this study is the production of one ton of this detergent.

Inventory analysis

To establish LCA for the multipurpose workshop, we tried to collect all the theoretical and experimental data from the various analyzes carried companions. These data include those relating to the consumption of raw materials (surfactants, fragrances, dyes, packaging material) and energy consumption (water, electricity). Which are related to the functional unit defined above.

<u>Balance incoming</u>

The raw material consumption and energy is presented in Table 1.

Tab.1: *Consumption of raw materials and energy*

Inputs	**consumption (kg)**
LAS (alkyl benzènesulfonâte)	21.207
AES (alkyl ethoxy sulfate)	26.414
NaoH	0.526
NaCl	4.260
Parfum	1.230
Formol	0.662
NI LT07	3.787
Dye	0.153
acetic acid	0.037
Dequest	0.568
Packaging material	**consumption (kg)**
cellulose Cards (Kg)	50
Labels (plastic) (Kg)	3.60
caps (PEHD) (Kg)	4.80
bottles (PET) (Kg)	48
Energy	**Consumption**
Electricity (KWh)	32.14
Water (m^3)	941.18

<u>Out going balance</u>

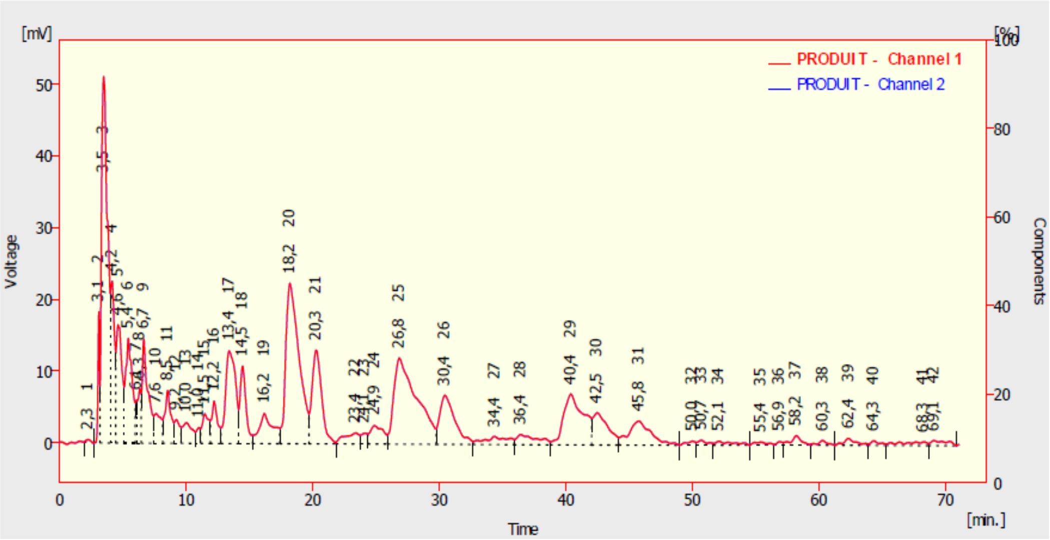
Outgoing balance consists of rejecting liquid (water) and solid (packaging waste), including pollution parameters are measured and calculated according to standardized methods of water analysis. (See the book by Rodier) [4]. But the concentrations of the surfactants (LAS, AES and NI07) are determined by the chromatographic method using a (HPLC).

***Tab. 2:** Analysis methods HPLC (In mobile phase at high ionic strength) [5]*

Extraction	Electrolyte	Elution	détection	LD	Références
	$NaClO_4$	G	SM	300 pmol.g^{-1}	Tolls *et al.*, 2003
Coacervation Milieu acide	$NaClO_4$	G	FL λ_{ex} = 225 nm λ_{em} = 295 nm		Ruiz *et al.*, 2004
SPE C18				10 µg.L^{-1} (eau) 100 µg.L^{-1} (boues)	De Henau *et al.*, 1989
REA + SPE C8	$NaClO_4$	G	UV λ = 250 nm		Matthijs et De Henau, 1987
aucune	$NaClO_4$	I	UV λ = 225 nm		Nakae *et al.*, 1981

with :

***Fig.1**: Chromatogram of surfactants*



- SPE : Solid phase extraction.
- SM :Mass Spectrometry.
- REA: anion exchange resin
- LD: limit dedétection.
- CTMA: cetyltrimethylammonium.
- G: gradient.
- I: isocratic.

***Tab.3:**physicochemical parameter of rejecting liquid*

Outputs	
physicochemical parameter	**Results**
temperature (°C)	20
Ph	9.07
COD (mg of o_2/l)	983.00
BOD_5 (mg of o_2/l)	103.33
LAS (g/l)	1.96
AES (g/l)	0.600
NI07 (g/l)	0.068
salinity (g/l)	3.50
turbidity (NTU)	71.11
The O_2 below (mg/l)	13.32
Phosphates (mg/l)	76.00
Sulfates (mg/l)	800.00
Nitrates (mg/l)	30.00
TDS (g/l)	3.45
Solid waste	
cellulose Carton	5
Label plastic	2

III. Results and discusion

Ecotoxicity tests surfactants on mussels

1st test :

The experiments were usually performed in continuous flow aquaria. In order to assure natural conditions, the aquarium is alimented by sea water at a constant continuous flow with variation of temperature between 14C° to 18C° and Ph varies between 7 to 8 for each 10 animals in 10L of sea water for 48 Hours for each experience. The standard sample is taken in sea water, that its characteristics are summarized in table 3. It's remarked that no mortality of animals (see table 4).

Tab .4: *Physicochemical characteristic of standard sample (only sea water)*

Physicochemical parameter	Results
O_2 (mg/ l)	8,60
Ph	7,42
Salinity (g/l)	29
Turbidity (NTU)	8 ,11
Total of dissolute Salt (TDS (F°)	26,4
Sulfate (mg/l)	0,02
Nitrate (mg/l)	2,72
TH (F°)	1060

Tab. 5: *Mortality of mussels in 1nd test (see water)*

Day of contact	1st Day	2nd Day	4th Day	6th Day	8th Day	9th Day	10th Day
% Mortality	0	0	0	0	0	1	3

Tab. 6: *Physicochemical characteristic of standard sample after the 1nd test*

Contact time Physicochemical parameters	1st Day	4th Day	9th Day	10th Day
O_2 (mg/ l)	8.46	8.10	7.89	7.72
Ph	7.41	7.38	7.40	7.42
Salinity (g/l)	30	29.8	29.8	28.7
Turbidity (NTU)	9.30	11.82	20.87	30.61
Total of dissolute Salt (TDS (F°)	28.5	28.3	28.4	28.3
Sulfate (mg/l)	0.022	0.018	0.024	0.019
Nitrate (mg/l)	59.36	75.44	133.21	195.38
TH (°F)	1056	1040	1048	1051

2nd test

The mussels are taken in three aquariums sea water, with addition for each one a surfactant that it's concentration is taken in the reject of Eagle factory (see table 3). These animals are taken contact with each solution for 48 Hours, that the results are summarizes in table 7.

Tab.7: *Mortality of mussels in contact with the actual concentrations.*

Concentration surfactant Mortality%	LAS (1,98 g/l)	AES (0,65g/l)	NI07 (68mg/l)
24h	60	80	70
48h	100	100	100

These results show that the:

- LAS LC_{50} for mussels is <1.98g / l.
- AES LC_{50} for mussels is <0.65g / l.
- NI07LC_{50} for mussels is <68mg / l.

The characteristic of solution after contacts are summarized in table 6
The characteristic of the environment solution of the 2nd experiment after contact is summarized in table 8

Tab.8. *physicochemical characteristic after the 2nd test*

Physicochemical parameters	LAS	AES	NI 07
O_2 (mg/ l)	9,73	9,57	9,75
Ph	6,80	6,68	6,83
Salinity (g/l)	32	32,5	32,4
Turbidity (NTU)	801	30,3	13,2
Total of dissolute Salt (TDS (F°)	29,8	30	30,2
Sulfate (mg/l)	710,20	689,79	0,026
Nitrate (mg/l)	5112,76	139,14	84,27
TH (°F)	850	870	700

3rd test

The animals are taken in one aquariums of sea water, with addition a mixture of three surfactant that it's concentration is taken in the reject of Eagle factory (see table 3). These animals are taken contact in this environment for 48 Hours, that the results of mortality are summarizes in table 9 and the characteristics of this environment after contact are summarized in table 10.

Tab. 9: *Mortality of mussels for the 3rd test*

Time of contact	% of mortality
24 H	90
48 H	100

Tab: 10. *Physicochemical characteristic after the 3rd test*

Physicochemical parameter	Results
O_2 (mg/ l)	9.70
Ph	6.80
Salinity (g/l)	32.5
Turbidity (NTU)	830

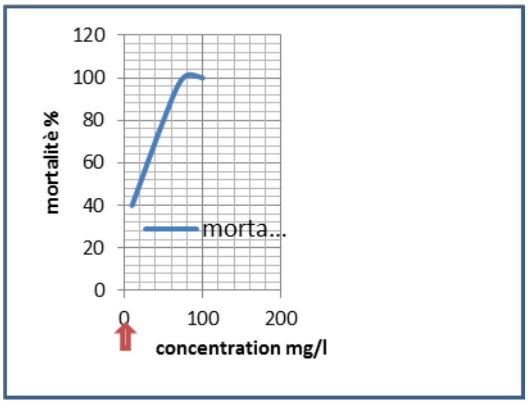
4th test

The animals are taken in four aquariums of sea water, with addition different concentrations (table11 of the anionic surfactant (LAS) contacting the animals for 48 Hours. The results of mortality are summarizes in table 11 and figure 2, the characteristics of this environment after contact are summarized in table 12

Tab: 11: *Mortality of mussels in contact with the concentrations of LAS*

Concentration of LAS Mortality %	10 mg/l	50 mg/l	75 mg/l	100 mg/l
24h	10	20	40	60
48h	40	80	100	100

Fig.2*: Mortality of mussels on function concentration of LAS*



Tab.12: *physicochemical characteristic after the 4th test*

Concentration of LAS Physicochemical parameters	10 mg/l	50 mg/l	75 mg/l	100 mg/l
O_2 (mg/ l)	7	7,10	7,05	6,90
Ph	7,20	7,24	7,30	7,10
Salinity (g/l)	29,8	29,8	29,7	28,6
Turbidity (NTU)	22	101	135	182
Total of dissolute Salt (TDS (F°)	28,3	28,4	28,3	28,2
Sulfate (mg/l)	3.51	17.59	26.39	143.31
Nitrate (mg/l)	644.68	861.70	1161.70	1440.42
TH (°F)	830	810	750	700

5th test

The mussels are taken in four aquariums of sea water, with addition different concentrations (table12) of the anionic surfactant (AES) contacting the animals for 48 Hours. The results of mortality are summarizes in table 13, the characteristics of this environment after contact are summarized in table 13.

Tab.13: *Mortality of mussels 5th test*

Concentration of AES Mortality %	10 mg/l	50 mg/l	75 mg/l	100 mg/l
24h	40	50	70	80
48h	50	90	100	100

The AES LC_{50} for mussels is 10 mg / l.

Tab.14: *physicochemical characteristic after the 5th test*

Concentration of AES Physicochemical parameters	10 mg/l	50 mg/l	75 mg/l	100 mg/l
O_2 (mg/ l)	8,01	7,10	6,87	6,70
Ph	7,27	7,08	7,03	7,10
Salinity (g/l)	30,00	29,8	29,8	28,7
Turbidity (NTU)	59,5	63,8	122	163
Total of dissolute Salt (TDS (F°)	28,5	28,3	28,4	28,3
Sulfate (mg/l)	3.51	17.59	26.39	35.19
Nitrate (mg/l)	379.68	407.75	778.72	1040.42
TH (°F)	900	870	850	830

6th test

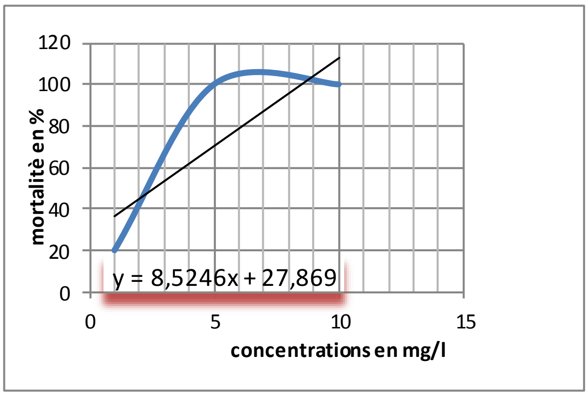
The animals are taken in four aquariums of sea water, with addition different concentrations (table15) of the nonionic surfactant (NI 07) contacting the animals for 48 Hours. The results of mortality are summarizes in table 15 and figure 3, the characteristics of this environment after contact are summarized in table 16

Tab.15: *Concentration surfactants and animals mortality in 6th test*

Concentration of NI 07 Mortality %	1 mg/l	5 mg/l	10 mg/l
24h	10	70	100
48h	20	100	100

It is found that the nonionic may cause 100% mortality of the population at a concentration of 10 mg/l. The $CL50_{48h}$ of NI07 is between 1 mg / l and 5 mg / L, and it is possible to graphically determine the mortality curve as a function of the concentration of NI07.

Fig.3: *Mortality of mussels on function concentration of NI O7*



Tab.16: *physicochemical characteristic after the 6th test*

Concentration of NI 07 Physicochemical parameters	1 mg/l	5 mg/l	10 mg/l
O_2 (mg/ l)	6.95	7.01	10.40
Ph	7.01	7.02	6.85
Salinity (g/l)	29 ?8	30	30?9
Turbidity (NTU)	30	64	86.5
Total of dissolute Salt (TDS (F°)	28.5	28.3	28.6
Sulfate (mg/l)	0.019	0.024	0.020
Nitrate (mg/l)	191.48	408.51	552.12
TH (°F)	910	870	800

Based on the results, a 48H of contact with different surfactants is sufficient to cause a mortality rate of 100% of the population, we note that the LAS 24H has a concentration [LAS] = 1.98g / l to cause 60% mortality, AES has de0.65g / l causes 80% mortality and the mortality rate of NI07 is 70% to 68mg / l.

Rather, the mixture of the three surfactants caused a mortality rate of 90% of the population after 24 hours of which we can conclude that the assemblement of these surfactants is more toxic than mètrent separately, something that does not happen in the manufacture of cleaning products.

It is noted that the hardness decreases with increase in the concentration of the LAS, the decrease is due to the ions of the complexities of the reactions with sulphate ions Mg^{++} and Ca^{++} forming precipitates: Ca $(LAS)^2$ and Mg $(LAS)^2$. 48 hours after contact, mussels with different concentrations of the AES, we find that:

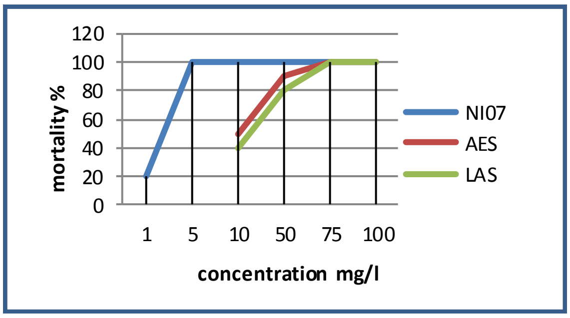
- pH decreases slightly, and this due to the acidification caused by the presence of sulphate ions in the aquatic environment by keeping the neutral medium.

-The reduction of dissolved O_2 is due to the breathing of the mussels, it is one of the nutrients necessary for survival and growth of the mussels.

In the control, test there's no real change in the water body except a slight decrease in hardness and dissolved O_2 that due to consumption by mussels and a nitrate concentration increased from nitrogenous waste mussels.

To compare the ecotoxicity of three surfactants with each other, a determination was performed per class, depending on the $CL50_{48H}$ each surfactant.

Fig.5*: Comparison ecotoxicity of three surfactants*



Finally we will justify the results of the tests of Ecotoxicological these three surfactants by applying the LCA approach that will allow us to make a toxicological classification of the three surfactants and assessing their impacts aquatic toxicity.

Application of life cycle assessment on multi user liquid detergent

Impacts assessment

The EDIP2003 method is used to assess the environmental impacts.

The impacts considered in this study are shown in figure 4 and summarized in table 17:

Aquatic eutrophication EP(N) expressed on kg N

Aquatic eutrophication EP(P) expressed on kg p

Human toxicity water expressed on m^3

Bulk waste expressed on Kg

Tab.*17: Impact generated by detergent liquid multi user-EDIP 2003 method*

Impact categories	Unit	Results
Aquatic eutrophication EP(N)	*Kg N*	4.07 E-6
Aquatic eutrophication EP(P)	Kg P	2.21 E-5
Human tocxicity water	m^3	0.105
Bulk waste	Kg	7.00

Contribution of components to the impacts generated

Edip2013 method allows us to explain the origin of some important impacts : human toxicity by the water. Which we are interested in their origins.

Tab.18: *Contribution to Human toxicity water impact generated*

Impact categories	Element contribution	Unit	Results
Human toxicity water	Alkyl Ether Sulfate (sulphonate)	m^3	1.78 E-4
	Fatty alcohol ethoxylate	m^3	0.103
	Linear Alkyl benzene sulfonate	m^3	5.28 E-4

The aquatic toxicity has received particular attention in the regulatory context, as the aquatic compartment is a typical sink for industrial pollution due to direct releases and indirect emission pathways. This impact category is primarily influenced by the emission of the surfactants in the various processes for the production of detergents

The multi pollutant in use is the impact of human toxicity by the water with a large contribution of NI07 surfactants, LAS and AES.

The surfactants are responsible aquatic human toxiicity, explain what these surfactants concentrations accumulated by aquatic species and transformation to the human food chain

Conclusion

Reviews conducted environmental toxicity of certain assets tensions in several marine species, and to complete these studies and to provide knowledge in the same perspective, our study was performed on a species called mussels , there was little toxicological studies in this context.

In The practical part, we tried to vary the concentrations of three active tension, two of which are anionic (LAS, AES) and one non-ionic (NI7), and put it in contact for a definite time with mussels and monitored physiological variations and the number of deaths of the species.

This study followed the results of the LCA approach that has allowed us to make an assessment of the impact of human aquatic toxicity of liquid detergent (multi use) and to determine the contribution of components to these impacts.

The ecotoxicity of the aquatic species studied shows that the nonionic is more toxic than anionic because it caused the death of all individuals contacted in time less than 24heurs with behavioral disturbance and physiology of this species.

Through this research we can propose the replacement of the most polluting power assets (non-ionic) with oils play an important role in detergents such as essential oils or ethoxylated oils that are low in toxicity.

Finally, wishing us by this research that will result in the initiative, and it will serve as a reference for future research.

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