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Experimental Variables in Biodegradation of Surfactant in Marine Environment

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Increasing use of surfactant culminates in the surplus of power dilution and fresh water self-depuration. This process is causing this substance to begin to appear in the oceans. Consecuently, the concentration of surfactant matter is going beyond the levels established in the literature as lethal for fish in certain areas with low rates of water renewal such as bays and estuaries.

The effects of such high concentrations are particularly damaging in an area like the Bay of Cádiz, were the marine species cultivated are higly sensitive, while the exploitation of biological resources for human consumption is especially intense.

Other authors (Dobarganes et al. 1977; Ruiz Cruz et al. 1972) have pointed to the importance of a number of external factors (aeration, agitation, temperature, etc.) in the process of surfactant degradation in fresh water. These factors may play a significant part in accelerating or slowing down the process of surfactant degradation, which in the latter case could constitute a danger to the flora and fauna in the ecosystem where surfactants are present; the more time undegraded surfactants spend in the medium, the more their toxic effects will be felt. A proper understanding of these variables, then, may be most useful in order to eliminate surfactants from seawater prior to its entry in tidal salt-ponds in this area.

Hence, this paper examines the influence of cartain environmental factors on the process of sodium dodecyl-benzene-sulphonate degradation in seawater in the presence of marine sludge for to reproduce the natural conditions.These factors are: light, aeration, darkness and salinity.

MATERIALS AND METHODS

A number of matrices were prepared, and they were added 25 g of moist sludge each, 100 mL of seawater and 2 mg of sodium dodecyl benzene sulphonate with 90.3% active ingredients. A full description of the degradation method employed and of the techniques for extracting surfactant from sludge is given in a previous paper (surfactant were extracted with a mixture of CH_3OH and 2N NH_4OH at a volume ratio of 2:1) (Sales et al. 1984).

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Analysis of the surfactant matter present in the medium at any time was performed using Abbot's Methylene Blue method (Abbot 1962) (yield of a complex Methylene Blue-Anionic surfactant, which can be extracted in chloroform), as this method produces the least interference in seawater.

To test the influence of light, samples were subjected to a constant luminosity of a 1254 lux, with visible light. Aeration was studied by keeping the flasks closed while an aerator introduced filtered, purified air at 1 L/min. The effect of darkness was tested by leaving the samples in a totally dark room for the entire duration of the assay. Finally, to test the influence of salinity, seawater was used from a tidal pool which had undergone intense evaporation (S=65‰). Salinity levels of 16‰ ,32‰ and 50‰ were also tested in order to cover all the possible concentrations occurring in the area under study. The latter salinities were obtained through dilution of the 65‰ salinity water with sterilized distilled water.

Table 1. Characteristics of the sludges employed.

Loss of weight at 110°C	23.1	Fe (%)	3.20
Loss of weigth at 450°C	4.9	Mn (µg/g)	375
Organic carbon (%)	0.52	Zn (µg/g)	330
Organic nitrogen (%)	0.03	Cu (µg/g)	13.7
Clay (%)	68	Pb (µg/g)	21.5
Silt (%)	10	Cd (µg/g)	2.17
Loam (%)	22		
Anionic surfactant matter (µg DSNa/g sediment dry)	3.25	Nº aerobic col./g sediment dry	240000

A parallel control assay was performed in natural conditions at the normal salinity for this area (32‰) without aeration. All assays were performed in duplicate at 25°C.

For realize the different assays (aeration, illumination etc.), the water used has S = 32‰ , from water S = 65‰ by dilution. Tables 1 and 2 show the characteristics of the sluge and sea-water employed.

Salinity (salino-meter YSY), pH (pH-meter Beckman) and dissolved oxygen (method Winkler) (Strickland and Parson 1968) were determined of the sea-water. Micro-organisms counts were conducted as described by Harrigan and McCance (dilution of samples in seawater sterilised and sows in Nutrient-Agar) (Harrigan and McCance 1976).

Sludge analysis included determination of organic carbon (Gaudette et al. 1974), and organic nitrogen (Anonymous 1983), weight loss at110 and 450°C, and assays for various heavy metals (Fe,Mn,Zn,Cu, Pb and Cd), all by atomic absorption spectroscopy (Gómez-Parra et al. 1984). Granulometric analysis was performed using the chain hydrometer method (De Leener et al. 1965).

Table 2. Characteristics of the sea-water employed

Salinity (‰)	16	Anionic surfactant	
Dissolved Oxygen (mg/L)	9.8	matter (µg DSNa/L)	30
pH	8.12	N° aerobic col./mL	4200
Salinity (‰)	32	Anionic surfactant	
Dissolved Oxygen (mg/L)	6.5	matter (µg DSNa/L)	70
pH	8.11	N° aerobic col./mL	8500
Salinity (‰)	50	Anionic surfactant	
Dissolved Oxygen (mg/L)	2.7	matter (µg DSNa/L)	98
pH	8.13	N° aerobic col./mL	12800
Salinity (‰)	65	Anionic surfactant	
Dissolved Oxygen (mg/L)	1.5	matter (µg DSNa/L)	115
pH	8.12	N° aerobic col./mL	16900

RESULTS AND DISCUSION

The results of the different assays are shown in Figures 1 and 3, which reflect the evolution with time of the percentage of residual surfactant matter. It will be seen in Figure 1 that although there are no significant differences in percentage degradation reached over the entire 21 d of experimentation, the aerated and illuminated samples attained 90% degradation in roughly 4 d less than the other cases.

To explain the greater degradation velocity in the aeration assays, it should be considered that degradation is basically an aerobic process, and hence the introduction of air to the solution will favor this process.

In the luminosity assays, increased velocity is probably to be explained by photosynthetic activity in the micro-algae present in the sea-water. Artificial ligh was used in these experiments, but of a spectrum very close to that of sunlight. There is further reason to believe that light in the presence of photosynthesizers may affect the degradation process.

These results are set forth in Figure 2, where we can see how the assays commence with a relatively small number of colonies (248 000) and exceeded 1 millon at the end of the induction period for the aeration and luminisity assays. Such growth in the number of colonies stems from increased surfactant consumption by the microorganisms, which logically results in a shorthening of this period. By applying the kinetic degradation model developed by the authors in a previous paper (Sales et al. 1987), coefficients were obtained for the proposed kinetic equation. Thèse are shown in Table 3. The theoretical values of initial concentration derived from these coefficients lead to results ranging from 1.05-1.09 of initial experimental concentration, which bears out the applicability of

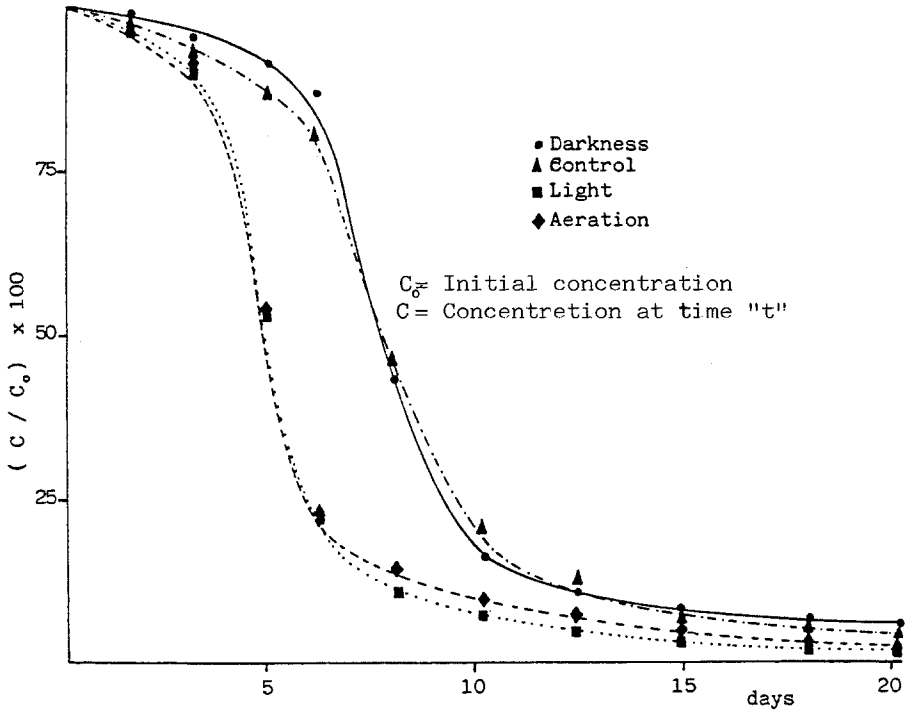

Figure 1. Charge with time of percentage of residual surfactant as influenced by aeration, luminosity and darkness.

the proposed kinetic model(Figure 3).

In the case of the assays at varying salinities (Figure 4), it can be seen that similarly, there are no significant differences in the levels reached after 21 d. The difference lies in the induction period, which is shorter for high salinities (65‰ and 50‰) than for lower ones (32‰ and 16‰). This may be due the

Table 3. Values of coefficients of equation $V= aC^2 + bC + d$ for the different assays realized

Assays	a	b	d
Control	-2.9×10^{-4}	0.49	-28.16
Light	-4.7×10^{-4}	0.85	-59.46
Aeration	-4.7×10^{-4}	0.85	-57.75
Darkness	-2.7×10^{-4}	0.46	-15.73
Salinity (16‰)	-4.7×10^{-4}	0.88	-71.40
Salinity (32‰)	-5.2×10^{-4}	0.94	-53.72
Salinity (50‰)	-4.0×10^{-4}	0.74	-36.80
Salinity (65‰)	-3.1×10^{-4}	0.61	-32.85

V = velocity C = Concentration

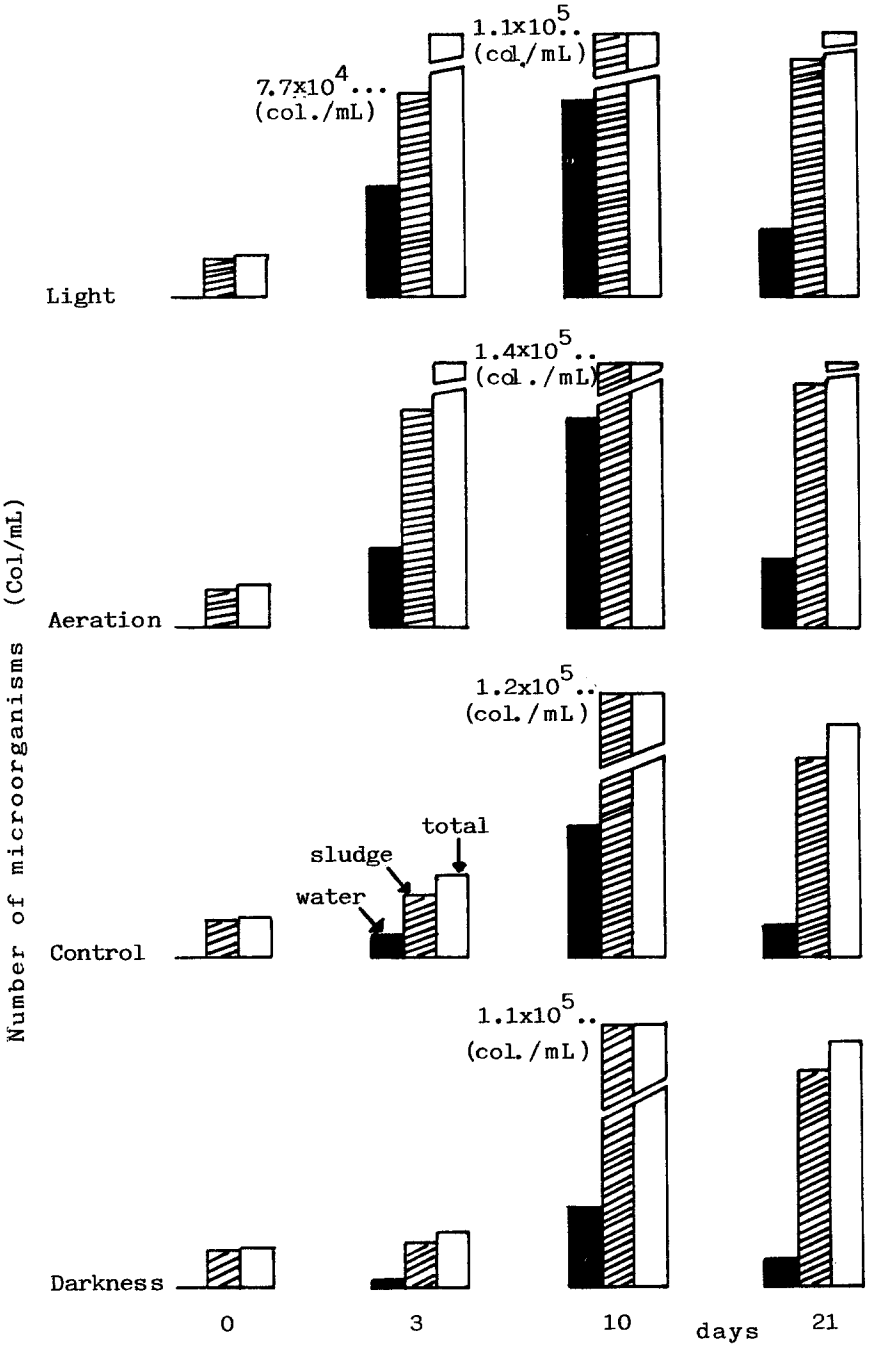

Figure 2. Change in number of micro-organisms as influenced by aeration, luminosity and darkness.

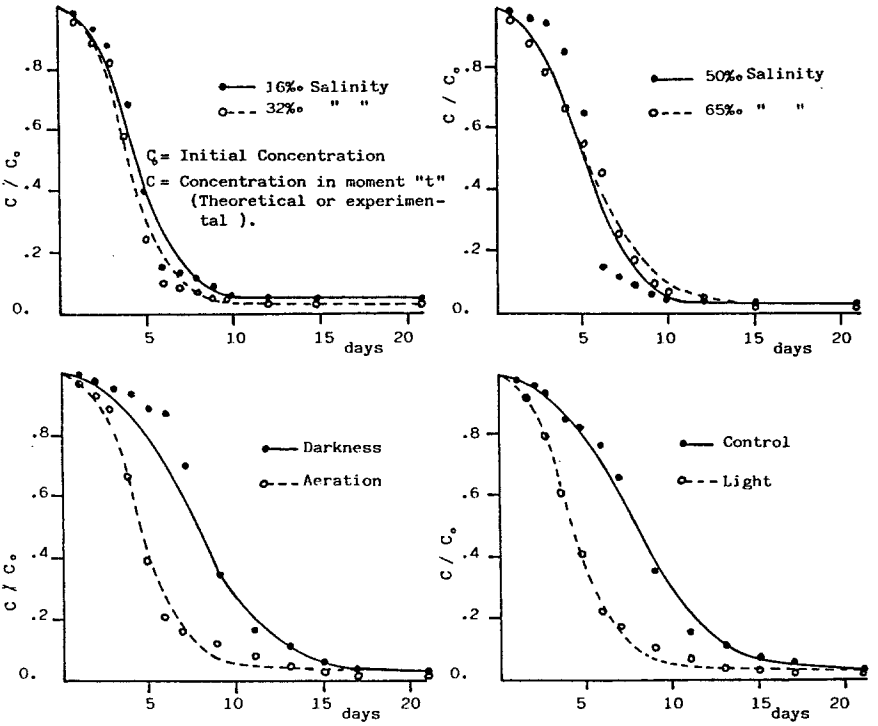

Figure 3. Variation of residual quantity of surfactant versus time for the different assays.

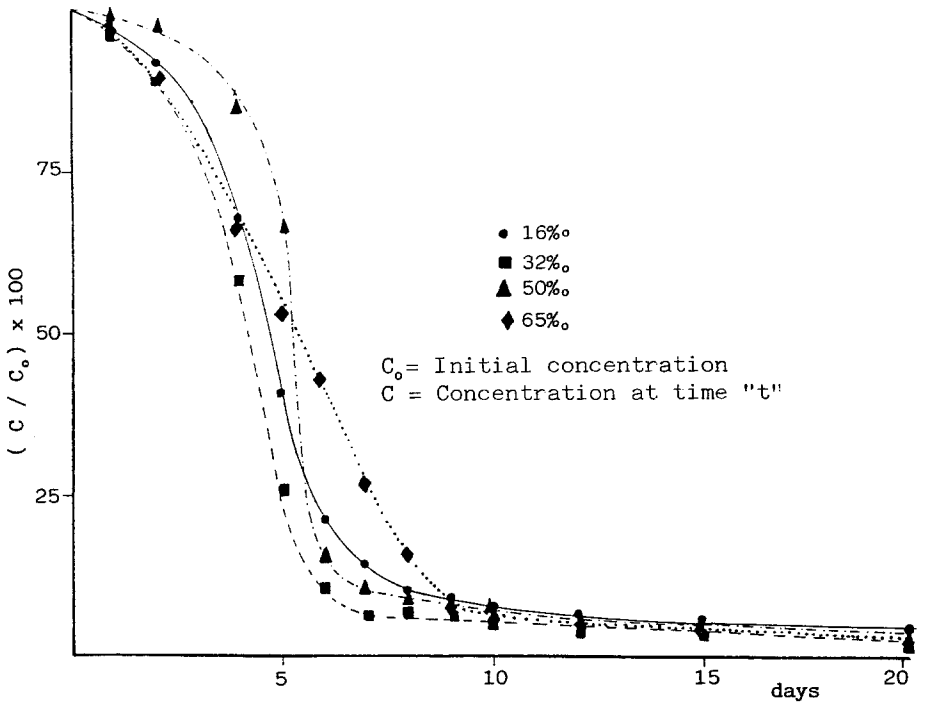

Figure 4. Change with time of percentages of residual surfactant matter for different salinity assays.

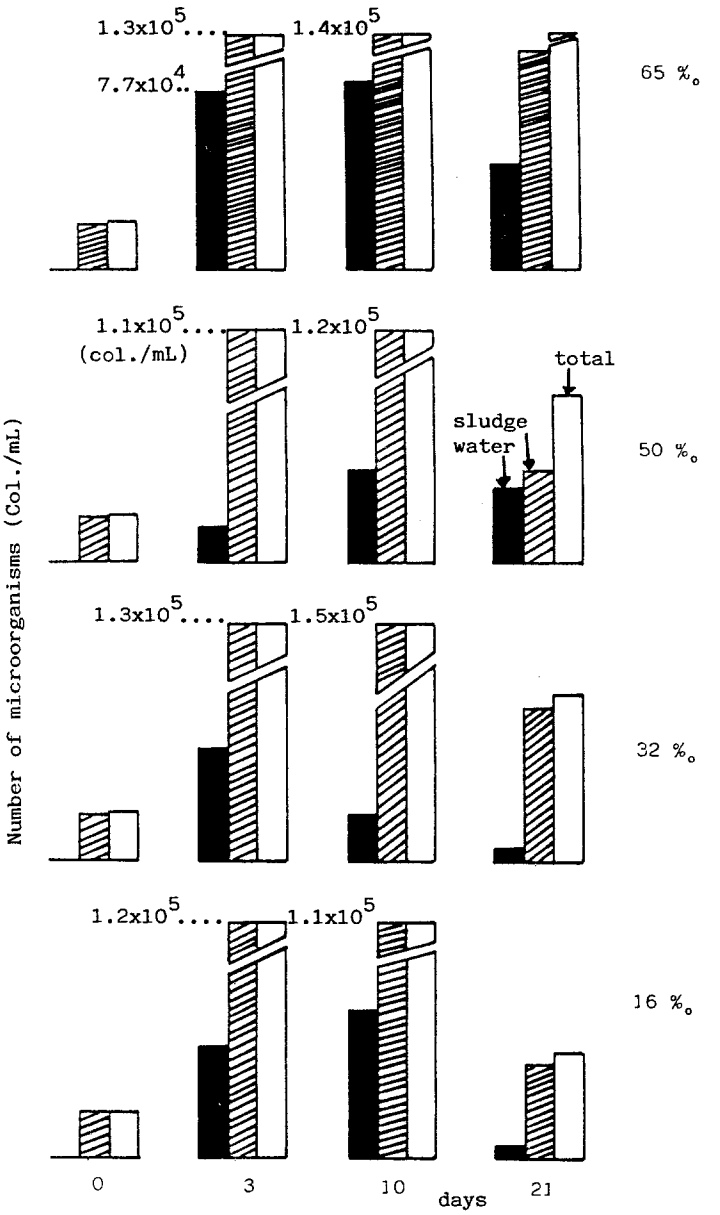

Figure 5. Change in numbers of micro-organisms for different salinities studied

fact that degrading bacteria are halophilous, accustomed to existence in very saline media, so that dilution would result in the disappearance of large numbers of them; then again, those remaining would require a longer period to adapt to the new medium. This is borne out by Figure 5 which shows how outset of the degradation process, the numbers of colonies decreased in the assays at lower salinities.

The values of the parameter "d", shown in Table 3, also reflect this tendency. In the proposed model, the independent term is related to the occurence of side effects inhibiting or enhancing bacterial growth. The lower absolute value of the term "d" in the higher salinity assays indicates that there is less resistence to degradation, which is therefore enhanced. This further concords with the previous supposition.

The reason for the lack of differences in percentage degradation reached at the end of 21 d for the various salinities studied, must be sought in the presence of sludge in the medium used for the degradation assays. As was pointed out in a previous paper (Sales et al. 1984), this is due to the high bacterial content of these sludges.

The agreement between the theoretical concentration derived from model proposed by authors (Sales et al. 1987) and the experimental values is shown in Figure 3.The continuous and dotted lines represent the ratio between the theoretical and the initial concentration. The points which appear in the Figure 3 are the ratio between the experimental and initial concentration.

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