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EFFECT OF TEMPERATURE ON KINETIC OF ANIONIC SURFACTANT DEGRADATION IN SEA-WATER

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ABSTRACT

This paper studies the effect of temperature on the velocity of degradation of a commercial surfactant (LAS) in sea-water. The tests were conducted in conditions designed to simulate those in which anionic surfactant matter is dumped into the Bay of Cádiz. A comparison is made between the results of surfactant degradation in sea-water only and degradation and sea-water in the presence of marine sludge.

Temperature is found to exert a profound effect on the degradation process; at temperature below 5-10°C there was no appreciable decomposition of the surfactant, while at high temperatures, 20-25°C, degradation was practically complete after 21 days of testing. In addition, were sludge was added degradation was faster at all temperatures studied.

As a prior step, a method was divised to extract the surfactant contained in the sludge.

INTRODUCTION

In certain coastal areas with low rates of water renewal such as bays and estuaries, the growing use of detergents has culminated in concentration of surfactant matter beyond the levels established in the literature as lethal for fish.

The effects of such high concentrations are particulary damaging in an area like the Bay of Cádiz, where the marine species cultivated are highly sensitive, while the exploitation of biological resources for human consuption is especially intense.

The poor solubility of this type of substance in sea-water (chiefly sodium dodecyl benzene sulphonate, the surfactant most widely used in the manufacture of domestic detergents), combined with the adsorptive phenomena which take place[1], results in the incessant aggregation of surfactant matter to the sludges close to the dumping points of urban effluent. Thus, while there is a considerable amount of literature extant on anionic surfactant degradation in sea-water[2-3], there are practically no studies on this type of degradation in sea-water and sludge.

This paper, then, compares the results described for degradation of LAS in sea-water only with those of assays where sea-water samples are in contact with marine sludge.

To this end a method had first to be devised for the extraction of the surfactant matter embedded in the sludge.

The tests were conducted at different temperatures in order to determine the effect of temperature on the kinetic of surfactant degradation.

METHODS

Description of the Assaying System Used

The assaying system was similar to the river-water test described in the bibliogrphy[4], as this is the system which best reproduces natural conditions.

For the experiments at the various temperatures programmed, 250ml erlenmeyer flask were taken; to these were added about 25gr of moist sludge water content 23,2% and 100ml of sea-water containing sodium dodecyl benzene sulphonate at a concentration similar to that often found in the effluents reaching the Bay of Cádiz[5]. A commercial linear-chain sodium dodecyl benzene sulphonate was used, whit 90,3% surfactant matter. Parallel controls consisted in monitoring the degradation process in matrasses containing only satured surfactant solution in sea-water.

Samples were taken 0,1,3,6,10,15 and 21 days after the start of the assay and residual surfactant matter analysed, both in water and sludge, always in duplicate. The nature of the system used to analyse surfactant matter in the sludges made it necessary to use a different matrass for each sample; nevertheless, in order to minimise the inconvenience inherent in the design of the experiment, all assays were conducted in duplicate.

Surfactant degradation was monitored both in water only and in water with sludge at 5,10,15,20 and 25°C in order to cover the range of temperatures normally occurring in surface waters at different points on the Spanish coastline. In all case, the water and sludge used came from an inlet close to the Bay of Cádiz, which generally speaking shows low levels of contamination[6]. The sea-water and sludge were characterised through the determination of a number of physical, chemical and bacteriological parameters.

Analytical Methods

To determine the anionic surfactant matter present in the medium, the metylen blue method was used, as proposed by Abbot[7]. In view of the scant literature existing on the subject[8], a method was divised for extracting the anionic surfactant matter from the slugde. The comparative results of the various extraction techniques employed are described in the following section.

Dissolved oxygen, salinity and pH were determined for the seawater using the techniques described by Strickland and Parsons [9].Microorganism counts were conducted according to the techniques described by Harrigan et al[10].

Characterisation of the sludge included measurement of organic carbon[11], organic nitrogen[12], losses through calcination at 110 and 450°C, and content in various heavy metals. These were determined by atomic absorption spectroscopy after extraction from the sludge samples with a mixture comprising ClH/NO H 10:1[13]

TABLE I

Characteristics of the sea-water and sludges used

SEA-WATER

pH	8,03	Anionic surfactant matter (µg DSNa/l)	62,7
Salinity (‰)	33,3		
Dissolved Oxygen (mg/l)	6,78	N° aerobic col./ml	17100

SLUDGES

Loss of weight at 110°C	23,20	Fe (%)	0,31
Loss of weight at 450°C	2,10	Mn (ppm)	304
Organic Carbon (%)	0,47	Zn (ppm)	288
Organic Nitrogen (%)	0,04	Cu (ppm)	6
Clay (%)	58,40	Pb (ppm)	19
Silt (%)	35,40	Cd (ppm)	2,07
Loam (%)	6,20	N° aerobic col./g	12.500
Anionic surfactant matter (µg DSNa/g sediment dry)	3,68	N° anaerobic col./ /g	800

Granulometric analysis of the sludges was carried out using the chain hydrometer method[14] .

Table I shows the characteristics of the sea-water and sludges used in these assays.

RESULTS AND DISCUSSION

Techniques for the Extraction of Surfactant Matter from Sludge

In order to analyse the surfactant matter embedded in sludge, the latter must first be solubilised with a suitable solvent which does not subsequently interfere with the determination process.

To this end, surfactant-free sludges was placed in contact with sea-water to which a precisely-measured quantity (20 mg/l) of surfactant had been added, then left in contact for 4 days so that the bulk of the surfactant would associate with the sludge. This operation was conducted at 2°C to avoid the degradation of the surfactant. After centrifuging for 20 minutes at 100g to separate the supernatant surfactant solution, two agents were tried for the extraction of the surfactant from the sediment: water at varying temperatures, and a 2N methanol-ammonium mixture in various volumetric proportions. The literature describes this mixture as suitable, but does not indicate proportions or other analytical conditions[8].

Two extraction techniques were tried:

- Extraction with Soxhlet
- Extraction with the help of a magnetic shaker

The first is recommended in the literature; it entails separating the sludge from the supernatant solution then placing it in a cartridge inside the soxhlet. After 2-3 hours of extraction, an aliquot is taken for analysis.

The second method entails the addition of a determied quantity of solvent to the sludge, shaking for 20-30 minutes, then separating by centrifuge. The supernatant fluid is removed and the sludge is once again subjected to the same operation. The process is repeated until the greatest possible amount of surfactant has beed extracted. Finally all the supernatants are mixed together and a fraction taken for analysis. Table II shows the mean values obtained after processing ten samples with each of the methods described.

It will be noted that while the water's extractive capacity increased with temperature, no more than 70% of the surfactant present was recovered at the best of times; the 2N methanol-ammonium mixture, on the other hand, showed much greater extractive capacities in all the different proportions tested. The greatest

TABLE II

Results of different extraction techniques

ASSAY	AGENTS FOR EXTRACTION	ASSAY CONDITIONS	RECUPERATION %
1	H_2O (20°C)	7 consecutive extractions of 2,9ml water/g sludge. Shaking for 20' each extraction	62,8
2	H_2O (60°C)	7 consecutive extractions of 2,9ml water/g sludge. Shaking for 20'each extraction	66,7
3	H_2O (100°C)	200 ml H_2O in Soxhlet during 2-3 hours	60,2
4	CH_3OH-NH_4OH 2N proportion 1:1v	3 consecutive extractions of 5,5;2,9 and 2,9 ml/g sludge.Shaking for 20'each extraction	92,9
5	CH_3OH-NH_4OH 2N proportion 1:2v	" " "	90,3
6	CH_3OH-NH_4OH 2N prop. 2:1	" " "	95,2
7	" " " prop. 3:1	" " "	93,6
8	CH_3OH-NH_4OH 2N prop. 2:1	200 ml in Soxhlet during 2-3 hours	93,4
9	" " " prop. 4:1	" " "	92,3

effects was obtained with a 2:1 methanol-ammonium (2N) proportion in volume; also,although the soxhlet produced good results, the magnetic shaker definitely accelerated the process.

Degradation of LAS in Sea-Water

Figure 1 shows the results of the degradation assays at different temperatures. Qualitatively speaking, it will be seen that degradation fails to occur at low temperatures (5-10°C), while at 25°C degradation had exceeded 90% after 15 days. At a medium temperature (15°C) degradation only took place to a very limited extent.

From the dependence on temperature of the speed of the process, which is clearly related to the metabolism of the microorganisms intervening in degradation, it follows that the contaminant potential of the surfactant-bearing effluents will be highly seasonal. Thus, in the winter months, in those places

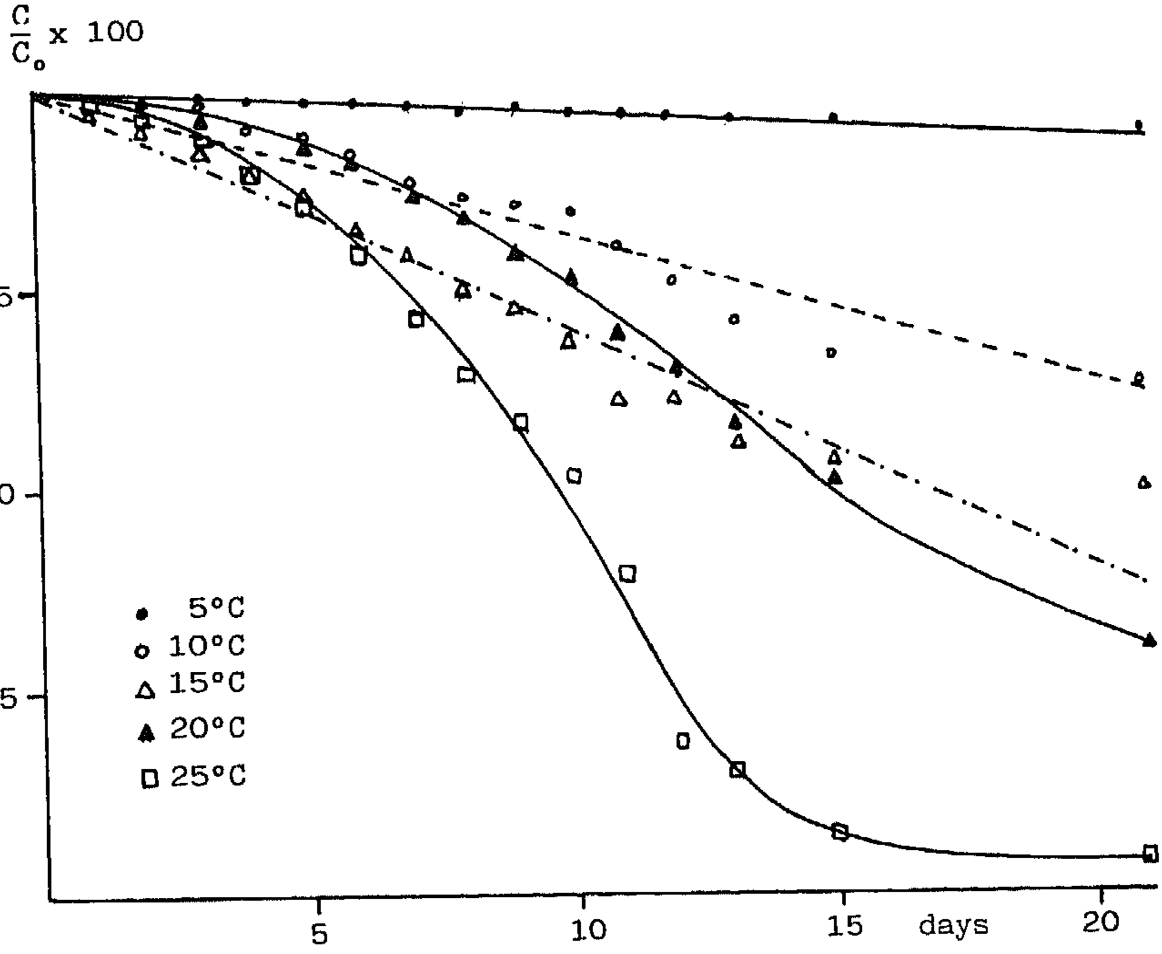

Fig. 1. Percentage of surfactant matter versus time at different temperatures.

where water temperature ranges from 5 to 10°C, the effects wrought by the dumping of such wastes must be particulary serious. Although temperature in the Bay of Cádiz are not normally as low as this, the falling-off degradation in winter is felt especially keenly, as this is the time for the laying and initial development of larvae in most of the species commercially produced in the local fish-farms[15-16].

For assays at 5-10-15°C, degradation velocity was not dependent on surfactant concentration, given that the values ob-

TABLE III

Values of coefficients a, b and d for different temperatures in absence of sludge.

Temperature (°C)	a	b	d
20	$-4,72 \times 10^{-4}$	0,28	-17,00
25	$-4,78 \times 10^{-4}$	0,28	-0,28

tained are best fitted to a zero order kinetic equation. Correlation coefficients are 0.98, 0.99 and 0.99 respectively.

The differential kinetic equation at 20-25°C best fits the model developed by the authors in previous work ,specifically a second-degree polynomial of the type:

$$v = \frac{dC}{dt} = a\,C^2 + b\,C + d$$

The values of coefficients a, b and d are shown in Table III

The above equation may be put in the following way:

$$v = \frac{dC}{dt} = K'\,C\,(\,1 - B\,C\,) + K_o$$

were : $K' = b$, $B = -b/a$ and $K_o = d$

which is formally identical to the model proposed by Pearl and Reed as developed by Volterra[17] . This non-structured mathematical model refers to bacterial growth in a culture processed in a discontinuous reactor and finds concrete for in the following expression for micro-organism growth:

$$\frac{dn}{dt} = K\,n\;(\,1 - B\,n\,) + K\,(t)$$

were : n is a measurement of the number of micro-organisms

B is the inverse of the bacterial population size in the situation reached at the end of the process

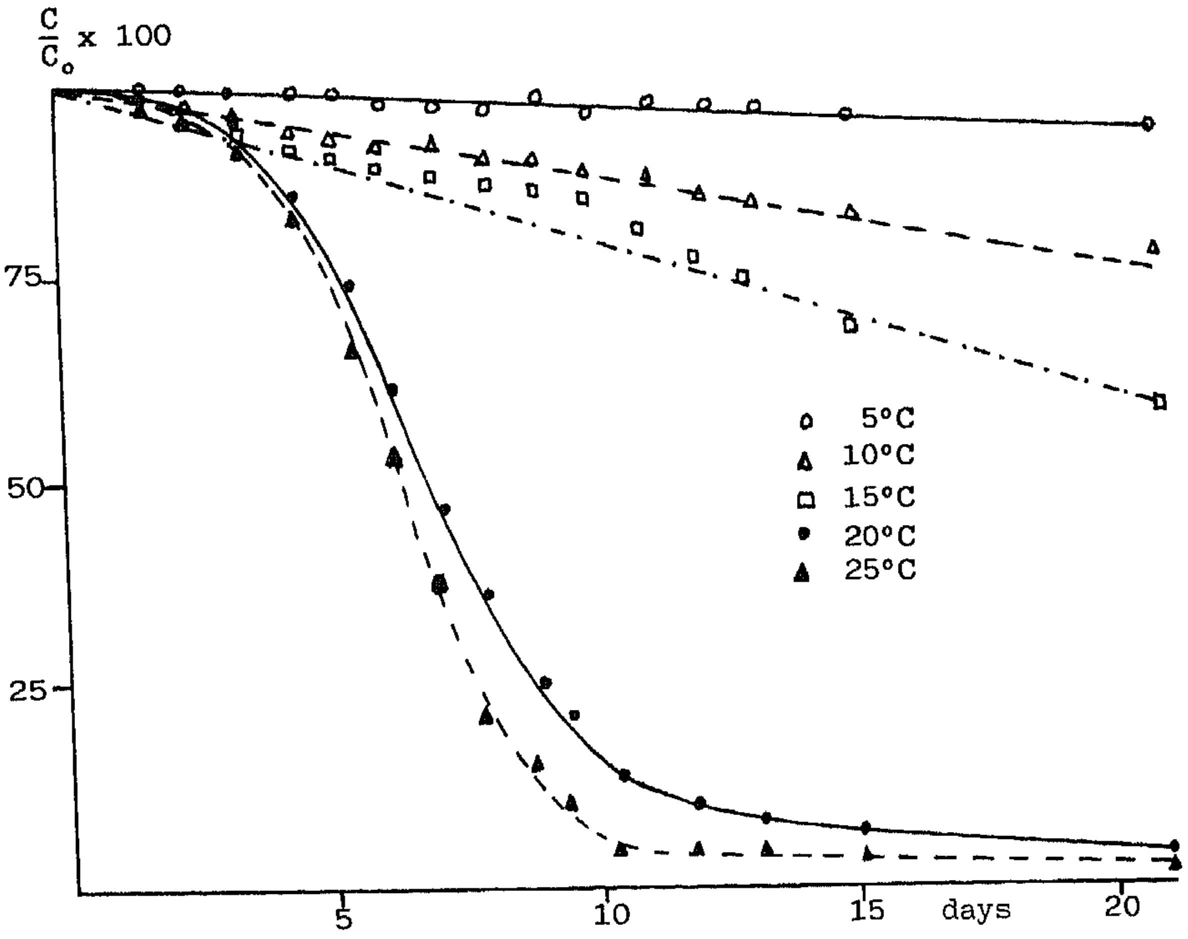

Fig. 2. Percentage of surfactant matter versus time at different temperatures in presence of sludge.

K(t) is a function related to the presence of side effects which inhibit or enhance bacterial growth.

In the opinion of the authors, the degradation process in the assays conducted in discontinuos mode can be interpreted in terms of an adaptive phase in the bacterial flora present in the medium, a phase of exponential development during which degradation actually occurs, and a final phase characterised by a residual substrate concentration veering asymptotically towards zero and coinciding with stasis in micro-organism growth.

TABLE IV

Values of coefficients a, b and d for different temperatures in presence of sludge.

Temp. (°C)	a	b	d	r
5	--	--	4,08	0,988
10	--	--	60,00	0,956
15	--	--	34,29	0,940
20	$-3,45 \times 10^{-4}$	0,760	-41,77	0,967
25	$-2,92 \times 10^{-4}$	0,638	-24,94	0,974

In Volterra's model, K(t) is a difficult term to interpret. In this case, as it possesses a negative sign, it could be associated with some inhibition of bacterial growth. This could arise from the production of toxins in the course of surfactant degradation, which in turn would slow the process down.

Degradation of LAS in Water and Sludge

Figure 2 shows the results of surfactant degradation in the water-sludge combination. In will be seen that only at the highest temperatures tested (20-25°C) was the statutory 90% degradation exceeded by the tenth day of the assay, while at lower temperatures the degradation process had scarcely begun in that time. Temperature, then, has a major effect on the velocity of degradation in the surfactant studied. Furthermore, at high temperatures the period required to acclimatise the micro-organisms to the added substrate (surfactant) is considerably reduced.

If we compare these results with those shown in figure I, we will see that by combining sludge with the water, the degradation process is accelerated. Such an improvement in degradation velocity must be connected with the nature of the sludge and with their high bacterial content. Because of the preponderant clay fraction, the sludges used have a large specific surface, as a results of which there may be adsorption of the surfactant, which would facilitate microbic degrading action.

Table IV shows the values of parameters **a**, **b** and **d** in the corresponding kinetic equations and their correlation coefficients. It will be seen that the best fit at 20 and 25°C is a secon-degree polynomial of the type described in the foregoing section. At lower temperatures zero order kinetics provide the best fit.

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