Toxicological and Environmental Chemistry, Vol. 37, pp. 85–93
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INFLUENCE OF SEDIMENT ON THE BIODEGRADATION KINETICS OF LINEAR ALKYLBENZENE SULPHONATES IN THE MARINE ENVIRONMENT

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(Received 28 November 1991; in final form 23 March 1992)

Primary degradation of a linear-chain sodium dodecyl benzene sulphonate was studied in the laboratory by using water and sediments taken from various points in the Bay of Cádiz and the surrounding tidal lands and marshes. The degradation, carried out in a testing system quite similar to the "river-die-away", was shown to depend on the granulometric characteristics of the sediment and on the initial surfactant concentration. In most test runs, the biodegradation kinetic equations derived from the process showed good agreement with the non-structured model of bacterial growth proposed by Velhurst and Pearld & Read[1], and subsequently modified by Volterra[1].

KEY WORDS: Detergents, biodegradation sediment, LAS, surfactant.

INTRODUCTION

Coastal waters receive a continuous input of surfactants delivered by rivers and coastal sewage effluents. The surfactant linear alkylbenzene sulphonate (LAS) accumulates in sediments, either through adsorption[2] or by precipitation due to its poor solubility in sea water[3]. Several authors have evaluated soil constituents for use as adsorbents of surfactants[4,5]. Recently, Urano *et al.*[6] in a limited study on river sediments related the adsorption of LAS with sedimentary organic carbon. Other authors[7] reported the relationship between the extent of adsorption process and the presence of clay minerals in the sediment.

Matthijs and De Henau[8] estimated the total and irreversible adsorption of LAS in sediment to be 57% and 31%, respectively. In the case of reversible adsorption, an equilibrium takes place between dissolved and sorpted LAS; an irreversible adsorption of LAS can lead to the accumulation of this surfactant. The physicochemical characteristics of the interstitial waters can differ considerably from those of the overlaying water[9], particularly for the concentrations of oxygen and some highly toxic metals. These differences in environmental conditions, combined with the high bacterial load normally found in coastal muds[10], can affect the rate of surfactant biodegradation.

In previous work[11] the optimum degradation temperature was determined and it was found that the rate of surfactant degradation increases when marine sediment is added to sea-water. Several authors[8,12,13] studied the content of surfactant matter in river and marine sediments. They found values of LAS up to 100 $\mu g\,g^{-1}$ on a weight (d.m.) basis in river sediments and between 10 to 30 $\mu g\,g^{-1}$ in marine sediments. However, the process of biodegradation has not been yet exhaustively studied. This paper reports on the influence of some sediment characteristics (i.e.: granulometry and organic carbon and heavy metal content) on the process of LAS primary degradation in marine environment.

EXPERIMENTAL

Study area

The Bay of Cádiz is a shallow marine embayment (average depth ≈ 6.5 m) extending over 120 km^2. The Bay is now strongly transformed by man in order to develop marine aquaculture. Because the nature of the bottom differs within the bay, sediments for this study were sampled from different locations in the Bay of Cádiz. The samples represented the different kinds of sediment present in the area. Locations of the sampling stations are indicated in Figure 1. The sediments designated E, B and C refer to the place of origin: E_1 and E_2 from salt-ponds; B_1, B_2 and B_3 from the Bay of Cádiz (B_1 next to waste outlet Puerto Real town; B_2 located in the tidal area and B_3 next to one of the wastewater effluents of Cádiz); C_1, C_2, C_3 and C_4 from a waterway surrounding the marshland (C_1 mouth S. Pedro river, C_2 mouth waterway S. Petri's inside of Bay, C_3 next to waste outlets S. Fernando town and C_4 mouth waterway S. Petri's into the Atlantic Ocean.

Testing apparatus and procedure

The biodegradation experiments were conducted using a modified "river-die-away-test"[14], described elsewhere[11]. For each type of sediment, a series of 15, 250 mL Erlenmeyer flasks (one flask for every day of analysis) were used, containing 25 g of wet sediment, 100 mL of sea-water and 2 mg of LAS with an active matter content of 90.3%. The ratio of sediment weight to water volume were similar to those reported by others who studied heavy metal and nutrient transference through the water-sediment interface[15]. The sediment at the Erlenmeyer flask bottom was 1 cm thick. During the assays, overlaying water in the flasks were always aired. Each test was started the same day of the sediment collection. Tests were carried out at 25°C.

The surfactant was extracted from the sediment using the technique of Sales *et*

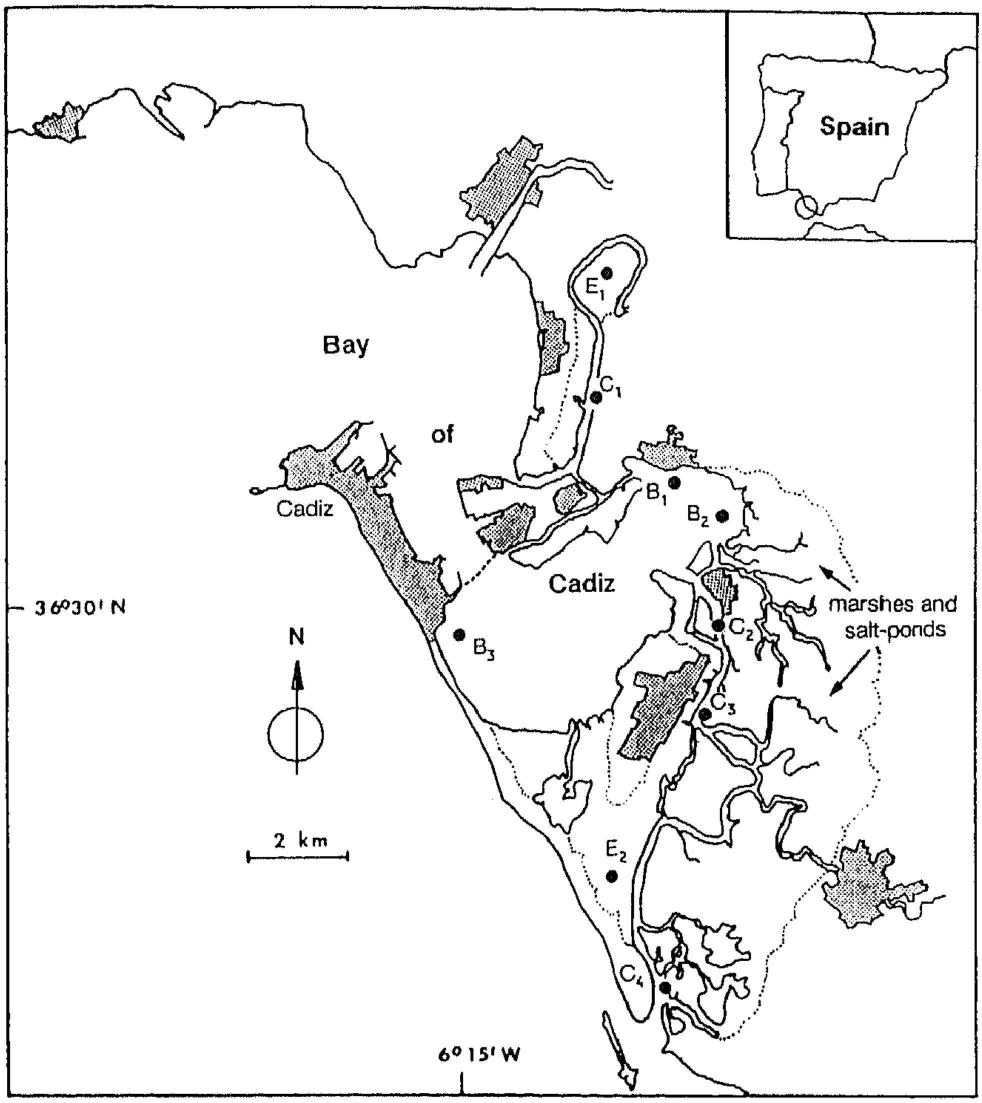

Figure 1 Location of sampling stations.

al.[11]. The residual surfactant matter was analyzed in duplicate in the supernatant water and the sediment extracts by a modification of Abbot's method[16].

Sea-water for all biodegradation tests came from an inlet close to the Bay of Cádiz. Its main physico-chemical characteristics were salinity (33.8 ± 0.7‰), pH (8.10 ± 0.15) and dissolved oxygen (7.1 ± 1.8 mg L^{-1}). Micro-organisms were counted according to Harrigan and MacCance[17]. The number of aerobic colonies per mL were $6 \cdot 10^3$–$8 \cdot 10^3$. Anionic surfactant matter (MBS) was 90 ± 25 μg L^{-1}.

Superficial sediments (0–5 cm) were collected using a Van Veen grab. The characteristics determined for the sediments included organic C[18], organic N[19], porosity (as weight-loss at 110°C), granulometry and some heavy metals (Fe, Mn, Zn, Cu, Pb and Cd). They were determined by atomic absorption spectroscopy after extraction from the sediment sample with $HCl–HNO_3$ (10:1)[20]. Granulometric analysis was determined by the "chain hydrometer method"[21].

RESULTS AND DISCUSSION

The features of the sediments used in these tests are reported in Table 1. Most of them are argillaceous, with the exception of those in stations C_1, B_1 and B_3, which are sandy. The concentration of heavy metals in the sediment samples were comparable to those previously found by Gómez-Parra *et al.*[20,22]. Nevertheless, especially high concentrations of Cu, Pb and Cd were found at stations B_1 and C_2, due to their proximity to the Puerto Real urban waste outlets (B_1) and the Bazan shipyard (C_2).

In general, the organic matter and heavy metal contents of these sediments depend primarily on the grain size distributions[23], although they are also affected by the proximity of the sampling stations to the urban and industrial waste outlets in the area[24]. For LAS accumulation in sediments, a similar trend has been found (Table 1).

The results of the degradation experiments are shown in Figure 2. The data show, that from the samples taken from the Bay inlets, only in the experiments performed by using sediment from the C_1 station degradation higher than 90% was found. Taking into account that sediment from station C_1 is highly sandy (Table 1), the observed higher biodegradation of LAS could be ascribed to the lower capacity of sand, compared with clay, to adsorb LAS. On the other hand, the degradation percentage reached at the end of the assay are inversely related with the original LAS concentration in sediment. A similar behaviour has been found for experiments performed with sediments taken from the bay. For this zone, the highest rates of primary biodegradation are found in sediments from stations B_1 and B_2. These stations also show a high concentration of surfactant in sediment (although not clay sediments) due to their proximity to urban wastewater effluents. This would be responsible for the highest degradation rate found, probably due to the greater adaptation of the bacterial flora.

Degradation figures for the tidal pool are lower, especially for station E_1. This may be due to the fact that the beds of the pool where the samples were collected display a high benthic oxygen demand, which often produces anoxic conditions, as well as relatively large quantities of easily degradable biological organic matter.

Utilizing the kinetic degradation model developed by the authors in a previous investigation[25], the adjustment coefficients (a, b, and d) of the equation

$$v = -|dC/dt| = aC^2 + bC + d$$

were calculated and reported in Table 2 (C is the actual quantity of surfactant (mg) at time t). In all instances, curves showed in Figure 2 are the integration of those equations. The obtained values suggest that a second degree polynomial fits well best is all cases, except the sediments B_1 and E_1, which followed a zero order kinetic. The kinetic behaviour of the B_1 sediment is the result of a high initial concentration of surfactant in the sediment, causing a relatively high amount of residual surfactant to remain practically unchanged throughout the process, in spite of the high average degradation recorded.

In the case of sediment E_1, the anomalous behaviour observed may be ascribed to

Table 1 Main characteristics of sediments used in the tests (O.C. = organic carbon, C/N = organic carbon to organic nitrogen ratio, MBAS = methylene blue active substances, M.D.V. = degradation values middle of 21 days).

Station	*Sediment class*	*Porosity (%)*	*O.C. (%)*	*C/N*	*Fe (%)*	*Mn (ppm)*	*Zn (ppm)*	*Cu (ppm)*	*Pb (ppm)*	*Cd (ppm)*	*MBAS μg/g(d.w.)*	*M.D.V. (μg/day)*
E_1	Clay	0.76	2.25	11.0	3.72	299	270	25	41	1.26	10	14
E_2	Clay	0.72	1.25	11.6	2.40	260	156	18	26	1.12	22	63
B_1	Sand	0.51	0.98	7.3	1.60	201	190	48	82	2.16	1210	377
B_2	Silt loam	0.64	2.73	8.0	3.31	356	166	40	71	1.55	99	91
B_3	Sandy loam	0.41	0.45	12.2	0.89	286	112	26	36	0.45	324	214
C_1	Silty clay	0.68	0.47	10.4	2.61	318	120	20	32	0.46	4	126
C_2	Clay	0.64	1.51	10.3	3.96	342	184	47	82	1.72	28	93
C_3	Sandy clay	0.60	1.88	8.5	3.40	286	189	52	81	2.70	94	112
C_4	Sandy clay	0.51	0.98	9.6	1.61	308	113	19	20	0.90	16	69

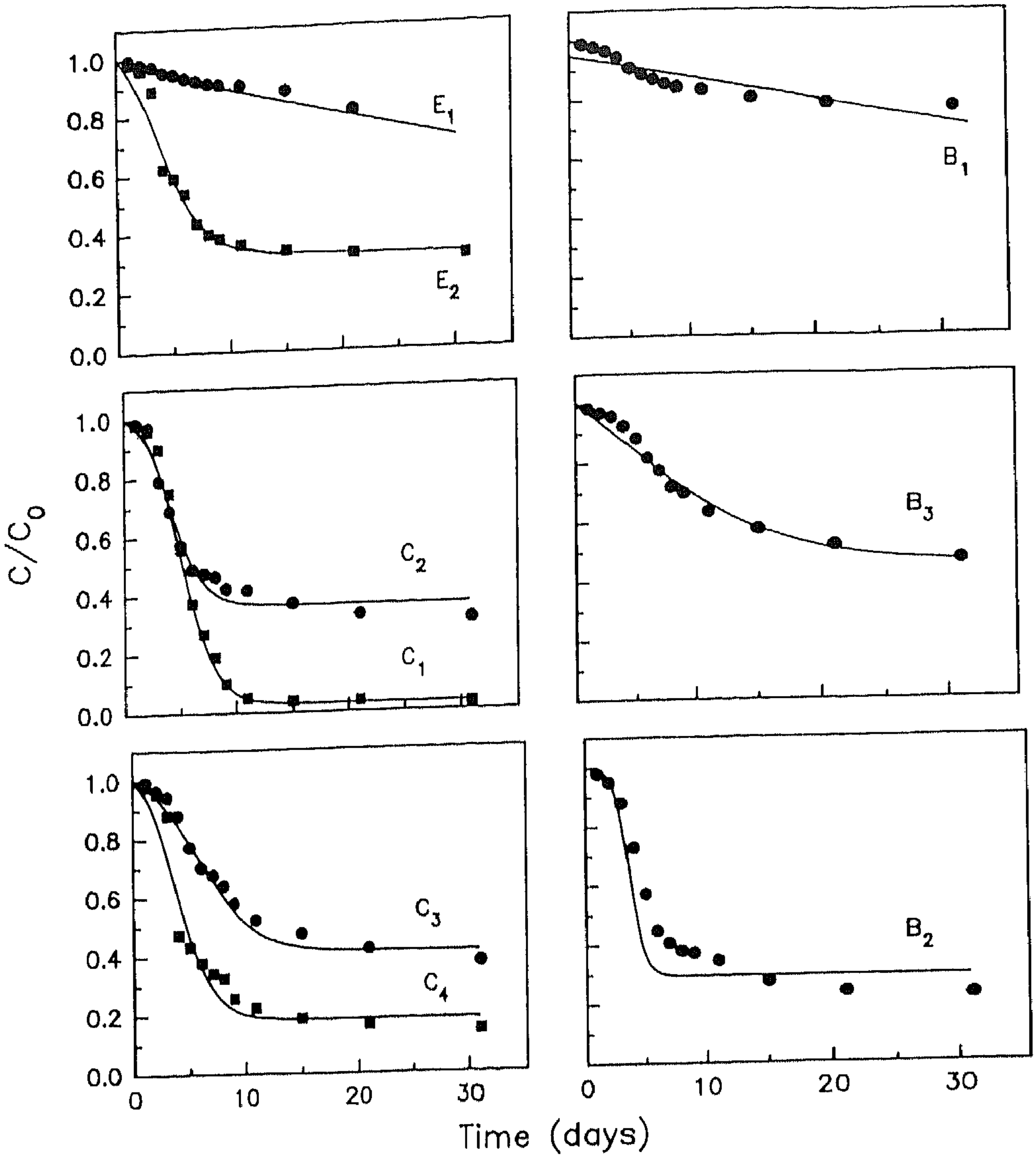

Figure 2 Residual relative quantity of surfactant (C/C_0) vs. time (C and C_0 are, respectively, actual and initial quantity of surfactant).

the peculiar environmental characteristics of the sampling point, which presents redox potential values around −400 mV. Under these strictly anoxic conditions, surfactant degradation, if any, must be carried out essentially by facultative anaerobic microorganisms. This explains the low daily degradation rate found in the tests carried out with this sediment, where 10% degradation was not attained until the 15th day.

No relationship was found between either sedimentary heavy metals and surfactant, matter degradation, or between the *a*, *b* and *d* kinetic coefficients and any other

Table 2 Values of the coefficients a, b and d, calculated according to the equation $v = aC^2 + bC + d$, for the different sediment considered $\{r$ is the regression coefficients for the integrated equations $C = f(t)\}$.

Sediment	a	b	d	r^2
E_1	0	0	21.7	0.87
E_2	$-3.23 \cdot 10^4$	0.91	−451.1	0.99
B_1	0	0	280.3	0.82
B_2	$-7.94 \cdot 10^{-4}$	2.97	−1592	0.97
B_3	$-2.23 \cdot 10^{-4}$	0.34	−999.8	0.99
C_1	$-3.50 \cdot 10^{-4}$	0.71	−39.1	0.99
C_2	$-4.58 \cdot 10^{-4}$	1.45	−887.0	0.98
C_3	$-1.92 \cdot 10^{-4}$	0.91	−864.8	0.99
C_4	$-3\text{-}65 \cdot 10^{-4}$	0.89	−275.0	0.98

parameter considered. According to Volterra[1], this suggests actual heavy metal concentrations in Cádiz Bay have no inhibiting effect on LAS biodegradation.

The results of counting of aerobic microorganisms, which are the chief operators in surfactant degradation[26,27], are shown in Figure 3. The biochemical characteristics of bacteria are described in a previous publication[28]. In Figure 3 we can also see, in most of the assays, the different stages of bacterial development during the biodegradation process: (i) lag phase, (ii) phase of exponential growth, (iii) maximum stationary phase and (iv) death phase. This tendency was not observed in the assays conducted on sediments E_1, E_2, B_1 and B_3. Sediments E_1 and B_1 did not follow this evolution since little degradation occurred and followed a zero order kinetic (Table 2: $a = 0$, $b = 0$). For sediment E_2 21 days testing the exponential growth phase of microorganisms was incomplete. In the experiments with sediment B_3, a sharp drop was noticed in the microbial load during the first few days. This may be related connected to the fact that this bacterial flora, assimilating large quantities of easily degradable organic matter from nearby urban waste outlets, adapted itself to the new substrate. The counting of anaerobic microorganisms shows that in every assay, population remains virtually unchanged during the whole degradation period.

CONCLUSIONS

The rate of surfactant degradation is remarkably high in the presence of sediment, except where the sediments are anoxic. In general, there are marked differences in the way in which the degradation process proceeds, according to the characteristics of the sediment used. The daily average degradation rate and the residual surfactant after 21 days testing, were affected by the following factors: (i) initial concentration of surfactant in the sludge, (ii) sediment proximity to the waste outlets in the area, (iii) physico-chemical conditions of the bottom, mainly the redox potential affecting the bacterial flora in the sediment, and (iv) granulometry of the type of sediment. From a kinetic point of view, LAS degradation in the presence of sediments can be

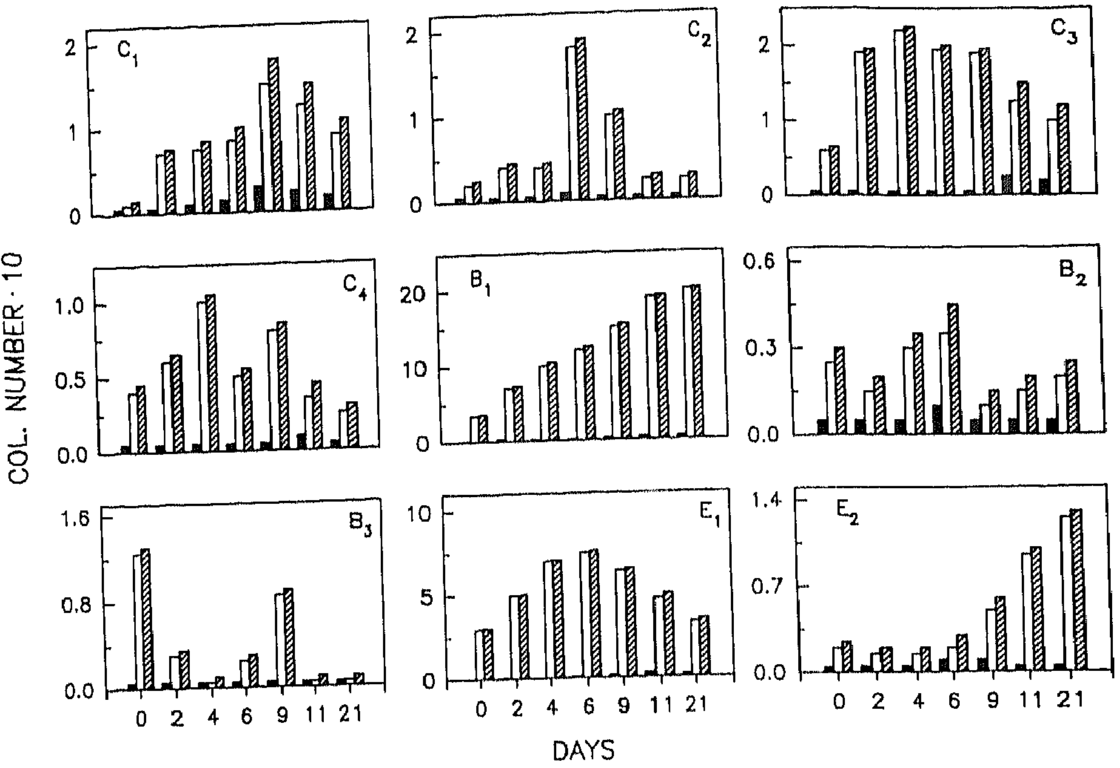

Figure 3 Number of aerobic micro-organisms during degradation vs. time.

explained taking into account the model proposed by the authors for the biodegradation of some anionic surfactants in seawater.

Acknowledgement

We are indebted to Dr. A. Marcomini for his critical review of the manuscript.

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