

C-9

BIODEGRADATION KINETICS OF LINEAR ALKYL BENZENE SULPHONATE (LAS) IN SEAWATER

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The biodegradation kinetics of commercial linear-alkylbenzene sulphonate (LAS), the major surfactant used in household detergents which was added to seawater samples originating from the nonpolluted open sea and polluted area of Rovinj harbour (Fig. 1) was investigated. Commercial LAS (Prva Iskra-Barič) contains 20 or more isomers and homologues, has an average molecular weight of 342 and an alkyl chain length of C₉-C₁₄, most of them C₁₁ and C₁₂. The biodegradation kinetics is expressed as the primary biodegradation, which was determined by the methylene blue active substance method (MBAS method, Longwell and Maniece modification) and as biodegradation of benzene-ring containing breakdown products, which was determined by the spectrophotometric method at 223 nm. Experiments were performed in batch culture under the temperature comparable to seawater temperature by using the method similar to the river water test. In order to compare the activity of bacterial culture from the polluted and nonpolluted area colony counts were performed by spreading the appropriate dilution of seawater with bent sterile glass rods on the surface of ZoBell agar. The results of biodegradation experiment were interpreted on the basis of an exponential decay model^{1,2}.

Table 1. Kinetics of primary LAS biodegradation determined by MBAS method during the batch culture experiment in seawater from Rovinj harbour.

LAS conc. (mg/l MBAS)	Temp. (°C)	Sampling location	Initial bact. conc. (CFU/ml)	Lag time (day)	Rate const. (day ⁻¹)	Half life (day)
10	9.0-10.0	harbour	130.000	8.1 ± 2.6	0.16 ± 0.08	4.3
		open sea	8.300	-	-	-
10	18.5-20.5	harbour	750.000	2.5 ± 1.2	0.57 ± 0.10	1.2
		open sea	720	-	-	-
5	15.0-18.3	harbour	640.000	2.7 ± 0.8	1.05 ± 0.05	0.7
		open sea	2.500	11.5 ± 3.4	0.38 ± 0.05	1.8
2	15.0-18.3	harbour	640.000	2.1 ± 0.1	1.10 ± 0.12	0.6
		open sea	2.500	5.8 ± 1.0	0.73 ± 0.15	1.0

- primary LAS biodegradation did not start within 30 days of experiment.

Table 1 shows that the kinetics of primary LAS biodegradation was faster in seawater from the harbour of Rovinj than in seawater from the open sea. This means that bacterial culture originating from the Rovinj harbour was more efficient in primary LAS biodegradation than the autochthonic bacterial culture in the open sea. None of the cultures was able to achieve ultimate LAS biodegradation, i.e. the biodegradation of benzene-ring containing intermediates formed by primary degradation did not start within 30 days of batch culture experiment.

Comparing the results obtained with seawater from the same location and the same initial LAS concentration (Table 1) it is evident that the half life of primary LAS biodegradation was smaller at higher temperatures. According to this fact it could be presumed that the rate of primary LAS biodegradation in seawater would be higher in summer than in winter.



Fig. 1. Rovinj harbour (Northern Adriatic) with sampling stations (A and B).

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C-10

INFLUENCE OF H₂O₂ GENERATED IN SEAWATER ON UO₂²⁺ SPECIATION

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All recent literature regards the Na[UO₂(CO₃)₃]²⁻ ion as the predominant uranium (VI) species in seawater. Values for this ionic form, as proposed by a number of workers, are around 90% of the total uranium concentration in seawater (app. 3.3 ppb).

Previous theoretical distribution studies (1) were based on the Pytkowicz model of ionic interactions among the macroconstituents of seawater (2). The distribution calculations referred to total soluble carbonate corresponding to a pCO₂ of 1 atmosphere at each pH value.

In order to obtain a closer correspondence to conditions in nature, the concept of a carbonate system for aqueous media open to atmospheric carbon dioxide at constant pCO₂, was introduced into Pytkowicz's model. This implies that the "used" or bound part of carbonate could be derived from the atmosphere. The relationships between free carbonate, hydrogencarbonate and dissolved carbon dioxide would thereby be satisfied for each pH value.

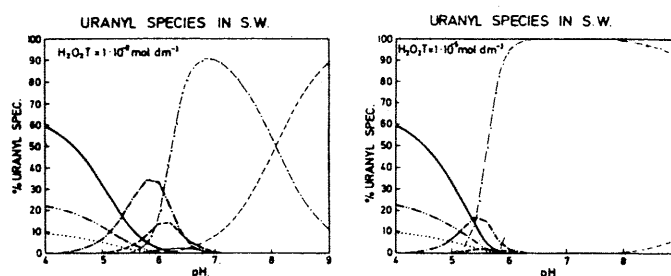


Fig. 1 and Fig. 2 pH dependant theoretical distribution curves

UO₂T = 1 × 10⁻⁸ mol dm⁻³
 pCO₂ = 0.00033 atm

--- UO₂CO₃
 — UO₂F₃
 - - - UO₂(CO₃)₃
 - - - UO₂(OH)₃
 - - - UO₂(CO₃)₂(HO₂)
 - - - UO₂SO₄
 - - - UO₂(CO₃)₂

However, recent research by Zika and coworkers (3) indicates that the ubiquitous humic material in seawater probably reduces oxygen through a photochemical process forming hydrogen peroxide in the sea. The hydrogen peroxide, generated by this mechanism, has in seawater a concentration of approximately 10⁻⁷ mol dm⁻³. Higher contents of humic material could bring the peroxide concentration in surface waters up to 10⁻⁵ mol dm⁻³.

For this reason we introduced the relevant stability constants for uranyl peroxy-carbonato (4) and uranyl hydrogenperoxy-carbonato species (5) into our model in order to estimate the possible influence of H₂O₂ on the distribution of uranyl ionic species in the photic zone of the ocean.

Calculated distributions are shown in Fig. 1 and 2. When the hydrogen peroxide concentration is 10⁻⁷ mol dm⁻³, about 50% of uranium present in seawater is in the form of the mixed uranyl carbonato-hydrogen-peroxy complex. At concentrations of 10⁻⁶ mol dm⁻³ and 10⁻⁵ mol dm⁻³ H₂O₂ respectively, 92% and 99.9% of the total uranium present should be in the form of the mixed UO₂(CO₃)₂(HO₂) complex.

The above distribution of the ionic species of uranium (VI) is compared with experimental results and will be discussed in detail.

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