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Biodegradability of Detergent Powder Surfactants in the River Water Die-A way Test*

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Abstract

A modified river water die-away test is developed for controlling the biodegradability of anionic surfactants (AS) and non-ionic surfactants (NS) of detergent powders. The tested powder undergoes a procedure replicating the washing process. An aliquot of the final solution is introduced into river water exhibiting good biodegradative ability. Primary biodegradation of both types of surfactant is monitored over 20 days and the MBAS method is used for determining AS and the indirect tensammetric method for NS.

Twelve detergent powders purchased in Polish supermarkets in 1995 are analyzed. AS in all tested powders exhibit relatively fast and complete biodegradation. NS are very diverse in terms of biodegradability: two powders had NS not satisfying the 80% biodegradability limit.

Keywords: detergent powders, biodegradation, river water die-away test, non-ionic surfactants, anionic surfactants

Introduction

A massive stream of surfactants is directed to the aquatic environment. Surfactants are probably the largest supplier of artificial organic carbon to the aquatic environment [1]. Most of the surfactants are used in the form of detergent powders [2-4], The condition for the relatively safe use of surfactants is their easy and complete biodegradation. Therefore, very strict control of the biodegradation of detergent powder surfactants is required.

A modern detergent powder is a complicated multicomponent mixture consisting of surfactants, builders (sodium phosphates, sodium carbonate, sodium silicate, zeolith), bleach (perborate, TAED, percarbonate) enzymes and auxiliaries (optical brightners, fragrance, sodium sulphate) [2]. Anionic and non-ionic surfactants are used. Normally, a detergent powder contains 20-25% surfactants. Producers are obliged by regulation to check the biodegradability of every component of a detergent powder. Surfactants used should be biodegraded at least 80% in terms of primary biodegradation. A series of screening tests is recommended for preliminary selection as well as the OECD Confirmatory test simulating dynamic conditions of sewage treatment plants as a final examination of the tested surfactant [5]. Despite such strict regulation, the Polish market offers a range of powders of poor biodegradability of surfactants [6]. One of the barriers for the successful elimination of poorly biodegraded detergents from the market may lie in their testing. However, testing a detergent powder is a more complex task than testing its components before mixing. Despite this, some form of an independent biodegradability control of producers should be organized, based on the testing of detergent powders randomly purchased in the market.

In a typical approach, components of a detergent powder under test are separated and their biodegradability checked separately. Apart from time consuming separation, chemical analysis of surfactants may also be a problem. On the one hand, anionic surfactants may be relatively easily analyzed using the relatively simple and inexpensive MBAS procedure [7, 8]. However, the analysis of non-ionic surfactants using the recommended BiAS procedure [9] is time-consuming and cumbersome and its performance requires well-trained staff. The CTAS method used in the USA is equivalent to the BiAS procedure both in terms of the detection limit as well as in time-consumption and complexity.

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* *This paper is dedicated to Professor S. Rubel on his 75 birthday.*

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The indirect tensammetric method (ITM) may be an alternative to these procedures. The ITM exhibits the detection limit by two orders of magnitude better than the BiAS or CTAS methods. Therefore, considerably smaller samples are required for analysis. The other advantage of the ITM is a high tolerance to anionic surfactants, and as a result of this non-ionic surfactants may be determined in the presence of non-separated anionic surfactants.

The aim of this work is to develop a simple screening test for the simultaneous investigation of primary biodegradation of non-ionic and anionic surfactants, without their separation prior to testing. Co-biodegradation of both types of surfactants used in formulation of detergents seems to be more adequate to the real situation in the aquatic environment than separate biodegradation. The river water die-away test was adapted for this task despite opinions that river water is relatively unstable as an inoculum. River water conditions seem to be the adequate medium representative for aquatic environments. It is worth mentioning that surface water is a direct receiver of the major stream of surfactant because only a portion of municipal sewage is biologically treated in Poland.

Prior to testing for biodegradability, a detergent powder should be treated in a manner adequate to washing (i.e. keeping the same temperature and time intervals as during real washing). This preliminary procedure will enable a bleach to be chemically degraded as in washing. The presence of such oxidants as perborates or percarbonates may seriously inhibit the biodegradation process.

Twelve detergent powders by world-known producers, available on the Polish market and purchased in supermarkets in Poland in 1995, were tested. The authors of this work are conscious that formulations of detergents may be changed and that the recent biodegradability of powders which sell under the same trade mark may be different. Therefore, this work served as a possible approach to the question of the control of the biodegradability of detergents rather than an evaluation of the recent situation in this area.

Materials and Methods

Twelve detergent powders purchased in supermarkets in Poland in 1995 were tested. They are shown in Table 1. However, names were hidden and only randomly selected numbers were used.

Table 1. List of tested detergent powders.

ARIEL	Procter and Gamble
BRYZA	Benckiser
DIXAN	Henkel
E-AUTOMAT	Cussons
E-TAED	Cussons
LANZA	Benckiser
OMO LIPOSYSTEM	Lever
ORION SUPER	Henkel
POLLENA 2000	Lever
PERSIL	Henkel
TORNADO	Benckiser
VIZIR	Procter and Gamble

Water from the River Warta in Poznan, showing normal biological activity, was used as inoculum. One sample of river water was used for testing three detergent powders. The same water was also tested for biodegradation of "native" surfactants of river water. All the twelve tested detergent powders were further investigated using four different, though very similar river water samples. The fifth water sample was also used as an inoculum in auxiliary experiments.

The tested detergent powder was processed according to the scheme shown in Figure 1. It was dissolved in distilled water at a concentration recommended for washing by its manufacturer. The solution was heated to 60"C over 50 minutes, simulating the washing process. An aliquot of cooled solution corresponding roughly to 1 mg•l^{-1} of non-ionic surfactants was introduced into 10 litres of river water. Samples for analyzis were taken each second day, preserved by an addition of 1 % of formaline and analyzed for concentration of anionic and non-ionic surfactants.

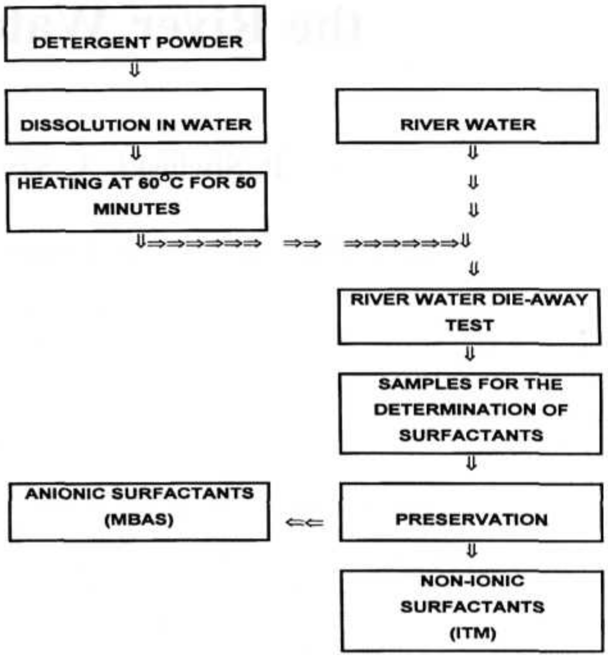

Fig. 1. Outline of the initial steps of the procedure.

The determination of anionic surfactants was performed according to the MB AS method [7]. A Carl-Zeiss Jena Specord M40 UV-VIS spectrophotometer and a Spectrocolorimeter SPECOL (also Carl-Zeiss) were used. The measurement of absorbance was performed at λ = 652 nm using sodium dodecylbenzene sulphonate as a standard.

The determination of non-ionic surfactants was performed using the indirect tensammetric method [10, 11]. A Radelkis OH-105 polarograph and ECO Chemie General Purpose Electroanalytical System µAUTOLAB were alternatively used for tensammetric measurements. A usual mode of measuring without phase sensitivity, a frequency of 60 Hz, a superimposed alternating voltage amplitude of 2 mV and a scan voltage rate of 400 mV min^{-1} were applied. Controlled-temperature Hanging Mercury Drop Electrode equipment (Radiometer), with an additional platinum wire auxiliary electrode, was used. A quartz (instead of glass) beaker and protection of a ceramic frit on the end of a salt bridge were applied to prevent adsorptive loss of surfactant [12].

The procedure for the determination of non-ionic surfactants in water or sewage samples was previously described [11]. Briefly, sodium chloride and sodium hydrogen carbonate were dissolved in the sample and non-ionic surfactants were extracted from the sample using two portions of ethyl acetate. An aliquot or whole extract was evaporated, the residue redissolved in a precisely measured 1.5 ml of ethyl acetate and introduced into a measuring cell already containing 0.5 M sodium sulphate base electrolyte. The tensammetric curve of ethyl acetate was recorded in the cathodic direction starting from -1.20 V vs. SCE, after dissolving of ethyl acetate and evaporation of residual droplets. The difference between the height of the peak of ethyl acetate (recorded in a separate measurement) and the peak height of ethyl acetate in the presence of NS was the analytical signal. The results were quantified using a calibration curve of Triton X-100.

Purified sodium sulphate and sodium chloride were used. All solutions were prepared in water triply distilled from a quartz apparatus. Only freshly distilled water was used.

Only freshly distilled ethyl acetate and chloroform purified by distillation were used. Other reagents were of Analar grade.

Results and Discussion

Five different river water samples were used as inoculum in the experiments. Each of them was taken at a different period of time and may differ from the others in terms of biodegradative power. In order to check and compare this power, die-away experiments with "native" surfactants of river water were performed. River water contains both anionic and non-ionic surfactants due to pollution, called in this work "native" surfactants. These "native" surfactants also undergo biodegradation and the pattern of this process may serve as a measure of the biodegradative power of a given sample of river water.

To check the biodegradation of "native" surfactants, the experimental water samples were left for 20 days and the analytical samples were taken at intervals of several days. These analytical samples were preserved with 1% formaline and analyzed for concentration of anionic and non-ionic surfactants. The results for anionic surfactants are given in Figure 2, and those for non-ionic surfactants in Figure 3.

All samples, independent of initial concentrations of both types of "native" surfactants showed relatively rapid decay of concentration of surfactants, which is a symptom of their good biodegradative power. A relatively small difference in the patterns of biodegradation curves and in the levels of concentrations of "native" surfactants is observed for different water samples used as inoculum. The decay of concentration is more pronounced for non-ionic than for anionic surfactants. The reason may be a more sensitive analytical method used for the determination of non-ionic surfactants. It is worth mentioning that this kind of die-away curve for "native" non-ionic surfactants is only possible using the ITM for their analysis. However, the simple version of the MBAS used for the determination of anionic surfactants is not sensitive enough to record precisely the changes of concentration at such a low level.

In order to check where any differences exist in the biodegradation of tested detergent powders due to differences in the inoculum used, one of the tested powders was investigated twice, using two different river water samples as an inoculum. The results are given in Figure 4. The pattern for the biodegradation of anionic surfactants (empty points) changes when different water is used as inoculum. A similar conclusion may be drawn for non-ionic surfactants (filled points). However, the changes caused by the use of a different inoculum are relatively small and do not affect the conclusion that:

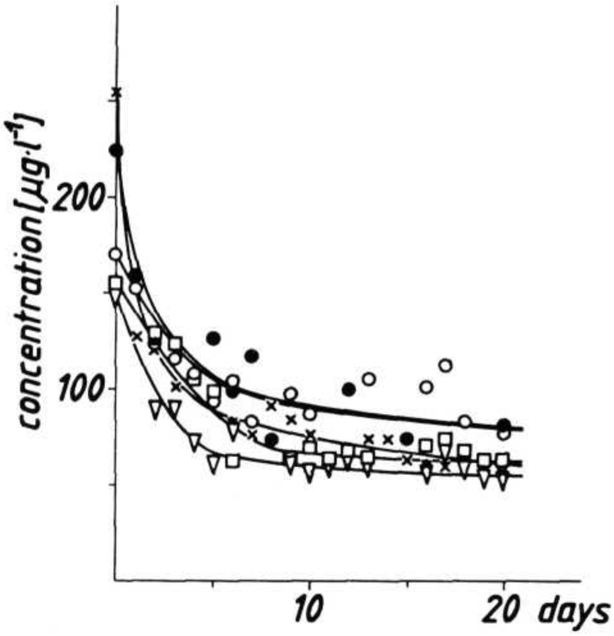

Fig. 2. Die-away curves of anionic surfactants for five different river water samples (the River Warta, Poznań) used as an inoculum in the experiments.

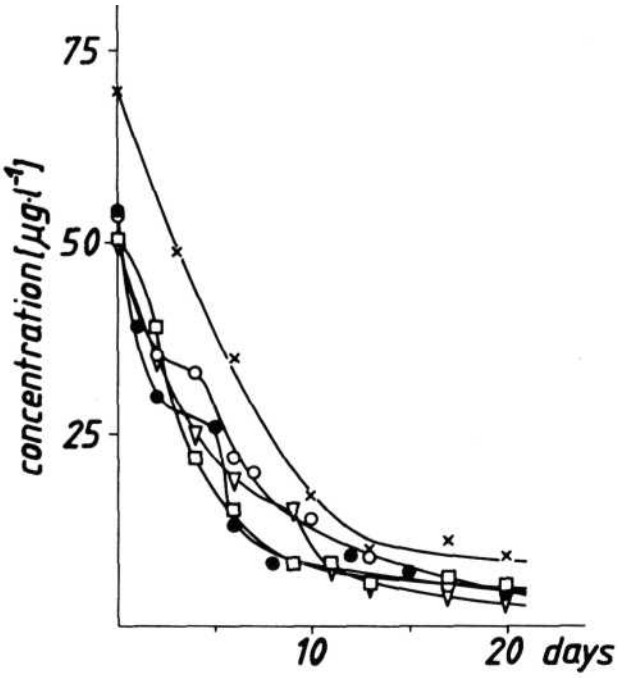

Fig. 3. Die-away curves of non-ionic surfactants for five different river water samples (the River Warta, Poznań) used as an inoculum in the experiments.

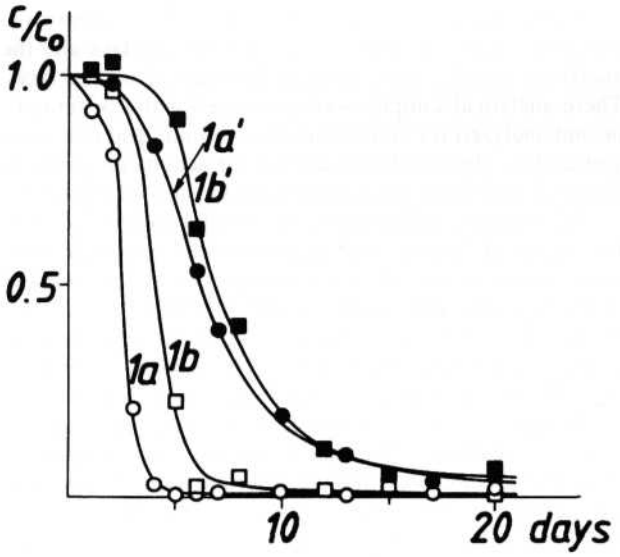

Fig. 4. Die-away curves of anionic surfactants (la and lb, empty points) and non-ionic surfactants (la' and lb', filled points) of detergent powder 1 (number randomly selected and not related to the sequence of powders in Table 1) in two different samples of river water used as inoculum (both the River Warta, Poznari).

i) both anionic and non-ionic surfactants are relatively quickly and completely biodegraded, and

ii) the biodegradation of anionic surfactants moves more speedily than the non-ionic one.

The main experiments were performed with 12 detergent powders in four groups corresponding to four water samples used as inoculum. The results were completed for each group separately and are shown in Figures 5-8.

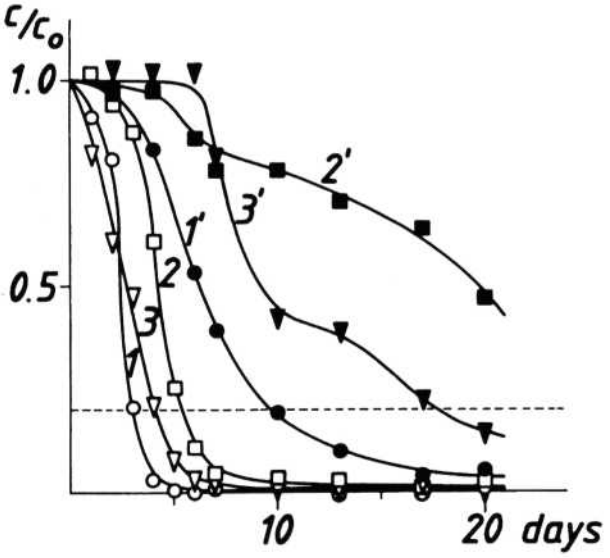

Fig. 5. Die-away curves of anionic surfactants (1, 2 and 3, empty points) and non-ionic surfactants (I', 2' and 3', filled points) of detergent powders 1, 2 and 3 (numbers randomly selected and not related to the sequence of powders in Table 1). The initial concentrations of anionic surfactants (mg•l^{-1}): (1) 4.76, (2) 4.19, (3) 4.98 and non-ionic surfactants: (1') 1.28, (2') 1.54, (3') 1.70. 80% biodegradation level is indicated by the dashed line.

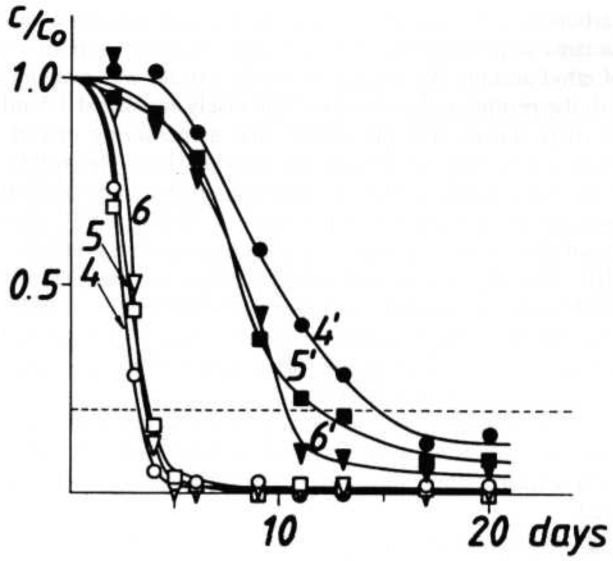

Fig. 6. As Figure 5 for powders 4, 5 and 6. The initial concentrations of anionic surfactants (mgl^{1}): (4) 3.47, (5) 4.26, (6) 3.19 and non-ionic surfactants: (4') 1.20, (5') 1.14, (6') 1.20.

In all instances anionic surfactants were complete and more quickly biodegraded than non-ionic surfactants. The biodegradation of non-ionic surfactants under these conditions is very divergent. Some of them were biodegraded easily and almost completely (powders 1,6, 11 and 5). The residual concentration on day 20 of the experiment was below 8% of the initial value. The others were biodegraded relatively slowly and incompletely (powders 3, 8, 10, 12 and 4). However, an 80% limit of primary biodegradation of non-ionic surfactants on day 20 of the experiment was satisfied in these cases. In one case (powder 8) initially relatively fast biodegradation stopped just on the boundary of 80 % of its biodegradation. Non-ionic surfactants of two other investigated powders were hardly biodegraded (powders 2 and 9) and the residual concentration on day 20 of the experiment was still of 37-47%. It is worth stressing that even the best pattern for non-ionic surfactants was

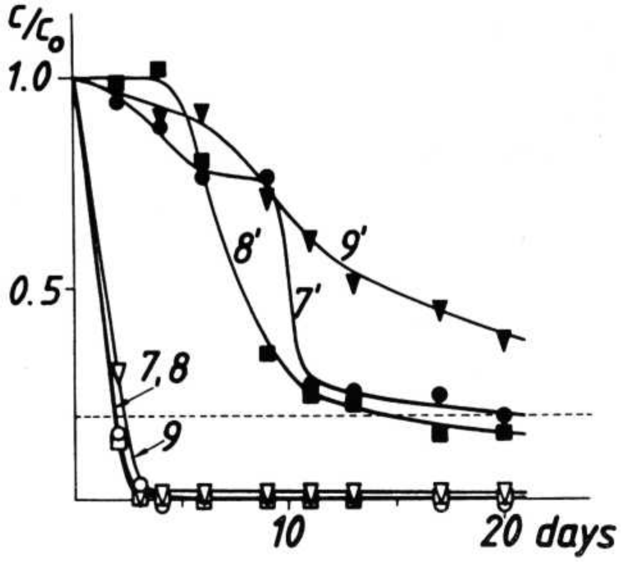

Fig. 7. As Figure 5 for powders 7, 8 and 9. The initial concentrations of anionic surfactants (mg•l^{-1}): (7) 4.98, (8) 3.19, (9) 3.55 and non-ionic surfactants: (7') 1.34, (8') 0.98, (9') 1.20.

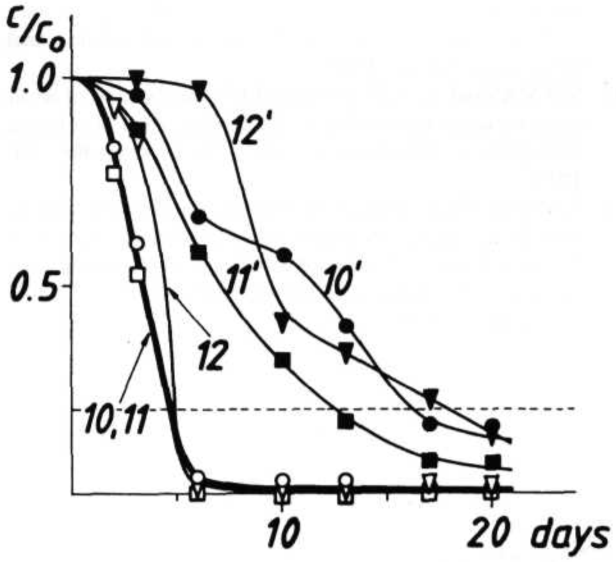

Fig. 8. As Figure 5 for powders 10, 11 and 12. The initial concentrations of anionic surfactants ($mg \cdot l^{-1}$): (10) 6.70, (11) 4.33, (12) 6.12 and non-ionic surfactants: (10') 1.63, (11') 1.13, (12') 1.68.

slower than any pattern of the tested anionic surfactants. Apart from the degree of primary biodegradation at the end of the test (day 20) the biodegradation curves shown in Figs. 5-8 allow for the evaluation of a number of stages of the primary biodegradation process, the determination of adaptation time of microfauna to tested surfactants as well as the prediction of the tendency of the further biodegradation of the residual surfactant beyond day 20 of the experiment.

All anionic surfactants and the majority of non-ionic surfactants of the tested powders show one-stage primary biodegradation. However, non-ionic surfactants of powders 2, 7 and 10 exhibit biodegradation in two stages. The presence of two non-ionic surfactants may be the reason for this phenomenon as well as the complicated pathway of a single component with inhibition of the further process by metabolites of biodegradation. Significantly non-ionic surfactants showing a two-stage primary biodegradation pattern can be classified as hardly or moderately biodegraded.

The adaptation time of anionic surfactants was relatively short - most frequently 2-3 days - while that for non-ionic surfactants was longer - usually 5-8 days - with the exception of non-ionic surfactants showing a two-stage pattern. Generally, the shorter adaptation time the more advanced primary biodegradation. The case of powder 2 shows that a poor biodegradation of non-ionic surfactants may be followed by a longer adaptation time of the anionic surfactant.

The pattern of primary biodegradation may allow for the prediction of further biodegradation of the surfactant beyond day 20 of the experiment. It may be predicted that the achieved level of biodegradation for non-ionic surfactants of powders 1, 4, 5, 6, 7, 8, 10 and 11 will not change substantially during the additional few days of the experiment. It seems to be a significant prediction for powders 7 and 8 whose non-ionic surfactants only achieved the required minimum of biodegradation. The hardly biodegraded non-ionic surfactants of powder 9 (Fig. 7) showed no tendency to achieve the 80 % limit of biodegradability during the further period. Contrary to powder 9, the non-ionic surfactants of powder 2 show the tendency to be accelerated during the further period. More advanced biodegradation of non-ionic surfactants of powders 3 and 12 in further days may also be expected.

It is necessary to emphasize that the differences which may be caused by the use of a different inoculum do not seem to be decisive. For example, powders 1, 2 and 3 (see Fig. 5) show very divergent biodegradability of their non-ionic surfactants, despite the fact that the same water sample is used as an inoculum: non-ionic surfactants of powder 1 are quickly and almost completely biodegraded, those of powder 3 are biodegraded slowly and incompletely (but still satisfying the 80% limit), while that of powder 2 is completely unsatisfactory. The measure of the possible role of an inoculum is the difference between curves 1 and 1' in Fig. 4. It is clear that the differences between curves 1, 2 and 3 in Fig. 5 (caused by differences in the biodegradability of non-ionic surfactants of tested detergent powders) are much bigger than the differences related to the use of different water samples as an inoculum (compare curves 1 and 1' in Fig. 4). However, the inoculum may have an influence on the value of adaptation time.

Conclusions

1. A relatively simple test for the simultaneous determination of primary biodegradation of anionic and non-ionic surfactants of detergent powders was developed
2. In the tested detergent powders:
   - anionic surfactants were much more easily biodegraded than non-ionic surfactants,
   - non-ionic surfactants were very divergent in terms of biodegradability; two of twelve investigated powders had non-ionic surfactants not satisfying the limit of 80% biodegradability
3. Die-away testing of "native" non-ionic surfactants of river water may be used as effective measure of the biodegradative power of the water.

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