Biodegradation of Synthetic Detergents Evaluation by Community Trials Part 2: Alcohol and Alkylphenol Ethoxylates

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ABSTRACT

The biodegradability of ethoxylates based on synthetic primary alcohols and on iso-octylphenol has been evaluated by field trials with a trickling filter sewage treatment plant serving a small community. Ethoxylates based on synthetic alcohols showed good biodegradability in the trickling filter even in winter. This is in line with laboratory tests. Effluents were practically nonfoaming and on further aeration an ultimate biodegradability of 99% was achieved. Ethoxylates based on iso-octylphenol biodegraded in winter to an extent of some 20% only. In summer, values as high as 80% were obtained. In general however ethoxylates of this type cannot be considered biodegradable. Effluents showed a considerable tendency to foam even under summer conditions.

INTRODUCTION

In Part I of this paper (1) we described the community trials carried out to evaluate the biodegradability of a range of alkylbenzene sulphonates. The present work extends the trials to cover ethoxylates based on synthetic primary alcohols and on iso-octylphenol.

Most workers have found ethoxylates, based on linear primary alcohols, to be readily biodegradable in laboratory biodegradation tests. Our own laboratory tests also showed these materials to be highly biodegradable but we wished to confirm this by trials conducted under practical sewage treatment conditions.

Published evidence concerning the biodegradability of branched chain alkylphenol ethoxylates is conflicting. The majority of workers have found in laboratory-scale tests that these materials are not biodegradable (2-7). Other workers, using both laboratory-scale and practical-scale tests have found them to be biodegradable (8-12). Swisher (13) attributes the main causes for these discrepancies to (1) failure to provide sufficiently for bacterial acclimation and (2) failure of the cobalti-thiocyanate analytical method to respond to biodegradation intermediates which still show substantial foaming and other surface activity. We wished to establish the order of biodegradation obtained on a material of this type under practical sewage treatment conditions with acclimatization already established and where the method of analysis was based on the thin layer chromatographic procedure of Patterson et al. (14).

TABLE I

Biodegradation of Dobanol 25-9

Date	Nonionic, mg/l		Per cent biodegraded
	Settled sewage	Effluent	
Jan. 3	4.2	0.6	86
17	5.5	0.5	91
18	5.5	0.5	91
24	7.0	0.9	87
25	7.0	0.9	87
31	7.0	1.0	86
Feb. 1	7.0	1.0	86
7	7.0	0.8	89
8	7.0	0.8	89
14	7.0	0.5	93
15	7.4	0.7	91
21	12.0	1.0	92
22	9.5	1.0	90

EXPERIMENTAL PROCEDURES

Conduct of the Trials

The community trials were conducted in the small trickling filter sewage treatment plant at Preston used in the trials described in Part I (1). The sampling and analytical work were done by the Water Pollution Research Laboratory (WPRL) using the same methods as in the previous trial.

An additional analytical method was required in these trials for determination of trace quantities of nonionics in the influent and effluent sewage streams. The WPRL employed the thin layer chromatographic procedure developed by Patterson et al. (14) which was found to be satisfactory for this analysis.

Materials Examined

Alcohol ethoxylates: Two ethoxylates derived from synthetic primary alcohols were employed in the trials. One of these was an ethoxylate containing nine oxyethylene groups per molecule, based on Dobanol (Shell trademark known as Neodol in U.S. and Canada) 25, a C_{12}-C_{15} alcohol with an average molecular weight of 207. Dobanol 25 is a synthetic primary alcohol mixture consisting of about 75% normal primary alcohols and 25% isomeric 2-alkyl (predominantly 2-methyl) primary alcohols. Its carbon number distribution is typically 20/30/30/20% of $C_{12}/C_{13}/C_{14}/C_{15}$.

The other ethoxylate contained an average of eight oxyethylene groups per molecule, based on Dobanol 91, a C_9-C_{11} alcohol with an average molecular weight of 160. Its normal and isomeric primary alcohol content is similar to that of Dobanol 25 and its carbon number distribution is 22/48/30% of $C_9/C_{10}/C_{11}$.

For simplicity these ethoxylates are referred to in the text as Dobanol 25-9 and Dobanol 91-8 respectively.

Alkylphenol ethoxylates: Two ethoxylates based on octylphenol were also used. The octylphenol base material was derived from diisobutylene giving the predominant alkyl structure 1,1,3,3-tetramethylbutyl.

These ethoxylates are sold under the trade names (Shell)

TABLE II

Biodegradation of Dobanol 91-8

Date	Nonionic, mg/l		Per cent biodegraded
	Settled sewage	Effluent	
Jan. 15	12.5	2.5	80
22	10.0	1.7	83
23	10.0	1.5	85
29	9.0	1.3	86
30	10.0	1.0	90
Feb. 6	10.0	2.0	80

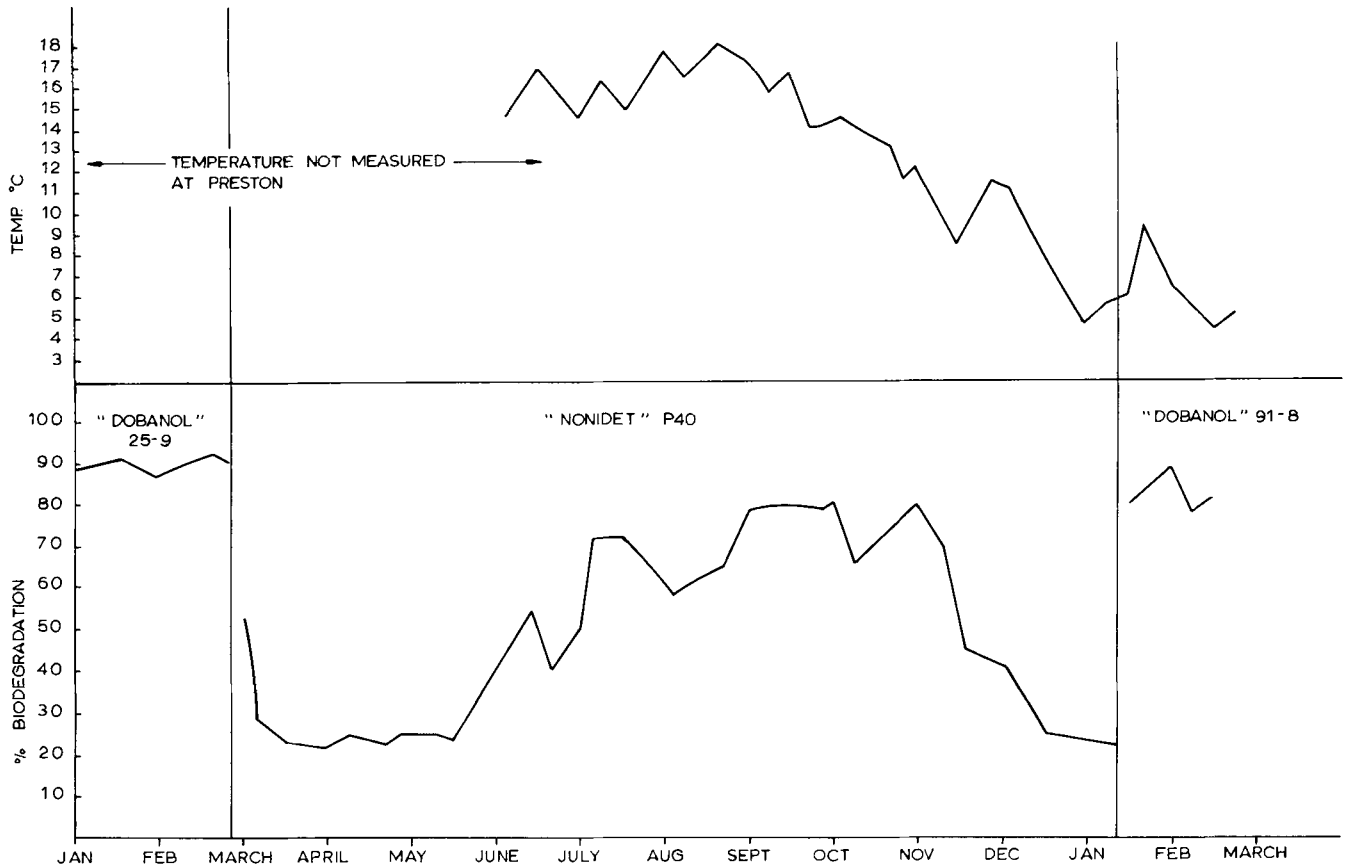

FIG. 1. Biodegradation of nonionic detergents in trickling filter.

of Nonidet P40 and Nonidet P100. Nonidet P40 has an average of 8-9 oxyethylene groups per mole and Nonidet P100 has an average of 14-15 groups per mole.

The nonionic detergents described above were distributed to the householders as a component of dishwashing liquids. The dishwashing liquids were blends containing 21 parts weight anionic detergent to 9 parts nonionic detergent with small additions of ethanol, sodium chloride or urea to achieve satisfactory physical properties.

Schedule of Trials

In the 20 months prior to detailed study of nonionic biodegradation, Nonidet P40 and Nonidet P100 were used as the nonionic components of the dishwashing liquid. Only a few analyses for nonionic surfactants were carried out on the sewage and effluent during this period: the results obtained are discussed later (see alkylphenol ethoxylates).

In the first comprehensive trial to study nonionic biodegradation we used Dobanol 25-9. Before starting this trial we attempted to wash out all traces of the previously used alkylphenol ethoxylate from the trickling filter by omitting this component from the trickling filter for a 5 week period. We were only partially successful because, at the end of this time, we could still detect about 0.2 mg/l nonionic in the settled sewage and effluent. Nevertheless we proceeded to test Dobanol 25-9 for a 9 week period of the winter.

An extended trial with Nonidet P40 followed, lasting for the remainder of that winter until about the middle of the following winter.

Dobanol 91-8 was tested for a 6 week period immediately following the Nonidet P40 trial.

RESULTS AND DISCUSSION

Dobanol 25-9

The trial with Dobanol 25-9 covered nine weeks of January and February. The results are shown in Table I.

The average value for biodegradation over the test period was 89%.

Dobanol 91-8

The trial with Dobanol 91-8 was conducted during January/February of the following year. The results are shown in Table II.

The average value for biodegradation over the 6 week period was 84%.

Alkylphenol Ethoxylate

In the earlier trials, for evaluating biodegradibility of the alkylbenzene sulphonates (1), Nonidet P100 was used as a component of the dishwashing liquids distributed to the villagers. The bacteria in the trickling filter thus had ample time (nine months) to acclimate to this ethoxylate before the first determinations of nonionic content were made. The first three determinations were made between March and the beginning of May and the results obtained indicated a low order of biodegradability (5-25%). This seemed to confirm conclusions that we and other workers had drawn from laboratory-scale tests, that alkylphenol ethoxylates were not biodegradable. However a much higher level of biodegradability (64%) was recorded in July. Then we replaced Nonidet P100 by Nonidet P40 and obtained results of 70% to nearly 90% removal in September and October. These levels of biodegradability of Nonidet P40 were far higher than we had ever found in laboratory-scale tests.

We were puzzled however as to why the earlier results on Nonidet P100 should have been so low in a presumably acclimated system. The only clue to the reason for this anomalous behavior lay in the fact that the low results were obtained in spring or early summer, whereas the high levels were recorded during summer and early autumn. We therefore tentatively concluded that climatic conditions

TABLE III

Comparison With Laboratory Tests

Product	Per cent biodegraded		
	Die-away test[a]	Activated sludge laboratory test[b]	Community trials
Dobanol 25-9	99	95-98 (three tests)	89
Dobanol 91-8	—	97-98 (two tests)	83
Nonidet P40	10	20	—
Nonidet summer	—	—	ca. 80
Nonidet winter	—	—	ca. 20

have a significant effect on biodegradation of these nonionics, much more so than on anionic detergents whose biodegradability is not much different in summer and winter (1). We decided to test this hypothesis by running a prolonged trial to measure biodegradability of Nonidet P40 throughout almost a complete year. The prolonged trial began in the winter (late February) following the Dobanol 25-9 trial, and continued to the following January. The results obtained are shown graphically in Figure 1 which also shows filter bed temperatures throughout the year.

Figure 1 shows clearly a gradual increase in biodegradability of Nonidet P40 from an average of about 26% in March to May to a level of about 80% in late August, September and October. During November and December biodegradation fell dramatically, until by the end of the trial in January it was again only about 20-25%. The reduction in biodegradation corresponded with a fall in temperature of the sewage and the filter bed from about 15 C to 5 C in the same period.

Two possible explanations are advanced for this behavior: (1) The bacteria in the trickling filter which are capable of degrading alkylphenol ethoxylates in the summer are absent or dormant in the winter; (2) The rate of bacterial film growth on the filter is affected by climatic changes and alters the characteristics of the sewage treatment process, for example residence time of sewage in the filter.

We have not attempted to find out by experiment which of these alternatives is true; perhaps both mechanisms play some part in the overall result. Our observation that biodegradation rose from ca. 50% in June to 80% in September, although during this period the sewage and filter bed temperatures were relatively constant, would seem to indicate that the bacteria required considerable time to acclimate to the detergent. This might suggest that we are dealing with a new bacterial population, not one that had remained dormant over the previous winter and which might be expected to be already acclimated.

Whatever the explanation for the variation in biodegradability on Nonidet P40 between summer and winter in the Preston trial, the fact remains that this ethoxylate, unlike the alcohol ethoxylates, was inadequately removed across the trickling filter in winter. Therefore on the basis of this evidence, Nonidet P40 must be regarded overall as "not biodegradable." It is a matter of conjecture whether its behavior in the Preston plant was typical of what might occur in other, larger filters or in activated sludge plants in which temperature variations in the plant may be less than in the small filter bed at Preston.

The data very clearly show the superior biodegradability of the alcohol ethoxylates to Nonidet P40 under winter conditions. In Figure 1 it is seen that, in the January/February period when Dobanol 25-9 was replaced by Nonidet P40 the biodegradability fell immediately from the 90% region down to the order of 20-30%. Conversely, the following winter when Nonidet P40 was replaced by Dobanol 91-8 the biodegradability rose immediately from 20-30% to the 80-90% region.

Biodegradation on Further Aeration

Periodically samples of effluent were taken to the laboratory and aerated for 28 days at 20 C. In these tests the alcohol ethoxylate Dobanol 91-8 reached an ultimate biodegradability of 99% compared with 84% under practical winter conditions.

Nonidet P40 effluents, even those sampled in winter when practical biodegradability values were below 30%, degraded in the laboratory to an average of 93%. The higher laboratory temperature probably contributed to this higher level of biodegradation but, as shown by the results in Table III, Nonidet P40 shows a low level of biodegradation in some die-away tests even at 20 C.

Comparison with Laboratory Tests

Table III compares the results obtained in the trials with those obtained using the following laboratory tests: (1) Simple die-away test at 20 C. This test was similar to the standard test of the British Standing Technical Committee on Synthetic Detergents (15) except that clear sewage effluent was used as inoculum instead of dried activated sludge. (2) Continuous activated sludge test as prescribed by German law (Husmann test).

It is seen that the winter community trials give results for Dobanol 25-9 and Dobanol 91-8 somewhat lower than those obtained by laboratory tests. This could be due to low filter-bed temperatures in the practical trial and presence of traces of alkylphenol ethoxylates referred to earlier. On further aeration at 20 C results more in line with laboratory tests are obtained.

Low values for biodegradability were obtained on Nonidet P40 in both laboratory tests. It is of interest however to note behavior of this material in the activated sludge laboratory test. When conducted in the normal way biodegradation of the order of 20% was obtained over a period of 46 days. At this point activated sludge taken from a municipal sewage treatment works in winter was added to the sludge normally developed in the test by airborne bacteria. An immediate rise to biodegradation in the 80-90% region occurred. This indicates that some strains of bacteria in the added sludge become active at laboratory temperature, but such strains are not present in the normal airborne seeding.

Foaming Property of Effluents

The tendency of an effluent to foam was evaluated by a standard method (16) in which air is passed through the effluent contained in a cylindrical vessel and the foam height measured. This provided a rough comparison of the relative foaming tendency of different effluents.

The trials with ethoxylates were conducted during periods when the anionic detergent employed consisted of alkyl sulphates based on either synthetic or natural alcohols: the alkyl sulphates were highly biodegradable and detailed results are reported in Part III of this paper. Effluents containing residual alkylphenol ethoxylate showed considerable tendency to foam even in summer

(10-12 cm foam height). Those with only residual alkyl sulphate or alkyl ethoxylate were practically nonfoaming (0-2 cm foam height).

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