Studies on Detergent Phosphate Replacements: I. Aerobic Biodegradation of Sodium 2-Hydroxyethyliminodiacetate

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ABSTRACT

The biodegradation of sodium 2-hydroxyethyliminodiacetate, a potential substitute for detergent phosphate, has been studied under aerobic conditions. The biodegradation of this material has been demonstrated in both river water die-away tests and in an activated sludge system which approximated an actual municipal sewage treatment plant. In the latter instance, degradation in excess of 90% has been observed in less than 6 hr.

INTRODUCTION

With the increasing concern over the eutrophication of our lakes and waterways, the development of nonpolluting substitutes for detergent phosphates acquired great significance. As a class, organic sequestering agents offer the greatest potential for yielding an acceptable altenative, and, even within this class, the number is limited. It has been well established (1) that the groups having important coordinating functions are, in order of decreasing affinity for metal ions, the following: the enolate ion, the amine group, the diazo group, a ring nitrogen, the carboxylate group, the ether group, and the carbonyl group. In addition, sulfonic acid, phosphonic acid, and hydroxyl and sulfhydryl groups may function as secondary donor groups.

The group of compounds which probably has received the greatest attention are the aminocarboxylic acids. A number of these materials has been commercially available for many years, however, economic considerations had limited the choice to nitrilotriacetic acid (NTA). When the teratogenic and mutagenic acceptability of NTA was questioned, the search was extended to other compounds of this class. It has been demonstrated that the amino acids derived from polyamines are not sufficiently biodegradable to be of interest (2). Of a list of 13 substitution derivatives of iminodiacetic acid investigated by Schwarzenbach (3), only 2 possessed desirable chelation properties and appeared to have the potential of being produced in commercial quantities at a cost commensurate with this application. These two compounds were acetamidoiminodiacetic acid and 2-hydroxyethyliminodiacetic acid, the disodium salts of which are, hereafter, referred to as SAND and HEIDA, respectively.

Studies were initiated to gather appropriate data related to these materials to provide a basis for assessing their potential as detergent builders. The results of these studies indicated that both of these materials were similar to NTA in their chemical, physical, and toxicological properties. This, along with an Environmental Protection Agency sponsored report (4), shows both to be possible substitutes for detergents phosphates. For a variety of developmental reasons beyond the scope of this paper, further studies were limited to HEIDA.

A major contributing factor leading to discontinuation of the use of NTA was the fear that, under certain conditions, it would not biodegrade and, thus, build up in the environment to levels at which it might pose a health hazard. With this in mind, the biodegradation of HEIDA was investigated under both aerobic and anaerobic conditions. The present paper deals with the aerobic biodegradation of this material; the anaerobic degradation studies will be reported in a later publication.

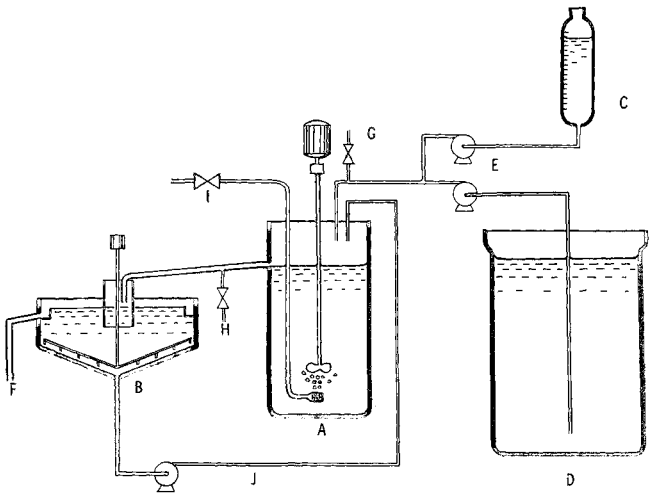

FIG. 1. Model activated sludge system: A. Aerator sludge bed. B. Clarifier. C. Concentrated 2-hydroxytethyliminodiacetate feed. D. Sewage feed tank. E. Metering pumps. F. Final effluent. G. Inlet sample. H. Outlet sample. I. Air supply.

EXPERIMENTAL METHOD

The aerobic degradation of HEIDA was studied in both a river water die-away test and in an activated sludge system. The river water die-away test (5,6) employed the simple technique of obtaining 1 liter samples of 3 river waters: the Lehigh River, which is subject to the impact of heavy industry; the Delaware River, at a location which coincides with a municipal water supply; and the Little Lehigh Creek, which is a popular trout fishing stream. Each of the waters was inoculated with 20 ppm C-14 tagged HEIDA and incubated at room temperature. No effort was made to exclude air, nor was any effort made to fortify the water with additional nutrients or bacterial seeds. Periodically, the waters were stirred well, and a sample taken for analysis.

Of equal or greater interest is the fate of HEIDA in a sewage treatment system. To this end, a model activated

TABLE I

Performance of Activated Sludge System

Operating parameters	Sludge bed residence times 5.6 hr	12.0 hr
Biological oxygen demand (BOD):		
Inlet BOD, ppm	150-190	
Outlet BOD, ppm	20-25	
BOD removal, %	85-87	
Ammoniacal nitrogen		
Inlet NH_3, ppm	25	
Outlet NH_3, ppm	<0.5	
pH		
Inlet pH	7-8	7-8
Outlet pH	7-8	7-8
Dry sludge concentration of bed, ppm	1500-2000	600-800
Feed rate, liters/hr	0.75	0.36
Recycle rate, liters/hr	0.75	0.36

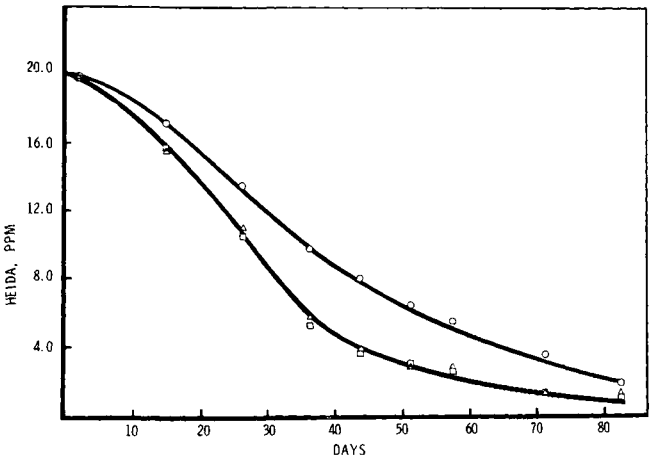

FIG. 2. Results of river water die-away tests. ○ = Little Lehigh Creek, □ = Lehigh River, and △ = Delaware River. HEIDA = 2-hydroxyethyliminodiacetate.

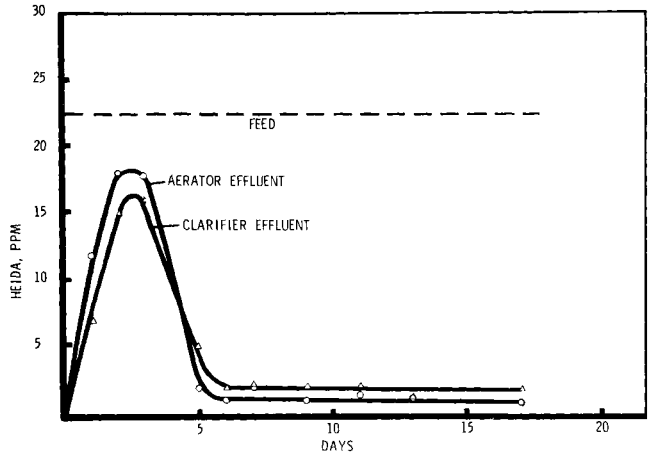

FIG. 3. Acclimation and biodegradation of 2-hydroxyethyliminodiacetate (HEIDA) in an activated sludge system.

sludge system (Fig. 1) was constructed and operated on a continuous flow-through basis at room temperature (22 C). The raw sewage feed stock was pumped into the aerator at a rate sufficient to yield a residence time of 5.6 hr. Aeration of the sludge bed was accomplished with air blown through fritted glass spargers at a rate in excess of stoichiometric requirements. A propeller stirrer was used to ensure good dispersion of both sludge and air bubbles. The overflow from the bed passed to a clarifier equipped with a continuous rake, which provided adequate separation and collection of sludge for recycle to the aeration bed. The clarified overflow was the final effluent.

HEIDA was introduced into the system by pumping a concentration feed solution prepared with distilled water into the sewage feed stream at a rate sufficient to maintain the desired concentration entering the sludge bed. This rate was never greater than 1/50 of the sewage stream so as to avoid any significant dilution effects upon the biochemical oxygen demand (BOD) loadings. A concentrated HEIDA solution of 1000 ppm was used to maintain a HEIDA concentration of 20-25 ppm in the feed. On a routine basis, samples of the feed, aerator effluent, and clarifier overflow were taken and analyzed for HEIDA.

The system was started with stock from the activated sludge beds of the Municipal Sewage Treatment Plant of Pottstown, Pa., and was operated continuously for 250 days. The raw sewage feed was obtained from the Bethlehem Municipal Sewage Treatment Plant and replenished every second day. Fifteen days were allowed for formation of a viable biota before introducing HEIDA into the system. Typical performance data, prior to starting the HEIDA, are shown in Table I and provide a clear indication of the system's efficiency.

In the early stages of these studies, carbon-14 tagged HEIDA was used to monitor the system. All samples were filtered through a millipore filter (0.45 μm), fixed by mixing 1 part sample with 2 parts distilled water and 15 parts Aquasol (a xylene based universal cocktail supplied by Nuclear Associates, Westbury, N.Y.). The radioactivity was measured with a Packard liquid scintillation counting spectrophotometer. This reading was related to concentration by standards made from the 1000 ppm feed solution appropriately diluted with sewage.

Two variations of C-14 tagged samples of HEIDA were used in these studies. In one, the 2-carbon of the acetic acid group was tagged; in the other, the 2-carbon of the ethanol group was tagged. As is evident, the disappearance of these carbons requires the cleavage of the carbon-nitrogen bond and also the disappearance of the 1-carbons. Their disappearance, thus, indicates the absence of any long lived degradation product.

It was recognized from the inception of this work that reliance on the C-14 radioactivity as an analytical tool yielded results which represented maximum possible HEIDA concentration, since this technique could not distinguish between HEIDA and its soluble degradation products. Early attempts at developing a polarographic analytical method specific to HEIDA were hindered by the weak stability constants of its metal ion complexes. At the concentrations present in the sewage, HEIDA could not compete successfully with the naturally occurring chelating agents present. It was only with the development of the polarographic technique using indium that a method specific to HEIDA became available. This technique involved measurement of the half-wave potential of the indium/HEIDA complex using a PAR model 174 polarographic analyzer and made it possible to determine HEIDA concentrations in sewage effluents to as low as 10 ppb. A fuller description of this technique will be published elsewhere.

RESULTS

River Water Die-Away Tests

The results of this study, presented in Figure 2, provide clear evidence of HEIDA's biodegradability. These data, obtained exclusively by using C-14 tracers, indicate complete biodegradation to gaseous products with very little soluble degradation products remaining. As might be expected, degradation occurs more rapidly in waters subjected to industrial wastes, the Lehigh, or farmland run off, the Delaware, and less in a rocky bedded trout stream, the Little Lehigh.

Activated Sludge System (7)

The HEIDA concentration for the first 17 days is shown in Figure 3. The results clearly demonstrate that after ca. 3 days, the activated sludge bed has been acclimated to HEIDA. Since these results were obtained using an equimolar mixture of the 2 differently tagged HEIDAs, it is evident that at least 90% of the HEIDA is removed from the system. Measurements of the sludge proved negligible. The minor difference between the aerator effluent and the clarifier overflow indicated the degradation is confined largely to the sludge bed.

A summary of the results of all tests is given in Table II. Test no. 1 corresponds to those shown in Figure 3. Doubling the feed concentration had little effect upon the removal efficiency as shown in test no. 2. A doubling of the residence time by reducing the feed and the recycle rate tends to diminish the efficiency only slightly. This was

TABLE II

Biodegradation of 2-Hydroxyethyliminodiacetate (HEIDA) in Activated Sludge System

Data source			Sludge bed residence time (hr)	Test time (days)	Cumulative operating time (days)	HEIDA concentration in feed		HEIDA concentration in effluent	
Test no.	Analysis[a] description	Test chemical				Mean concentration (ppm)	Standard deviation	Mean concentration (ppm)	Standard deviation
1	LSC(E-A)	HEIDA	5.6	13	32	23.7	2.7	1.4	0.11
2	LSC(E-A)	HEIDA	5.6	8	41	40.3	3.0	3.5	0.62
3	LSC(E)	HEIDA	5.6	9	75	21.7	2.0	1.1	0.22
4	LSC(A)	HEIDA	5.6	15	94	21.9	4.1	2.0	0.20
5	LSC(A)	HEIDA	12.0	22	125	26.0	4.8	3.5	1.0
6	LSC(E)	HEIDA	12.0	24	147	26.0	5.7	3.1	0.7
7	HRL(Pol)	HEIDA	5.6	49	250	24.4	7.1	0.8	0.6

[a]LSC = liquid scintillation counting spectrometry; (E-A) = both ethanol and acetate no. 2 carbon tagged with C-14; (E) = ethanol group tagged only; (A) = acetate group tagged only; and HRL(Pol) = in-house developed polarographic method specific to HEIDA.

expected, since such a modification in the operation decreases the BOD loading to the system and thereupon the sludge concentration. A comparison of the polarographic data of test no. 7 and the C-14 tracer data of tests no. 3 and 4 indicates that more than 90% of the degradation results in gasification, probably to carbon dioxide, and, of the remainder, ca. half is intact HEIDA, with the other half some soluble degradation product associated with the acetate moiety. The polarographs, however, in all cases had shown no additional chelating agents having a stability constant above that found in normal sewage. Consequently, there is a good possibility the soluble product is glycine.

This work demonstrates conclusively that HEIDA will degrade readily under aerobic conditions in the presence of an appropriate biota which will form readily from those naturally occurring in river water and aerobic sewage systems. There is little possibility of appreciable amounts of HEIDA accumulating in such environments.

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