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AN INVESTIGATION INTO THE BIODEGRADABILITY OF METALWORKING LUBRICANTS WITH REGARD TO BOD/COD PARAMETER DATA

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ABSTRACT

Biochemical oxygen demand, combined with chemical oxygen demand ratios, provide a profile that can be used in the interpretation of an effluent water system's environmental health. The biochemical oxygen demand (BOD) and the chemical oxygen demand (COD) are commonly used as parameters for determining the degradation of organic compounds. The biological oxygen demand testing measures only the biodegradable part of an organic waste process. BOD parameters are an indication of the ability for specified microorganisms to oxidize available organic matter. The chemical oxygen demand provides a means of measurement of the environmental health of the system in terms of the oxygen demand placed upon organic matter needed for degradation. Both BOD and COD parameters have been investigated for straight oil, water-soluble chlorinated oil, and water-based synthetic type metalworking lubricants to determine their degree of biodegradation within a waste system such as found in industrial effluents. Results indicate that the petroleum oil-containing systems exhibit a generally low initial BOD value, while COD values are high. Synthetic compounds tested exhibit the opposite profile — high BOD values, low COD values — indicating that synthetic systems are more easily oxidized and degraded in an aqueous matrix than conventional petroleum-base compounds. This trend indicates active bacterial action to achieve degradation of organics without placing a strong chemical demand on the effluent. It has therefore been observed that BOD/COD testing does enable environmental monitoring and a degree of biodegradability to be established for organic systems.

1. INTRODUCTION

Industrial pollution control can benefit from the study of oxygen content and its effect on the oxidation of organic matter. Such studies incorporate the usage of BOD and COD data to provide a profile that can be used in the interpretation of a water system's quality.

In this investigation, the environmental ramifications of the usage of metalworking lubricants are considered by regarding the compiled BOD/COD data for straight oil base, water-soluble oil base, and non-petroleum water-based synthetic lubricant systems.

The metalworking compounds currently in use by the majority of manufacturers consist largely of fatty additives for lubricity, sulfur and chlorine additives for extreme pressure performance ability, and a mineral oil base. By adding a specialized emulsifier package, such systems not only become more water soluble, but increased chlorine content is possible, thereby increasing the processing capabilities of such soluble oil systems.

The present synthetic technology consists largely of the amine-soap polymer base type of compounds. Such synthetics are being developed with the purpose of achieving a completely biodegradable product which can be safely used without the disposal problems encountered by their petroleum-based counterparts.

2. OBJECTIVE OF RESEARCH

Dissolved oxygen is the key element in the life cycle of any body of water. It is the demand on such oxygen that is used as a measure of determining the efficiency of a wastewater treatment process. In this study, the biochemical oxygen demand (BOD) and the chemical oxygen demand (COD) values are used as the measuring device to determine the quality of a given pollutant-containing system.

If the assumption is made that the BOD testing procedures measure only the biodegradable part of the organic waste sampling, then by taking such measurements over varying time spans, a realistic picture of degradation within a waste treatment system can be observed. This data, coupled with the chemical oxygen demand values, offers a profile not only of water quality, but also of the extent of the biodegradation of the contained pollutants.

Within the body of this paper, the author has attempted to show the degradation profile based on BOD as well as COD parameter data.

3. EXPERIMENTAL METHOD

BOD and COD values were obtained for diluted samples of petroleum based straight oil lubricants, chlorinated soluble oil lubricants, and water-based synthetic metalworking lubricants. Samples were tested at 500:1 and 1000:1 dilutions (water:product). Standard BOD analyses, incorporating the Winkler titration method for oxygen content determination, were performed for diluted samples and specified standards. The BOD was determined by adding a microbial seed to the diluted samples, saturating them with air, incubating for 5-, 7-, 20-, 30-, 45-, 50- and 60-day intervals, and then determining the dissolved oxygen content remaining. Samples were incubated in standard BOD bottles in a constant water bath set at $37^{o}C \pm 1^{o}C$. A water seal was used to prevent air from entering bottles and contaminating samples. The BOD values of the samples were determined by measuring the dissolved oxygen content before and after the incubation periods. The BOD values were calculated as follows:

$$\text{BOD, mg/l} = \frac{D_1 - D_2}{P} \qquad (1)$$

where D_1 is the initial dissolved oxygen value,

D_2 is the dissolved oxygen value after incubation, and
P is the fraction of sample used.

This method for determining the observed BOD value of samples measures the oxygen demand produced by carbonaceous and nitrogenous compounds, and their immediate oxidation.

The chemical oxygen demand (COD) testing was used to provide a rapid measure of organic waste concentration. The COD use was defined as a measure of oxygen equivalent to that portion of organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant (potassium dichromate/50% sulfuric acid solutions as oxidants). Such oxygen equivalents were studied by refluxing diluted samples with the potassium dichromate-sulfuric acid solution. Upon completion of the oxidation processes, the samples were titrated for chromate content using standard ferrous ammonium sulfate reagent as described by the standard EPA analysis method [1] for COD testing.

Because of the large amount of water present in the samples, it was impossible to measure an increase in any of the reaction parameters, and therefore became necessary to measure the change occurring in the dichromate (the increase in Cr^{3+}) to determine the oxygen demand. Titrating the amount of Cr^{6+} that remained after the reaction was complete enabled oxygen levels to be calculated. The COD values were determined by a simple mathematical relationship:

$$\text{COD, mg/l} = \frac{(a - b)\, N \times 8000}{\text{ml of sample}} \qquad (2)$$

where COD is the chemical oxygen demand,
a is the mls of ferrous ammonium sulfate used for blank
b is the mls of ferrous ammonium sulfate used for sample, and
N is the normality of the ferrous ammonium sulfate.

4. RESULTS

Chemical trends in BOD and COD values have been easily identified for the ten products studied here (Table 1; Figures). The straight oil-based metalworking lubricants (Figs. 1 - 3), consisting of chlorine and sulfur derivatives, fat additives, and phosphates with a straight mineral oil base, are easily distinguishable from the emulsifier-containing water-soluble oil systems (Figs. 4 - 6) by their initial 5-day BOD readings. With the conventional oil-based compounds, the initial BOD values are generally lower and the COD values substantially higher. But when these values are taken at the 30 - 60 day incubation period, it becomes apparent that BOD values increase slowly to a maximum and then diminish to a minimal plateau.

With the addition of an emulsification system to the straight oil lubricant, the initial 5-day BOD readings show a slight increase, seen in the plots for products D, E and F (Figs. 4 - 6). The 30- and 60-day values were substantially lower than those obtained for the non-soluble oil samples (products A, B and C; Figs. 1 - 3).

TABLE 1. TESTING SAMPLE KEY AND CHEMICAL OXYGEN DEMAND VALUES

Key	Product	Chemical Oxygen Demand (COD) Values 500 : 1	1000 : 1
A	Straight Oil	3250 mg/l	1317 mg/l
B	Straight Oil	3922 mg/l	2122 mg/l
C	Slightly Soluble Straight Oil	3500 mg/l	1875 mg/l
D	Chlorinated Water-Soluble Oil	2731 mg/l	979 mg/l
E	Chlorinated Water-Soluble Oil	1926 mg/l	1011 mg/l
F	Chlorinated Water-Soluble Oil	2519 mg/l	1392 mg/l
G	Water-Based Synthetic	976 mg/l	525 mg/l
H	Water-Based Synthetic	1011 mg/l	742 mg/l
I	Water-Based Synthetic	1262 mg/l	681 mg/l
J	Non-Chlorinated, Naphthenic-Based Oil	2300 mg/l	1506 mg/l

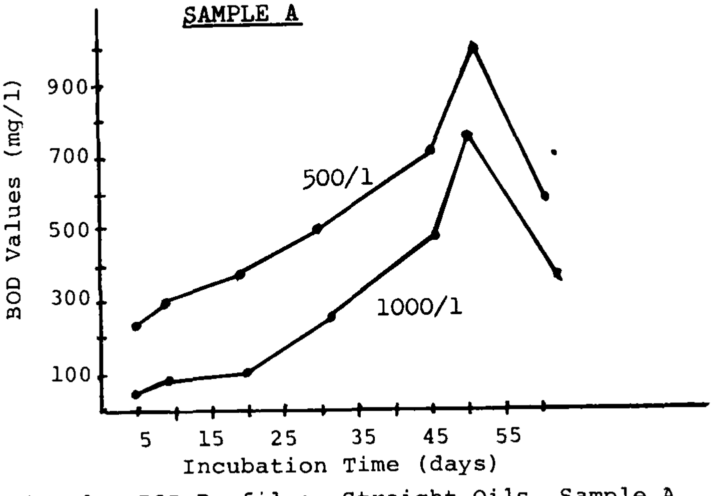

Fig. 1. BOD Profiles, Straight Oils, Sample A.

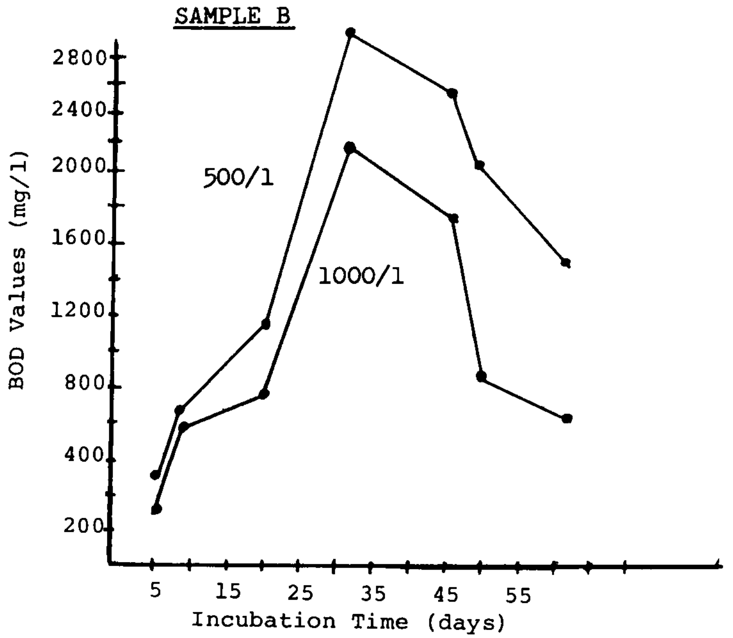

Fig. 2. BOD Profiles, Straight Oils, Sample B.

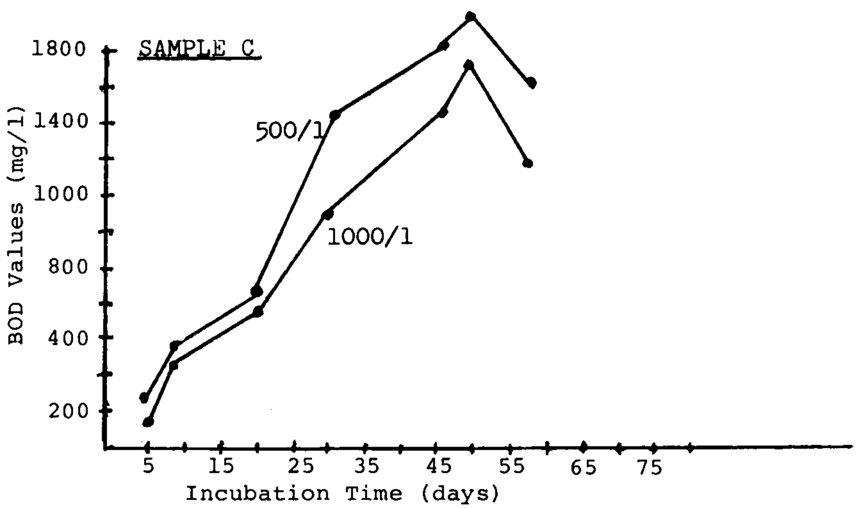

Fig. 3. BOD Profiles, Soluble Oils, Sample C.

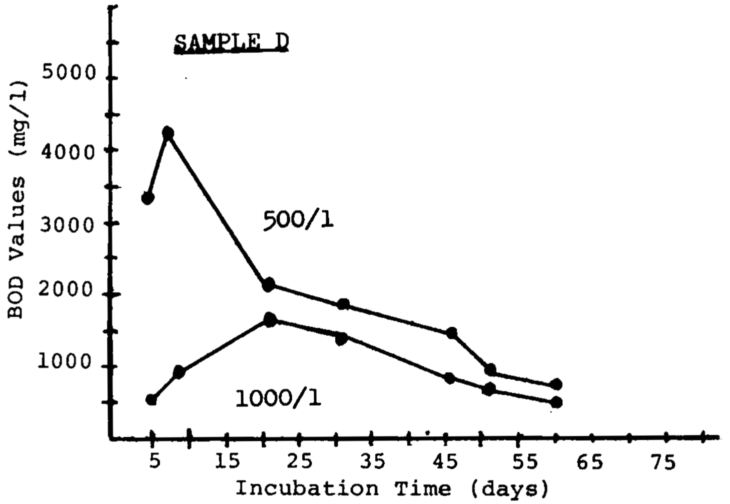

Fig. 4. BOD Profiles, Soluble Oils, Sample D.

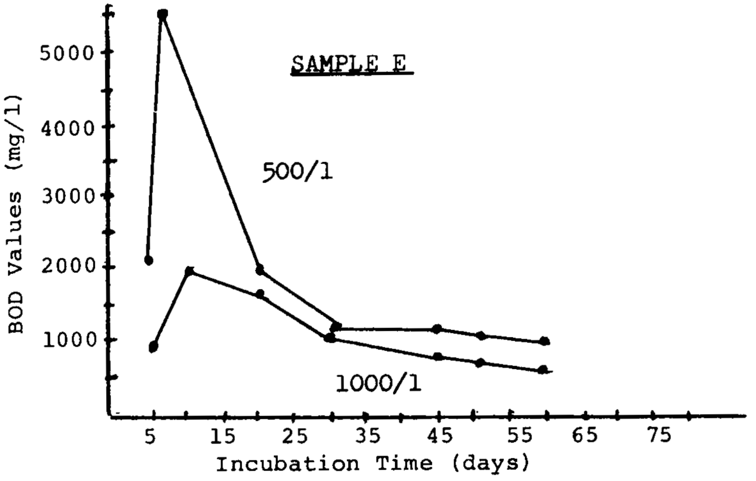

Fig. 5. BOD Profiles, Soluble Chlorinated Oils, Sample E.

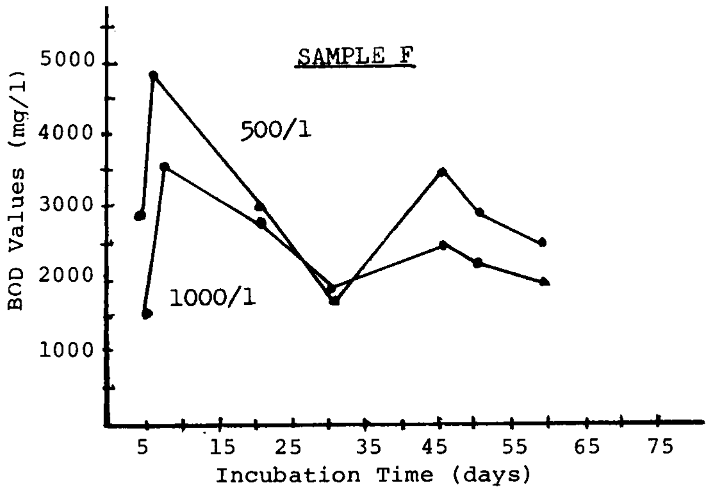

Fig. 6. BOD Profiles, Soluble Chlorinated Oils, Sample F

4.1 BOD Values

From the plots of incubation time versus BOD value for petroleum-based samples (Figs. 1 and 2), it is obvious that the addition of emulsifier systems (consisting of straight- and branched-chain amines with polyethoxylated nonionic surfactants) to the straight-oil type lubricant systems decreases the incubation time necessary to reach the maximum BOD level for the tested samples (Figs. 4 and 5).

For the highly chlorinated, water-soluble oil systems tested (Samples D - F), the high initial BOD values obtained indicate that such samples are readily oxidized — more so than observed for the straight, nonsoluble oil systems. From the data obtained for products D and E (Figs. 4 and 5), the amine/sulfonate/nonionic surfactant emulsifier system these products contain to increase water solubility tends to exhibit a lower dissolved oxygen content, as the oxygen necessary for biodegradation must be taken from the environment.

Product F (Figure 6) exhibited a different type of BOD profile which is easily correlated with its composition. Product F incorporates a highly sophisticated emulsion and inhibitor system into a basic chlorine/sulfur-containing petroleum oil. The two distinct maximums observed in the plots of incubation time versus BOD value can be attributed to the ratios of the base components of the system. For each of the major contributing organic components within the product, there is a separate and distinct oxidation point which exists without interference from the petroleum base component.

The non-petroleum, water-based synthetic lubricant systems (Products G, H and I; Figs. 7 - 9) all exhibit similar BOD profiles: high initial BOD levels quickly tapering off to an absolute minimum. In all of these synthetic systems, maximum BOD values were observed at the 5-7 day incubation period.

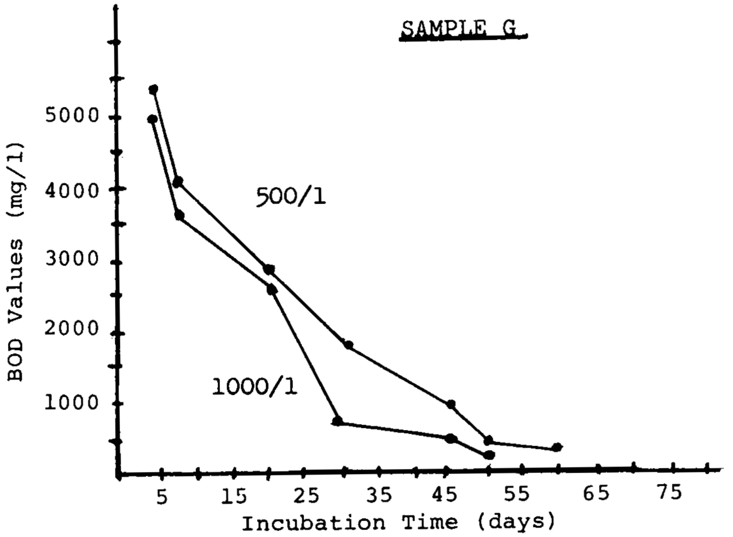

Fig. 7. BOD Profiles, Synthetics, Sample G.

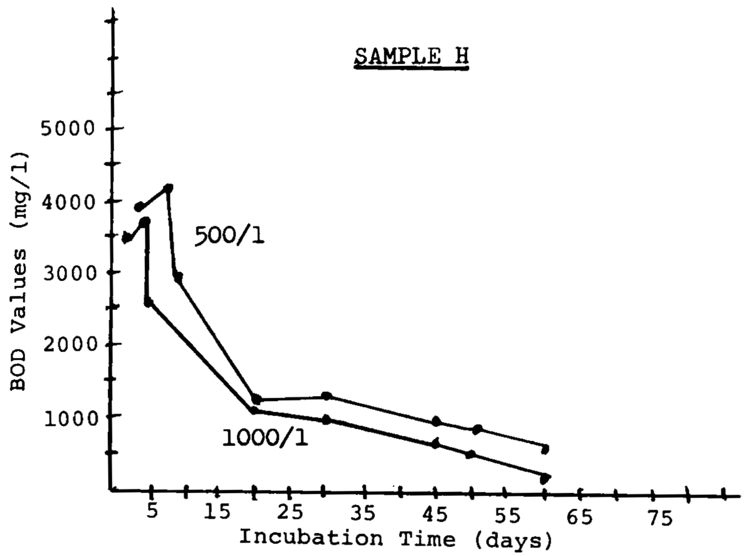

Fig. 8. BOD Profiles, Synthetics, Sample H.

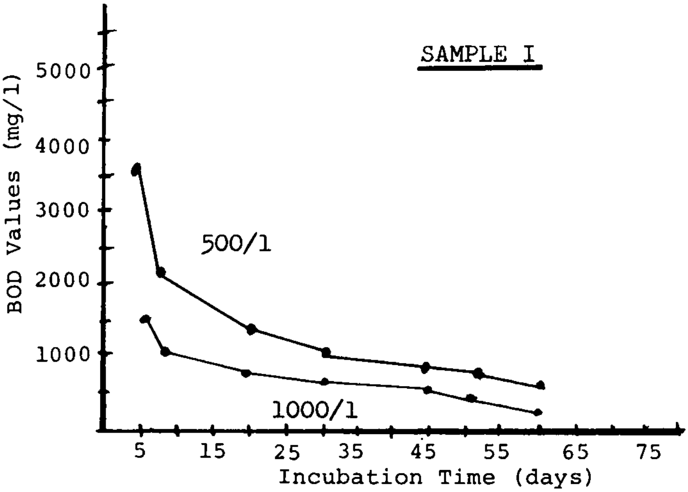

Fig. 9. BOD Profiles, Synthetics, Sample I.

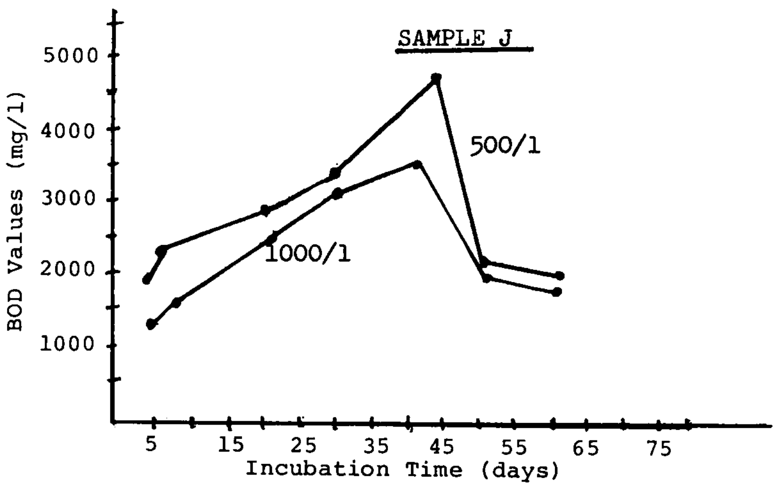

Fig. 10. BOD Profile, Straight Base Oil (Naphthenic), Sample J.

Variations among the three synthetic lubricant samples can be attributed to the unique chemistry encountered for each product. Product G (Fig. 7) was a synthetic soap containing polymers and polycyclic rust-inhibitor additives. Product H (Fig. 8) was also an amine-soap base system, but with a slightly different additive base. The observed BOD levels for product H reached their maximum at the 7-day incubation period. BOD levels for product H were also slightly lower than for product G, indicating a possible decrease in oxidation potential. Sample I BOD levels (Fig. 9) were most similar to the profile obtained for Product H. Samples H and I are chemically similar and vary only slightly in their defoaming capability.

Sample J is a straight naphthenic oil and exhibits very predictable BOD values (Fig. 10). It exhibits a much higher initial BOD reading than do the chlorinated oil systems (Figs. 4 - 6) since it contains neither chlorine or sulfur additions, nor any specific emulsification systems.

4.2 COD Values.

Since COD is a measure of the oxidizable organic content of a sample, the results of the COD tests obtained (Table 1) are considered to be a measure of the gross organic pollution content of a wastewater sample [2]. All organic components should be oxidized to carbon dioxide and water, with nitrogen from amines and amino compounds converted to the ammonium ion and not oxidized, and resulting COD values that are extremely low (Samples F and G, Figs. 6 and 7).

Both straight oil-based and chlorinated, water-soluble oil-based lubricants presented expected COD profiles: high COD values. In comparison, lower COD values were observed for those samples containing synthetic chemistries. The high COD levels obtained for the petroleum-containing products attest to the degradative difficulties encountered in bacterial as well as chemical oxidation processes for petroleum oils. The increasingly lower COD values observed for the synthetics tested indicated an increased degree of biodegradability for the organic content, inasmuch as a low COD value indicates that only a small amount of organic matter is present after the oxidative processes have occurred.

4.3 Summary

Clearly, the results indicate predictable trends for BOD and COD data as obtained for the oil-based and synthetic-based lubricant systems tested and compared.

5. DISCUSSION

Although both BOD and COD testing are widely used as a rationale for the interpretation of conditions in various waste systems, both methods have extremely low sensitivities. Because of their high degree of manipulation as well as their extensive analysis preparation, BOD and COD testing have become extremely sensitive to minor discrepancies in their techniques. The quality of the dilution water, the effectiveness of any seed components used, and the technique of the analyst are all parameters that must be constantly monitored. Many other factors also affect BOD and COD testing.

Toxic substances in the sample inhibit or may even prevent bacterial growth, and therefore the oxidation of the organic matter in the system. This will cause a resultant decrease in the actual BOD value obtained and possibly an increase in the COD value. The time factor involved in the incubation of BOD samples tends to vary BOD values if not properly controlled. Bacteria grow somewhat slowly, so that it may take considerably longer than a 5-day interval for completion of the biological oxidation. Interfering substances can also greatly alter actual results. In performing BOD testing, interference from other organic materials, which may produce the same oxidation reaction as the Winkler titration, yield high values resulting from what is interpreted as positive interferences. On the other hand, reducing agents could possibly produce the opposite effect, resulting in lower-than-expected BOD values [2].

It is important to note that, unlike BOD testing, toxic substances do not interfere with COD testing. However, high levels of chlorine will drastically reduce the accuracy of the method. To overcome such interferences encountered in chlorinated oils, an addition of mercuric sulfate was introduced to the samples tested [3].

Despite the obvious inaccuracies of BOD and COD testing, they remain the widely accepted method of determining pollution criteria of water systems. Systems containing organic matter exhibiting large BOD values will be oxidized by the natural bacteria present. The bacterial oxidation processes will consume oxygen from the wastewater faster than it is able to dissolve oxygen back into the system from the air. This condition results in extreme loss of oxygen within the water system, creating a life-threatening environment for the oxygen-requiring organisms. It is for this reason that a waste treatment plant removes as much as possible of the BOD load passing through it.

In reviewing the results obtained for industrial lubricants tested in this study, it becomes obvious that at the 5-day incubation stage, it is the synthetic compounds that use much more oxygen in the process of degradation. But by studying the extended incubation effect of time on the stability of such lubricants, it becomes apparent that petroleum-base lubricants do not begin their oxidation degradation until a much later time interval after the initial inoculation into a system.

Observing the BOD and COD parameter data from this study, one would expect the synthetic type of lubricant system to place a much higher oxygen demand on any water system it encounters. The slowly-degrading petroleum oils do not exhibit the same oxygen profiles and can be characterized, as can all the samples tested, from the time/BOD plots obtained.

6. CONCLUSIONS

The conclusions of this study are as follows:

1. As seen from the data of BOD versus incubation time, effluent systems that exhibit initially high BOD values with relatively low COD values can be characterized as being in a state of increased degradation, in which the system has nearly depleted its organic content or is in the process of doing so.

2. The opposite trend is foreseen for the conventional oil-based compounds tested. Initially low BOD levels coupled with extremely high COD levels indicate that the product effluent contains an increased amount of organic components which can be readily oxidized by chemical methods, but cannot be degraded by bacteria-induced oxidation (as observed in activated sludge processing).

3. Petroleum-containing lubricants would require a much longer degradation period to reduce oxygen-demanding components than have been observed for the water-based synthetic samples tested. This trend remains clearly a function of time and chemistry.

4. The overall view of the environmental studies and results obtained indicate a predictable pattern of biodegradation for waste-containing effluents. It is the synthetic compound that offers the best ability for control, since there total degradation appears to occur more rapidly than the petroleum-based systems. It is the contention of this study that high BOD levels can be tolerated if encountered early enough in the effluent treatment cycle, to be controlled by conventional methods.

5. Metalworking lubricants are varied in character, as are their environmental effects. By categorizing the oxygen depletion brought about by lubricant-containing industrial waste (since it is not always possible to determine the exact chemical breakdown of waste-contributing effluents, the initial BOD/COD values become more important criteria with which to evaluate water quality.

If all the above points are taken into consideration, a feasible characterization plot of organic effluent waste will have been established and can aid environmentalists in further defining the biodegradation within a system.

ACKNOWLEDGMENT

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