PNL-SA-7795
CONF-790663--2

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CONTRIBUTION OF THIOSULFATE TO COD AND BOD IN OIL SHALE PROCESS WASTEWATER

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Paper presented at the American Society for Testing and Materials Symposium on Analysis of Waters Associated with Alternate Fuel Production. Pittsburgh, PA, June 4 and 5, 1979.

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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT EY-76-C-06-1830

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CONTRIBUTION OF THIOSULFATE TO COD AND BOD IN OIL SHALE PROCESS WASTEWATER

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ABSTRACT: Thiosulfate accounted for a significant portion of the COD (7-20%) and BOD (14-41%) of the four oil shale process waters studied. As such, accurate measurement of the thiosulfate oxygen demand of retort water is critical in assessing its environmental impacts on receiving waters and in designing biological treatment systems to treat it. The contribution of thiosulfate to the COD of oil shale retort waters can be accurately measured in a standard COD test. The BOD of thiosulfate in retort water is more difficult to determine and may require the development of a special thiosulfate acclimated seed. Thiosulfate recovery of a known thiosulfate spike ranged from 92-100% in the COD test and from 54-119% in the BOD test. Considerable variability in recovery was found between the process waters studied. When determining the BOD of oil shale process waters, care must be taken to insure a viable population of thiosulfate oxidizing bacteria.

KEY WORDS: Chemical oxygen demand (COD), biochemical oxygen demand (BOD), thiosulfate, sulfur oxidizing bacteria, thiobacilli, BOD interferences, oil shale, retort water, wastewater evaluation, characterization, thiosulfate, oxidation.

INTRODUCTION

Thiosulfate is a common constituent of process wastewater produced during the retorting of oil shale. Like many of the organic constituents

of this wastewater, it is unstable with respect to air oxidation and will exert an oxygen demand in the receiving waters to which it is discharged. A substantial volume of process wastewater can be produced by a moderate-sized shale oil recovery facility. A 50,000 barrel per day in situ oil recovery operation, for example, may produce on the order of two million gallons of process wastewater per day. If improperly treated prior to discharge, this wastewater could have a significant impact on the quality of the relatively small volume of receiving water available in the oil shale regions of Colorado, Utah, and Wyoming. The amount of process wastewater generated depends on several factors such as the type of retorting process used, the mineralogical characteristics of the oil shale, the amount of free water present in the shale, and the use of steam in the retorting process. Water to oil volume ratios reported for in situ retorting have ranged from 0.4 to 22 [1]. The high water to oil ratio resulted from groundwater intrusion during the retorting process.

Thiosulfate concentrations have been found to range from a few hundred to over 20,000 milligrams as S per liter in the oil shale process water studied. Thiosulfate can be completely oxidized both chemically and biochemically to sulfate, however, partial oxidation to other species can also occur under specific conditions. Since thiosulfate may be present in oil shale wastewaters at high concentrations, oxidation of the thiosulfate could exert a substantial oxygen demand on receiving waters. In addition, one of the processes considered for the treatment of oil shale retort water is the activated sludge process which uses a mixed culture of microorganisms to biochemically oxidize organic and other oxidizable constituents (reduced sulfur and nitrogen compounds). The effectiveness of biological treatment on retort water is, therefore, dependent both on organic and inorganic oxidation.

This work was undertaken to determine the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of pure thiosulfate solutions and known additions of thiosulfate to actual process wastewater samples. These measured values could then be compared with theoretical values computed by assuming complete oxidation to sulfate.

THIOSULFATE REACTIONS

Chemical Behavior of Thiosulfate

Thiosulfate concentrations were observed to undergo little or no change in retort water samples stored at 4°C for periods up to one year. The alkalinity of the retort water (pH 8-9) is a contributing factor to the stability of the thiosulfate. Acidification to low pH levels will bring about immediate dissociation of the thiosulfate as follows [2]:

$$S_2O_3^{=} + 2H^+ \rightarrow SO_{2(g)} + S_{(s)} + H_2O \qquad (1)$$

This reaction may also occur slowly under mildly acid conditions due to the presence of dissolved CO_2. The addition of alkaline reagents to high pH levels may also cause decomposition, especially at high temperatures.

Ordinary air oxidation of thiosulfate in solution proceeds at a negligible rate to produce sulfite which is rapidly oxidized by air to sulfate. The presence of catalysts such as Cu(II) and Fe(III) can accelerate air oxidation of thiosulfate. A relatively weak oxidant such as iodine (I_3^-) in neutral or acidic solution will stoichiometrically oxidize thiosulfate to tetrathionate:

$$I_3^- + 2\ S_2O_3^{=} \rightarrow 3\ I^- + S_4O_6^{=} \qquad (2)$$

This reaction is commonly used in iodometric titrations. Strong oxidants would be expected to oxidize thiosulfate to sulfate. Under the conditions of the COD test, Cr(IV) acts as a strong oxidant:

$$4\ Cr_2O_7^{=} + 3\ S_2O_3^{=} + 26\ H^{+} \rightarrow 6\ SO_4^{=} + 8\ Cr^{+3} + 13\ H_2O \qquad (3)$$

On the basis of this reaction, eight equivalents of dichromate would oxidize one mole of thiosulfate, therefore:

1 mg/l S as $S_2O_3^{=}$ = 1 mg/l O_2

It has been reported, however, that strong oxidizing agents will generally oxidize thiosulfate to a mixture of tetrathionate, sulfate, and sulfur [3]. Therefore, it is of interest to establish the experimental COD value as determined by Standard Methods for the Examination of Water and Wastewater [4].

Biochemical Reaction of Thiosulfate

Several Thiobacillus species are known to biologically mediate thiosulfate oxidation. When growing on a thiosulfate medium, these bacteria use the energy derived from thiosulfate oxidation as an energy source and inorganic carbon as a carbon source. Each thiosulfate molecule is split into sulfite and sulfur. The sulfite is oxidized to sulfate with the subsequent production of energy. The sulfur molecule is converted to elemental sulfur, which can later be oxidized for energy if the thiosulfate concentration is low. In solutions with low thiosulfate concentrations, the elemental sulfur is used up as fast as it is produced. Incomplete oxidation of thiosulfate to polythionates may also occur at low pH.

All thiobacilli can grow autotrophically at the expense of sulfur compounds, and some species can grow heterotrophically on organics. The presence of organics may, however, inhibit growth of other Thiobacillus species. Salt tolerance, like organic substrate and acid tolerance, varies through the genus.

A working relationship can be generated for the biochemical oxidation of thiosulfate to sulfate by a method developed by McCarty [5]. A mass balance separates the energy derived from the substrate into two fractions: the fraction used for cell synthesis and the fraction used for cell maintenance. By coupling relevant oxidation-reduction equations, an overall stoichiometric equation is obtained. Necessary assumptions for this analysis include biological rate and yield coefficients which have already been experimentally determined. These assumed coefficients are:

$a_e = .11$

$b = .15/day$

$f_d = .80$

$\theta_c = 5$ day (for BOD_5)

where a_e = the cell yield coefficient

b = the coefficient of organism decay

f_d = the biodegradable fraction of an active organism

θ_c = the solids retention time

The fraction of substrate energy going to cell synthesis has been described by the equation:

$$f_s = a_e \left(1 - \frac{f_d b \theta_c}{1+b\theta_c}\right)$$

$f_s = .07$

Since $f_s + f_e = 1$, $f_e = .93$

The overall reaction is developed from the following oxidation-reduction equations (all on electron equivalent basis):

R_d: $1/8\ S_2O_3^{=} + 5/8\ H_2O = 1/4\ SO_4^{=} + 5/4\ H^+ + e^-$

R_a: $1/2\ H_2O = 1/4\ O_2 + H^+ + e^-$

$$R_c: \quad 1/20\ C_5H_7O_2N + 9/20\ H_2O = 1/5\ CO_2 + 1/20\ HCO_3^- + 1/20\ NH_4^+ + H^+ + e^-$$

where R_d = electron donor reaction

R_a = electron acceptor reaction

R_c = cell synthesis reaction

The overall equation, R, is composed of these equations together with their fraction of substrate energy as follows:

$$R = R_d - f_e R_a - f_s R_c$$

The overall reaction for the biochemically mediated oxidation of thiosulfate to sulfate is:

$$S_2O_3^= + 1.86\ O_2 + 1.03\ H_2O + .112\ CO_2 + .028\ HCO_3^- + .028\ NH_4^+ \rightarrow .028\ C_5H_7O_2N\ (\text{"cells"}) + 2\ H^+ + 2SO_4^= \qquad (4)$$

This shows that complete biochemical oxidation of one mole of thiosulfate would use 1.86 moles of molecular oxygen, or

$$1\ mg/l\ S\ as\ S_2O_3^= = 0.93\ mg/l\ O_2$$

This represents the theoretical BOD of thiosulfate.

Wastewater Treatment Evaluation

Preliminary laboratory analysis of an activated sludge treated retort water showed a 95% thiosulfate removal efficiency at a two day hydraulic detention time. Since thiosulfate can be oxidized either chemically or biochemically, experiments were conducted to determine the contribution of each oxidative process to the observed thiosulfate oxidation. Both COD and BOD tests were performed on a nutrient enriched thiosulfate solution. The COD of thiosulfate was close to the theoretical value; however, the BOD could not be determined because no oxygen depletion occurred in any of the dilutions using activated sludge

seed. This indicated that thiosulfate removal was either due to chemical oxidation or that interferences were causing inaccurate BOD results.

To test the former hypothesis, two chemical oxidation experiments were performed. The purpose of the first test was to determine the rate at which a continuously aerated thiosulfate solution is chemically oxidized. The test involved daily sampling of a sterile air-sparged, thiosulfate solution and subsequent analysis for thiosulfate. Any decrease in thiosulfate concentration could be attributed to chemical oxidation. The effect of chemical oxidation due to aeration was important to determine also because of its possible interference in the BOD test.

One liter of sodium thiosulfate solution (1000 mg/l S as $S_2O_3^{=}$) was made up using boiled deionized water. Sodium borate (400 mg) and mercuric iodide (10 mg) were added to prevent bacterial growth. The thiosulfate solution was placed in a two liter graduated cylinder and continuously air sparged and mechanically stirred. Each day before sampling the volume was brought up to one liter with deionized water. A ten milliliter sample was then taken and stored at 4°C to deter decomposition. All samples were analyzed for thiosulfate at the end of the eight day period. The results of the thiosulfate analysis indicate that there was a negligible change in the thiosulfate concentration over the eight day period. This shows that thiosulfate solutions are not readily oxidized by dissolved oxygen provided by simple aeration. It implies that chemical oxidation is not responsible for the removal of thiosulfate during activated sludge aeration.

The second chemical oxidation experiment was based on the hypothesis that other chemical catalysts which enhance thiosulfate oxidation are present in the retort water. Treated effluent from the bench-scale

retort water activated sludge unit was filtered through a .45μm filter. This procedure insured that the soluble chemical makeup of the treated effluent was unchanged while removing essentially all bacteria. The filtered effluent was air sparged to saturation and put in a BOD bottle. Two milliliters of a 10 g/l S as $S_2O_3^=$ solution were added to the effluent. No oxygen depletion occurred within the five day time period. Stoichiometrically, this amount of thiosulfate would produce an oxygen uptake of 67 mg/l. The conclusion was that simple aeration would not chemically oxidize thiosulfate to sulfate in the retort water.

Since thiosulfate was not chemically oxidized under controlled experimental conditions, microbial action was implicated in the thiosulfate loss observed during activated sludge treatment. Stanier, et al. [6], reports that when thiobacilli are grown in thiosulfate media, they may have generation times as short as two hours. Energy utilization during rapid growth could account for complete thiosulfate oxidation within the two day hydraulic detention time. To test the microbial oxidation hypothesis, rates of biochemical thiosulfate oxidation were studied with the aid of a bench-scale fill and draw activated sludge aeration unit. The unit, which consisted of a two liter graduated cylinder filled with 500 ml of mixed liquor, was air sparged to saturation. The air sparge was cut off and the DO was measured periodically over a period of time. When the DO dropped to a low level, the air sparge was resumed to saturate the mixed liquor with DO. Eighty mg/l S as $S_2O_3^=$ was then added and thoroughly mixed. The DO was again measured periodically following the thiosulfate addition and again an hour later. To prevent oxygen absorption from the air, the mixed liquor was either blanketed with N_2 gas in the graduated cylinder, or run in a standard BOD bottle.

The DO depletion curves in Figure 1 show oxygen uptake was much faster immediately after thiosulfate was added, indicating that microbial activity was responsible for thiosulfate oxidation. An hour later, after further sparging, the sludge showed a slow depletion rate indicating that the added thiosulfate was nearly completely oxidized. Therefore, the acclimated activated sludge unit appeared to be efficiently oxidizing the thiosulfate present in the retort water.

SAMPLE ANALYSIS

Methods and Materials

Four process wastewater samples were used in these studies. Two were obtained at different times from an in situ test site in Utah, one from a simulated in situ retort in California, and another from an above-ground retort in Colorado. All of the samples were filtered through a .45μm membrane filter and stored at 4°C to deter microbial decomposition.

The thiosulfate solution used for both the COD and BOD analyses was prepared from analytical reagent grade sodium thiosulfate in boiled deionized water. Sodium bicarbonate and ammonium chloride were added in stoichiometric amounts to provide carbon and nitrogen sources. This solution was also stored at 4°C to prevent microbial degradation.

COD tests were conducted according to Standard Methods for the Examination of Water and Wastewater. The COD was determined for each retort water, the test thiosulfate solution, and each retort water spiked with a known amount of thiosulfate solution. A 20 milliliter sample size was used with corresponding reagent concentrations as specified in Standard Methods for the Examination of Water and Wastewater.

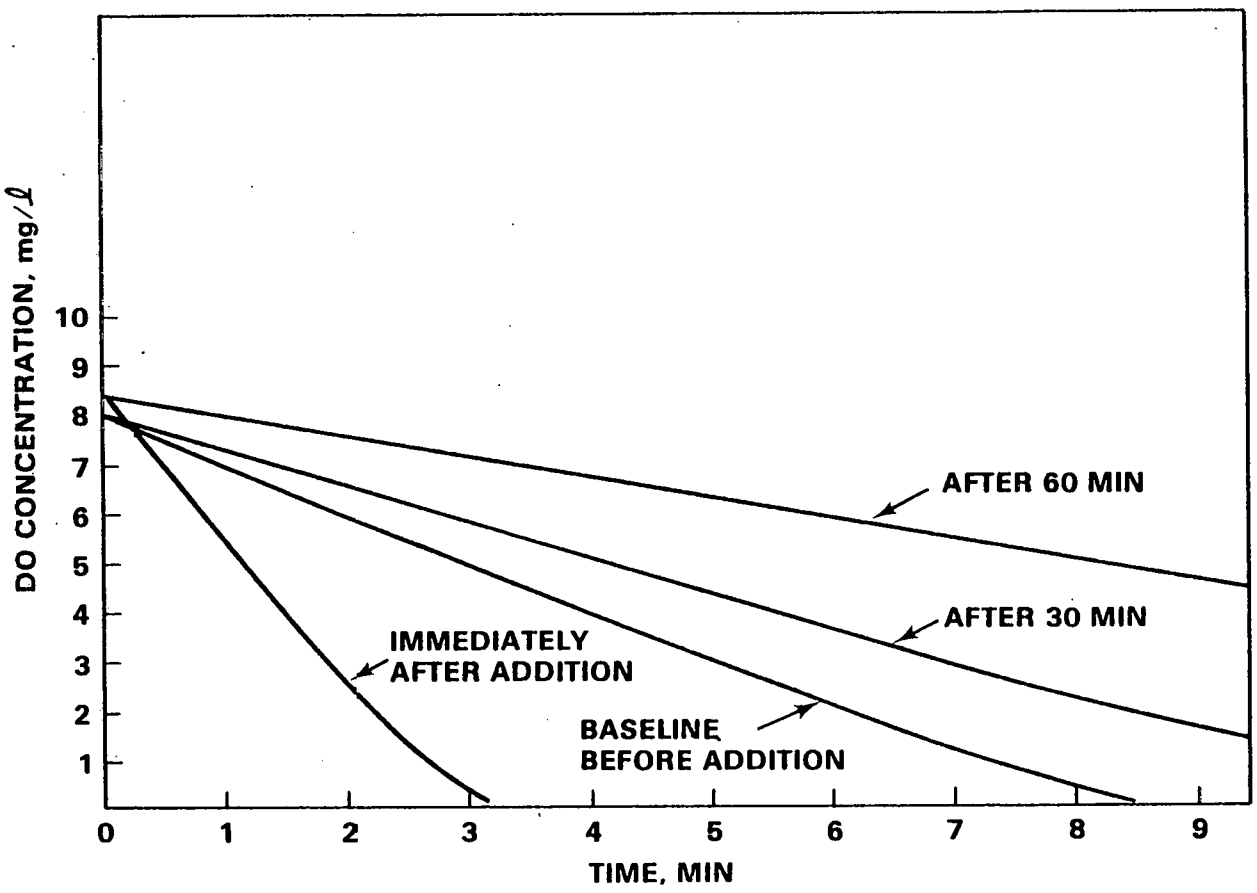

FIGURE 1. Dissolved Oxygen Depletion with Thiosulfate Addition in Activated Sludge

BOD tests were conducted according to Standard Methods for the Examination of Water and Wastewater with the modification suggested by Sawyer and McCarty [7] to use the five day dissolved oxygen (DO) blank to represent the 0-day corrected value. DO concentrations were determined with a membrane electrode. The dilution water was prepared with 2 ml of seed per liter for each analysis. Seed for the BOD tests was obtained from two different sources. Seed used in the initial test consisted of effluent from an activated sludge bench-scale unit used for treatability studies on shale oil process wastewater. The second seed was prepared from thiosulfate solution which was inoculated with soil and is referred to as a Thiobacillus enrichment culture.

Most of the analyses utilized a combined seed of activated sludge and the Thiobacillus enrichment culture. This activated sludge seed differed from that initially used in that frozen activated sludge samples (not effluent) were reconstituted and slowly reconditioned before use in the BOD tests. Reconditioning involved thawing, slowly diluting the sludge with deionized water, aerating, and feeding with diluted (1:100) process wastewater containing added thiosulfate (100 mg/l as S). The Thiobacillus enrichment culture was aerated and fed a dilute thiosulfate solution (240 mg/l as S). The BOD dilution water was seeded with 1 ml/l of the diluted activated sludge and 1 ml/l of the Thiobacillus enrichment culture.

Thiosulfate concentrations were determined by iodometric titration as given in Standard Methods for the Examination of Water and Wastewater for sulfite after testing for the absence of sulfide and complexing any sulfite present with formaldehyde. An independent analysis was also made using an ion chromatograph.

Chemical Oxygen Demand

Chemical oxygen demand was determined on four different process wastewater samples, a standardized sodium thiosulfate solution (5.47 g/l S as $S_2O_3^=$) and samples of process wastewater with known additions of thiosulfate. Sample aliquots were selected to consume 50 to 75% of the dichromate oxidant. The amount of added thiosulfate was adjusted to react with approximately half of the total dichromate consumed. The average of ten determinations for the known thiosulfate solution yield 0.92 mg/l COD for each 1.00 mg/l of S as $S_2O_3^=$. The average COD value is therefore 92% of the theoretical value computed from equation 3.

Results of COD analyses on process wastewater samples with and without known additions of thiosulfate are presented in Table 1 along with thiosulfate and total organic carbon data. The recovery of COD from known additions of thiosulfate ranged from 92.1 to 99.7% of the expected COD value which was calculated from experimental values for each retort water and the thiosulfate solution. This indicates that there is minimal interference with other constituents in the process wastewater. The contribution of COD from the thiosulfate naturally present in these samples ranged from 7.6% for the simulated in situ retort water to 20% for the Utah in situ No. 2 retort water.

Biochemical Oxygen Demand

Initial testing of a sodium thiosulfate solution for BOD failed to show any DO depletion over the standard five day incubation period. Only a small depletion was noted over a 14 day period in spite of an excess of thiosulfate in most of the test dilutions. The seed used in these tests consisted of activated sludge produced in bench-scale units used in treatability studies on oil shale process wastewater. A second

TABLE 1. Process Wastewater Analytical Data

Wastewater Sample Source	Total Organic Carbon, mg/l	Thiosulfate mg/l as S	Experimental COD, mg/l	Percent COD Contribution from Thiosulfate	Percent Recovery of COD from Known Addition of Thiosulfate
Utah In Situ No. 1	1,000	860	4,480	17.8	92.1
Utah In Situ No. 2	1,400	1,380	6,240	20.3	98.4
Simulated In Situ Retort	2,000	700	8,420	7.6	99.7
Above-Ground Retort	42,000	27,000	153,000	16.2	98.1

series of tests using activated sludge seed on one set of sodium thiosulfate dilutions and seed from a Thiobacillus enrichment culture on another set of sodium thiosulfate dilutions also failed to produce a significant DO depletion over a five day incubation period.

In view of the strong evidence for biochemical degradation of thiosulfate in the bench-scale activated sludge units receiving oil shale process wastewater, efforts were continued to develop a seed culture which would give an appropriate DO depletion in the BOD test dilutions. Feeding and aeration of the seed cultures was carried out over a period of several weeks after the initial tests during which time the seed developed the ability to degrade the thiosulfate in the test dilutions. An average of 0.60 mg of BOD per mg of S as $S_2O_3^=$ was obtained for 11 determinations. This value is 64% of the theoretical BOD computed from equation 4.

BOD was determined on samples of oil shale process wastewater with and without known additions of thiosulfate using a mixture of seed developed from activated sludge inoculum and soil inoculum which degraded thiosulfate in test dilutions. The results of these analyses are presented in Table 2. The BOD values are approximately one-third of the COD values for a given sample, which indicates a large fraction of refractory material in these wastewaters. Results with activated sludge treatment of the Utah in situ wastewaters revealed that about half of the organic carbon was removed by biological oxidation. The percent BOD contribution from the thiosulfate naturally present in these wastewaters ranged from 14 to 41% of the total BOD and could, therefore, exert a significant impact on the operation of an aerobic biological treatment plant.

TABLE 2. Process Wastewater BOD Results

Wastewater Sample Source	BOD with Mixed Seed, mg/l	Percent BOD Contribution from Thiosulfate	Percent Recovery of Known Additions of Thiosulfate*
Utah In Situ No. 1	1,600	32	54
Utah In Situ No. 2	2,400	35	75
Simulated In Situ Retort	3,000	14	119
Above-Ground Retort	40,000	41	56

*Based on experimental BOD, 0.60 mg BOD/mg S as $S_2O_3^{=}$.

The percent recovery of BOD from known thiosulfate additions to the wastewaters was quite variable. The 75% recovery value for Utah in situ No. 2 represents an average of nine determinations which ranged from 32 to 99%. The BOD data without known additions of thiosulfate were more precise, ranging from 2200 to 2600 mg/l. Insufficient data are available on the other samples to evaluate precision.

The use of activated sludge seed alone for BOD analysis of Utah in situ No. 1 and No. 2 gave much lower values than the mixed seed. In addition, this seed was ineffective for oxidizing a sodium thiosulfate solution. The difference between the BOD values determined with the different seed cultures was nearly equivalent to the BOD computed for the thiosulfate naturally present in these wastewaters using the experimental value of 0.6 mg BOD per mg of S as $S_2O_3^{=}$.

The reason for the failure of seed prepared from activated sludge to oxidize thiosulfate in the standard BOD test is unknown at the present time, but is suspected to be related to the difference in salinity between the activated sludge mixed liquor or effluent and the BOD test solutions. Dissolved solids concentrations in the wastewater from the Utah in situ samples varies between 15,000 and 20,000 mg/l while that in the BOD test dilution is less than 300 mg/l. The microorganisms responsible for thiosulfate oxidation in the activated sludge units may be more susceptible to damage from osmotic shock than other microorganisms which oxidize carbonaceous materials.

SUMMARY AND CONCLUSIONS

Thiosulfate accounted for a significant portion of the COD and BOD determined in the four oil shale process wastewater samples used in this study. The contribution of thiosulfate to COD ranged from 7.6 to 20%

while that for BOD ranged from 14 to 41%. Oxidation of the thiosulfate in bench-scale activated sludge units was quite rapid and resulted from biological activity rather than chemical activity. However, seed obtained from the bench-scale units did not effectively biodegrade thiosulfate in the BOD test. It was found necessary to develop a special seed prepared by inoculating diluted thiosulfate solutions with soil and use this in combination with activated sludge seed for the BOD tests.

The average COD and BOD values obtained on a sodium thiosulfate solutions were 92 and 64%, respectively, of the theoretical values computed for complete oxidation of thiosulfate to sulfate. Based on experimental values, the recovery of known additions of thiosulfate to the process wastewater samples ranged from 92.1 to 99.7% for COD and from 54 to 119% for BOD. Considerable variation in test results was experienced for recovery of known thiosulfate additions in the BOD method.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support provided by Ms. Dee Long, Mr. Brian Sheldon, and Mr. Marvin Mason for assisting with the analytical work, and Ms. Nancy Painter for typing and Ms. Sue Gano for editing the manuscript. Appreciation is also expressed for the support of the U.S. Department of Energy which provided funding for this program through Contract No. EY-76-C-06-1830.

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