PHOTOLYSIS MECHANISMS FOR POLLUTION ABATEMENT

ADVANCED WASTE TREATMENT RESEARCH LABORATORY—XIII

PHOTOLYSIS MECHANISMS FOR POLLUTION ABATEMENT

by

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for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

October, 1969

FOREWORD

In its assigned function as the Nation's principal natural
resource agency, the United States Department of the Interior
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ABSTRACT

Photocatalytic oxidation of dissolved organic matter by irradiation of slurries of zinc titanate (Zn_2TiO_2), zinc oxide (ZnO), titanium dioxide (TiO_2) and beach sand by sunlamps has been demonstrated. The reaction appears to follow first order kinetics in most cases. Zinc oxide appears to be superior for this purpose. At concentrations of 100 to 200 mg/l organic carbon, 80% of phenol, 67% benzoic acid, 44% acetic acid, 40% sodium stearate, and 16% sucrose were oxidized in 24 hrs with 10 gr/l zinc oxide catalyst. Continued illumination reduced organic carbon to a few mg/l in most cases.

The photocatalytic properties of illuminated beach sand (87% of phenol removed in 72 hr) strongly suggest that photocatalysts are widely distributed in nature and that photocatalytic oxidation is a mechanism whereby dissolved organic matter is oxidized in the natural environment in streams and lakes.

Dissolved organic matter in a sample of domestic sewage was reduced 50% in 24 hours and 75% in 70 hours. The limiting factor appears to be the activity of the photocatalyst since sunlamp intensity dropped approximately 80% without measurable decrease in oxidation rate. Improving catalyst activity by quenching from high temperature and/or by doping is proposed. The effects of ionizing radiation should be studied to determine the economic and technical advantages over UV. A recent publication[6] describing ZnO sensitized polymerization with both UV and gamma radiation reports that zinc oxide caused an enormous enhancement of the polymerizing effect of ionizing radiation in an aqueous system of calcium acrylate and acrylamide which suggests a corresponding increase in free radical generation.

At the present state of knowledge the most promising area of application appears to be in problems of industrial disposal where high concentrations of organic matter are involved since

the amount removed at constant irradiation intensity increases
with increased concentration. Small residual concentrations
might be economically removed by conventional means.

INTRODUCTION

This study was based on photocatalytic phenomena described in the literature and on experimentation conducted in IITRI laboratories. The interaction of photocatalysts with radiation below about 4200Å should produce active oxygen species which could destroy organic matter by complete oxidation to carbon dioxide and water.

Certain oxides, notably zinc oxide and titanium dioxide, are known to be photosensitizers or photocatalysts. Goodeve and Kitchener[1] obtained powerful photosensitization with TiO_2, studied by bleaching a blue dye under near-UV irradiation. Jacobsen[2] correlated outdoor chalking behavior of TiO_2 pigmented paints with the loss of reflectance of various TiO_2 pigmented media under sunlamp exposure. Weyl and Forland[3] proposed that atomic oxygen was dislodged by photons from rutile and other oxides; e.g., SiO_2 due to the asymmetric force field acting on the surface oxygen atoms.

Although photo-oxidation by zinc oxide has been much more extensively studied than TiO_2, no method to make it non-photo-active for outdoor pigment use has been found. The use of zinc oxide as a photoconductor in electrophotography has stimulated a great deal of study. Bauer and Neuweiler[4] were first to report the formation of hydrogen peroxide in near-UV-irradiated aqueous suspensions of zinc oxide. Markham et al.[5] studied zinc oxide photocatalysis extensively in aqueous systems and showed that sharply increased hydrogen peroxide concentrations were formed in aqueous media containing organic substances.

Yamamoto and Oster[6] reported that ZnO under UV excitation causes polymerization of vinyl monomers if water and oxygen are present. They concluded, on the basis of end group titration of polymethylmethacrylate polymers formed under these conditions, that hydroxyl radicals initiate the polymerization.

Work at IITRI showed that UV irradiated aqueous slurries of a specially prepared TiO_2, produce an oxidant similar to the

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hydrogen peroxide formed in UV irradiated zinc oxide slurries. However, this oxidant does not give the amber pertitanic acid coloration specific for hydrogen peroxide. The formation of hydrogen peroxide in irradiated zinc oxide slurries has been confirmed by other investigators[5] by the titanic sulfate reaction. Both oxidants liberate, of course, iodine from potassium iodide. It was first thought the unknown oxidant was ozone; however, the absence of ozone odor at high concentrations and its appreciable solubility in water (concentrations of 500 ppm have been obtained) rule out this possibility.

Either oxidant (produced in situ by UV irradiation of ZnO and/or TiO_2) might provide a means of oxidizing dissolved organic matter in polluted water, since manufactured hydrogen peroxide and ozone have been used for this purpose.

EXPERIMENTAL

SCREENING OF PHOTOCATALYSTS

Because the level of oxidant obtainable in our previous work was low (8-10 mg/l), an investigation was undertaken to determine if greater concentrations of catalyst would produce higher levels of oxidant.

Initially, the light source was 4 G.E. 100W Fluorescent Daylight lamps on 4-inch centers in an aluminun foil lined reflector 18 inches from the sample. Samples of one-liter volume, in 180 by 100 mm crystallizing dishes, were stirred by magnetic stirrers separated from the dishes by Coolplates* which limited heating by the stirrer motors to about 2°C above ambient.

Catalysts initially examined included Photox 801, zinc oxide, (New Jersey Zinc Co.), titanium dioxide prepared by our own process, and a sample of zinc titanate. The latter had been found to be destructive to organic vehicles under UV light.

Initial experiments conducted at 25 ppm verified previous data and indicated that zinc titanate was a photocatalyst on the basis of an initial equilibrium oxidant level of approximately 5 mg/l as H_2O_2.

In an effort to raise oxidant concentrations, catalyst loadings were increased from 1-5%; however, this had the opposite effect in that equilibrium concentrations dropped substantially.

We concluded that the catalyst was decomposing the oxidants and that once the shaded fraction exceeded the irradiated oxide, the equilibrium concentration dropped.

This effect was quite unexpected, since Markham and Laidler[5], working with fairly concentrated slurries (0.1 g ZnO/25 ml H_2O) had obtained high concentrations (170 mg/l) of H_2O_2. Their results are attributable to the fact that the various organic substances they worked with inhibited the decomposition reaction,

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*Thermodyne Corporation Dubuque, Iowa.

thus strongly favoring oxidant formation.

Since the dilute slurries absorb only a small fraction of the radiation, use of an oxidized metal surface as the photo-catalyst was investigated. In this way access of the solution to shaded surfaces would be decreased or prevented. Also, in many cases, it was thought the oxidized surface would be a more efficient absorber of radiation than the white pigments. On this assumption a number of metals were examined including zinc, copper, nickel, bronze, titanium, and tin.

In some cases the metal was heavily oxidized by heating and in others it was used with the normal invisible oxide of the metal. Many of these materials, especially zinc and copper, looked quite promising at first, on the basis of oxidant levels which in the case of zinc rose rapidly at first to about 25 mg/l H_2O_2; however, as the formation of zinc oxide proceeded it dropped to 2.5 mg/l in about 3 days.

In addition to oxidized metals it was found that a number of other substances show photocatalytic properties, for example, Ottawa silica sand and two man-made pigments which were largely Fe_2O_3 and Fe_3O_4. Two dimensional catalyst surfaces such as ceramic porcelain ware and Pyrex as well as films of zinc undecylate developed oxidant concentrations of 5-10 mg/l when illuminated for a week or so. Of the oxidants formed, all were of the non-hydrogen peroxide variety (with the exceptions of irradiated zinc and tin metal plates) as determined by their negative pertitanic acid tests with titanic sulfate reagent. Since we have not yet identified oxidant "x", as we call it, and since it is detected by the oxidation of potassium iodide these oxidants were both reported as hydrogen peroxide as deter-mined by a spectrophotometric starch iodide method described in detail in the Appendix.

We concluded that there must be many substances, other than man-made, which exhibit photocatalytic properties; in all probability ordinary beach sand contains photocatalytic minerals. To test this hypothesis, sand was obtained from a nearby beach

and exposed to daylight fluorescent radiation.

After 2 days of exposure, of a thin layer of sand, the oxidant level rose to 3.5 mg/l. A thick layer of sand produced a faint but definite trace of oxidant which remained constant after a few days of exposure. The difference is attributed to the enhancement of the reverse reaction in the thick layer. Apparently, our hypothesis was correct. Oxidant "x" is being formed and decomposed on shores and beds of streams where natural photocatalysts are illuminated by solar energy. We theorized that photocatalysis is a mechanism of nature to remove organic pollutants in addition to non-catalytic photolysis, autoxidation and biodegradation. This theory was subsequently verified by brief, but conclusive, experiments demonstrating the removal of organic contaminants from water by simulated sunlight. These experiments are described in the following section.

The site from which sand samples were obtained was substantially that from which Pettijohn[7] obtained his. Since this is natural beach, it is assumed the mineral content is similar to that he reports. The principal minerals found by Pettijohn were garnet (Mg, Ca, or Fe-Al silicate); augite $(CaO \cdot MgO \cdot 2SiO_2)$; Hornblende $(3[MgFe]O \cdot CaO)$; SiO_2; ilmenite (FeO 48%, TiO_2 52%), and magnetite (Fe_3O_4) along with calcium and magnesium carbonaceous minerals.

PHOTOXIDATION OF ORGANIC SUBSTANCES

Although we had hoped to find a catalyst superior to the powdered oxides initially investigated, it became increasingly evident that oxidant level, per se, was not a valid indication of organic oxidation effectiveness. Consequently, efforts were directed toward actual oxidation studies which were monitored by the Beckman Total Organic Carbon Analyzer.

The first experiments, run in zinc pans, were inconclusive. Although linear alkylate sulfonate (LAS) was oxidized, we suspected that galvanic factors due to the formation of oxygen concentration cells were involved since oxidation in dark samples

approached that of illuminated samples. For this reason further work with oxidized metal surfaces was abandoned.

The first definite photo-oxidation of an organic substance obtained is shown in Figure 1. The apparent initial rise in organic carbon is not understood; it may have been due to desorption of an organic substance from the catalyst (20 g zinc titanate in 350 ml H_2O). The superiority of the sunlamps* whose emission is almost entirely in the 3000-4000Å region over the G.E. Daylight fluorescent lamps, is clearly evident from the Figure. This superiority was somewhat surprising since oxidant levels were about the same under each source. This demonstrates that oxidant level alone is not a valid indication of organic oxidation rate. With few exceptions, subsequent tests were run under sunlamps. These samples were exposed in 180 mm-diameter Pyrex dishes, 75 mm deep without agitation. In view of its poor showing in these tests, further work with $ZnTiO_4$ was discontinued.

Figure 2 demonstrates oxidation of both phenol and benzoic acid and the H_2O_2 concentration does increase in the presence of organic matter as reported by Markham and Laidler[5]. The higher values obtained by those authors are probably due to the fact they used pure oxygen. Markham and Laidler, as well as Oster and Yamamoto[8], showed oxygen to be essential to the photo-oxidation by zinc oxide.

The samples in Figure 2 were exposed in 180 x 100 mm crystallizing dishes and stirred magnetically. Dishes were placed eccentrically which helps to prevent the catalyst from settling. Analyses for total organic carbon (TOC) and oxidant were made on "whole samples", i.e., catalyst and solution which avoids artifacts due to adsorption of degradation products on the catalyst which appears to vary in the course of the test. In hundreds of tests, the small quantity of oxide introduced into the combustion zone of the organic carbon analyzer had no apparent effect.

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*8 twenty watt sunlamps on 4" centers with an aluminum reflector 18" from the sample.
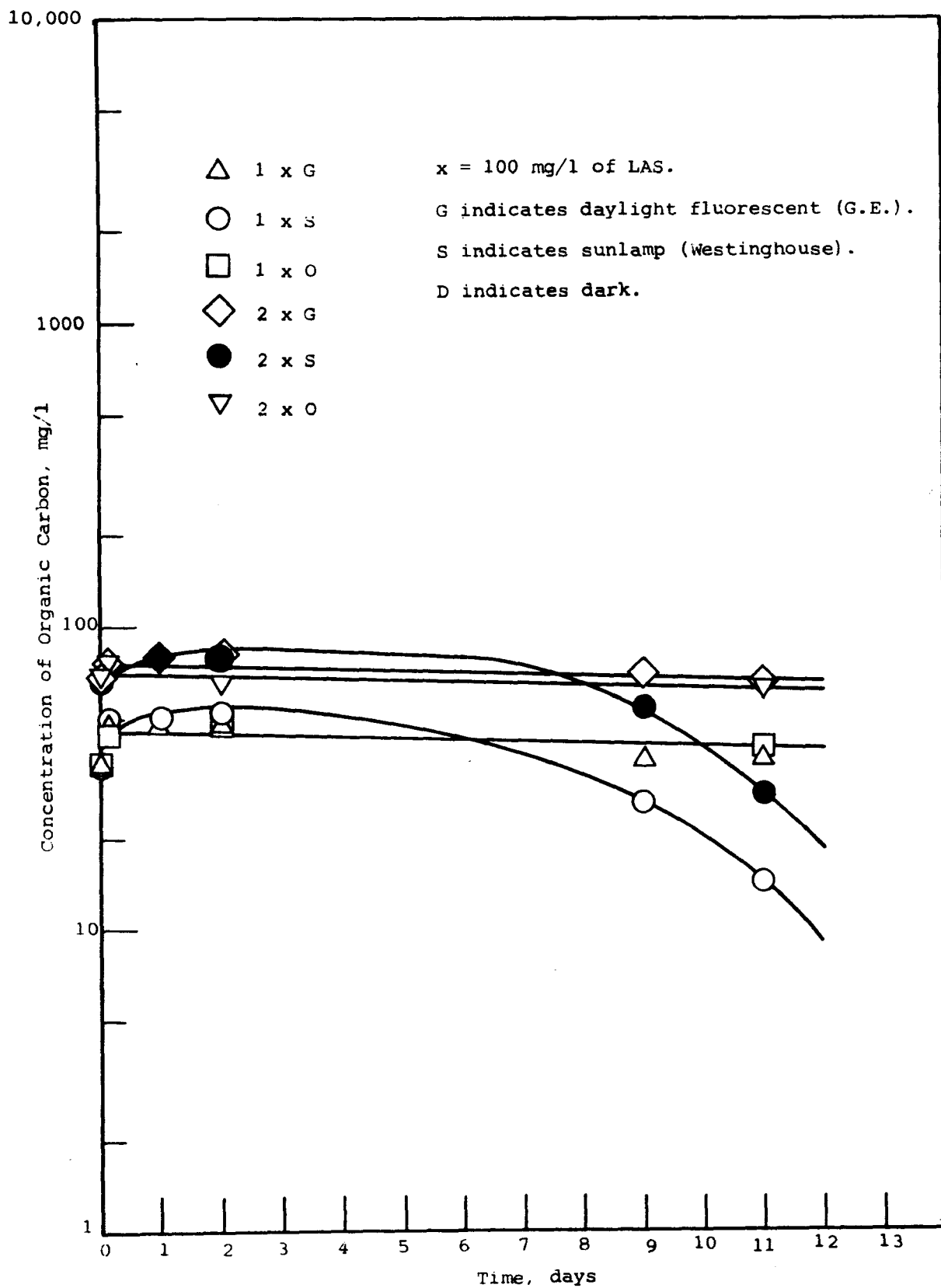
Figure 1

EFFECT OF LIGHT SOURCE ON LAS REMOVAL
BY ZINC TITANATE

Table 1

EFFECT OF LIGHT SOURCE ON LAS REMOVAL BY ZINC TITANATE

Concentration of Organic Carbon, mg/l

Time, day

Sample	0		3[a]		1		2		9		11	
	Carbon	pH	Carbon	pH	Carbon	pH	Carbon	pH	Carbon	pH	Carbon	pH
1xG	35.0	7.2	47.5	6.1	47.5		48.5		36.0	5.9	36.0	6.0
1xS	35.0	7.2	48.5	6.3	50.0		51.0		26.0	6.1	14.5	6.0
1xD	35.0	7.2	45.0	6.4			50.0				39.0	5.8
2xG	69.5	7.0	76.0	6.2	81.0		80.0		69.5	4.8	65.0	5.4
2xS	69.5	7.0	74.0	6.2	80.5		81.0		53.5	4.7	28.0	5.8
2xD	69.5	7.0	74.0	6.4			66.0				62.0	5.8

[a]Hours.

x = 100 mg/l of LAS.

G indicates daylight fluorescent (G.E.).

S indicates sunlamp (Westinghouse).

D indicates dark.

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Figure 2

EFFECT OF DEPTH OF SAMPLE ON OXIDATION OF PHENOL
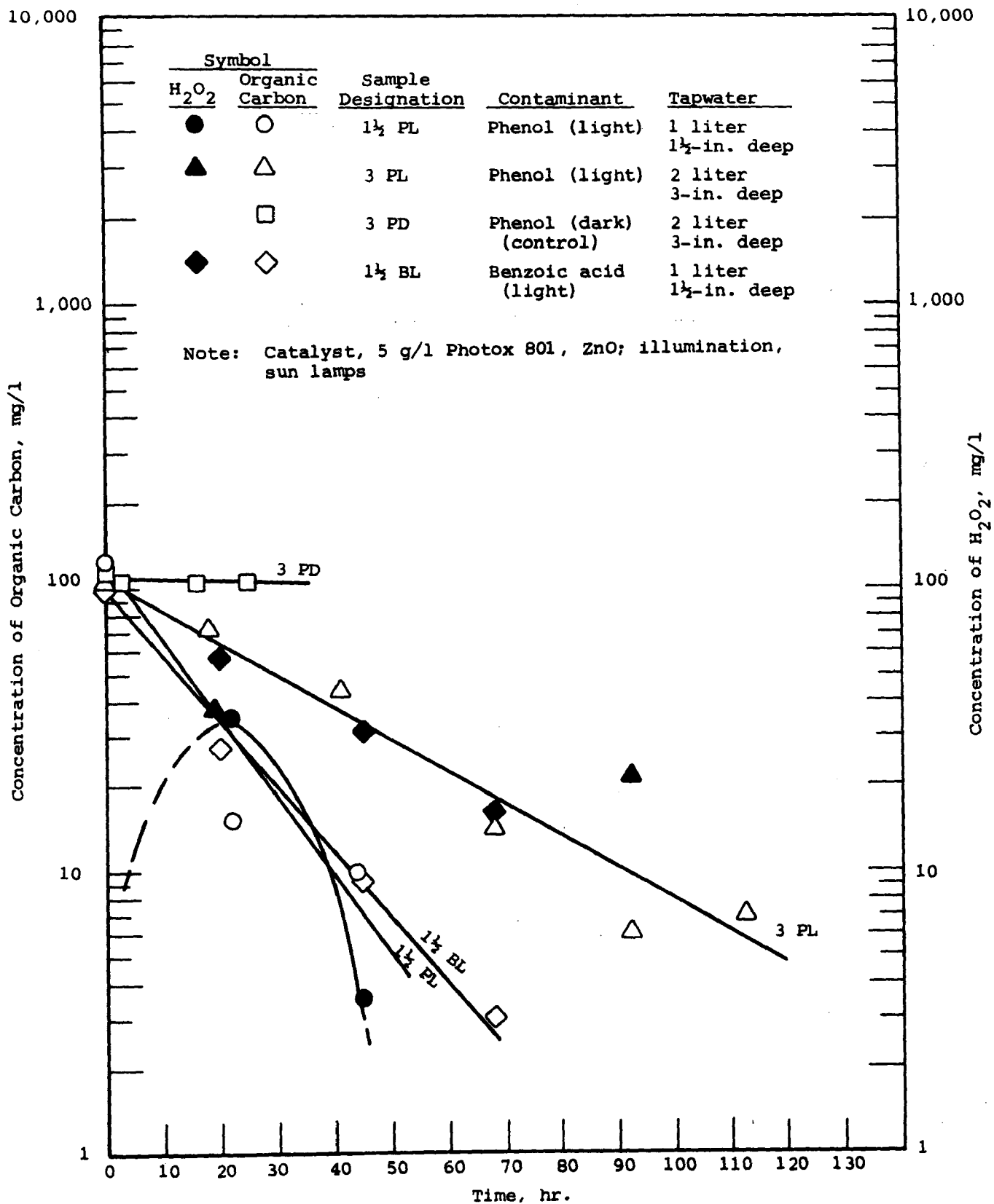AND COMPARISON OF PHENOL AND BENZOIC ACID OXIDATIONS

Table 2

EFFECT OF DEPTH OF SAMPLE ON OXIDATION OF PHENOL
AND COMPARISON OF PHENOL AND BENZOIC ACID OXIDATIONS
(Catalyst, 5 g/l, Photox 801 (N.J.Z.)

	Concentration of Organic Carbon and H_2O_2, mg/l						
	Sample						
	1-1/2[a] PL		3 PL		3 PD[b]		1-1/2 BL	
Time, hr	Organic Carbon	H_2O_2	Organic Carbon	H_2O_2	Organic Carbon	H_2O_2	Organic Carbon	H_2O_2
0	122		104		114		101	
3					106			
18					106			
19			73	38				
20							27	56
22	15	35						
25					104			
41			44					
44	11	3.5						
45							9	32
68			14				3	16
92			6	23				
112			7	8				

[a]1-1/2-in. depth, 3-in. depth, etc.

[b]Control sample kept in dark.

Note: The phenol sample concentrations were approximately 0.15 g/l, and the benzoic acid sample concentration was also approximately 0.15 g/l.

Sample Designation	Contaminant	Tapwater
1½ PL	Phenol (light)	1 liter 1½-in. deep
3 PL	Phenol (light)	2 liter 3-in. deep
3 PD	Phenol (dark) (control)	2 liter 3-in. deep
1½ BL	Benzoic acid (light)	1 liter 1½-in. deep

First order kinetics were observed for the oxidation of both phenol and benzoic acid. The decrease in hydrogen peroxide concentration after a sharp initial rise appears to follow a similar path, though the data are incomplete. Control samples stored in the dark showed no reaction between either photo-catalytically produced oxidant or H_2O_2 with organic matter. This suggests that the oxidation is directly associated with the active oxygen species released by the radiation.

Figure 3 represents an effort to assess the importance of catalyst loading on phenol oxidation. Samples were magnetically stirred in 100 mm by 180 mm crystallizing dishes. The data indicate only slight gains by increased catalyst loading from 2.5 g/l - 10 g/l, whereas at 0.5 and 0.1 g/l proportionately lower oxidation rates were encountered. This suggests that once all the incident light is absorbed, additional catalyst gives only slightly improved removal of organic carbon.

Despite the apparent lack of effect of excess catalyst, a recirculation system was devised to keep all the catalyst in suspension.

Several three gallon Pyrex bottles were cut off 2 inches from the mold line at the shoulder and the bottom was discarded. The neck was reduced in diameter and a 29/42 standard taper female fitting was fused to the reduced neck. A male taper fitting with a suitable opening for drainage was attached by springs and the assembly was inverted on an iron tripod. The bottom drain was connected to a the suction side to a peristaltic pump with a Viton tube after first passing the slurry through a water-cooled condenser. The discharge of the pump was connected to a 10 mm tube with a right angle bend terminating in a 3 mm nozzle which was arranged at the outer periphery of the vessel so that the discharge imparted a circular motion to the contained slurry. In this manner the mixture was constantly recirculated at a rate of about 1 l/min. Additional aeration was provided by a sintered glass gas dispersion tube immersed to within about 1 inch from the pump intake. Air from an aquarium
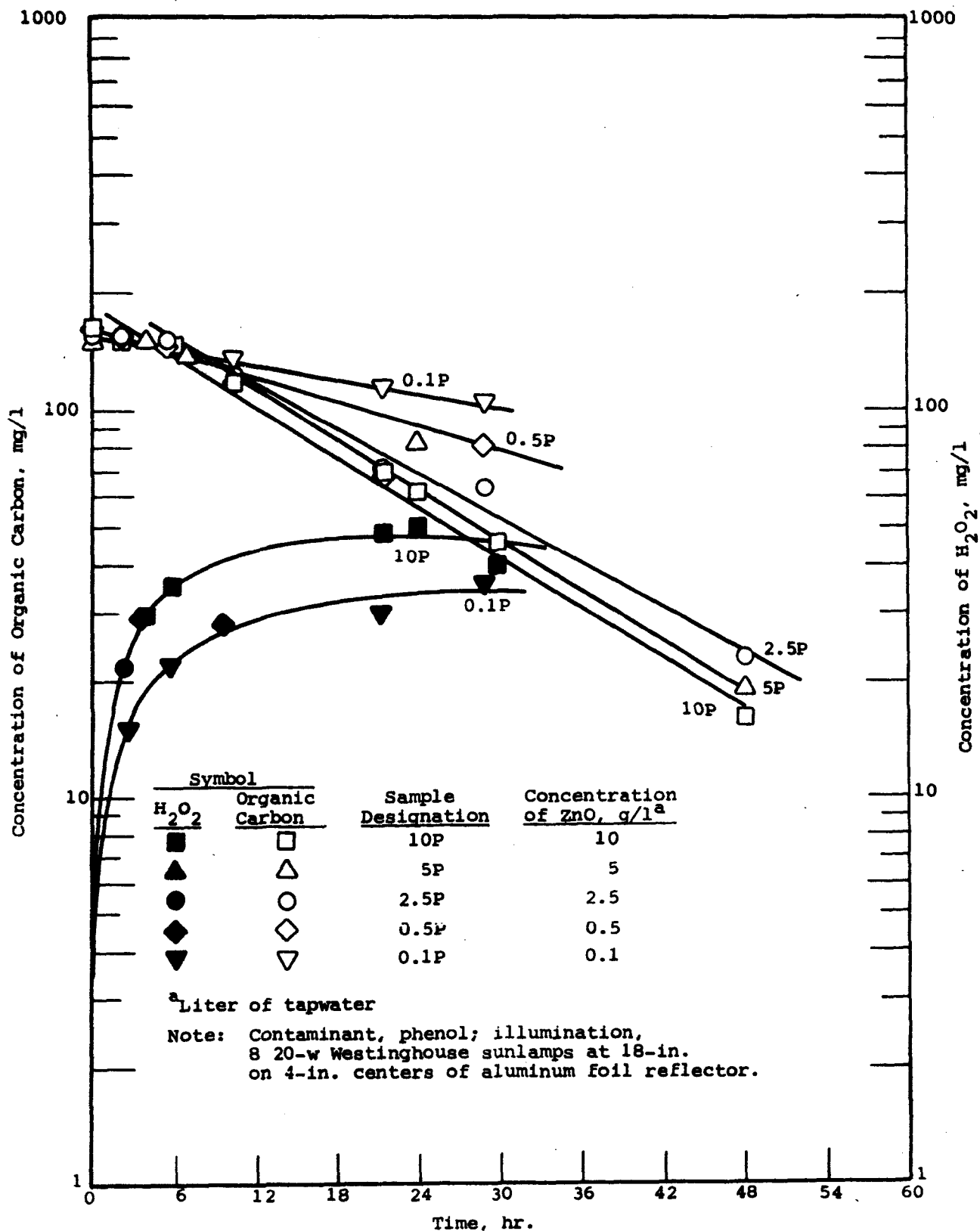
Figure 3

EFFECT OF VARIOUS ZnO LEVELS
ON MAGNETICALLY STIRRED SAMPLES

Table 3

EFFECT OF VARIOUS ZINC OXIDE LEVELS ON MAGNETICALLY STIRRED SAMPLES

Sample	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2
10P	0	161		2.3	152		4		29.6	5.8	144	35	10.7	118	
5P	0	150		4	150					7	137				
2.5P	0	155		2.2	162	22				5.4	151		10.7	125	
0.5P	0	161		2.2	154		3.5		28.5	5.6	149		10.7	118	28
0.1P	0	155		2.2	152	15				5.8	153	22	10.5	134	
(cont.)															
10P	21.7	68	48	24	61 / 51[a]	50	30	45	38	48	16 / 6[a]				
5P	24	83								48	19				
2.5P	21.5	71		29	63					48	23				
0.5P	21.5	72		29	82										
0.1P	21.7	111	30	29	103	36									

[a]Centrifuged.

Sample Designation	Concentration of ZnO, g/l[a]
10P	10
5P	5
2.5P	2.5
0.5P	0.5
0.1P	0.1

pump was provided at a rate of 60 ml/min.

Figure 4 depicts results of recirculation at various catalyst loadings and shows a sharp increase at 10 g/l. At catalyst loadings of 2 and 5 g/l, however, there seems little effect. Even with the recirulcation system sedimentation of the catalyst occurred in certain instances. It is interesting to note the behavior of the H_2O_2 concentration in these tests. With phenol contaminant the level drops more rapidly with higher catalyst loading and shows a general relationship to the residual contaminant. This does not hold true for acetic acid however, since the concentration drops sharply while the residual contaminant is still high. The H_2O_2 concentration for sucrose (Figure 7) appears to level off and remain high despite the high catalyst loading. A better understanding of these phenomena might provide useful insights into the effects of pollutants in the natural environment.

Figure 5 shows little difference between magnetic stirring or recirculation if one takes into account the lower starting concentration of samples 5P, 1½Bl, and 1½Pl. The curve for the 1½Pl sample may be the result of sampling errors.

Figure 6, on the other hand, shows a clearcut advantage of recirculation over magnetic stirring. Figure 7 shows a comparison of phenol with sucrose, sodium stearate and two examples of acetic acid oxidation. The difference in the two acetic acid runs is due to the sequence of adding the zinc oxide and acetic acid. The acetic acid curve on Figure 4 was obtained by first adding the acid to tap water and then adding the zinc oxide. This method removes all of the inorganic carbon. However, over the course of the oxidation inorganic carbon returned to the original value. In a later experiment, shown in Figure 7, the zinc oxide was added before the acetic acid, which results in the formation of zinc acetate which is more slowly oxidized, accompanied by a substantial rise in inorganic carbon means that one product of oxidation of zinc acetate is zinc carbonate. From Figure 7, it can be seen that phenol, acetic acid (added
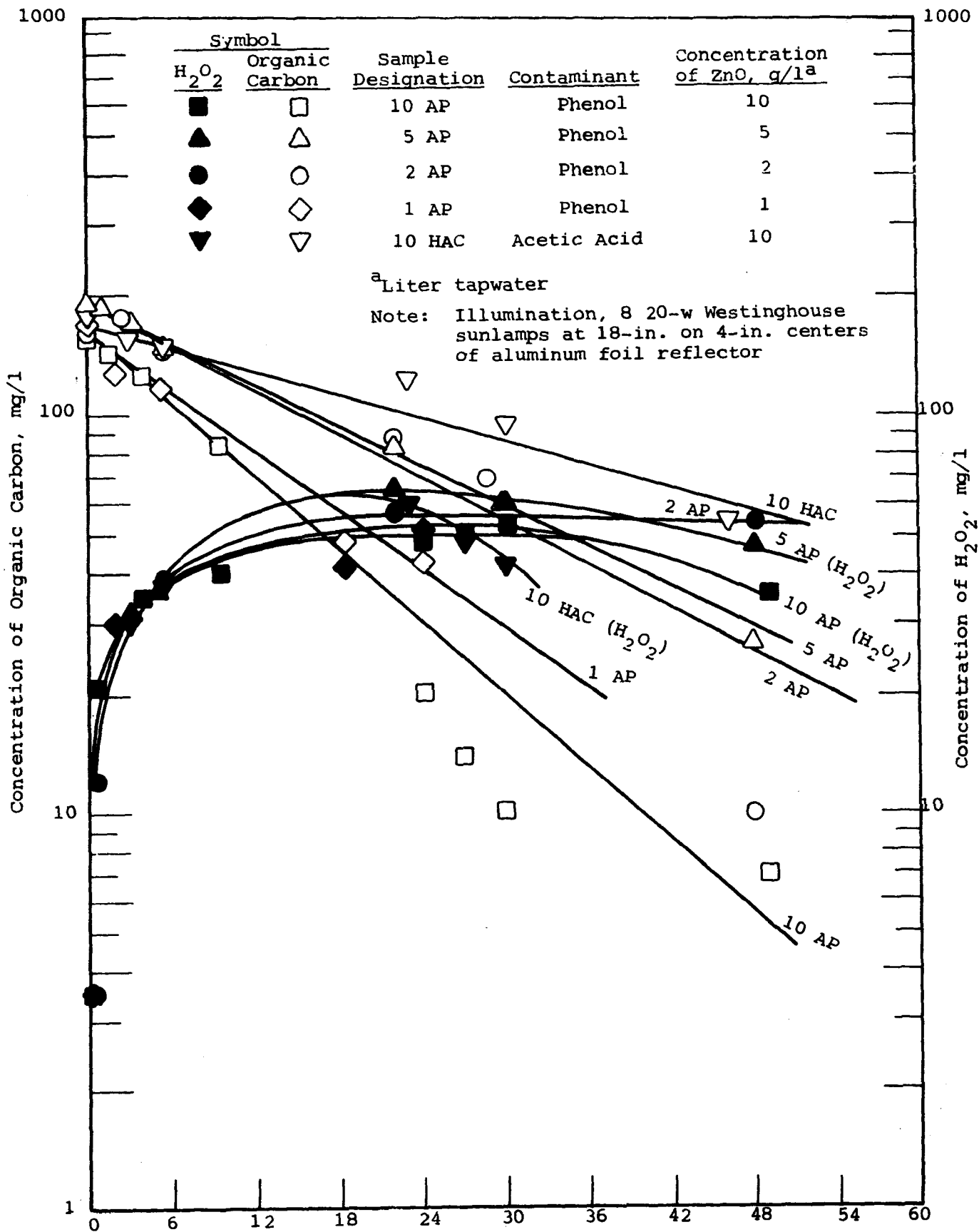
Figure 4

EFFECT OF ZINC OXIDE LOADING
ON RECIRCULATED SAMPLES

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Table 4

EFFECT OF ZINC OXIDE LOADING ON RECIRCULATED SAMPLES

Sample	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2
10 AP	0	157.5	3.5	.75		21	1.5	141		4	126	35	9.5	82	40
5 AP	0	190		1	183		3.1	170	31	5.3	146	37	22	82	66
2 AP	0	160	3.5	.3		12	2.4	175		5.2	147	38	22	88	57
1 AP	.	170	3.5	2	139	30	5.3	115	39	18.7	48	42	24	43	52[a]
10 HAC	0	178		3	156	30	5.5	148	37				23	124	60
(cont.)															
10 AP	24	20	48	27	14	50	30	10	53	49	7	36			
5 AP	29.7	60	60	48	27	47									
2 AP	28.8	70	60	48	10	54									
10 HAC	30	95	42	46	55	50									

[a]Discontinued.

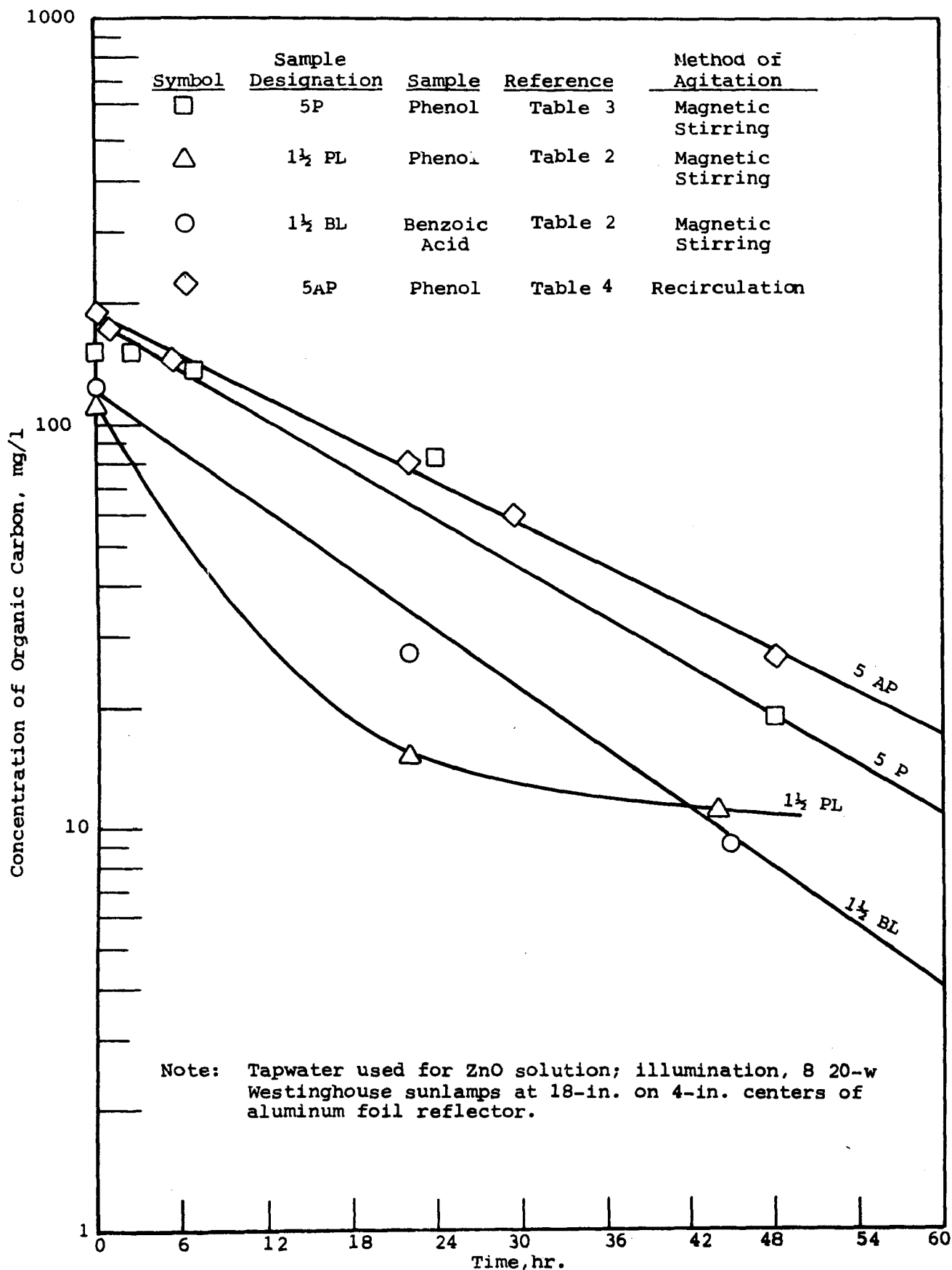| Sample Designation	Contaminant	Concentration of ZnO, g/l[a]
10 AP	Phenol	10
5 AP	Phenol	5
2 AP	Phenol	2
1 AP	Phenol	1
10 HAC	Acetic Acid	10

Figure 5

COMPARISON OF AGITATION METHODS
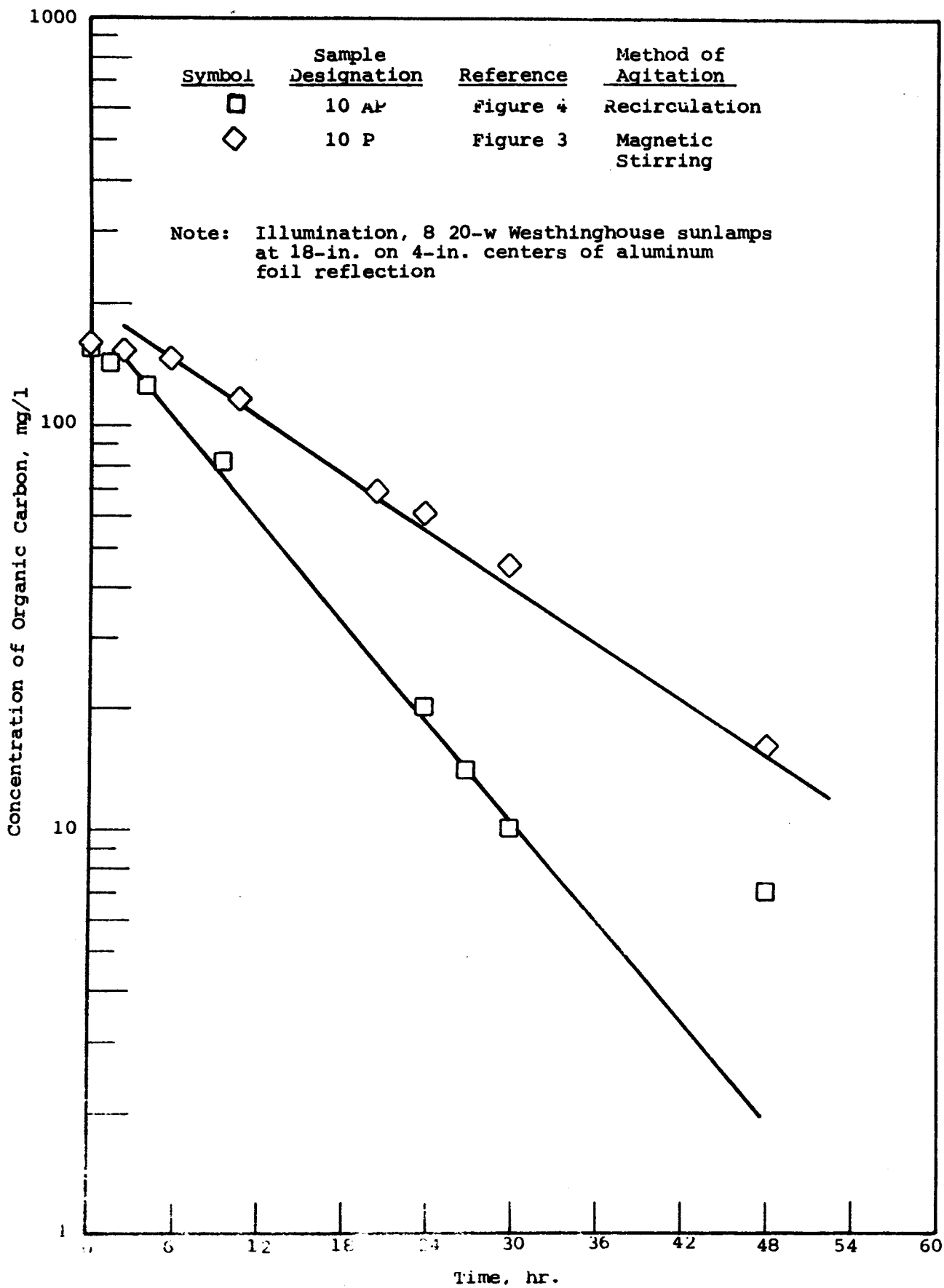USING A ZnO CONCENTRATION OF 5 g/l

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Figure 6

COMPARISON OF AGITATION METHODS ON OXIDATION OF PHENOL
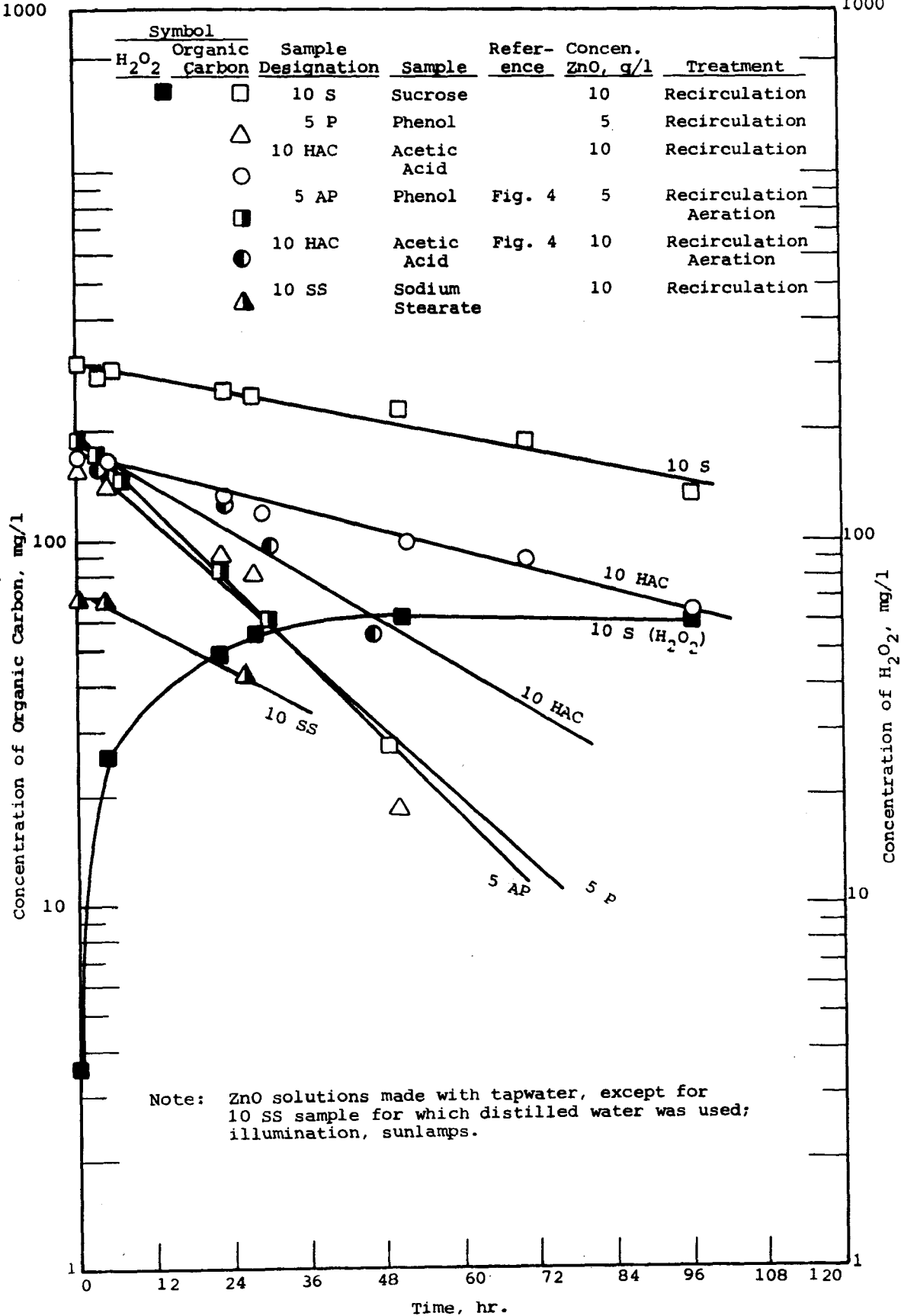USING 10 g OF ZINC OXIDE

Figure 7

COMPARISON OF AERATED WITH NONAERATED RECIRCULATED SLURRIES, ALSO OXIDATION OF ACETIC ACID, SUCROSE, PHENOL, AND SODIUM STEARATE

Table 5
(Data plotted in Figure 7)

COMPARISON OF AERATED WITH NONAERATED RECIRCULATED SLURRIES,
ALSO OXIDATION OF ACETIC ACID SUCROSE, PHENOL, AND SODIUM STEARATE

Sample	Contaminant	Concentration of ZnO, g/l	Time, hr	Concentration mg/l Organic Carbon	H_2O_2	Time, hr	Concentration mg/l Organic Carbon	H_2O_2	Time, hr	Concentration mg/l Organic Carbon	H_2O_2	Time, hr	Concentration mg/l Organic Carbon	H_2O_2
10S[a]	Sucrose	10	0	296		3.5	276	25	5.3	289		22.9	252	48
5P[a]	Phenol	5	0	152		4.3	139	--	--	--		22.3	92	
10HAC[a]	Acetic Acid	10	0	166		5.0	166	--	--	--		22.7	130	
10SS[a]	Sodium Stearate	10	0	69		4.1	67	8	25	42		discontinued		
(cont.)														
10S			27.7	249	55	50	228	62	70	188		46	133	60
5P			27.3	80	--	50	18		70	discontinued				
10HAC			28.5	118	--	51	97		70	89		96	64	--

[a]Samples recirculated without aeration.

Sample Designation	Sample	Reference	Concen. ZnO, g/l	Treatment
10 S	Sucrose		10	Recirculation
5 P	Phenol		5	Recirculation
10 HAC	Acetic Acid		10	Recirculation

Sample Designation	Sample	Reference	Concen. ZnO, g/l	Treatment
5 AP	Phenol	Fig. 4	5	Recirculation Aeration
10 HAC	Acetic Acid	Fig. 4	10	Recirculation Aeration
10 SS	Sodium Stearate		10	Recirculation

before zinc oxide), sodium stearate and sucrose are oxidized with increasing difficulty in that order. The sodium stearate curve represents zinc stearate oxidation. Figure 7 also compares re-circulated aerated samples with non-aerated recirculated samples.

These results demonstrate that aeration does not enhance the oxidation mechanism. No differences in dissolved oxygen were noted, being in both cases, saturated at the temperature of the tests.

To obtain a more coherent picture of the effects of agitation as well as to assess the degree to which air stripping and/or autoxidation are involved, the experiments illustrated in Figure 8 were conducted.

This figure shows a comparison of various methods of agitation with respect to phenol removal. Comparison of the aerated samples in the dark and the illuminated samples, without catalyst in each case, shows that part of the phenol removal is by strip-ping and/or autoxidation. The additional removal under illumin-ation (without ZnO catalyst) are photocatalytic oxidation by Pyrex which is a weak photocatalyst*. A similar acceleration occurs with magnetically stirred samples in the light without catalyst compared to similar samples in the dark. Phenol added to distilled water stirred in polyethylene (not shown) had a slope closely paralleling the magnetically stirred sample in the dark.

Since much of the increase in oxidation rate was due to air stripping in both the recirculated and the aerated samples, we decided to return to magnetic stirring because this method shows the greatest effect due to the presence of catalyst. However, none of the methods keeps the catalyst entirely in suspension. Initially we thought as long as sufficient catalyst was in sus-pension to absorb all the incident radiation, an excess would do no harm. This is true if the pigment all remains in suspension;

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*Distilled water magnetically stirred reaches an equilibrium concentration of oxidant "x" as H_2O_2 of 4 mg/l when illuminated by G.E. Daylight fluorescent lamps for 6 days.
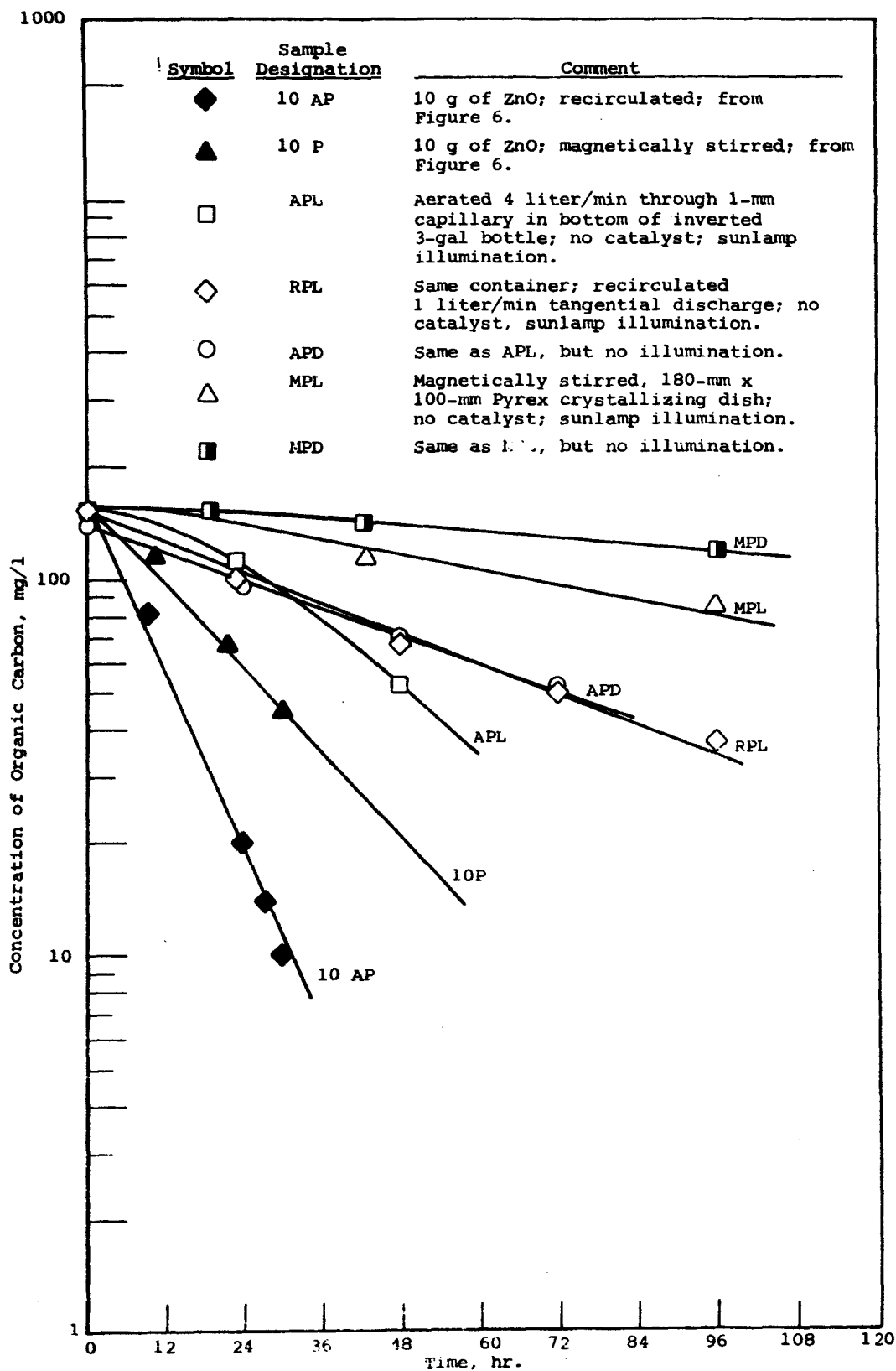
Figure 8

COMPARISON OF VARIOUS AGITATION METHODS
IN REMOVING PHENOL

Table 6
(Plotted in Figure 8)

COMPARISON OF METHODS OF AGITATION ON OXIDATION OF PHENOL USING 10g OF ZINC OXIDE

Sample	Time, hr	Organic Carbon	H_2O_2	Time, hr	Organic Carbon	H_2O_2	Time, hr	Organic Carbon	H_2O_2	Time, hr	Organic Carbon	H_2O_2
		Concentration mg/l			Concentration mg/l			Concentration mg/l			Concentration mg/l	
APL	0	154		23	112	--	48	52	--	72	--	
RPL	0	153		23	101	--	48	67	3.0	72	50	
APD	0	140		24	97	--	48	70	--	72	51	
MPL	0	155		19	152	1.5	43	115	--	96	85	
MPD	0	157		19	155	--	43	140	--	96	112	

Sample Designation	Comment	Sample Designation	Comment
APL	Aerated 4 liter/min through 1-mm capillary in bottom of inverted 3-gal bottle; no catalyst; sunlamp illumination.	APD	Same as APL, but no illumination.
RPL	Same container; recirculated 1 liter/min tangential discharge; no catalyst, sunlamp illumination.	MPL	Magnetically stirred, 180-mm x 100-mm Pyrex crystallizing dish; no catalyst; sunlamp illumination.
		MPD	Same as MPL, but no illumination.

however, if the contaminant is appreciably adsorbed on settled catalyst, it is protected from oxidation and may only become available for oxidation through diffusion, thereby slowing the process.

PHOTOCATALYTIC OXIDATION OF PHENOL WITH TiO$_2$ AND BEACH SAND

Since we had on hand only limited amounts of the special TiO$_2$ catalyst prepared in our previous work, it was necessary to prepare it. The TiO$_2$ was obtained from New Jersey Zinc Co. in slurry form and did not contain the stabilizing additives, e.g., silicates that are normally added to minimize photocatalysis in commercial pigments. This slurry was washed chloride-free and nearly sulfate-free. The resultant cake was dried at 100°C. Figure 9 compares oxidation of phenol by various types of TiO$_2$. Based on limited tests the optimum calcination temperature is about 850°C since at 48 and 72 hrs, the 850°C sample is better than either the 825°C or 875°C sample. The apparent increase in rate of oxidation with time is interesting. In subsequent tests (not shown), a commercial anatase and an active TiO$_2$ prepared some years ago by the IITRI technique were also compared under the same conditions; both were definitely inferior to the samples shown in Figure 9 in oxidation of phenol under the same conditions.

A brief experiment was conducted to determine the effectiveness of beach sand. These data are shown graphically in Figure 10 and support our previously stated conviction that photo-oxidation by natural catalysts under solar irradiation is a mechanism of nature for the removal of organic matter from streams and lakes. In these tests, 300 g of water washed beach sand were placed in the recirculation container described previously and 4 1/min of room air was pumped through from the bottom. This produced much less agitation in sand than anticipated and much less than sample APD, since the column of water being agitated was about six times longer due to the absence of sand. The true comparison is between 300 PBD and 300 PBL. The leveling off of 300 PBL at 22 mg/1 is believed due to the presence of a refractory organic substance leaching out of the sand or possibly
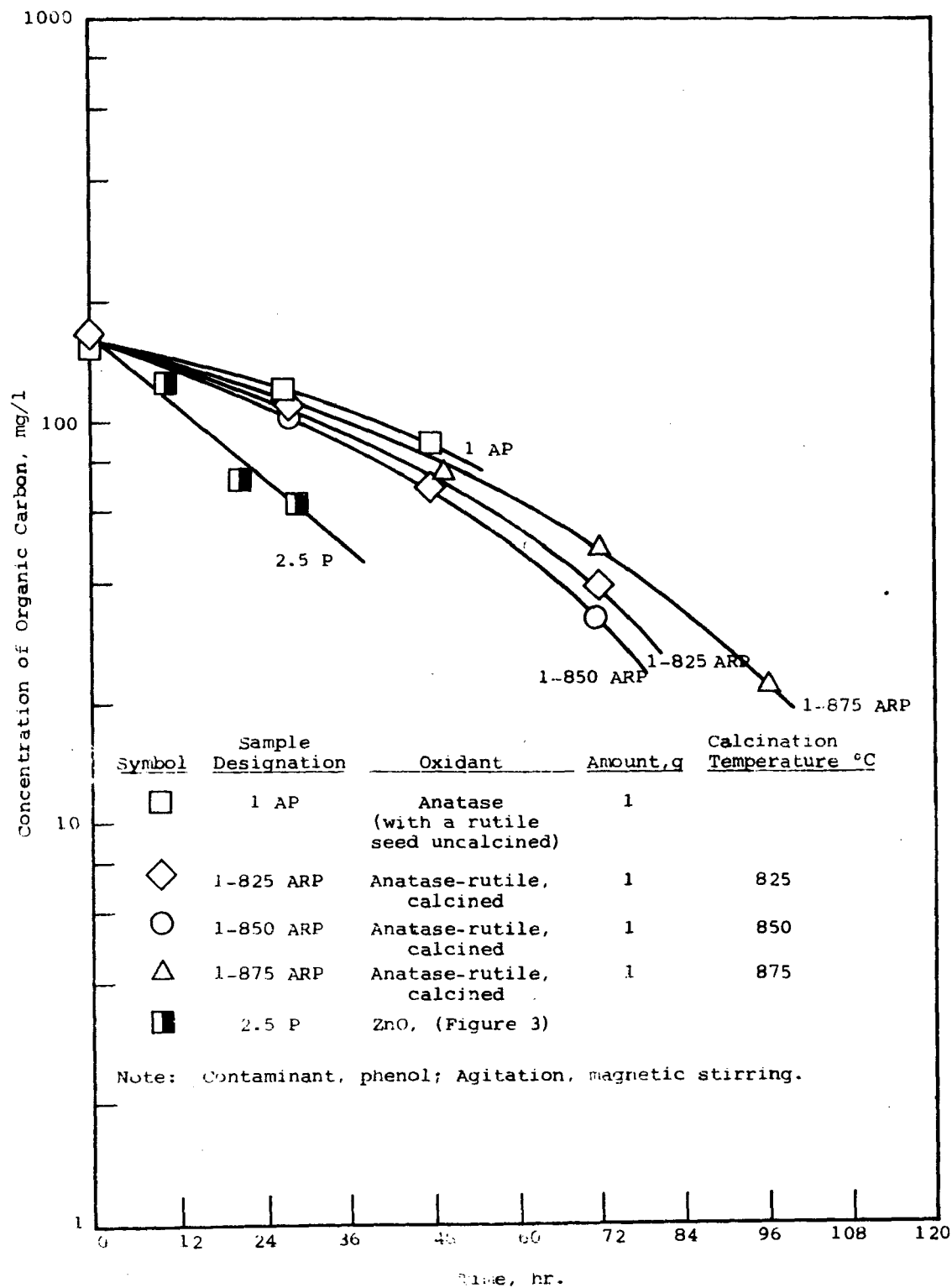
Figure 9

OXIDATION OF PHENOL WITH ANATASE AND ANATASE-RUTILE
PREPARED BY CALCINATION AT DIFFERENT TEMPERATURES

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Table 7
(Plotted in Figure 9)

OXIDATION OF PHENOL WITH ANATASE AND ANATASE-RUTILE
PREPARED BY CALCINATION AT DIFFERENT TEMPERATURES

Sample	Catalyst	Calcination Temperature °C	Time, hr	Concentration mg/l Organic Carbon	H_2O_2	Time, hr	Concentration mg/l Organic Carbon	H_2O_2	Time, hr	Concentration mg/l Organic Carbon	H_2O_2
1-AP	Anatase	Not calcined	0	155	0	25.7	120	0	48	89	--
1-825 ARP	Anatase-Rutile	825	0	166	0	26	110	3.3	48	70.0	--
1-850 ARP	Anatase-Rutile	850	0	168	0	26	105	3.5	48	67	3.0*
1-875 ARP	Anatase-Rutile	875	0	156	0	23	137	2.8	50	75	--
(cont.)											
1-825 ARP			72	39							
1-850 ARP			72	32							
1-875			72	49		96	24				

*Oxidant, reported as H_2O_2

Note: All samples contained 1 g of pigment

1000

Concentration of Organic Carbon, mg/l

100

300 PBD

PEL

APD

300 PBL

10

Symbol	Sample Designation	Sample	Illumination
□	300 PB	Aerated Beach Sand	Sunlamp
◇	300 PBD	Aerated Beach Sand	None
○	APD	Aerated Beach Sand (no catalyst) control	None
△	PEL	Polyethylene dish, magnetically stirred (no catalyst)	Sunlamp

Note: Contaminant, phenol.

1

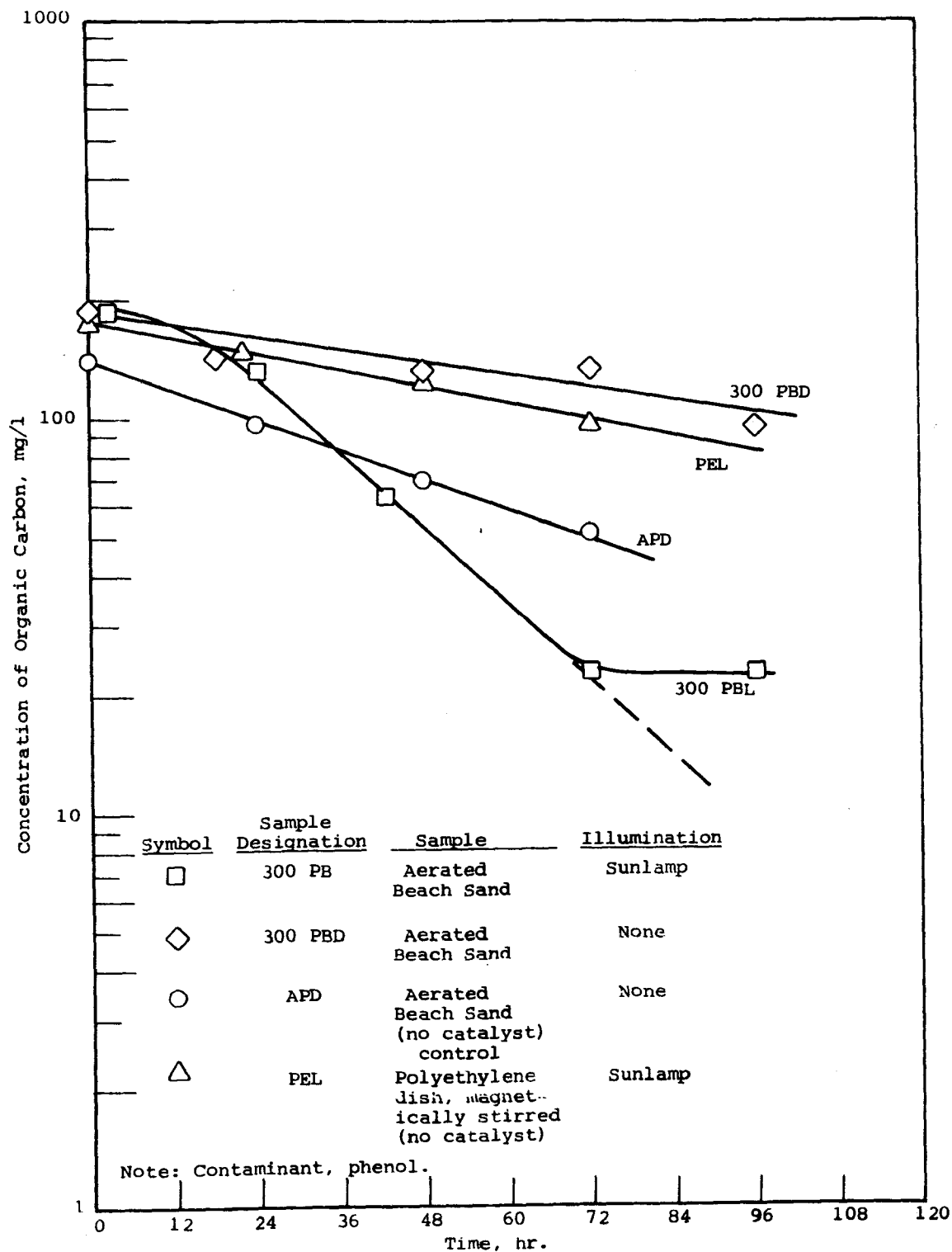0   12   24   36   48   60   72   84   96   108   120

Time, hr.

Figure 10

EFFECT OF ILLUMINATION ON OXIDATION OF PHENOL
BY BEACH SAND

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Table 8
(Plotted in Figure 10)

EFFECT OF ILLUMINATION ON OXIDATION OF PHENOL BY BEACH SAND

Sample	Time, hr	Concentration mg/l Organic Carbon	H_2O_2	Time, hr	Concentration mg/l Organic Carbon	H_2O_2	Time, hr	Concentration mg/l Organic Carbon	H_2O_2
300 PBL	0	172		3.1	187		24	132	13*
300 PBD	0	185	0	16	144		48	131	
PEL	0	181		22	149		48	124	
(cont.)									
300 PBL	42.5	54		72	23	11*	94	23	
300 PBD	72	134		96	96				
PEL	72	96							

Sample Designation	Sample	Illumination	Sample Designation	Sample	Illumination
300 PBL	Aerated Beach Sand	Sunlamp	APD	Aerated Beach Sand (no catalyst) control	none
300 PBD	Aerated Beach Sand	none	PEL	Polyethylene dish, magnetically stirred (no catalyst)	Sunlamp

*Oxidant, reported as H_2O_2

to particulate organic matter. All samples were whole samples, i.e., they included any particulates generated by the agitation. Sample PEL shows that the oxidation is primarily photocatalytic and not simply due to photolysis.

The intensity of 3000-3800$\overset{o}{A}$ of sunlight is somewhat lower than that of the sunlamps so the natural process may be somewhat slower. On the other hand, in the range of about 3800-4200$\overset{o}{A}$, sunlight is much stronger than the sunlamps, thus the oxidation rates of sunlamp vs. solar irradiation is a question of the relative effectiveness of radiation bands. Unfortunately time did not permit further exploration of this matter.

OXIDATION OF PHENOL WITH THE ACE GLASS COMPANY PHOTOCHEMICAL APPARATUS

The photochemical apparatus consists of a medium-pressure mercury arc contained in a water-cooled quartz jacket which in turn is immersed in a Pyrex jacket. The sample to be irradiated is introduced into the annular space between the quartz and Pyrex containers, where it receives virtually all of the irradiation. Provision is made for sparging, and the exposure space may be pressurized.

The 450-watt mercury arc lamp provides about 0.063 watts/cm^2 of effective illumination vs. about 0.0032 watts/cm^2 for the sunlamps. The increase in oxidation rate due to the higher intensity was quite modest, as can be seen from comparing Figures 8 and 11. Figure 11 also represents an attempt at acceleration of oxidation by dye sensitization which is widely used to broaden the range of spectral absorption in electrophotography. Without a Pyrex filter (sample RB#1 ⌊rose bengal⌋)(Figure 11) the dye is bleached in a few minutes. We believe RB#2 (Figure 11) represents true dye sensitization but the dye oxidized too rapidly for dye sensitization to be of practical interest.

Sudan orange is much more oxidation-resistant than rose bengal but does not increase photosensitivity. The use of high
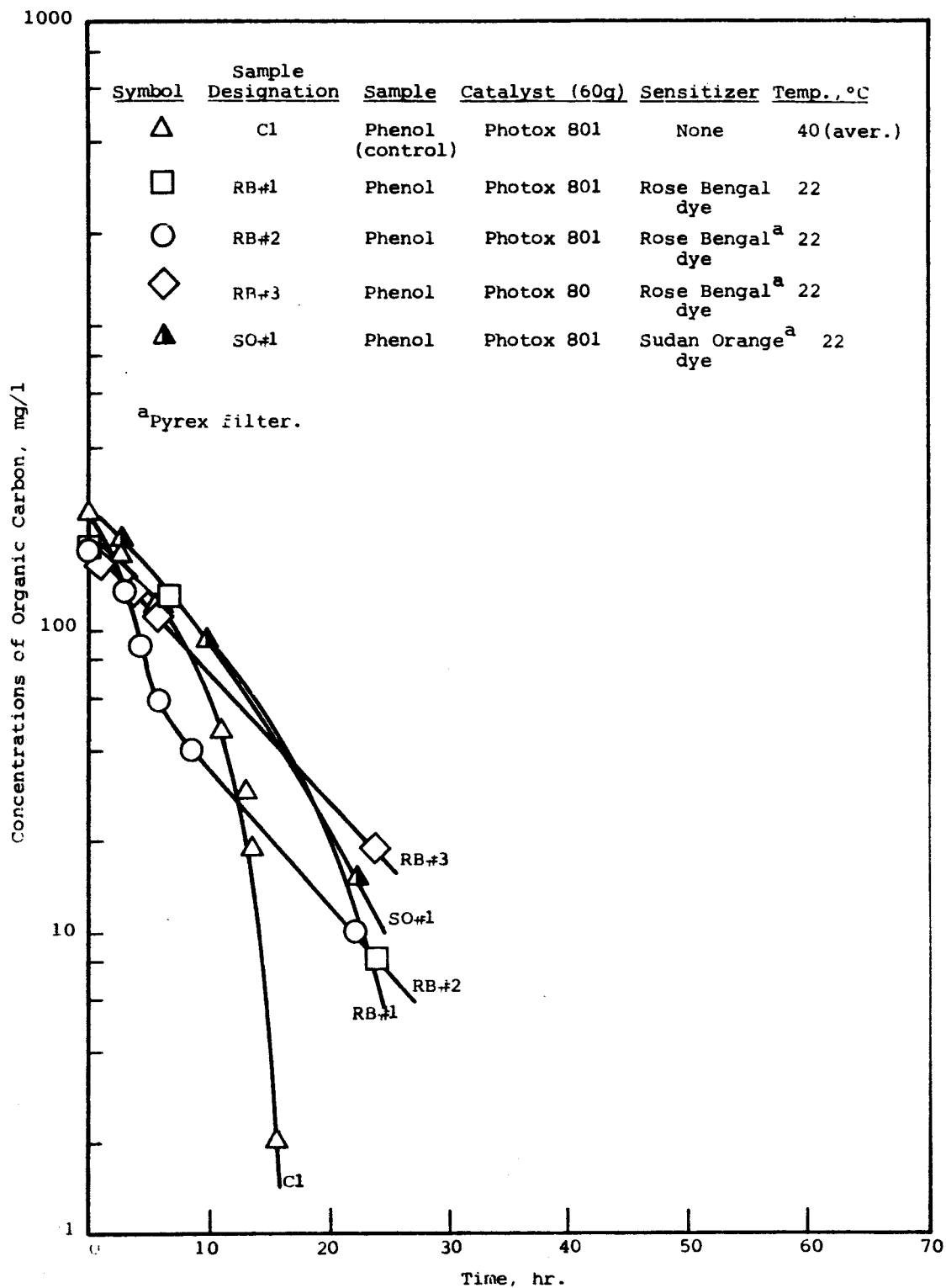
Figure 11

EFFECT OF DYE SENSITIZER ON PHOTOCATALYTIC OXIDATION
IN 'ACE GLASS PHOTOCHEMICAL APPARATUS

Table 9
(Data plotted in Figure 11)

EFFECT OF DYE SENSITIZER ON PHOTOCATALYTIC OXIDATION
IN ACE GLASS PHOTOCHEMICAL APPARATUS

Sample	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2	Time, hr	Concentration, mg/l Organic Carbon	H_2O_2
C1	0	213		0.5	219		1.0	195		2.75	177		6.5	122	
RB#1	0	184		0.25	180	25	8	130		24	14	44 (8 centrifuged)			
RB#2	0	184		0.5	184		3	133	56	4.5	88	62	5.5	58	60
RB#3	0	215		0.16	189		1.3	169	46	3.4	135	56	5.4	110	
SO#1	0	248		0.75	227		2.6	201		6.1	118		9.75	93	
(cont.)															
C1	11	46		13.5	19		16.5	2							
RB#2	8.5	41	58	22.5	10										
RB#3	24	19													
SO#1	22.5	15													

Sample Designation	Sample	Catalyst (60g)	Sensitizer	Temp., °C
C1	Phenol (control)	Photox 801	None	40(Aver.)
RB#1	Phenol	Photox 801	Rose Bengal dye	22
RB#2	Phenol	Photox 801	Rose Bengal[a] dye	22
RB#3	Phenol	Photox 80	Rose Bengal[a] dye	22
SO#1	Phenol	Photox 801	Sudan Orange[a] dye	22

loadings of ZnO (60 g/l) was an attempt to compensate for the
short path exposed to the radiation, approximately ½ inch in the
photochemical apparatus as compared to 1½ inch for the magneti-
cally stirred samples. This may have been ill-advised since
data at 10 and 20 g ZnO per liter showed somewhat faster oxida-
tion rates. However, it was assumed that since 20 g/l was better
than 10 g/l (not shown) still higher loadings would be better.
The 10 g/l ZnO sample dropped to 10 mg/l organic carbon in 12
hours whereas the 20 g ZnO/l dropped to 10 mg/l organic carbon
in 8 hours. Comparable time for 60 g/l ZnO loading from Fig-
ure 12, sample Cl, 10 mg/l organic carbon was reached in 14 hours.
All tests started at about 220 mg/l organic carbon. The temper-
ature of the solution in these runs fluctuated from 30° to 50°C.

RB#3, on Figure 11, is a comparison of Photox 80, a zinc
oxide reputed to be about twice as sensitive as Photox 801 in
the visible when dye sensitized and is directly comparable to
RB#2. It appears that this oxide is perhaps less effective
than Photox 801 under these conditions. From this it is evident
there is only a general relationship (if any) between the photo-
conductor properties of the pigment and its photocatalytic prop-
erties. Thus, Photox 801 may have been a poor choice. In view
of the very large number of variables, it was imperative to
standardize on one ZnO catalyst.

After brief raw sewage oxidation studies, described sub-
sequently, work with the Ace glass equipment was discontinued.
It was only recently discovered that the catalyst had a tendency
to adhere to the quartz envelope during the course of the oxida-
tion. While this did not appear to block much light, the adsorp-
tion of phenol oxidation products caused a black tar to form
in the early stages which retards the oxidation to an unknown
degree.

The tar film was discovered when a test was halted in the
early stages of oxidation. It is not known if this was a factor
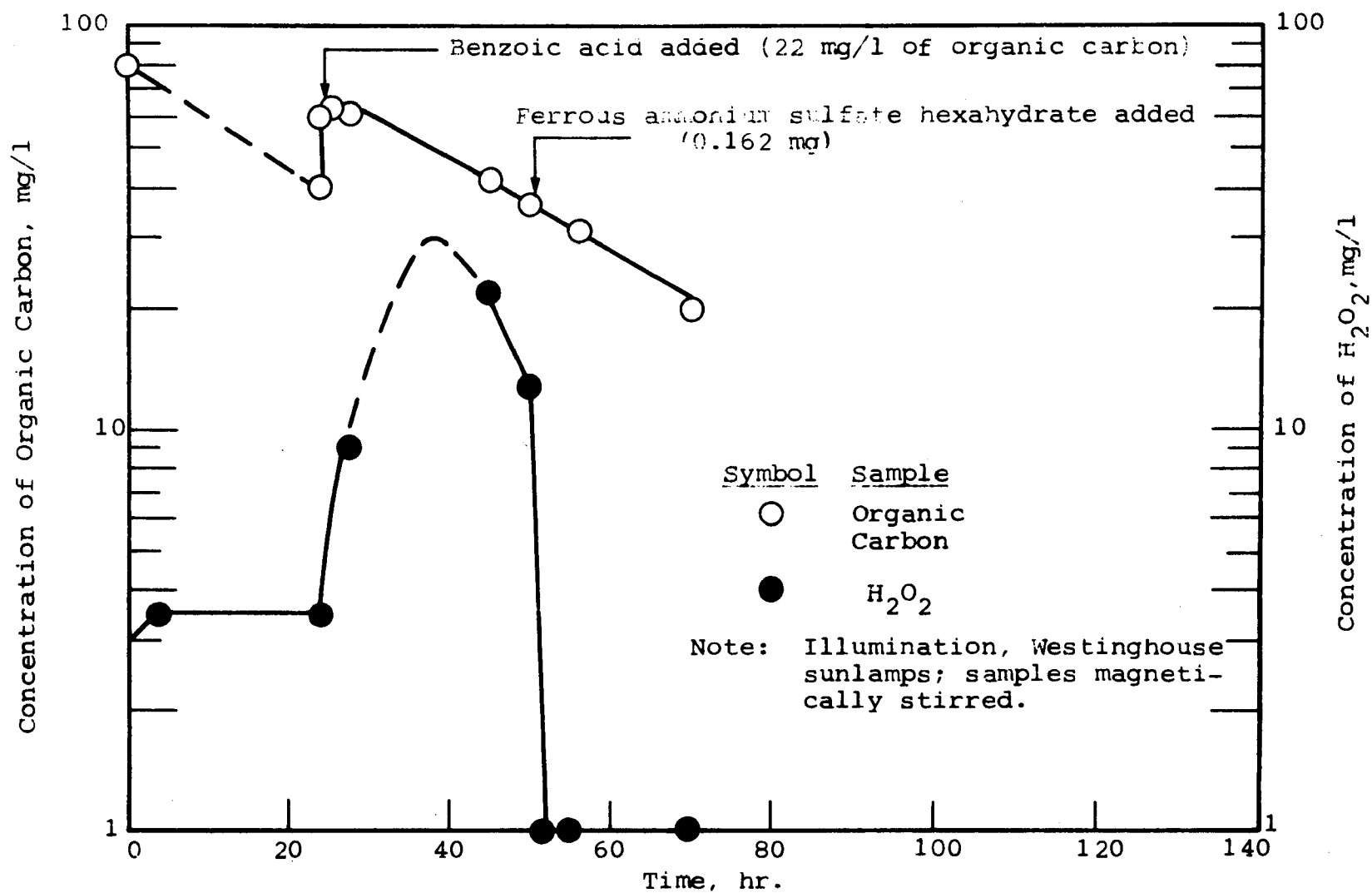in the sewage oxidation studies.

Figure 12

OXIDATION OF RAW SEWAGE

Table 10

OXIDATION OF RAW SEWAGE
(Mixed industrial and
domestic, Park Forest, Ill.)

| Time, hr | Concentration, mg/l | |
	Organic Carbon	H_2O_2
0	80	--
After catalyst addition	28[a]	--
24	28[a]	--
24	40	3.5
After benzoic acid addition	60	--
28	63	9.0
27	60	
45	42	22
50[b]	37	13
51	--	0
56	31	0
70	20	0

[a]Values not reliable as explained in the text.

[b]Added Fe^{2+} catalyst.

OXIDATION OF RAW SEWAGE

One experiment, (Figure 12), was conducted with mixed sanitary and industrial sewage magnetically stirred under sunlamps. Although our initial organic carbon oxidation data at 5 minutes and 1 hour are now known to be faulty, the experiment did represent an attempt at homogeneous catalysis. Bishop, et al.[9] have shown that ferric and ferrous ion catalyze H_2O_2 decomposition with formation of hydroxyl radicals, which, at about pH 4, oxidizes substantial amounts of organic carbon.

Chambron and Giraud[10] reported up to 98% catalytic oxidation of sodium lauryl sulfate by H_2O_2 with cupric, ferrous and manganous ion. However, they used H_2O_2 concentrations of approximately 3 wt %.

In our experiment, mixed industrial and domestic raw sewage was filtered through S & S 597 filter paper and the organic carbon was determined at the outset. This value started at 80 mg/l organic carbon and dropped almost immediately to 28 mg/l organic carbon. This rapid drop was subsequently proved to be a sampling error. This sewage contained varying amounts of "soluble" oil as evidenced by its typical opalescent appearance. In tests of known "soluble" oil concentration, ZnO breaks the emulsion and allows the oil to float on the surface. This fact is obscured by the zinc oxide; unless great care is taken to agitate the sample thoroughly, wide variations occur. In the case of the actual sewage, a fortuitous check value at 2 hours gave the reading undeserved credency, initially. For this reason, we have omitted data prior to the 22 hour point, which we believe to be valid, as well as subsequent measurements, since the oxidation follows the usual first order kinetics. The principal objective here was an attempt to produce hydroxyl radical by decomposing H_2O_2 with Fe^{2+} catalyst after first enhancing H_2O_2 formation by the addition of benzoic acid. Although, as can be seen from Figure 12, the H_2O_2 dropped immediately to zero upon addition of the Fe^{2+} catalyst, there was no effect on the organic removal rate.

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Two samples of sewage (not shown) were run in the photo-chemical apparatus at 60 g/1 zinc oxide. One sample consisted of mixed industrial and domestic sewage and the other was domestic sewage only. Due to heavy spring rains, we were unable to obtain samples with appreciable soluble organic matter as a result of rain-water dilution. The domestic sewage dropped from an initial 20 mg/1 to 10 mg/1 organic carbon in 7 hours; the mixed sewage dropped from an initial 33 mg/1 to 20 mg/1 in about 3 hours. Both samples leveled off, and further illumination for 3-4 hours had no effect. Both samples had been filtered through fiber glass filter paper. The residual organic may have been in colloidal form.

BACTERICIDAL PROPERTIES OF IRRADIATED ZINC OXIDE SLURRIES

A final experiment was conducted to determine the bactericidal properties of illuminated zinc oxide. The test was conducted in saline solution with E. coli under the Westinghouse sunlamps in 2500 ml culture flasks in a low speed shaker. Although the zinc oxide showed a higher kill rate at 30 minutes and at 2 hours, the differences, compared with an illuminated control, were not considered statistically significant. The validity of the test was further diminished by the fact that oxidation of phenol in the same apparatus was substantially less than in crystallizing dishes with the same illumination and ZnO concentration and time of exposure. The reason for this is not clearly understood, since Pyrex transmits about 90% of the radiation in this region (3000-4000Å). It may be that the angle of incidence (variable from 0 to about 45° due to the contours of the flask) resulted in a much higher reflectance than if it had been normal to the light source. Zinc oxide of both 1 g/1 and 10 g/1 ZnO had no inhibitory effect on the growth of E. coli in the dark in nutrient.

While repeating the photo-oxidation tests with nutrient in open containers was considered desirable, expiration of time and funds did not permit this; thus, the question of the bactericidal

and/or bacteriostatic properties of illuminated photocatalysts
is left in doubt.

DISCUSSION

Although our original concept looked for the reaction of
oxidant with organic materials, it is probable that the mechanism
entails the direct reaction of an active oxygen species, atomic
oxygen or singlet excited state molecular oxygen. From Figures
3, 4, and 7, it is evident that beyond a certain level of organic
matter, the oxidant concentration has little relationship to
organic level. In the case of zinc oxide, Markham and Laidler[5]
attributed this result to the fact that organic molecules are
adsorbed at the H_2O_2 decomposition sites, thus favoring the
formation reaction and inhibiting the decomposition reaction.
This apparently holds true for our oxidant as well (see Table 8).
It must also be inferred that oxidant level is not a direct
measure of catalyst effectiveness. Although zinc oxide
apparently produces the highest oxidant level and apparently is
the most effective oxidizer (Table 7), the actual oxidation
data must be viewed with some reservation since they may repre-
sent merely differences in absorption of sunlamp irradiation of
TiO_2 vs. ZnO. The actual surface area of the pigment is also
an important factor.

We suggest that three conditions must be satisfied to
achieve oxidation of an organic molecule.

    (a)   the molecule must be adsorbed at, or be in
        the vicinity of the active site on the catalyst.

    (b)   light energy of suitable wavelength (below about
        4200Å) must impinge on the active site.

    (c)   dissolved oxygen must be present to replace the
        active oxygen species displaced by the radiation.

From these considerations, everything else being equal,
the higher the concentration of contaminant the faster the rate
of oxidation. Thus it would appear that photocatalytic oxidation
will find its greatest utility in problems of industrial waste
treatment where massive contamination is involved.

In our sunlamp exposures, we exceeded the manufacturer's
recommended use period of 2000 hours by a factor of 2.5; however,

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not until the end of this period did a noticeable decrease in oxidation rates appear. Extrapolation of the manufacturer's life-intensity curves, shows that the tubes dropped to perhaps 20% of their original value before a decrease in efficiency could be noted. From this, we infer that with this light source, the limiting parameter is the number of active sites on the catalyst surface and not the intensity of the source until it is greatly attenuated.

Despite a very large number of tests, we find ourselves without firm data on such a basic factor as the performance of various zinc oxides. The selection of Photox 801 on the basis of the H_2O_2 equilibrium was perhaps unfortunate; Photox 80 is a much better electrophotographic material, but as Figure 11 indicates, it is evidently not as good a photocatalyst.

Time did not permit a definitive investigation of temperature-dissolved oxygen relationships; however, we think the level of dissolved oxygen is not as important as the rate at which dissolved oxygen is replaced. Thus, vigorous agitation at elevated temperature would favor faster kinetics, despite lower dissolved oxygen level.

The premise upon which the investigation was undertaken has been amply confirmed. It is definitely possible to oxidize a number of known organic materials as well as a substantial portion of those in sewage by photocatalytic techniques. The evidence that this process occurs in nature is convincing and of great potential significance in pollution control.

FUTURE WORK

Since it appears that with sunlamps, at least, the limiting factor is the number of reactive sites on the catalyst particle, examination of the wide variety of photocatalytic materials available would be fruitful. A brief investigation under the present program produced a substantial advance in TiO_2 performance. The anatase used contained a rutile seed crystal, which probably produces more crystallites in the anatase-rutile transition stage, with consequent greater photosensitivity. This result might further be enhanced by water quenching from the calcination temperature and/or by impurity doping.

An examination of the various grades of zinc oxide might reveal much more active types than the ones we used. The experiments with one type of beach sand suggest that a large number of catalysts are available in natural form which might be isolated and adapted to photocatalytic applications.

INTERACTION OF IONIZING RADIATION WITH METAL OXIDE CATALYSTS

This approach is based on work of Yamamoto and Oster[6] who studied the polymerization of calcium acrylate and acrylamide in aqueous media under the influence of ionizing radiation. These investigators reported an "enormous" increase in polymerization effect when zinc oxide was added to the system. It appears reasonable that photo-oxidation would show a similar acceleration.

In such a system, a number of advantages over the photochemical system would accrue. Most importantly, the radiation would penetrate the slurry to a considerable depth so that much less surface area would need to be exposed. Higher efficiency should result because of the increased likelihood of the radiation striking an active site. Finally, the energy cost should be much lower and the time of exposure much shorter.

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APPENDIX

Analytical Procedures for the Determination of Low Concentrations
of Hydrogen Peroxide in Aqueous Solutions

I.   INTRODUCTION

The following outlines in detail the step-by-step proce-
dures to be followed in analyzing for hydrogen peroxide by the
potassium iodide method. None of the theoretical aspects will
be included in this description; however, the precautions to be
observed and special techniques to be followed will be described
in each step.

II.   EQUIPMENT

1 - 5 ml micro burette	2 - glass stirring rods
1/100 ml graduations	1 - wash bottle distilled
2 - 1 ml pipette	water
1 - 2 ml pipette	2 - 1 qt stoppered bottle
1 - 10 ml pipette	1 - 1 pt stoppered bottle
2 - 10 ml graduate	Eye droppers
1 - 25 ml graduate	1 - acid dropping bottle
4 - 150 ml Erlenmeyer Flasks	1 - trip balance
	1 - stop watch

Bausch and Lomb Spectrophotometer "Spectronic 20"
with constant voltage transformer.

III.   CHEMICAL REAGENTS

1. Distilled water

2. 0.01 N standardized sodium thiosulfate $(Na_2S_2O_3 \cdot 5H_2O)$.
   Supplies of this solution may be obtained from chemical
   supply houses. It should be kept in ordinary stoppered
   bottles to avoid contamination or concentration changes.
   (Dilute 0.1 N standardized solution to 0.01 N).

3. Use H_2SO_4 acid in KI to maintain acid pH.

4. 1 N potassium iodide solution: The potassium iodide (KI)
   solution should be prepared daily by adding sufficient
   distilled water to approximately 150 g of reagent grade
   KI to make up 900 ml of solution. This solution must

be stored in an amber bottle and cannot be used if over 24 hours old.

5. Indicator: Starch indicator is prepared daily by adding 5 g of reagent grade soluble starch to 100 ml of boiling distilled water and stirring vigorously. The solution must be clear upon cooling. The indicator is useable only on the day prepared.

Sampling Procedure

We assume a 10 ml sample is representative of the solution we want to determine.

In a 20 ml beaker we place 10 ml of our unknown. Add 5 drops of 0.5 N H_2SO_4 - 20 drops of KI (in solution) - 5 drops of starch solution.

The stop watch is started as the KI is added.

Pipette 1 ml of sample, add to 10 ml graduate, dilute to 10 ml -- label "A".

Pipette 1 ml of sample, add to 25 ml graduate, dilute to 20 ml -- label "B".

Pipette 2 ml of sample, add to 10 ml graduate, dilute to 10 ml -- label "C".

After diluting, shake to evenly distribute solution.

Take B graduate, rinse the B & L test tube and fill to mark. Use spectronic 20 - record transmission.

Take A graduate, rinse the B & L test tube back and forth, fill to mark - record transmission.

Take C graduate, rinse the B & L test tube back and forth, fill to mark - record transmission.

The dilutions and reading should be all done in a 5 minute period. Total time on stopwatch should be under 10 minutes.

The transmission values are then used on Figure A-1 to determine the concentration of unknown solution.
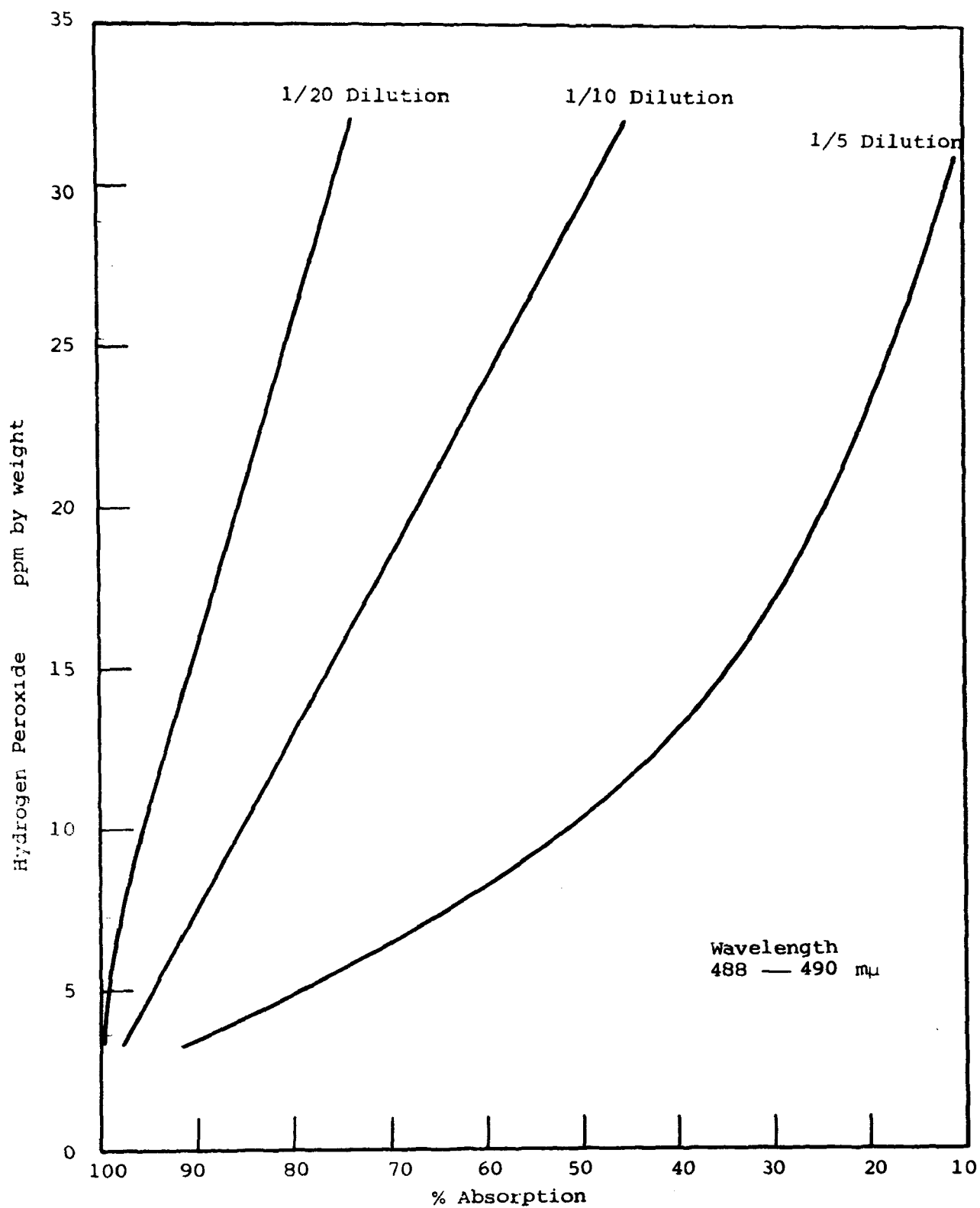
Figure A-1

ABSORPTION OF STARCH IODIDE
AT VARIOUS CONCENTRATIONS

A3

Table A-1

ABSORPTION OF STARCH IODIDE AT VARIOUS CONCENTRATIONS

Sample No.	Dilution Value	Titration Value	1/5 Dilution	1/10 Dilution	1/20 Dilution
				Absorption Values	
A	3.29 ppm	4.25 3.4*	92	97	99-100
B	6.58	7.47 6.62*	71	93	98
C	9.87	10.07 9.85*	54	86	96
D	13.16	13.2 12.4*	43	81	93
E	16.45	16.3 15.4*	34	75.5	91
F	19.74	19.9 19.0*	29.5	70.5	87
G	23.03	22.8 21.9*	19	61.0	83.5
H	26.32	25.8 25.0*	18	59.0	81
I	29.61	28.6 27.7*	14	54.0	82
J	32.90	32.4 31.6*	11	47.0	73

*Corrected for distilled water blank.
 Dilution was made with distilled water.

10 ml tap water ≃ 3 drop   (0.14 ml Thiosulfate solution)
10 ml distilled water ≃ 1 drop   (0.05 ml Thiosulfate solution).

Titration Procedure can be used as a check.
Titrant 0.01 N Sodium Thiosulfate
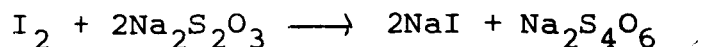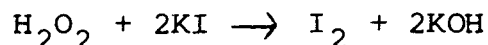
    20 ml of 1 N Potassium Iodide (KI)
    20 drops of 0.5 N H_2SO_4
    10 ml of sample solution   Start stopwatch
     5 ml of starch solution

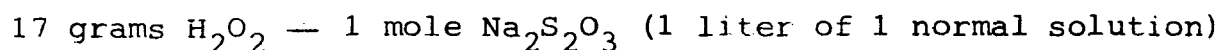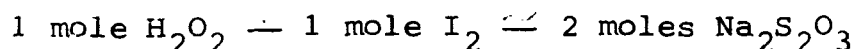Start titrating after 5 minutes of reactive digestion.

When solution starts going from purple $\rightarrow$ brown, add the thiosulfate dropwise at a very slow rate until a sharp color change from purple brown to water white is obtained. Wait 5 seconds between drops at this stage to avoid going past the end point.

Amount of thiosulfate used is recorded.

Equations:

$$H_2O_2 + 2KI \rightarrow I_2 + 2KOH$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

Equivalent:

1 mole H_2O_2 — 1 mole I_2 — 2 moles $Na_2S_2O_3$

17 grams H_2O_2 — 1 mole $Na_2S_2O_3$ (1 liter of 1 normal solution)

1 cc of 0.01 N $Na_2S_2O_3$ = $\dfrac{17 \times 0.01}{1000}$ = 0.00017 grams H_2O_2