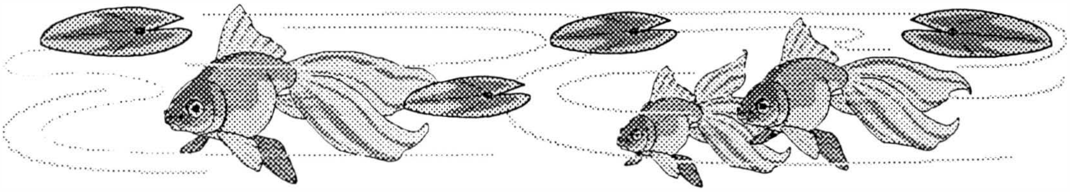
1995

Effluent Color Removal by Dimethyldioxirane

Lori Jo Shafer
Western Michigan University

Recommended Citation

Shafer, Lori Jo, "Effluent Color Removal by Dimethyldioxirane" (1995). *Paper Engineering Senior Theses*. 470.
https://scholarworks.wmich.edu/engineer-senior-theses/470



EFFLUENT COLOR REMOVAL BY DIMETHYLDIOXIRANE

by

Lori Jo Shafer

A Thesis submitted to the Faculty of the
Department of Paper Science & Engineering
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan

ABSTRACT

This project was done to determine if the chemical dimethyldioxirane was effective in removing color from various effluent types. Experimentation indicated that optimum conditions for color removal by dimethyldioxirane occurred at high pHs, increased temperatures, and applying the chemical in stages.

TABLE OF CONTENTS

PAGE
NUMBER

EXPERIMENTAL SCHEMATIC

LIST OF FIGURES

LIST OF TABLES

PAGE NUMBER

INTRODUCTION

Color in an effluent is an important parameter of interest to the public. If an effluent turned a river red, the public would consider the river toxic; they would not use the river for recreational or sanitary purposes, and they would force governmental intervention to prevent future episodes. However, if someone reported to the constituents that the effluent contained only dietary products and that the products should not be of environmental concern, the public authority would still consider the river as a potential hazard. In other words, it is the psychological trauma inflicted by industry on an individual that provides many concerns for the public and future environmental regulations.

Although current, national, environmental regulations neglect to address the topic of color, it is becoming a concern. Regionally, officials dictate and mandate certain limits involving color, but enforcement can vary between different locales due to political pressures from industry on public officials.

Once enforcement becomes mandatory throughout the United States, many facilities will be forced to implement a treatment to negate and/or reduce color in effluent. If this should happen, industry will want to utilize a method of treatment that will work effectively, produce a non-hazardous effluent/waste after treatment, and be relatively inexpensive.

Previous experimentations have established the positive effects of oxidation treatments over physical treatments; however, each method induced further public concerns (i.e., dioxin generation with the use of chlorine) or created costs that exceeded previous methods of treatment. One chemical that was neglected in research for possible color removal is dimethyldioxirane.

Dimethyldioxirane is an effective oxidant that has been proven to effectively treat organic material. The chemical's advantage is that it does not contain chlorine or any compounds containing chlorine. This will curb any possible negative feelings from the public which establishes a means to research the chemical further.

LITERATURE SURVEY

The USEPA (United States Environmental Protection Agency) has not restricted the color in an effluent. Legal obligations for industry for the removal of color in an effluent is set forth by an individual state in a National Pollution Discharge Elimination System Permit or by a publicly owned treatment works. The current statutes on color are, however, under scrutiny and due to public concern, color may become a regulated parameter (1).

Currently, the only regulation involving color is for drinking water. The maximum value allowed for drinking water is 15 color units (2). 15 color units is very hard to see but 100 color units will be perceived to be similar in color as tea (3).

Color can be caused by "colloidal iron and manganese complexes," or it can be attributed to the formation of organic compounds (4).

The major contributor of color is from the natural decay of organic matter. The other source of color is from the discharge of effluent (3).

The color of concern is called "True Color". "True Color" is the amount of color remaining in a sample after the turbidity is removed from the sample. In other words, it is the color that remains in the solution after sedimentation and filtration is performed on a solution (3).

The reason that color in an effluet is a major concern is that an individual without technical and/or scientific knowledge will perceive a colored water as being hazardous to one's health. Due to the psychological impact of color in water, consumption and/or use of a water containing color will decrease significantly. When consumption and use of water decreases dramatically, human health and welfare may suffer (3).

The experiment by Montgomery (5) noted that the catalysis of peroxymonosulfate will create oxidation capabilities to dyes. The oxidation of Polar Brilliant Blue GAW utilizing activated oxygen demonstrated that color will disappear in a first order reaction after its application. In other words, as the concentration of activated oxygen was increased, the amount of color in solution decreased. The activated oxygen proved to be an effective method in removing color from a dye treated solution.

Tozer (6) demonstrated with his experiment that color removal by oxidation methods on three direct dyes are not only effective but are also efficient. Tozer's data noted that the color removal methods of coagulation and adsorption produced sludges with varying levels of toxicity and the systems were extremely difficult to control. The oxidation methods utilizing chlorine and ozone were not only easier methods to provide treatment to an effluent and did not produce sludge but the treatments significantly enhanced the aesthetic qualities of the wastewater.

Tozer did note that there were two slight problems associated with the use of chlorine or ozone oxidation treatments. The first problem dealt with the public's concern about the use of chlorine for the treatment of water (i.e., another psychological parameter that can not be avoided by industry). The second problem dealt with the economic feasibility of ozone oxidation. In other words, the generation of ozone created costs that were significantly higher than the other methods of treatment (6).

The dyes used in Tozer's experiment were direct azo dyes. Azo dyes are the most popular dyes utilized in industrial processes. Direct dyes, popular in the paper industry, are azo dyes that can readily "dye cellulose fibres without the aid of mordants" (7).

The printing industry utilizes dyes for inks. The different dyes utilized in inks are: acid, basic, solvent, and disperse dyes. Acid and basic dyes are soluble in water. Solvent dyes are soluble in organic solvents and disperse dyes are insoluble in water (8).

As determined through Montgomery's experiment, the importance of dimethyldioxirane in aesthetically enhancing an effluent is of significant interest. The production of the chemical of interest occurs in the reaction seen in Figure 1, page 4. To effectively produce dimethyldioxirane, the use of acetone is most effective (9).

The use of the chelating agent EDTA (Ethylenediaminetetra-acetic Acid) removed metal ions from the testing subjects. If EDTA is not used during production and utilization, the peroxide compounds will decompose, unwanted reactions will occur, and oxygen reactions will reduce (10).

To drive the reaction in the proper direction, a neutral pH must be maintained during the production of the dimethyldioxirane. A pH of 7.3 to 7.5 must be maintained or else the reaction will follow a destructive path (9).

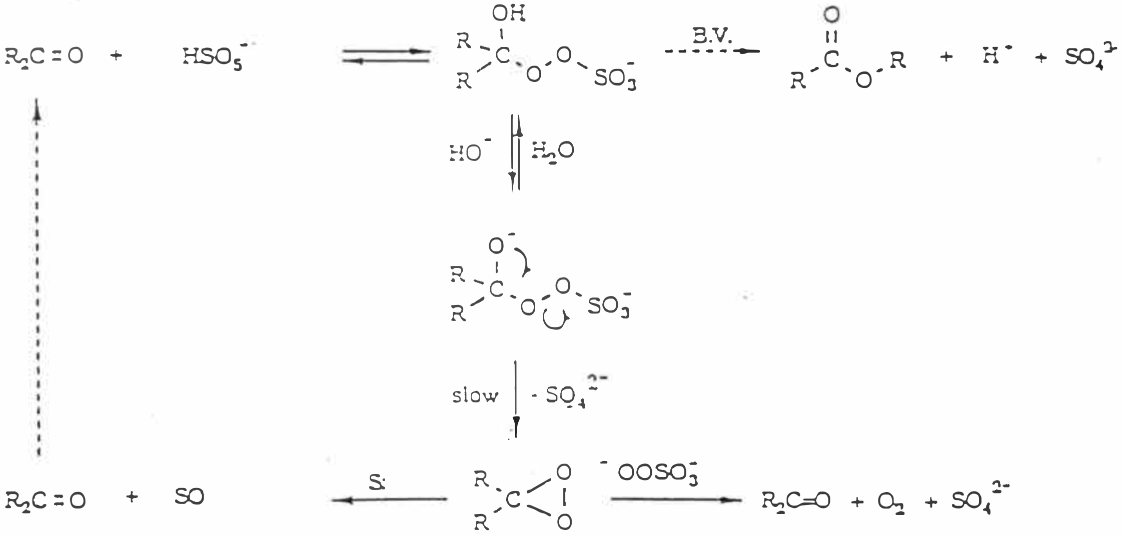


Figure 1. Chemical Reaction

The dimethyldioxirane is an efficient oxidant with organic compounds. The dimethyldioxirane structure (Figure 2) demonstrates the chemical's capabilities to deliver oxygen to an organic compound. Also, dimethyldioxirane produced in situ is an "efficient oxidant transfer agent" (9).

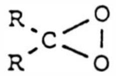


Figure 2. Dimethyldioxirane Structure

The parameters of interest in this study are absorbance, percent color removal (demonstrated below), pH, visual appearance of the "effluent" after treatment, time, quantity of chemical applied to the effluent, type(s) of dye(s), sludge produced, and the cost of treatment. These parameters are necessary to establish the efficiency of the use of dimethyldioxirane for environmental improvement (6).

Percent Color Removal = (((Raw Water Absorbance - Treated Water Absorbance)(100))/ Raw Water Absorbance)

The instruments of importance are: the spectrophotometer (to measure the absorbance levels of the raw and treated effluents) and the pH meter. The absorbance is proportional to "the length of the light path through the sample and to the concentration of the absorbing material" (11).

LITERATURE ANALYSIS

Based on the past experimentation with dimethyldioxirane, color can be removed from a dye. The effectiveness of this procedure, however, was neglected by Ronald Montgomery. Also, the areas of interest neglected in Ronald Montgomery's experiment were: cost analysis, sludge production after treatment, time to achieve certain levels of color removal, concentrations applied to the dye, visual appearance of the dye after treatment, and pH.

Ronald Montgomery neglected to administer these tests due to the fact that he was trying to determine the activity of the chemical of peroxymonosulfate with a ketone catalyst to obtain the crucial information needed to prove that the chemical will oxidize an organic fraction. His work was done in 1974 when environmental concerns dealing with color had not yet unfolded in governmental regulations.

PROBLEM STATEMENT

The topic as prescribed will define the parameters of interest involving dimethyldioxirane with an effluent. The effluent will be made of dyes to provide an experimental design dealing only with "True Color."

The parameters of interest are: a) sludge production, b) absorbance and wavelength, c) pH, d) visual appearance of "effluent" after treatment, e) time, f) quantity of chemical applied, g) type of dyes, h) percent color removal, and i) concentration of dyes in the sample. The other problems are generation of the chemical on-site and the technological and economical feasibility of using dimethyldioxirane for effluent treatment.

OBJECTIVES

Dimethyldioxirane (DMD), an oxidant, was used to remove color from water tainted with direct dyes. The dyes consisted of Pergasol Yellow 2GL LIQ (DIR YEL 004), Pergasol Blue GD LIQ (DIR BLU 281), and Pergasol Red 2G LIQ (DIR RED 239). Also, the effluent was generated on-site to reduce the probability of "apparent" color. The water was treated to different levels of pH to create varying visual appearances. The effectiveness of DMD as a color-removing agent under these conditions were studied. Experimentation consisted of measuring the variations in absorbance (using a spectrophotometer) between untreated samples and those bleached with DMD. Absorbance variations occurred with increased mixing times, pH variations, the levels of DMD, and temperature.

PROCEDURES

The effluent was produced by taking three different colors of direct dyes and mixing them together on a 1:1:1 basis into distilled water. The effluent was dilute in nature to allow the penetration of visible light. The mass of dye per liter of distilled water was approximately 0.0002 grams per liter.

The effluent was stirred to allow the dyes to be evenly distributed throughout the solution. After mixing, the wastewater was filtered to remove suspended particles to prevent "apparent" color readings.

The filtered effluent then had the pH altered to the levels of 4, 7, and 11. If needed, the pH altered effluent was filtered to remove any suspended particles that occurred after adjusting the wastewater to the various pH levels.

All tests were performed at room temperature (unless noted). The pH was adjusted by administering H_2SO_4 and HCl to enhance acidity or NaOH to make the effluent alkaline in nature.

To perform the tests at each pH level, a half-liter effluent sample was prepared. A sample was drawn from each aliquot to provide the blank readings for absorbance and to determine the initial appearance of the samples (i.e., sight evaluation).

Each half-liter sample was mixed by a magnetic stirring bar and a known quantity of Oxone and acetone was administered to each of the aliquots. The treated samples were then timed.

At time intervals of 2, 10, 30, and 60 minutes (unless noted), samples were withdrawn from each of the different aliquots and, if needed, the samples were filtered. The samples were evaluated for the appearance of color, sludge, and then tested for appearance.

EVALUATIONS

To provide standard statistical analysis, five samples at each time interval were withdrawn from each aliquot. The determination of treatment costs were based on the amount of Oxone applied to the samples. The amount of "sludge" produced after treatment was zero which eliminated the need to filter the treated effluent and testing samples.

To measure absorbance and wavelength (to determine percent color removal), a spectrophotometer was utilized. The instrument used in this experiment was the Beckman DU 7500. This machine, using sample cells of 1 centimeter, measures wavelengths of 190 to 800 nanometers.

The spectrophotometer, however, created some problems. One problem of interest was the inability to calculate absorbancy reductions below 0.3000 (i.e., if the initial absorbancy was 4.5000, the final absorbancy was 4.2000). The other problem was the inability to perform multiple scans for new wavelengths in the standard testing times (for each wavelength analysis, only one sample was experimented on the spectrophotometer which created the lack of statistical analysis in the body of the report).

Even though absorbancy removal could not achieve a value greater than 0.3000, the percent color removal must be noted as 100% and a new wavelength determined. Because of this problem, standard statistical analysis could not be performed on the raw data. Analysis, however, was performed by averaging similar raw data and applying the new data to tables and charts. Based on the data in the tables and charts, the discussion and conclusions were developed.

EXPERIMENTAL SCHEMATIC

Stage 1 - Effluent Preparation

The effluent was prepared by taking 500 milliliters of distilled water and adding 1 drop (approximately 0.1 milliliters) of Pergasol Yellow 2GL LIQ (DIR YEL 004), 1 drop of Pergasol Blue GD LIQ (DIR BLU 281), and 1 drop of Pergasol Red 2G LIQ (DIR RED 239). After the dyes were added, the temperature was increased to 50^{o}C (50 degrees Celsius) for stages requiring temperature enhancement. Otherwise, the temperature of the effluent was 20^{o}C (room temperature).

Stage 2 - pH Adjustment

The pH of the effluent was adjusted to 4, 7, and 11 with the chemicals H_2SO_4, HCl and NaOH. For the pH of 7, the effluent was buffered with sodium bicarbonate to maintain a steady pH level. The pH adjusted effluent was then filtered to remove turbidity.

Stage 3 - Treatment

To treat the effluent, different loads of Oxone and acetone were applied to the effluent. For each pH variation and temperature enhancement set, the Oxone and acetone additions were: 3.84 grams Oxone with 1.1 milliliters acetone, 7.68 grams Oxone with 2.2 milliliters acetone, and 11.52 grams Oxone with 3.3 milliliters acetone.

The stage set treatment was performed at pH = 7 and at room temperature. Treatment was applied in three stages of 1.28 grams Oxone with 0.4 milliliters acetone. Application of the dosages occurred at 0, 15, and 30 minutes.

Stage 4 - Sampling Procedures

The samples were withdrawn after 2, 10, 30, and 60 minutes (unless noted). Visual observations were made at the time of sampling. For the tests of absorbance and color removal, 5 samples were utilized and tested in the spectrophotometer. Wavelength analysis was performed on the effluent prior to treatment and after 100% color removal was achieved or a 0.3000 absorbancy reduction occurred. Only 1 sample was withdrawn for each wavelength test.

For the stage set, samples were taken 10 minutes after each treatment. At the times of 10, 25, 40, and 60 minutes, visual observations were noted and 5 samples were withdrawn for the tests of absorbancy and percent color removal. After 25 minutes of treatment, 1 sample was withdrawn for wavelength analysis because absorbancy reduction values achieved 0.3000.

Stage 5 - Optimization Studies

To minimize the use of Oxone and acetone, tests were performed to seek a visual change that was similar to normal testing procedures. The effluent was prepared the same as the previous tests and the pH was enhanced to a level of 11. The temperature was maintained at room temperature.

Application of the Oxone and acetone was 0.5 grams Oxone with 0.2 milliliters acetone and 1.0 grams Oxone with 0.4 milliliters acetone. Visual observations were made 10 minutes after the initial treatment.

Stage 6 - Color Removal Attempt Without Acetone

At a pH of 11 in 500 milliliters of effluent, 1.0 grams Oxone was added. 10 minutes after the initial treatment, the visual appearance was noted.

Stage 7 - Analysis

Analysis was performed by averaging similar raw data generated by the spectrophotometer. Visual observations were done in the 1 centimeter testing cells for the spectrophotometer in front of a white background to negate optical illusions.

DISCUSSION

To calculate the percent difference between data averages, the formula of:

Percent Difference = (((High Data Number - Low Data Number)(100))/(High Data Number))

will be utilized in the following discussion. This will be done to make a numerical notification of the differences that occurred between data sets and points.

Table 1 (Average Absorbancy Reduction Readings For pH = 7) demonstrates the degree of absorbancy removal from an effluent with the increase of time. The 60 minute values for the 3.84 grams Oxone addition exceeded the 2 minute values by as much as 93.1%. The 60 minute samples, also, exceeded the 10 minute samples by as much as 77.4% and exceeded the 30 minute samples by as much as 28.5%. Table 1 also demonstrated similar results for different Oxone concentrations at pH = 7.

Table 1
Average Absorbancy Reduction Readings For pH = 7

Oxone Addition (grams)	Initial Wavelength (nanometers)	Initial Absorbancy	Absorbancy Reductions 2 minutes	10 minutes	30 minutes	60 minutes
3.84	663.0	0.52596	-0.0194	-0.0632	-0.2003	-0.2802
7.68	661.0	0.35525	-0.0085	-0.0756	-0.2360	-0.3000
11.52	666.0	0.17579	-0.0159	-0.0462	-0.1095	-0.1493

The introduction of heat produced 100% absorbancy removal at the time of 10 minutes in Table 2 (Average Absorbancy Reduction Readings For pH = 7 and 50^{o}C) on page 14. By increasing the dosages to 7.68 grams of Oxone and 11.52 grams of Oxone, the data demonstrated that 100% absorbancy removal occurred within 2 minutes after the application of the Oxone.

With the reduction of the effluent's pH to a level of 4 for the 3.84 grams Oxone addition, absorbancy reduction levels, for the 60 minute sampling time in Table 3 on page 14, exceeded the 2

Table 2
Average Absorbancy Reduction Readings For pH = 7 And 50°C

Oxone Addition (grams)	Initial Wavelength (nanometers)	Initial Absorbancy	Absorbancy Reductions 2 minutes	10 minutes	30 minutes	60 minutes
3.84	651.0	0.40539	-0.0476	-0.3000	-0.3000	-0.3000
7.68	653.0	0.51519	-0.3000	-0.3000	-0.3000	-0.3000
11.52	648.0	1.19565	-0.3000	-0.3000	-0.3000	-0.3000

Table 3
Average Absorbancy Reduction Readings For pH = 4

Oxone Addition (grams)	Initial Wavelength (nanometers)	Initial Absorbancy	Absorbancy Reductions 2 minutes	10 minutes	30 minutes	60 minutes
3.84	651.0	0.51640	-0.0851	-0.0787	-0.0916	-0.2002
7.68	647.0	0.44035	-0.0865	-0.0855	-0.1609	-0.2798
11.52	646.0	0.58539	-0.1298	-0.1300	-0.2195	-0.3000

minute time by as much as 57.5%. The 60 minute absorbancy reduction readings also exceeded the 10 minute sampling time by 60.7% and the 30 minute sampling time by 54.2%. Similar results occurred when the pH maintained a level of 4 but DMD dosages were increased to 7.68 grams Oxone and 11.52 grams Oxone. The slight drop in absorbancy reduction readings from 2 minutes to 10 minutes could have been due to the fact that the oxidation reaction did not occur at a significant rate until the time of 10 minutes.

At a pH of 11 (Table 4), 100% absorbancy reduction occurred within 2 minutes of the initial treatment. This suggests that the oxidation reaction at the higher pH occurs at a much faster rate than the previously mentioned data. In other words, the pH = 11 produces optimum results.

Table 4
Average Absorbancy Reduction Readings For pH = 11

Oxone Addition (grams)	Initial Wavelength (nanometers)	Initial Absorbancy	Absorbancy Reductions 2 minutes	10 minutes	30 minutes	60 minutes
3.84	554.0	4.5000	-0.3000	-0.3000	-0.3000	-0.3000
7.68	544.0	4.5000	-0.3000	-0.3000	-0.3000	-0.3000
11.52	552.0	4.5000	-0.3000	-0.3000	-0.3000	-0.3000

When the application of the DMD occurred in stages (please view Table 5, page 16), the initial sampling time of 10 minutes produced a 0.0355 absorbancy reduction average. After the second stage application (i.e., 2.56 grams of Oxone total) and 25 minutes after the initial application, the absorbancy reduction achieved 100%. At the 25 minute sampling time, the absorbancy reduction reading exceeded the 10 minute sample by as much as 88.2%. This effect may have been due to the fact that the Oxone and acetone reacted together more efficiently than as a shock charge or a one dose application.

Tables 6, 7, and 8 demonstrated the effects of pH on percent color removal data. At the pH of 7 (Table 6, page 16), the Stage Set and the temperature enhanced effluent yielded 100% color removal

Table 5
Average Absorbancy Reduction Readings For Stage Set

Oxone Addition (grams)	Initial Wavelength (nanometers)	Initial Absorbancy	Absorbancy Reductions			
			10 minutes	25 minutes	40 minutes	60 minutes
1.28 (Stage 1)	663.0	0.51499	-0.0355			
2.56 (Stage 2)				-0.2993		
3.84 (Stage 3)					-0.3000	-0.3000

Table 6
Percent Color Removal For pH = 7

Average Wavelength Values = 658.0 nanometers

Time (minutes)	Percent Color Removal						
	3.84 g.n	7.68 g.n	11.52 g.n	3.84 g.t	7.68 g.t	11.52 g.t	Stage Set
2	3.68	2.38	9.04	11.8	100	100	
10	12	21.3	26.3	100	100	100	6.9
25							100
30	38.1	66.4	62.3	100	100	100	
40							100
60	53.3	84.4	84.9	100	100	100	100

NOTE: g.n = Grams and Application of Oxone Was At Room Temperature
g.t = Grams and Application of Oxone Was At 50°C

values within 25 minutes of the initial treatment. At room temperature (approximately $20^{o}C$), percent color removal values achieved results as low as 53.3% (3.84 grams application) and as high as 84.9% (11.52 gram application). Oxidation, in other words, was enhanced with the introduction of heat and stage applications (please view Figure 3, page 18).

Oxidation decreased with the lowering of the pH level (please view Figure 4, page 19) but increasing the application of Oxone resulted in 100% color removal after 60 minutes for the 11.52 grams Oxone application. As demonstrated in Table 7 (Percent Color Removal For pH = 4) on page 20, the 11.52 gram application exceeded the 3.84 gram trial by 61.% and the 7.68 gram trial by 36.5% after the 60 minute sampling.

Again, as the pH is raised and the concentration of the dosages are increased, the oxidation process increases substantially. In Table 8 (Percent Color Removal For pH = 11) on page 20, 100% color removal was achieved in every sample and trial.

Tables 9, 10, and 11 on pages 21 and 22 reported the percent color removal values for similar concentrations and pHs. Figures 5, 6, and 7 on pages 23, 24, and 25 provided graphical representations of the values presented in the indicated tables. At a pH of 7 and 3.84 grams Oxone application, the room temperature trial at 60 minutes was exceeded by the other trials by as much as 46.7%. The room temperature trial at a pH of 7 and 7.68 grams of Oxone application was exceeded by the other trial by as much as 15.6% after a time of 60 minutes. For the 11.52 grams Oxone application, the room temperature trial at 60 minutes' time was exceeded by the enhanced temperature trial by as much as 15.1%. These tables and graphs indicated that temperature and concentration enhancement contributed to the reaction between the organic fraction and the oxidation agent of DMD.

Table 12 (Percent Color Removal For pH = 7 With Oxone Addition Variations) presented on page 22 clarified further that increasing concentrations increases the level of color removal (graphically represented as Figure 8 on page 26). After 60 minutes following the initial treatment, the 11.52 grams of Oxone exceeded the 3.84 grams of Oxone by as much as 37.2% and the 7.68 grams of Oxone application by as much as 0.589%.

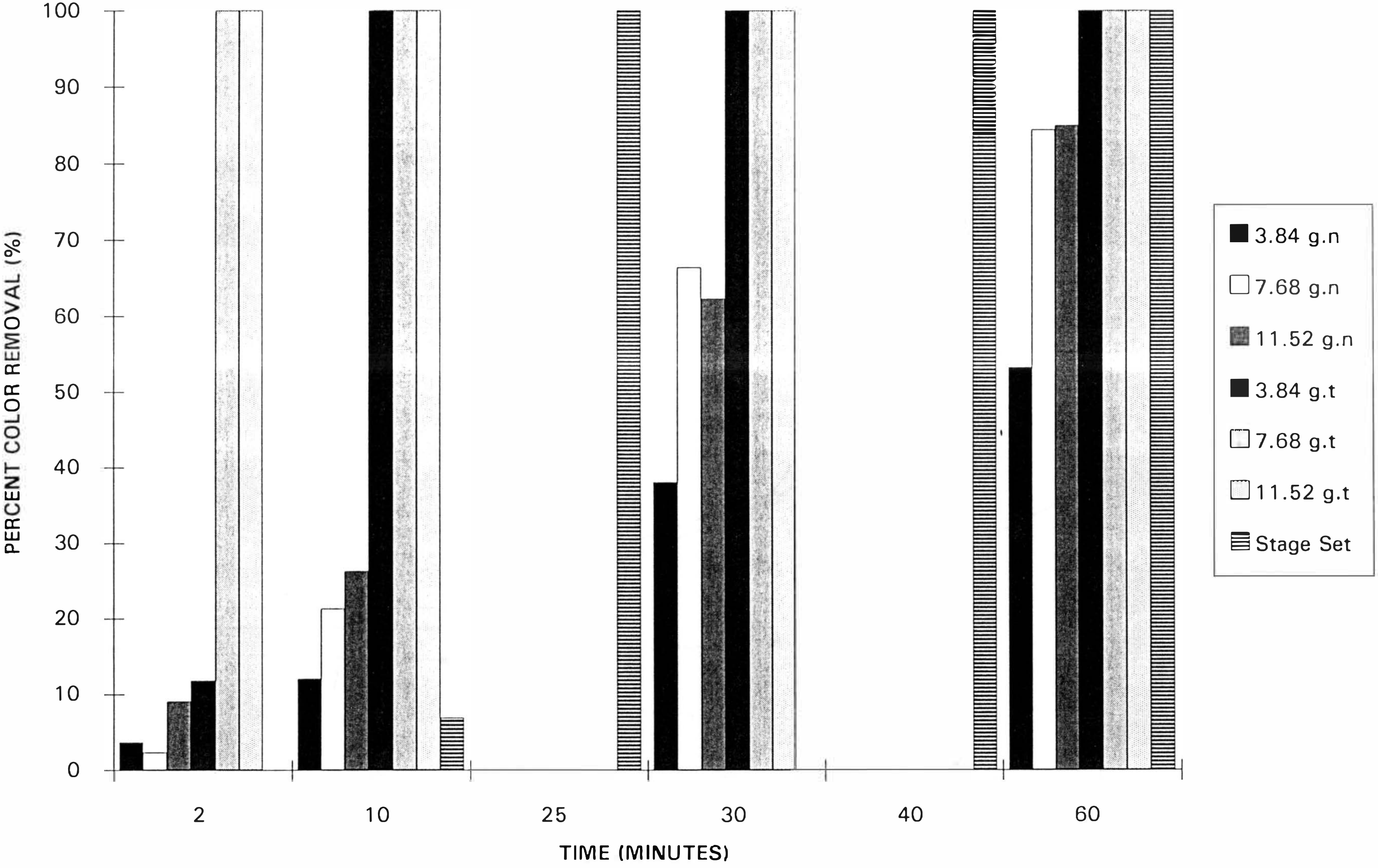


FIGURE 3. Percent Color Removal For pH = 7

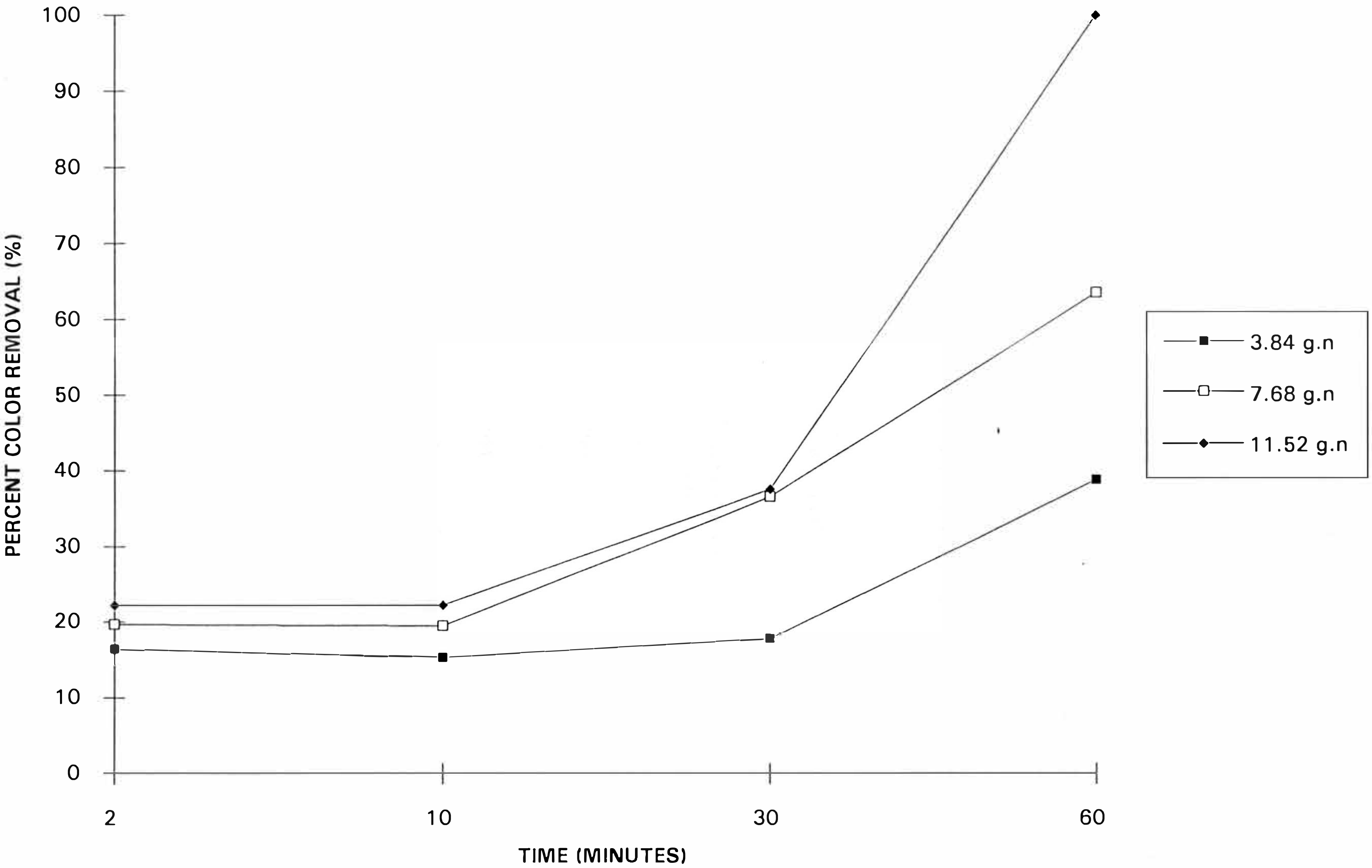


Figure 4. Percent Color Removal For pH = 4

Table 7
Percent Color Removal For pH = 4

Average Wavelength Values = 648.0 nanometers

Time (minutes)	Percent Color Removal 3.84 g.n	7.68 g.n	11.52 g.n
2	16.5	19.6	22.2
10	15.2	19.4	22.2
30	17.7	36.5	37.5
60	38.8	63.5	100

NOTE: g.n = Grams and Application of Oxone Was At Room Temperature

Table 8
Percent Color Removal For pH = 11

Average Wavelength Values = 550.0 nanometers

Time (minutes)	Percent Color Removal 3.84 g.n	7.68 g.n	11.52 g.n
2	100	100	100
10	100	100	100
30	100	100	100
60	100	100	100

NOTE: g.n = Grams and Application of Oxone Was At Room Temperature

Table 9
Percent Color Removal For pH = 7 And 3.84 Grams Oxone

Average Wavelength Values = 659.0 nanometers

Time	Percent Color Removal		
(minutes)	3.84 g.n	3.84 g.t	Stage Set
2	3.68	11.8	
10	12	100	6.9
25			100
30	38.1	100	-
40			100
60	53.3	100	100

NOTE: g.n = Grams and Application of Oxone Was At Room Temperature
g.t = Grams and Application of Oxone Was At 50°C

Table 10
Percent Color Removal For pH = 7 And 7.68 Grams Oxone

Average Wavelength Values = 657.0 nanometers

Time	Percent Color Removal	
(Minutes)	7.68 g.n	7.68 g.t
2	2.38	100
10	21.3	100
30	66.4	100
60	84.4	100

NOTE: g.n = Grams and Application of Oxone Was At Room Temperature
g.t = Grams and Application of Oxone Was At 50°C

Table 11
Percent Color Removal For pH = 7 And 11.52 Grams Oxone

Average Wavelength Values = 657.0 nanometers

Time (Minutes)	Percent Color Removal 11.52 g.n	11.52 g.t
2	9.04	100
10	26.3	100
30	62.3	100
60	84.9	100

NOTE: g.n = Grams and Application of Oxone Was At Room Temperature
g.t = Grams and Application of Oxone Was At 50°C

Table 12
Percent Color Removal For pH = 7 With Oxone Addition Variations

Average Wavelength Values = 663.0 nanometers

Time (minutes)	Percent Color Removal 3.84 g.n	7.68 g.n	11.52 g.n
2	3.68	2.38	9.04
10	12	21.3	26.3
30	38.1	66.4	62.3
60	53.3	84.4	84.9

NOTE: g.n = Grams and Application of Oxone Was At Room Temperature

FIGURE 3

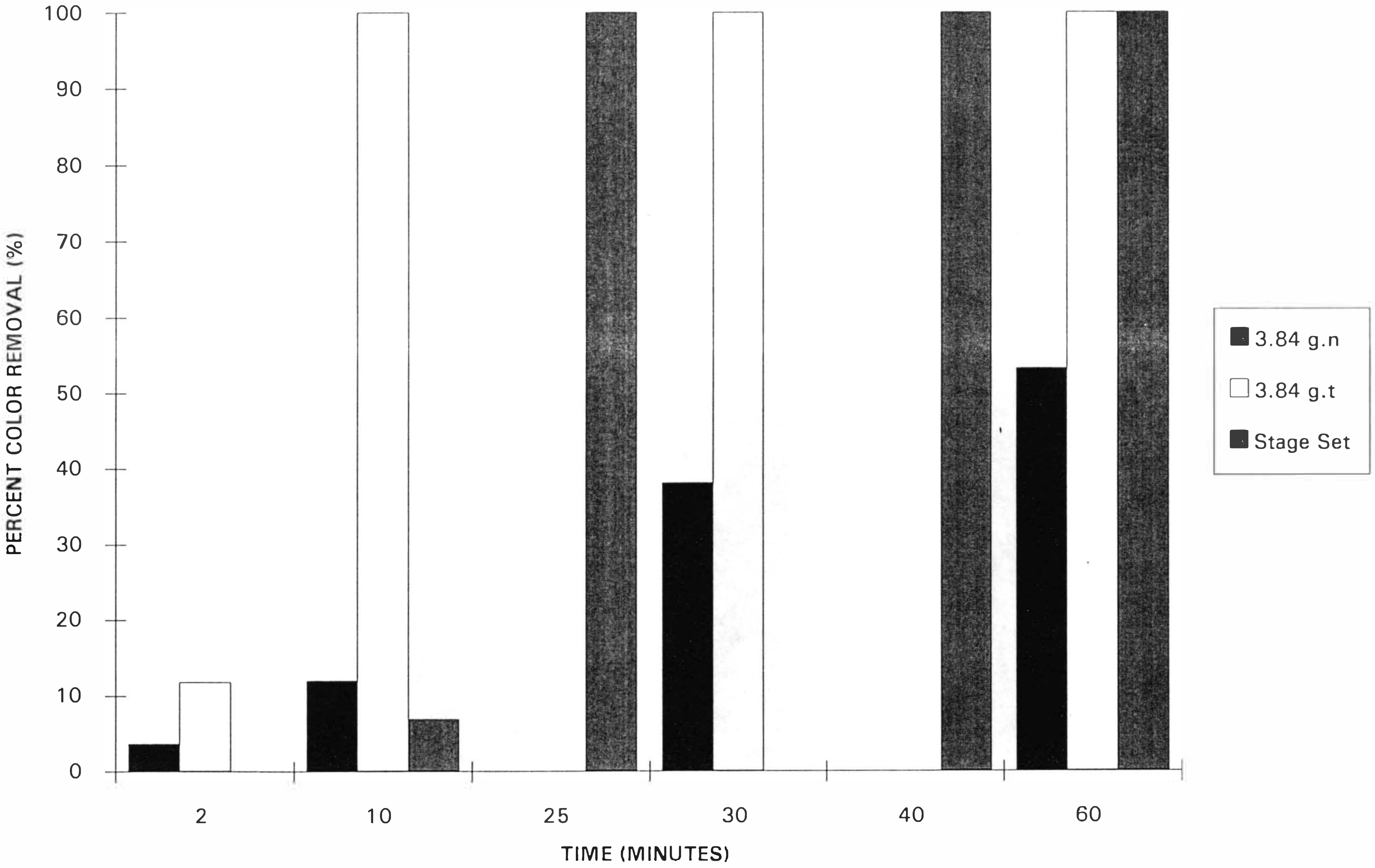


Figure 5. Percent Color Removal For pH = 7 And 3.84 Grams Oxone

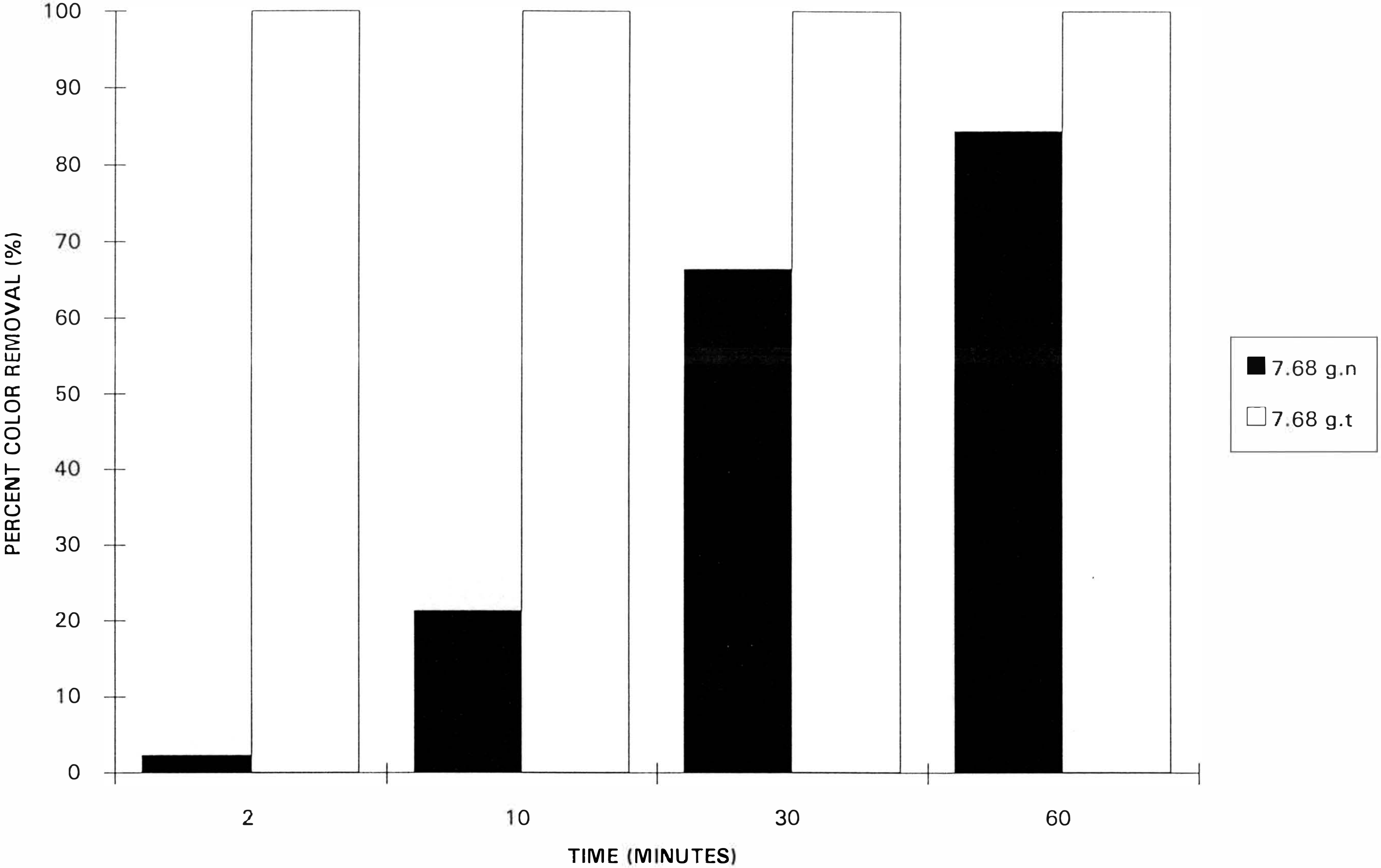


Figure 6. Percent Color Removal For pH = 7 And 7.68 Grams Oxone

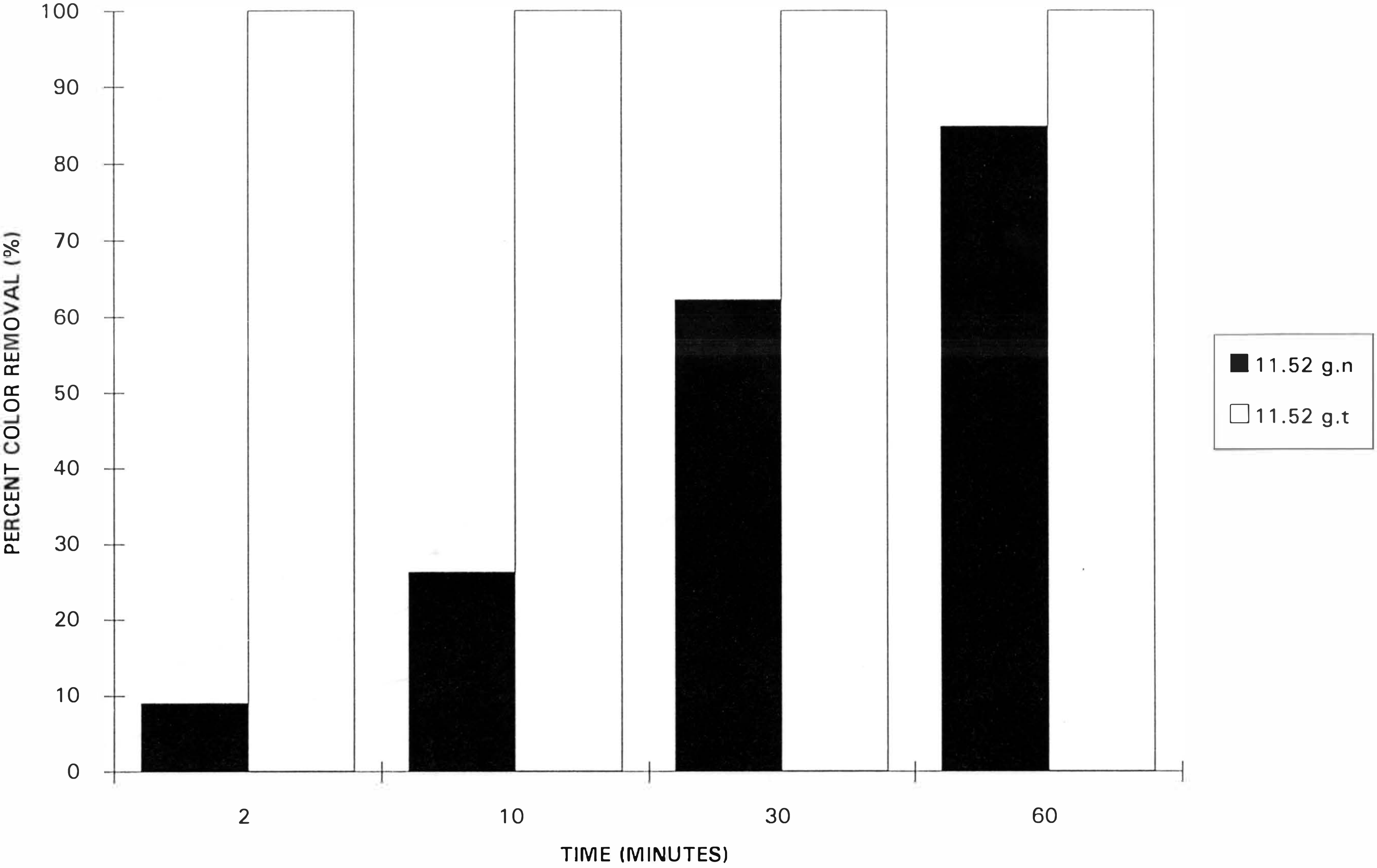


Figure 7. Percent Color Removal For pH = 7 And 11.52 Grams Oxone

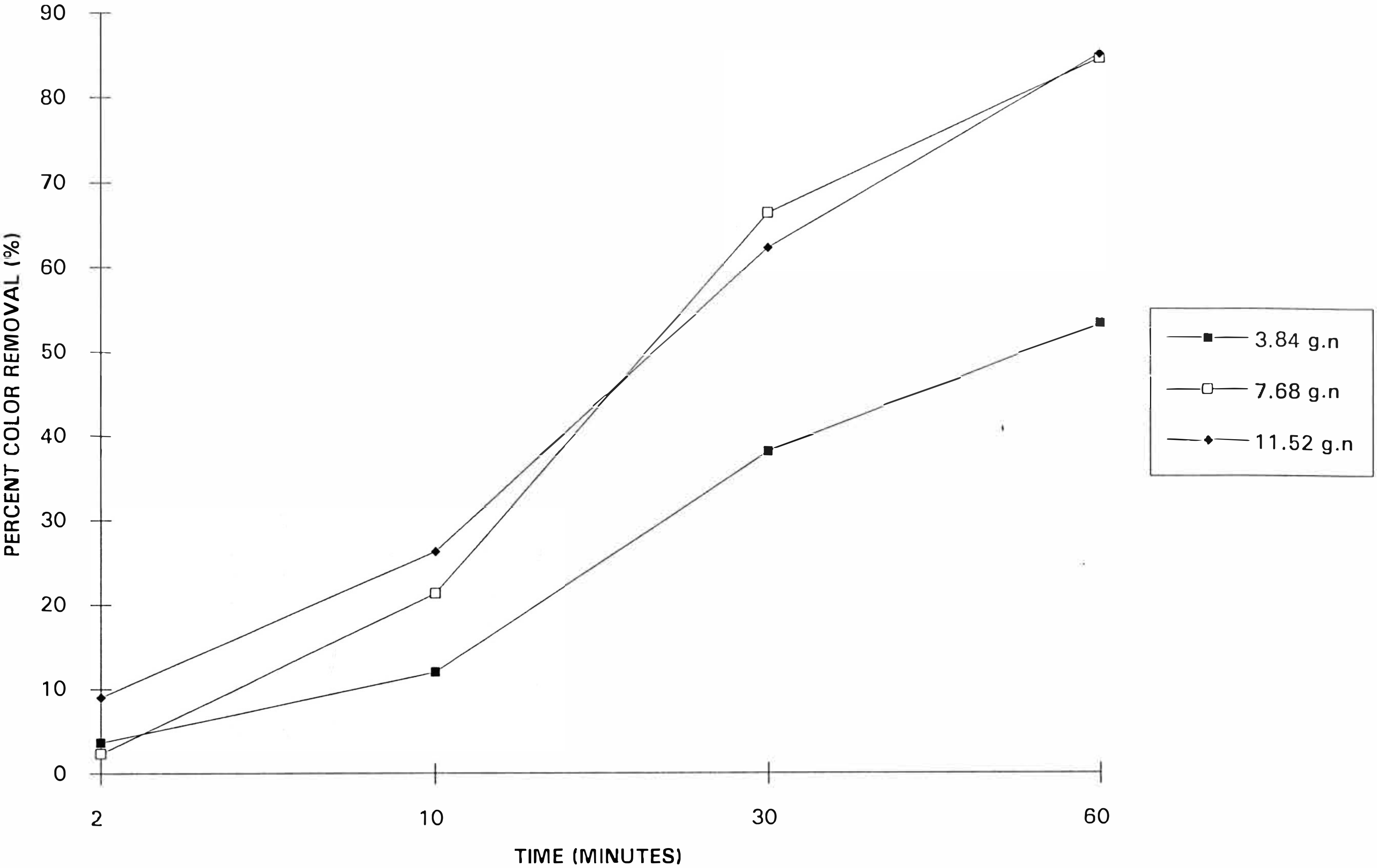


Figure 8. Percent Color Removal For pH = 7 With Oxone Addition Variations

Table 13 (Percent Color Removal For pH = 7 With Temperature Increase) indicated that the oxidation reaction was enhanced with the utilization of heat. Within 10 minutes after the initial treatment, 100% color removal was achieved.

Table 13
Percent Color Removal For pH = 7 With Temperature Increase

Time (minutes)	Average Wavelength (nanometers)	3.84 g.t	Percent Color Removal 7.68 g.t	11.52 g.t
2	651.0	11.8	100	100
10		100	100	100
30		100	100	100
60		100	100	100

NOTE: g.t = Grams and Application of Oxone Was At 50^{o}C

Table 14 (Percent Color Removal For 3.84 Grams Oxone With Varying Conditions), Table 15 (Percent Color Removal For 7.68 Grams Oxone With Varying Conditions), and Table 16 (Percent Color Removal For 11.52 Grams Oxone With Varying Conditions), demonstrated on pages 28 and 29, presented the factors that drove the oxidation reactions at a faster pace within the same chemical application concentration. Figures 9, 10, and 11 (also shown on pages 30, 31, and 32) presents the graphical contrasts for the different trials. At the lower concentrations, the pH of 11 yielded a 100% color removal value within 2 minutes after the initial application. The next trial to achieve 100% color removal was the temperature induced system at the time of 10 minutes. The Stage Set, after 25 minutes of reaction time, achieved 100% color removal. At the 60 minute time sampling, the pH = 7 produced a percent color removal value that exceeded the pH = 4 trial by 27.2%. This data indicates that an increase in pH produces a substantially more effective system in removing color than the temperature increased system and the other test conditions.

Table 14
Percent Color Removal For 3.84 Grams Oxone With Varying Conditions

Average Wavelength Values = 636.0 nanometers

Time (minutes)			Percent Color Removal		
	3.84 g.n7	3.84 g.t7	3.84 g.n4	3.84 g.n11	Stage Set
2	3.68	11.8	16.5	100	
10	12	100	15.2	100	6.9
25					100
30	38.1	100	17.7	100	
40					100
60	53.3	100	38.8	100	100

NOTE: g.n7 = Grams, Application of Oxone At Room Temperature, And pH = 7
g.t7 = Grams, Application of Oxone At 50°C, And pH = 7
g.n4 = Grams, Application of Oxone At Room Temperature, And pH = 4
g.n11 = Grams, Application of Oxone At Room Temperature, And pH = 11

Table 15
7.68 Grams Oxone With Varying Conditions

Average Wavelength Values = 626.0 nanometers

Time (minutes)		Percent Color Removal		
	7.68 g.n7	7.68 g.t7	7.68 g.n4	7.68 g.n11
2	2.38	100	19.6	100
10	21.3	100	19.4	100
30	66.4	100	36.5	100
60	84.4	100	63.5	100

NOTE: g.n7 = Grams, Application of Oxone At Room Temperature, And pH = 7
g.t7 = Grams, Application of Oxone At 50°C, And pH = 7
g.n4 = Grams, Application of Oxone At Room Temperature, And pH = 4
g.n11 = Grams, Application of Oxone At Room Temperature, And pH = 11

Table 16
Percent Color Removal For 11.52 Grams Oxone With Varying Conditions

Average Wavelength Values = 628.0 nanometers

Time	Percent Color Removal			
(minutes)	11.52 g.n7	11.52 g.t7	11.52 g.n4	11.52 g.n11
2	9.04	100	22.2	100
10	26.3	100	22.2	100
30	62.3	100	37.5	100
60	84.9	100	100	100

NOTE: g.n7 = Grams, Application of Oxone At Room Temperature, And pH = 7
g.t7 = Grams, Application of Oxone At 50°C, And pH = 7
g.n4 = Grams, Application of Oxone At Room Temperature, And pH = 4
g.n11 = Grams, Application of Oxone At Room Temperature, And pH = 11

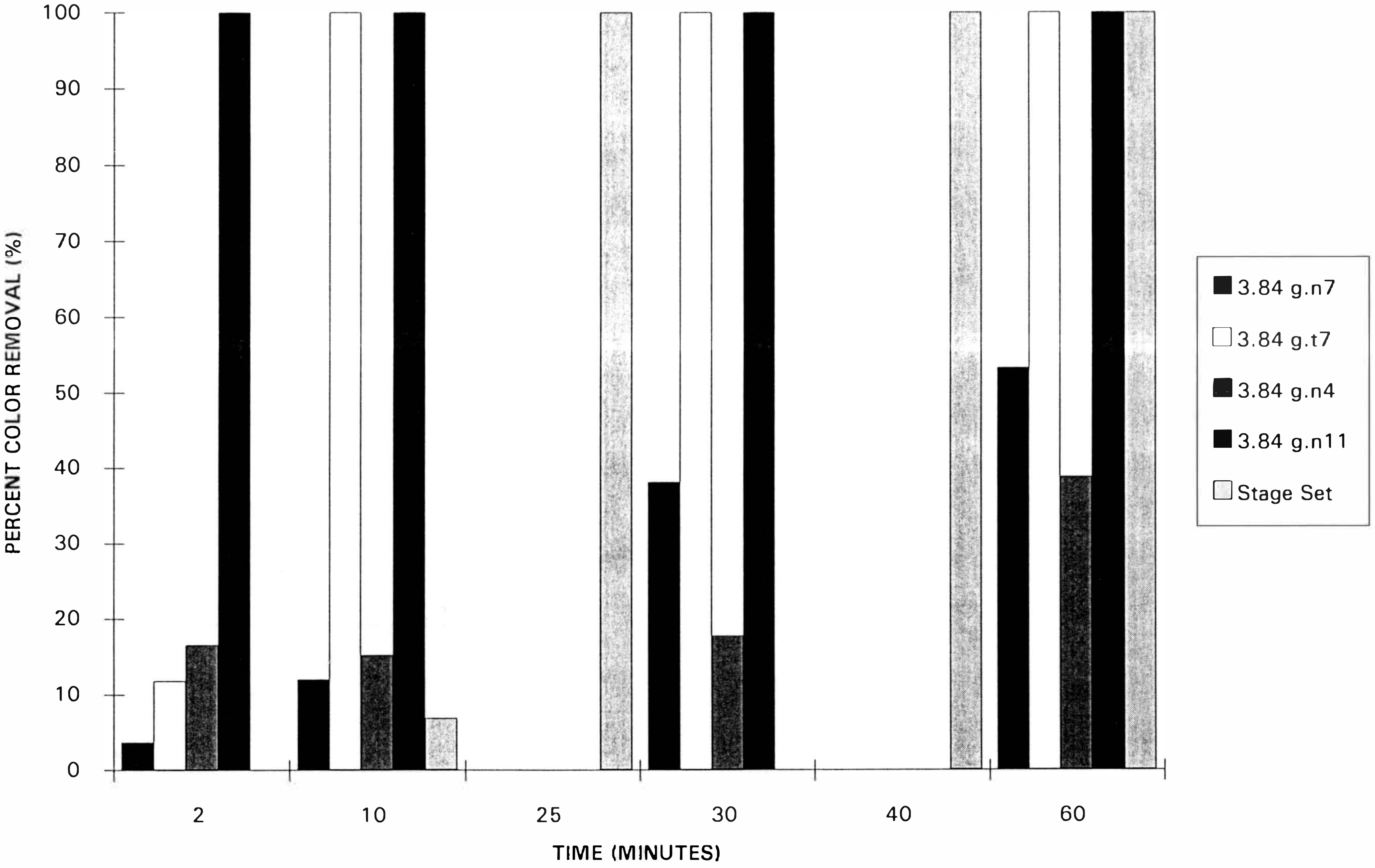


Figure 9. Percent Color Removal For 3.84 Grams Oxone With Varying Conditions

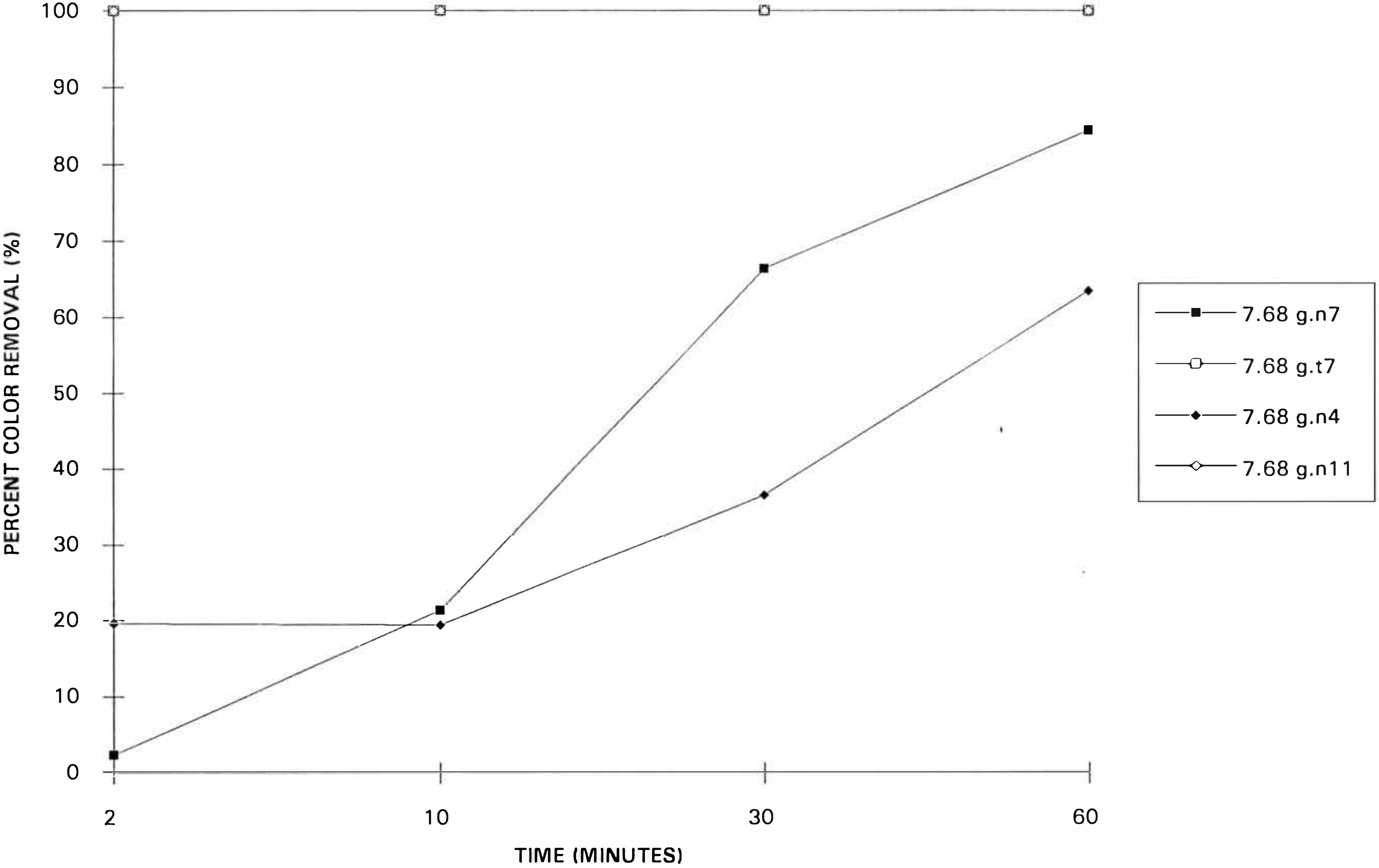


Figure 10. Percent Color Removal For 7.68 Grams Oxone With Varying Conditions

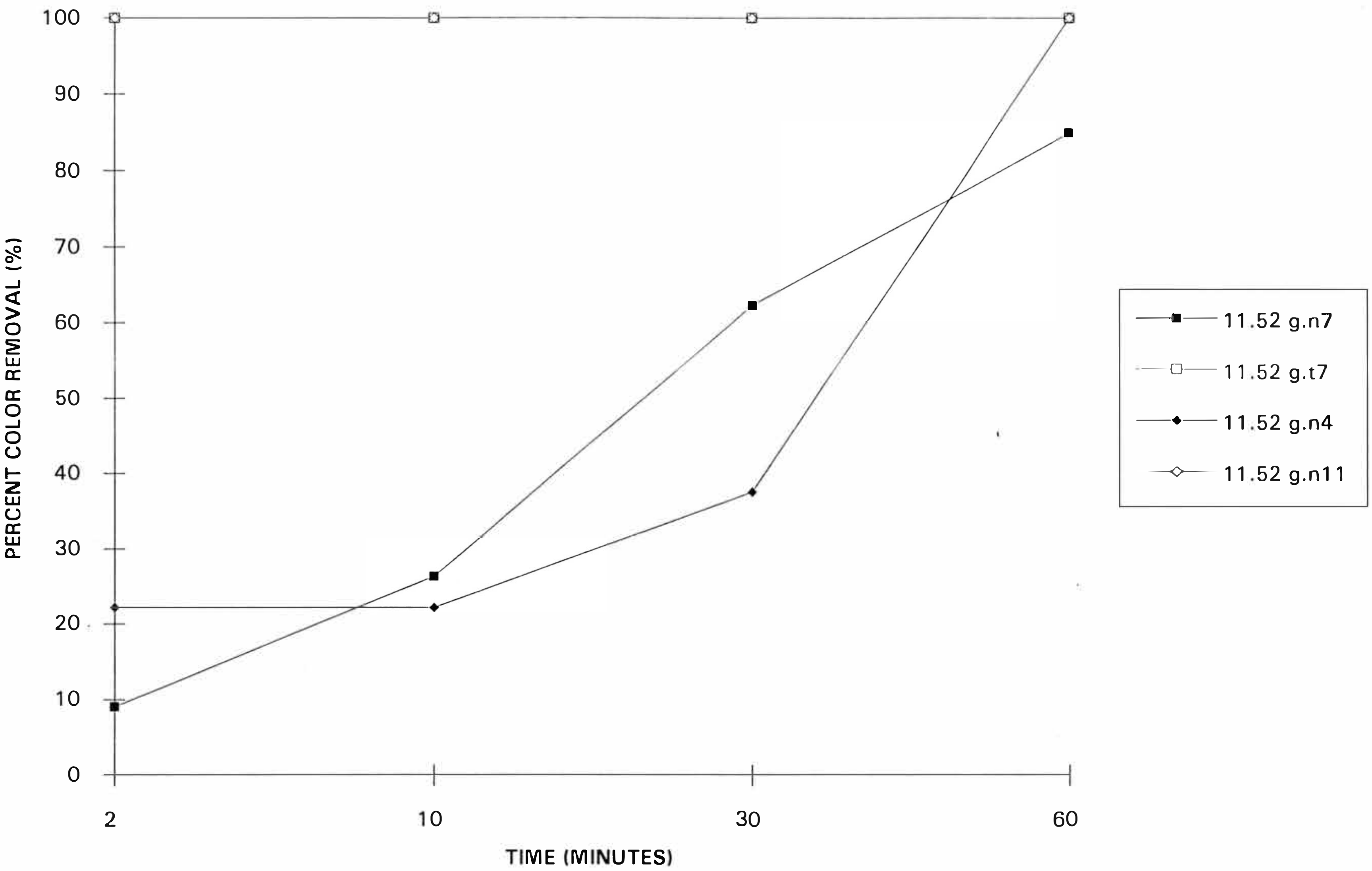


Figure 11. Percent Color Removal For 11.52 Grams Oxone With Varying Conditions

Tables 17 through 19, presented on pages 34 and 35, numerically detailed the changes in wavelengths due to the previous conditions described. These values are graphically represented in Figures 12 through 14 (demonstrated on pages 36 through 38).

During the experimentation, visual observations were made. Visual observations were performed in a 1 centimeter cell to reduce the effects of volume and a white backing was utilized to negate visual distortions due to color differences.

Generally, the initial color started as a dark brown and changed, with time, to various colors of pink and yellow. Tables 20 through 25 (demonstrated on pages 39 through 41) identifies the different visual variations during the various trials.

At the 60 minute sampling time, all of the 11.52 grams applications yielded the best results. After 180 minutes, to lower concentrations produced visual appearances that were substantially better than the highest dosage. With the introduction of temperature (Table 23, page 40), the 3.84 gram application at 10 minute sampling time produced a result similar to the 2 minute observation for pH = 11 and 11.52 gram application of Oxone (Table 23, page 40). The Stage Set after 60 minutes produced a appearance similar to the 10 minute sampling time for the 3.84 gram application with temperature enhancement. In other words, the light yellow appearance indicated that the highest concentrations yielded better results than lower concentrations with temperature enhancement and stage application. This result was also verified in the numerical and graphical results presented earlier.

Table 25 (pH = 11 Optimization Observations), page 41, yielded visual data that indicates the "minimum" application of chemical allowed to produce a oxidation reaction similar to the earlier trials. After 10 minutes, both the 0.5 and 1.0 gram trials indicated that visual changes occur. The 1.0 gram trial, after 10 minutes, produced a visual effect similar to the 2 minute and 3.84 gram addition. This data allows the possibility to substantially reduce the chemical treatment application meanwhile providing color removal enhancements.

It must also be noted that the Oxone did not become oxidative without the presence of acetone and/or a ketone. In other words, DMD was being generated during experimentation and was the driving force of the oxidation processes to help remove color from the effluent samples.

Table 17
Wavelength Changes For 3.84 Grams Oxone With Varying Conditions

Time (minutes)	Wavelengths (nanometers) 3.84 g.n7	3.84 g.t7	3.84 g.n4	3.84 g.n11	Stage Set
0	663	651	651	554	663
30		361		512	
40					357
60	543	356	651	511	321
120	532	321	-	510	
180	383	304			

NOTE: g.n7 = Grams, Application of Oxone At Room Temperature, And pH = 7
g.t7 = Grams, Application of Oxone At 50^{o}C, And pH = 7
g.n4 = Grams, Application of Oxone At Room Temperature, And pH = 4
g.n11 = Grams, Application of Oxone At Room Temperature, And pH = 11

Table 18
Wavelength Changes For 7.68 Grams Oxone With Varying Conditions

Time (minutes)	7.68 g.n7	Wavelengths (nanometers) 7.68 g.t7	7.68 g.n4	7.68 g.n11
0	661	653	647	544
10		360		505
30		320		503
60	512	311	647	382
120			405	
180			361	

NOTE: g.n7 = Grams, Application of Oxone At Room Temperature, And pH = 7
g.t7 = Grams, Application of Oxone At 50^{o}C, And pH = 7
g.n4 = Grams, Application of Oxone At Room Temperature, And pH = 4
g.n11 = Grams, Application of Oxone At Room Temperature, And pH = 11

Table 19
Wavelength Changes For 11.52 Grams Oxone With Varying Conditions

Time		Wavelengths (nanometers)		
(minutes)	11.52 g.n7	11.52 g.t7	11.52 g.n4	11.52 g.n11
0	666	648	646	552
10		308		385
30		303		363
60	528	302	532	360

NOTE: g.n7 = Grams, Application of Oxone At Room Temperature, And pH = 7
g.t7 = Grams, Application of Oxone At 50°C, And pH = 7
g.n4 = Grams, Application of Oxone At Room Temperature, And pH = 4
g.n11 = Grams, Application of Oxone At Room Temperature, And pH = 11

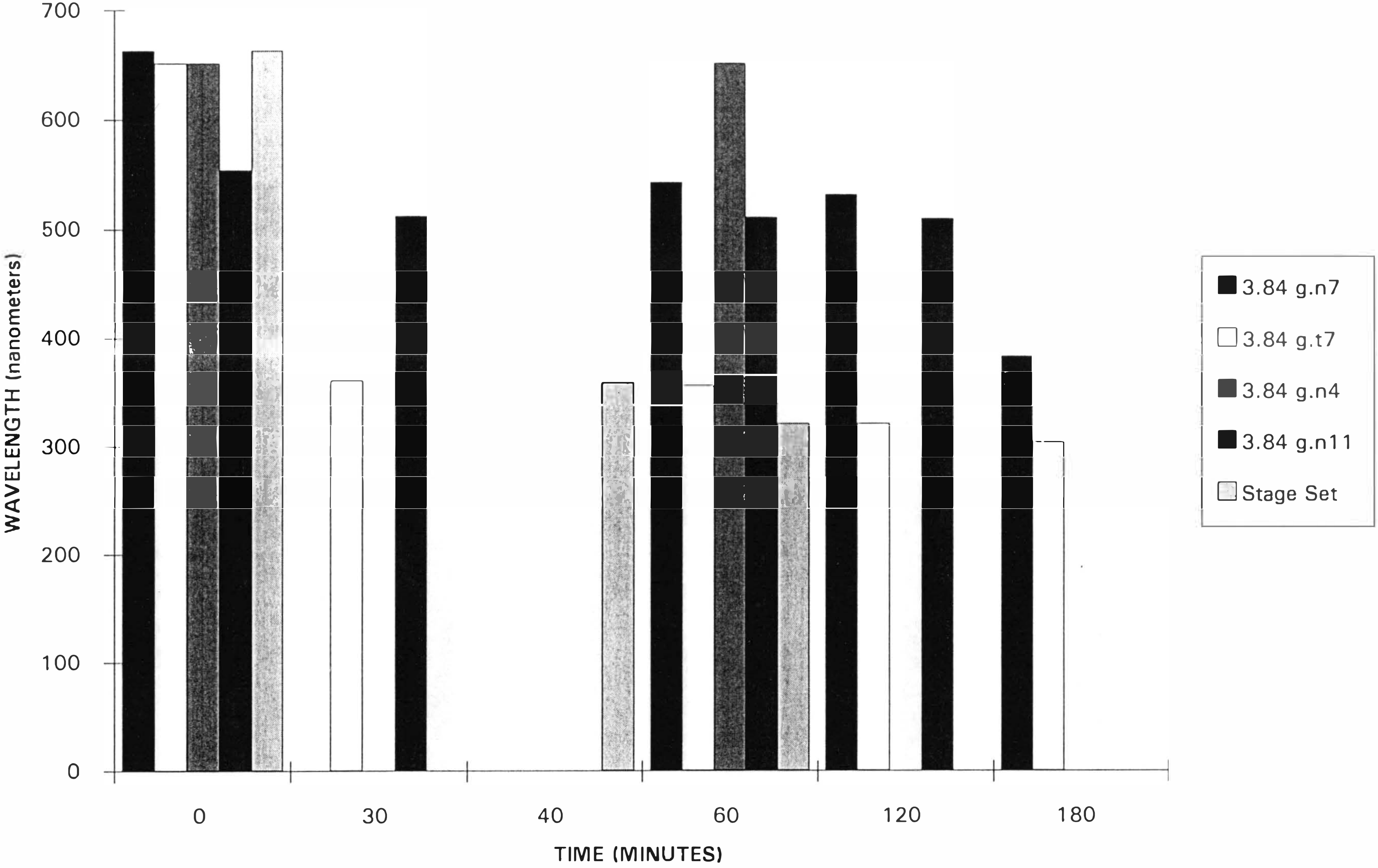


Figure 12. Wavelength Changes For 3.84 Grams Oxone With Varying Conditions

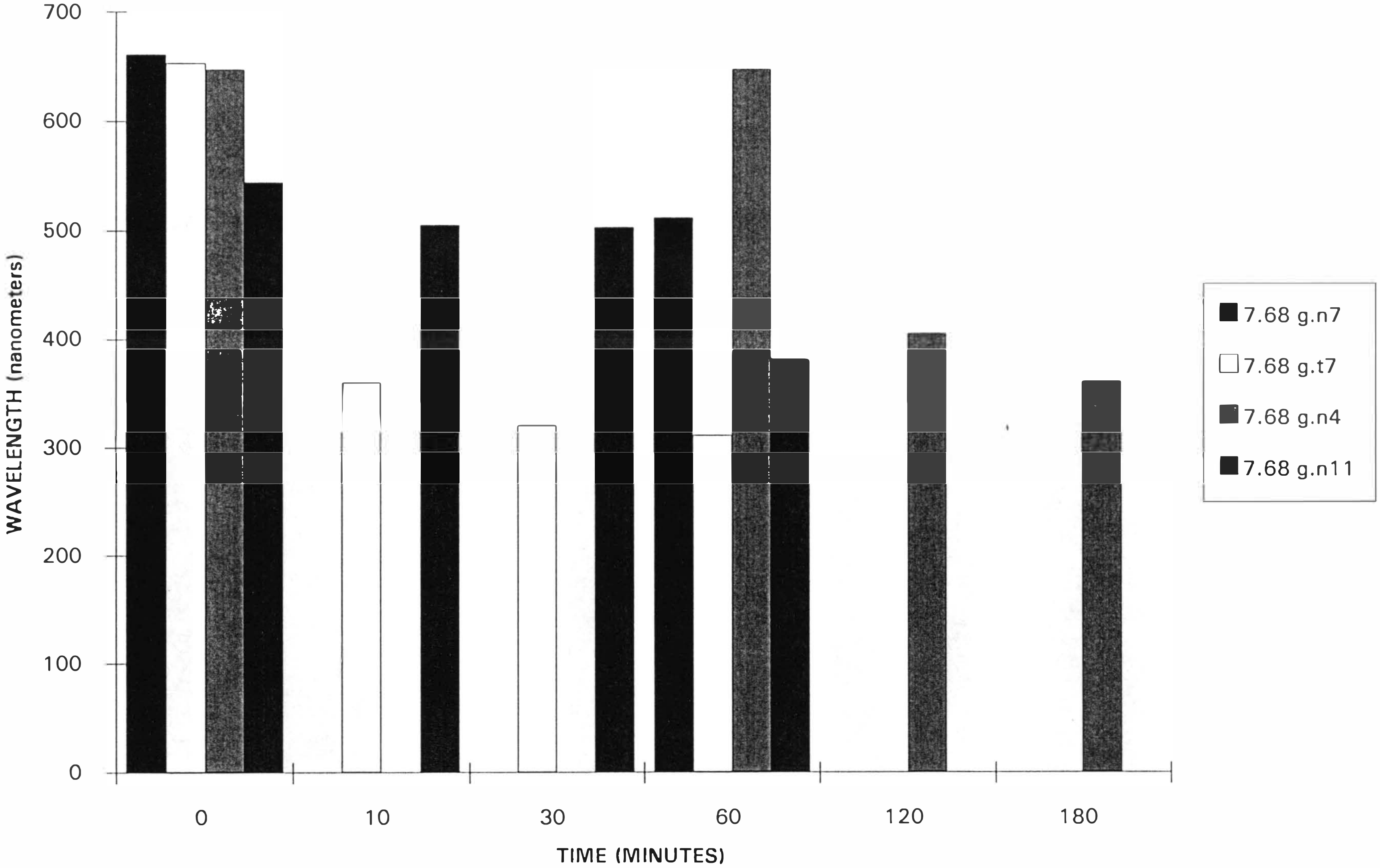


Figure 13. Wavelength Changes For 7.68 Grams Oxone With Varying Conditions

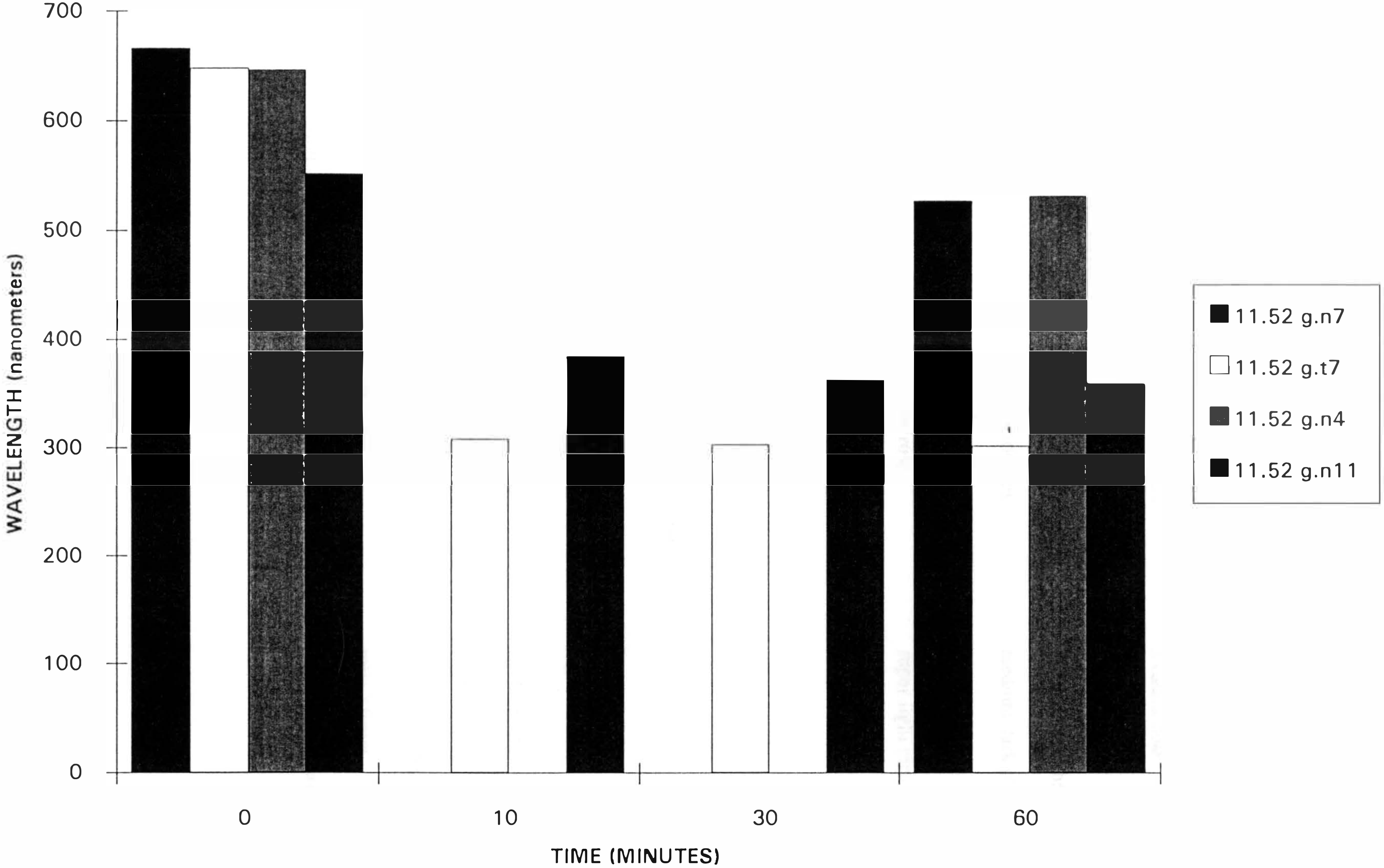


Figure 14. Wavelength Changes For 11.52 Grams Oxone With Varying Conditions

Table 20
pH = 7 Visual Observations

Time	Visual Observations		
(minutes)	3.84 grams	7.68 grams	11.52 grams
0	dark brown	dark brown	dark brown
2	medium brown	medium/light brown	medium/light brown
10	dark pink	medium dark pink	medium dark pink
30	purplish/pink	light pink	light pink/rose
60	light pink	light pink/rose	super light pink
120	very light pink (undetectable)		
180	light yellow		

Table 21
pH = 4 Visual Observations

Time	Visual Observations		
(minutes)	3.84 grams	7.68 grams	11.52 grams
0	dark brown	dark brown	dark brown
2	insignificant	insignificant	medium brown
10	insignificant	insignificant	insignificant
30	insignificant	light brown	light brown/dark tea
60	light brown	dark tea	light tea
120		light tea	
180		light yellow	

Table 22
pH = 11 Visual Observations

Time (minutes)	Visual Observations 3.84 grams	 7.68 grams	 11.52 grams
0	dark brown/red	dark brown/red	dark brown/red
2	medium light pink	light pink	light yellow
10	light pink/red	slightly pink	slightly yellow
30	pinkish/yellow	pinkish/yellow	lighter yellow
60	insignificant	insignificant	insignificant
120	insignificant		

Table 23
pH = 7 With Increased Temperature - Visual Observations

Time (minutes)	Visual Observations 3.84 grams	 7.68 grams	 11.52 grams
0	dark brown	dark brown	dark brown
2	medium brown	light purple	light yellow
10	light yellow	light yellow	very light yellow
30	slightly yellow	almost clear	almost clear
60	slightly yellow	almost clear	appears clear
120	almost undetectable		
180	appears clear		

Table 24
pH = 7 With Addition In Stages - Visual Observations

Time (minutes)	Oxone Additions (grams)	Visual Observations (appearance)
0	1.28	dark brown
10		insignificant change
15	1.28 (2.56 total)	
25		light pink (absorption complete)
30	1.28 (3.84 total)	
40		medium yellow
60		light yellow

Table 25
pH = 11 Optimization Studies - Visual Observations

Time (minutes)	Oxone Additions (grams)	Visual Observations (appearance)
0	0.5	dark brown/red
10		dark pink
0	1.0	dark brown/red
10		medium light pink (similar to 2 minute and 3.84 grams addition)

NOTE: 1.0 GRAM OF OXONE WITHOUT ACETONE DID NOT WORK. DMD WAS NOT GENERATED!

Table 26 (Application Costs) denotes the price value assigned for the treatment of 1,000,000 gallons with the dosages used for the experimental purposes of this project. The optimization project with a dose of 0.5 grams of Oxone for 500 milliliters of effluent yielded a value of $7,800,000. The 1.0 gram of Oxone for 500 milliliters of effluent yielded a cost 51.3% greater than the 0.5 gram application. In other words, the optimization study substantially reduced the costs of treatment but these values are not appropriate for daily treatment.

Table 26
Application Costs

Dosage of Oxone (grams/liter)	Cost Per Pound ($/Pound)	Assumed Flow Treated (gallons)	Total Cost ($)
1.0	0.94 *	1,000,000	7,800,000
2.0	0.94 *	1,000,000	16,000,000
7.68	0.94 *	1,000,000	60,200,000
15.4	0.94 *	1,000,000	121,000,000
23.04	0.94 *	1,000,000	180,700,000

NOTE: 1.0 grams/liter = 0.5 grams Oxone in 500 milliliters of effluent
2.0 grams/liter = 1.0 grams Oxone in 500 milliliters of effluent
7.68 grams/liter = 3.84 grams Oxone in 500 milliliters of effluent
15.4 grams/liter = 7.68 grams Oxone in 500 milliliters of effluent
23.04 grams/liter = 11.52 grams Oxone in 500 milliliters of effluent

* = Bulk Price Quote From DuPont's Chemical Sales Representative
Phone Number: 312/ 774-7068
(Monday, March 27, 1995)

CONCLUSIONS

Increasing the pH of the effluent, raising the temperature of the effluent, and applying DMD dosages in stages allowed the removal of color from an effluent to occur at a much faster rate. Because of this knowledge, chemical use could be minimized substantially by utilizing all of the effluent treatments together.

At the dosage levels used in these experiments, chemical costs would be too significant to warrant use. Further optimization studies utilizing the techniques of raising the pH and temperature of the effluent and applying the DMD in stages, further reduce treatment costs from the $7,800,000 treatment cost.

RECOMMENDATIONS

There are several areas in which future experimentation could explore with the use of DMD to remove color from an effluent. One area of greatest concern is to minimize the use of Oxone and acetone in a large effluent flow to make color treatment more profitable and efficient. If this is not performed, DMD use for effluent improvement should not be attempted.

Another area in which DMD experimentation for effluent improvement should explore is the use of DMD treatment with other chemical and/or physical processes. A hybrid system may prove to be more cost efficient and effective than a system focused solely on one application.

DMD use for color removal should be done to an effluent with varying dye concentrations. Also, the types of dyes should be altered during experimentation due to the possibility that color removal by DMD may be dependent on the type of dye.

Experimentation with DMD for color removal should also be attempted with different ketones. As EPA regulations increase, ketone use may become the limiting factor for DMD generation.

REFERENCES

1. Murphy, J.K., Hulsey, R.A., and Amarnath, R.K., "Advanced Oxidation Treatment of Pulp and Paper Mill Wastewater," Proceedings of the 48th Industrial Waste Conference May 10, 11, 12, 1993 held at Purdue University, West Lafayette, IN, Lewis Publishers, Chelsea, MI, 1994, pp. 621-628.

2. Safe Drinking Water Act: Amendments, Regulations, and Standards, edited by Calabrese, E.J., Gilbert, C.E., and Pastides, H., Lewis Publishers, Inc., Chelsea, MI, 1989, p. 11.

3. De Zuane, J., Handbook of Drinking Water Quality: Standards and Controls, Van Nostrand Reinhold, New York, NY, 1990, pp. 22-23.

4. Davis, M.L. and Cornwell, D.A., Introduction to Environmental Engineering, Second Edition, McGraw-Hill, Inc., New York, NY, 1991, pp. 123-124.

5. Montgomery, R.A., Journal of the American Chemical Society, "Catalysis of Peroxymonosulfate Reactions by Ketones," 96 (25): 7820 (1974).

6. Tozer, H.G., "Color Treatment of a Dye-Bearing Paper Mill Wastewater: A Case Study," Proceedings of the 48th Industrial Waste Conference May, 10, 11, 12, 1993 held at Purdue University, West Lafayette, IN, Lewis Publishers, Chelsea, MI, 1994, pp. 611-620.

7. Rys, P. and Zollinger, H., Fundamentals of the Chemistry and Application of Dyes, John Wiley & Sons Ltd., New York, NY, 1972, pp. 42-71.

8. The Printing Ink Manual, Fifth Edition, edited by Leach, R.H. and Pierce, R.J., Blueprint, London, 1993, pp. 199-210.

9. Organic Peroxides, edited by Ando, W., John Wiley & Sons Ltd., New York, NY, 1992, pp. 195-217.

10. McGrouther, K.G. and Allison, R.W., Appita, "Improved Oxygen Delignification with Peroxyacid Treatment," 47 (3): 238 (1994).

11. Spectroscopy Source Book, editor in chief Parker, S.P., McGraw-Hill, Inc., New York, NY, 1988, pp. 247-253.