

\OZONE TREATMENT OF A SELECTED
TEXTILE DYEING AND FINISHING WASTEWATER,

by

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To the honor and glory of God:

And whatever you do in word or deed, do all in the Name of the Lord Jesus, giving thanks through Him to God the Father.

Whatever you do, do your work heartily, as for the Lord rather than for men;

(Colossians 3:17, 23)

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I. INTRODUCTION

Water is considered today to be one of man's most precious resources, used in nearly every process known to civilization. The quality of the available water greatly affects its suitability for intended purposes. Water quality is degraded easily largely due to its strong solvent properties. As a result of these properties, many contaminants enter into solution in the water with each use and re-use. Industrial processes in general are known for their additions of contaminants to water. The textile dyeing industry, in particular, adds large quantities of solids, BOD, COD, phosphates, and heavy metals to the water used in its processes. In addition, the dyes and coloring agents used in the dyeing processes pass through the process equipment and cause color in the wastewater effluents. Even at high dilutions, these solutions are highly colored, and textile dyeing plants whose effluents flow into streams of low flow are finding that color itself is a pollution problem.

In the earlier days of untreated effluents, color was used as an indicator of the potential of a wastewater for killing fish. Water research showed that the effects of a waste on aquatic fauna were primarily due to oxygen depletion, rather than to chemical toxicity, and waste treatment systems were developed to alleviate the problem of deoxygenation. Conventional treatment systems included primary treatment for the removal of settleable solids

and secondary treatment for biological oxidation of organic matter in the effluent. These conventional systems have had conspicuous success in removing the materials in an effluent which are responsible for oxygen depletion, as witnessed by the growing infrequency of fish kills.

A major remaining problem with dyeing operation effluents involves the removal of the waste fraction of the effluents which is responsible for color. Biological oxidation has had virtually no effect on the color of these effluents, as the color-producing components are largely biologically refractive. The compounds have not generally been found to be toxic to fish species, at least in normal effluent concentrations. However, high color in effluents is meeting increased criticism on several grounds: 1) by reducing sunlight penetration, color might inhibit the growth of desirable aquatic plant life; 2) while not toxic to fish, colored components might be toxic to some of the lower organisms in the aquatic ecosystem; 3) at some point downstream, colored wastewater may become part of a municipal supply system, where color removal may become troublesome; 4) regulatory bodies at all levels are becoming less tolerant of any organic materials in an effluent; and 5) esthetically, strong color in a water is inconsistent with present public attitudes. Since pressure on dyers to remove color from their effluents is increasing, effective methods of doing so must be found.

The research described in this thesis consisted of an investigation of the suitability of a system which used ozone as a chemical

oxidant for removing color from a textile dye waste. The purpose of this investigation was to evaluate the feasibility of using ozone to achieve a high degree of color removal. In addition, the effect of ozone on several waste constituent parameters was studied. The waste chosen for this study was the dyehouse effluent of the Martin Processing Company plant located in Rocky Mount, Virginia.

II. LITERATURE REVIEW

Ozone was first noticed by Van Marum in 1785 as a result of a pungent odor in the vicinity of an electrical machine (9). Cruickshank noted the occurrence of the same smell during the electrolysis of water in 1801. Schonbein attributed the odor to a new chemical substance in 1840, and proposed the name ozone, deriving it from the Greek word "ozein," which means "to smell" (21). The tri-atomic oxygen formula was established in 1867.

General Properties of Ozone

Physical properties. Ozone is the tri-atomic form (O_3 , molecular weight 48) of oxygen. Unlike normal molecular oxygen, ozone has a characteristic pungent odor, detectable in concentrations as low as 1 part per million (16). It is colorless at room temperatures, and condenses to a dark blue liquid at $-112^{\circ}C$. Liquid ozone is easily exploded, as are concentrations of ozone in air-oxygen mixtures greater than 30 percent.

Ozone strongly absorbs light in the infrared, visible, and ultraviolet spectrums at several specific wavelengths, with an absorption maximum measured at 2537 angstroms (16). This characteristic makes the use of spectrophotometric methods of measuring ozone concentrations in the atmosphere and the laboratory very convenient.

The ozone molecule, after studying its microwave spectrum, is found to be diamagnetic, with an obtuse angle of $116^{\circ}49'$, and with oxygen-oxygen bonds of equal length of 1.278 angstroms, possessing a dipole moment of 0.49-0.58 debye (2). The molecular configuration

can best be described as a resonance hybrid, with four forms possible. As a result, an ozone molecule does not behave as a radical, but as a 1,3-dipole (2).

Ozone is much more soluble in water than is oxygen, but due to its much lower available partial pressure, it is very difficult to obtain a concentration much higher than a few parts per million under normal atmospheric and operating conditions of temperature and pressure (16). Regular di-atomic oxygen is soluble in distilled water up to 8.92 ppm at 25°C, while ozone is theoretically soluble up to 500-600 ppm at the same temperature. This theoretical concentration is rarely, if ever, reached. Determination of actual concentrations from theoretical concentrations involves many complicated calculations (24). The need for and use of these calculations has been eliminated by the development of a physical relationship between concentrations of ozone in air and water, as expressed by the distribution co-efficient,

$$S = \frac{A}{B}$$

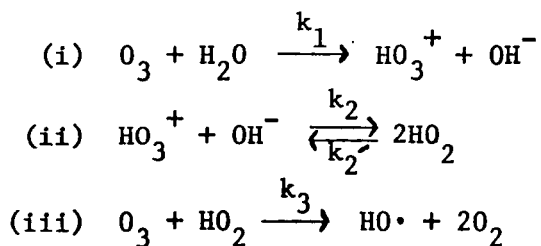
where A is the concentration of ozone in water at a given temperature and pressure, and B is the concentration of ozone in air under the same conditions. In many cases, however, it is the amount of organics present in water that will determine the quantity of ozone dissolved in the water, rather than the distribution co-efficient.

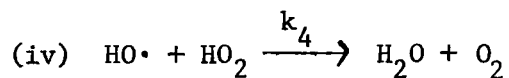
Chemical properties. Ozone gas is a powerful oxidizing agent, possessing an electronegative oxidation potential of -2.07 mv at 25°C (16). This value is exceeded only by fluorine, nascent oxygen,

and F_2O , and is approximately double that of the OCl^- ion. Such a high electronegativity makes ozone a very versatile, highly reactive oxidant. This activity is even more valuable, as ozone retains this oxidative power in aqueous solution, attacking nearly all organics and most metals, except gold and platinum. This strong oxidative power could possibly be a drawback, were it not for another of ozone's properties, that of its relatively rapid breakdown, with a half-life of approximately 15 minutes in dry air. The decomposition of ozone is even more rapid in the presence of water, and the half-life may be as low as 9 minutes in an aqueous solution. Several substances may act as a catalyst to further increase the decomposition rate, including sodium hydroxide, soda ash, lime, halogens and halides, silver, platinum, manganese dioxide, and nitrogen pentoxide (16). The decomposition of ozone, and the effects of its breakdown products on both organics and inorganics in water, is extremely important in understanding the usefulness of ozonation as a water and wastewater treatment process.

Ozone Kinetics

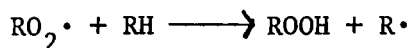
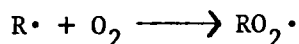
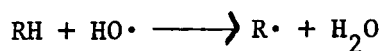
The decomposition mechanism of ozone in water is somewhat unsure, but is generally accepted as following the mechanism suggested by Alder and Hill, involving the reactions below (15):



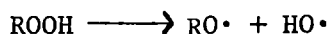
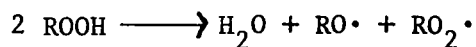


Reactions (i) and (iii) are the steps responsible for the disappearance of ozone, and are the rate controlling reactions. Reaction (ii) is an equilibrium state maintained as long as any ozone exists in the system. Reaction (iv) is the final, chain-breaking step. This mechanism has been supported by several kinetic experiments.

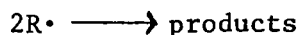
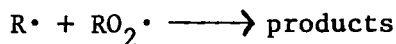
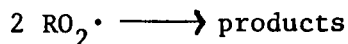
The reaction of ozone decomposition products with organics is postulated to occur through the action of the generated free radical, $HO\cdot$, on the organics present in solution, as follows (35).



The hydroperoxide decomposes in the following manner:



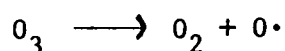
The chain-terminating reactions would then be:



This particular mechanism, called auto-oxidation, is only one of three types of decomposition reaction which occur upon the introduction of ozone into water containing organic or inorganic constituents, the other two being regular oxidation and ozonolysis. Auto-oxidation

is an enhancing action by ozone on the oxidizing capacity of oxygen. The products of this type of action may be greatly different than those of a pure ozone reaction.

Regular oxidation involves the splitting off of the third atom in the breakdown of the ozone molecule:



The third atom, commonly called nascent oxygen, is very unstable and reacts quickly with oxidizable matter. It is hypothesized that ozone-produced nascent oxygen is responsible for oxidizing most inorganic substances in an ozone reaction, particularly in the case of metals (11).

Ozonolysis is the true decomposition, or cracking, of unsaturated organic matter by ozone. An unstable, intermediate product is formed when all three atoms in ozone attach to a carbon-carbon double bond in an organic molecule, (i). This product is called a molozonide. The instantaneous breakdown of the molozonide, (ii), produces two ozonides as by-products, which are an aldehyde and a highly reactive dipolar ion, normally called a Criegee Zwitterion. This Criegee Zwitterion contains both acidic and basic functional groups. Addition of water to the Zwitterion produces a hydroperoxyalcohol (iii). This latter step has two possible further decomposition reactions as alternatives, with one yielding water and an organic acid (iv), while the other possibility produces a second aldehyde and hydrogen peroxide (v). These steps are shown as follows (22):

in Paderborn, Germany, in 1891, utilizing a system designed by Frölich (12). Schneller, Van der Sleen, and Tindal constructed the first industrial apparatus for ozone sterilization of water in Oudshoorn, Holland in 1893 (9). The plant followed up sedimentation and filtration with ozonation, and treated raw water from the Rhine River. Weisbaden, Germany, put the first full-scale municipal ozonation plant into operation in 1896 (12). Otto-ozone equipment was used at Nice, France, in the first major ozone disinfection plant which involved treatment of more than one million gallons per day (9). The degree of success at Nice led quickly to the construction of similar installations throughout Europe. The growth of ozone use stopped abruptly with the advent of World War I, but increased rapidly again after the war ended. Today, there are more than 1000 ozone disinfection installations in 50 countries around the world. Ozone is the method of choice for disinfection of water in continental Europe.

In this country, however, the use of chlorine in water treatment became prevalent after World War I, as cheap chlorine gas was a by-product of the war's research into poison gases. Only two major municipal installations in the United States have used ozone as part of their treatment schemes (9). Whiting, Indiana, opened a plant in 1940 which used ozone as a pretreatment process for the removal of taste and odor from Lake Michigan water. Philadelphia, Pennsylvania, in 1949, put into operation the worlds' largest ozonation installation. Ozone was used to remove taste, odor, and manganese from water drawn

from the Schuylkill River. This plant was closed in 1959 due to increased operational costs when the main treatment plant was expanded.

As can be seen, the principle use of ozone in the United States has been as an oxidant for taste and odor removal, while in Europe ozone is primarily used as a disinfectant. The use of ozone as a disinfectant is perhaps the most wide-spread application. Ozone exhibits an effect commonly called the "all-or-nothing" mechanism upon bacteria and virus (26). By this it is meant that little effect is noted on the microbial population until a critical dosage is reached, whereupon the population is almost completely eliminated. It has been found that when this critical dosage is reached, an ozone residual appears in the water. Nice, France, reaches a coliform count of zero with an ozone dosage of two grams per cubic meter for 5 minutes, obtaining an ozone residual of 0.1 ppm at one minute after ozonation ends (11). Paris, France, has reported similar results for the same dosage, with reduction of C. perfringens cells to zero, and spores to near zero. Hoather found that a coliform MPN of 50 per 100 ml was reduced to zero by a dose of 2 ppm (23). In a test performed by Houston, Bacterium coli were present in 1 ml. of filtered Thames River water in more than 70% of untreated water samples (37). After treatment with 1.5 ppm of ozone, B. coli were absent in 100% of samples of 100 ml.

Ozone has also been shown to be a powerful viricidal agent. Kessel found that poliomyelitis virus was completely inactivated by two minutes of contact with 0.05-0.45 ppm of ozone (37). The same

virus required contact of 1.5 to 3 hours at 0.5-110 ppm of chlorine to achieve the same level of inactivation. The normal applied dosage of ozone for disinfection purposes is 0.5-1.5 ppm for up to five minutes. The residual is then measured five minutes after ozone injection has stopped to determine the degree of disinfection, with a residual of 0.1-0.2 ppm considered sufficient for complete bacterial kill and 0.4 ppm adequate for virus deactivation (20).

Ozone is also used as a method of controlling taste and odor in water (9). At Whiting, Indiana, the introduction of ozone reduced threshold odor numbers by 58 to 83 percent. At Philadelphia, an ozone dose of 1.27 ppm reduced threshold odor numbers from 43 to 19. Valin has reported, from results at the Dusseldorf, Germany, plant that thresholds for tastes up to 18 and those for odors up to 10 were completely eliminated at a dose of 0.7-1.0 ppm for 10 minutes (13).

The oxidative power of ozone in water has been applied to industrial wastes as well as to municipal waters and wastewaters. An oil refinery near Lake Ontario in Canada currently uses ozone to destroy phenols and cyanides in the plant effluent. Ozone dosage is maintained at 20 to 50 mg/l, yielding a phenol level in the effluent of less than 3 ppb (8).

A plant in Kansas includes ozonation as part of a waste treatment scheme to remove chromium, phenols, sulfides and sulfites, cyanides, and miscellaneous oils (21). Treatment occurs in two packed towers, with the second tower acting as an air scrubber to remove ozone from the exhaust gases. The ozone is applied at a

dosage level of 20 ppm. After filtration, the effluent is discharged to a lagoon where live fish thrive in the non-toxic water.

Many industrial uses of ozone involve a frothing action, where materials are concentrated in an ozone-induced froth and removed for disposal or re-use, or where the froth is being broken down by the treatment. Foulds found that in an ozone frothing pond, there was an 83% removal of ABS (10). The surfactants which remained in the water after treatment were biodegradable, while those before ozonation were not. He also showed that nitrates, phosphates, and suspended solids were concentrated in the froth and could be easily removed by a skimming operation.

Buescher studied the destruction of lindane, aldrin, dieldrin, and other pesticides by various oxidants (9). He reported destruction of lindane and aldrin and decreased concentrations of dieldrin by ozonation, while other oxidants, such as calcium hypochlorite, KMnO_4 , Na_2O_2 , (each at up to 40 mg/l dose), showed either no measurable effect or only partial removal, and in some cases, increased toxicity. Gardiner and Montgomery observed substantial reductions of hydrocarbon pesticides upon ozonation (9). Dieldrin and γ -BHC were removed at the same rate, with approximately 50% of each disappearing with the absorption of 20 ppm of ozone. A more rapid removal was observed with both DDT and TDE.

Ozone has also been applied in both primary and tertiary treatment schemes to reduce the carbonaceous content of waters and wastewaters, as measured by BOD, COD, and TOC (6,7,34). Ozone can

theoretically oxidize organic materials completely to carbon dioxide and water. This result would be reflected by a decrease in the TOC level of the effluent. If the oxidation is not complete, the TOC level will not change. COD reduction is a result of incorporation of oxygen into the molecular structures of the ozonated organic materials. The organics in a waste in such a case will also show a reduction in BOD, as the initial oxygen demand will be satisfied by the ozone. After this initial oxygen demand has been met, ozone will begin to attack refractory materials, making them biodegradable. This increased biodegradability is caused by the action of ozone introducing oxygen functional groups into the refractory materials. These new oxygen-containing groups afford bacteria a site where metabolism can occur, possibly yielding an increase in the BOD. Continued ozonation of the refractory materials further oxidizes them and the BOD once again decreases.

Evans and Ryckman have reported an 80% reduction of the COD in the effluent of a secondary treatment plant after ozonation (9). The Air Reduction Company studied the effect of ozonation on a trickling filter effluent (9). The results showed a reduction in the COD from 32 to 13 mg/l and a TOC reduction of 12 to 9 mg/l, at a contact time of one hour. At Hanover Park in Chicago, Illinois, results of an ozone dose of 6 mg/l showed an average BOD reduction, after refractory materials were oxidized, of 30% (9).

Even though ozone has been shown to be effective in many instances, occasions have occurred where the results did not meet

expectations. These "failures" have generally been related to the normal occurrence in the waters of colloidal and suspended solids. Colloidal and suspended solids exert a masking effect on the intended target of ozonation, driving up the required dosages, and reducing the effectiveness of the ozonation process (24).

In order to combat this masking effect, two ozonation and microstraining processes for water treatment have been developed. They are called the Microzon process and the M.D. (Micellization/Demicellization) process (3). Micellization refers to an increase of turbidity due to ozonation from the formation of negatively charged micelles. Demicellization refers to the neutralization of these charged particles by the addition of a small dose of polyelectrolyte, and their subsequent removal by sand filtration. This effect comes about as a result of ozone's attack on both the hydrophilic groupings and the hydrophobic groupings-peptizing agent complexes which cause colloidal stability, with the final result being precipitation of the dispersed particles.

Both processes provide microstraining immediately before ozonation to remove solids that would mask the action of ozone on the water. If turbidity is not produced by ozonation, the water is discharged as finished: clarified, sterilized, and containing the appropriate ozone residual. This is the complete Microzon process. The Micellization/Demicellization process is used if ozonation has generated turbidity in the water.

Reasons for using ozone in the water and wastewater treatment processes are varied, but may be placed into two main categories (19,32).

The first category is the effect of ozone on the receiving stream. Here, the advantages of using ozone include an increase in dissolved oxygen, the disinfective action of ozone, decrease in organic pollutants, the unincreased salt content, hardness, and aggressiveness of the water, and the fact that the oxidized products are non-toxic or less toxic than the unoxidized materials. The second group of reasons for using ozone involve physical design concepts. Ozone is easily applied to a water or wastewater, yielding lower application costs. The high reactivity of ozone, combined with its ability to react with some materials without actually being in solution, leads to more rapid reaction rates, which may lead to shorter detention times.

Decolorization of Effluents

The causes of color. Color in waters and wastewaters is caused by both organic and inorganic compounds. Inorganic color-forming materials most commonly are complexes of metals called pigments (22). Pigments generally are readily removed during sedimentation processes, although some inorganic color is removed by flotation and frothing.

Most generally, color in waters and wastewaters is caused by materials of organic origin. This feature is particularly true in the textile dyeing industry. Almost all organic compounds are colored, but most do not absorb light in the visible spectrum (22). Color problems in dyehouse effluents are caused by organic compounds which do sorb light in the visible spectrum. The mechanism of light sorption is accomplished by organic functional groups, linked in

long chains, which have excesses of electrons (2). These groups are called chromophores, and include such functional groups as carbon-carbon double and triple bonds, nitro groups, benzene rings, and heterocyclic compounds which have sulfur, oxygen, or nitrogen in the ring (14). The shade of the color displayed will depend on the length of the molecular chain and the nature of the chromophoric groups involved.

Effluents from dyeing operations include both naturally occurring color and color imparted from the dyes added to the water. There are many types of dyes used in the textile industry, but they may be put into four main categories: vat dyes, disperse dyes, reactive dyes, and the most common type, soluble dyes (28). Soluble dyes include basic, acidic, and direct dyes, and may or may not be complexed with metals to increase dye fastness. Basic dyes are large cationic organic molecules and are the brightest class of soluble dyes, thereby causing the greatest color problem. Acidic dyes, either of the azo or anthraquinone variety, are small molecules complexed with sulfonic acid, and have poor light fastness. Direct dyes are medium length molecules complexed with inorganic salts, and are the most resistant to light degradation.

Methods of color removal. There are five major methods of waste treatment for color removal: oxidation, filtration, co-precipitation, ion exchange, and centrifugation. Each treatment type has its advantages and disadvantages. No single commercial treatment process, with the exception of reverse osmosis, a filtration process, has been found to be effective in removing color in all cases.

Co-precipitation is perhaps the most widely used type of color removal process in the textile dyeing industry (14,27,28,29,30,38). This method physically removes the color bodies from the effluent by adding coagulating aids to the waste and then settling the solids out of solution. Packham has found that most color bodies are not colloids, but are in true solution (14). However, the bodies are of sufficient size to exhibit colloidal properties, and thus are easily coagulated and flocculated out of solution. The most popular chemicals for use in a co-precipitation system are alum, alum-cationic polymer mixtures, massive lime dosages, lime-anionic polymer mixtures, and ferric salts. Results have shown up to 95% color removal, combined with up to 35% BOD removal (28,24,30,38). This type of system works best with a raw waste, rather than with a secondary effluent, as the sludge produced will cause problems in biological treatment when recycled. The quantity of sludge produced by a co-precipitation process is the major drawback to its use.

Centrifugation is another method for color removal, although it is not widely used (36). In fact, it is probably the least employed of all color removal methods. It has been used mostly for the recovery and re-use of soluble materials from dilute solutions of azo dyes. The method involves the addition of a specific liquid ion exchange solvent to strip the color from the stream, centrifugation, the addition of another specific solvent to act as a carrier, and more centrifugation (36). This process will concentrate a dye about 700 times and is not prohibitively expensive.

Filtration, a general process classification, could be said to be the most widely used for color removal, but the various individual types of filtration are different and must be categorized separately. These individual methods include reverse osmosis, ultra- and hyper-filtration, sand filtration, and carbon adsorption filtration. Reverse osmosis and hyper-filtration, in addition to merely removing color, have been used to recover color bodies for re-use in the dyeing process (1,18). However, fines and colloids tend to clog membranes and can not normally be backwashed out, unless very small pore sizes are used. If the waste has been previously treated biologically, pore size may be increased up to 10-20 microns. Sand filtration generally requires the addition of chemicals to aid in color removal to get more than a 5% removal of color (1). Carbon adsorption has been found to remove color quite efficiently from most dye wastes, with the exception of disperse dyes (30). Depending upon the particular plant set-up, pretreatment may be required to prevent clogging, and carbon regeneration may be carried out either by thermal or biological methods. One plant in Georgia has achieved 99% color removal and an excess of 64% removal of TOC by using a carbon adsorption system involving a 10-hour carbon adsorption run, followed by 14 hours of biological regeneration under aerobic condition (31,33).

Ion exchange has not been widely used as a color removal process, as it has been relatively difficult to remove the color bodies from the resins once they are sorbed onto the solid phase. However, the

introduction of some new styrene-sulfonic acid resins has begun to eliminate this problem, especially when the backwash liquid used is a caustic soda solution (1). Color removals of up to 95% have been noted. The resin influent must be free of suspended and colloidal materials, and the resins have not been effective in removing disperse dyes.

Oxidation, the last of the categories of color removal processes, is a process in which decolorization occurs by alteration of the chemical structure of the color bodies, resulting in a change in the light absorption spectrum away from the visible spectrum, and yielding products easily assimilated into the environment. The color causing materials are not removed, but are only changed in form. In the past, oxidation has meant the addition of chlorine or hydrogen peroxide to the waste (22). Hydrogen peroxide has such a low oxidation potential that its application is limited to those materials which are easily oxidized. Even then, long detention times and high dosages are required. Chlorine, in both its gaseous and hypochlorite salt forms, is effective in removing color, although it has been recently shown that the products generated have detrimental effects upon the receiving stream. As a result, dechlorination has begun to be required in several areas before discharge is allowed.

Recently, experimentation has begun involving oxidation of color-causing compounds by gamma-irradiation, using cobalt-60 as the source of the gamma rays (5). In the initial experiments, the process has been shown to be effective in removing color, yielding

CO₂ and H₂O as the ultimate products, in the presence of sufficient oxygen in the water. Gamma irradiation works especially well in conjunction with the carbon adsorption and reverse osmosis processes. The carbon is reactivated under radiation, and the concentrated color from the R.O. membrane is destroyed easily. However, the process is very expensive, both in capital and operating costs and has not been fully examined by the Atomic Energy Commission for safety considerations and environmental aspects.

Ozone and color removal. Ozone, as noted before, has a very high oxidation potential. The advantages of using such a high potential for color removal were noted in the past, but only recently has the application of ozone for color removal become popular. As a result of its reactivity, ozone is theoretically more suited to an oxidation process than the oxidants commonly in use.

The first applications of ozone for color removal were in the water treatment field, as a method for removing color caused by natural organics (24). This type of color is a result of soluble vegetable dyes leached into the water from decaying vegetable matter, possibly complexed with iron or manganese. This type of color is not generally a problem in the United States, but occurs frequently in Europe. The best known applications of ozone in this area are the plants at Baerum and Skedsmo, Norway, and Loch Turret, Scotland. The Loch Turret plant uses raw surface water as its influent, utilizing the Microzon and M/D processes (4). The ozone dose is 1.4 grams per cubic meter. With waters of 30^o Hazen or less, all

color is removed, before an ozone residual of 0.1 ppm appears. However, with waters of high color, the ozone residual appears before complete color removal occurs. In some cases, a color residual remains which is not removable.

When oxidation is incomplete, some return of color is possible when the water is stored for a sufficient period of time. At the Redbridge plant in London, England, an ozone dose of 20-25 ppm was sufficient to reduce an influent color of 38-41^o Hazen to 2-5^o Hazen, at a flow rate of 2000 gallons/hour (25).

Relatively few applications have been made of the oxidative power of ozone in decolorizing industrial effluents. The major applications so far have been in the textile and in the pulp and paper industries. The pulp and paper industry has a large problem with color in the effluent, especially in those plants which use the draft pulping process. Nebel, studying kraft process plants, found that ozone dosage levels from 70 to 143 ppm yielded color removals of 78-88%, involving reductions of color from 520 to 1600 APHA units down to 100 to 200 units (22). These color removals were complimented by turbidity removals of up to 67% and COD removals of 21 to 37%. Snider and Porter used ozone to treat several typical dyes and dye-wastes, and found that good color removal was achieved (35). However, they noted low COD reductions and even a few COD increases. Color removal occurred at varying times, depending upon dye type, with 15 to 30 minutes of ozonation suitable for soluble dyes, and up to 150 minutes required for comparable results with disperse dyes.

III. MATERIALS AND METHODS

All wastes used in this study were obtained from the wastewater recycle station of the Martin Processing Company plant located in Rocky Mount, Virginia. The wastewater treatment plant is designed to treat the spent textile process waters. The samples were drawn from the influent to the treatment plant and were stored in five-gallon nalgene bottles in a refrigerator at approximately 35° F. Due to the varied nature of the analyses performed on the samples, no preservatives were added to the samples.

Analytical Procedures

Determinations performed included color, chemical and five-day biochemical oxygen demand, total organic carbon, dissolved oxygen, ozone residual, pH, total and suspended solids, and turbidity. The following methods of analysis were used:

1. Color analyses were performed according to the Spectrophotometric Method described in the 13th edition of Standard Methods for the Examination of Water and Wastewater, utilizing the tenordinate technique, with one exception (39). The waste was filtered through Reeve Angel grade 934AH filter paper, rather than through the standard filter aid. A Perkin-Elmer Model 124 Double-Beam Spectrophotometer was the instrument used for the analyses, with a spectral band width of one m μ .

2. Chemical oxygen demand was determined using the dichromate method described in Standard Methods (39).
3. Biochemical oxygen demand (five-day) was determined using the procedure outlined in Standard Methods (39), utilizing a seed acclimated to the waste. The solids used for the seed were drawn from the aeration basin of an activated sludge unit which treats only domestic waste. Four liters of the mixed liquor were placed in a aeration chamber, and mixed there with a four liter volume of the waste diluted in a 1:4 ratio. This mixture was aerated and the microbes fed new waste daily on a batch draw-and-fill basis. The mixture was settled for one hour, and one liter of the supernatent removed. One liter of diluted waste was then added, and aeration resumed. This procedure occurred for one week, with the strength of the waste added increased daily. After this, the waste was fed to the mixture at full strength for another week.
4. Total organic carbon was measured through the use of a Beckman Model 915 Total Organic Carbon Analyzer. Due to a malfunction in the inorganic carbon channel, TOC was measured on the total carbon channel by the following process: a 100 ml aliquot was stripped of CO₂ by acidification with concentrated HCl and sparging with nitrogen gas, as is suggested in Standard Methods (39). The sample was then ready for injection.

5. Dissolved oxygen was measured using a YSI Model 54 Oxygen Meter, immediately before and after treatment.
6. The ozone residual of the treated waste was determined by the Iodometric Method discussed in Standard Methods (39). The measurements were carried out in such a way as to find the ozone residual at five minutes after the end of ozone contact with the water.
7. The measurement of pH was performed on a Fisher Accumet Model 120 pH Meter, standardized against pH buffer solutions of pH 7.0 and pH 10.0.
8. Total solids and total volatile solids analyses were performed according to the method given in Standard Methods (39). Total and volatile dissolved solids were determined using the Gooch crucible method found in Standard Methods (39).
9. Turbidity was measured using a Hellige Model 8000-TS Turbidimeter, with a 10 cm. light path length and no filter.

Experimental Procedures

Laboratory system. The ozone generator used throughout the study was an Airox ozonator, model C2P-3C-2, a product of Pollution Control Industries, Incorporated, having a capacity of 2.8 grams of ozone per hour. Bottled dry air, grade II with zero hydrocarbons with a dewpoint of -60°C was used as the air source for the ozonator. Tygon tubing with an inside diameter of 3/8 inches was used to deliver the ozone to the reaction chamber. The tubing coming from the ozone generator was branched so that one branch ran to the

reaction chamber and the other was vented directly to be exhausted. The branching of the tubing permitted the wasting of gases produced during the generator's warmup period.

The reaction chamber consisted of a glass column, four feet long and three inches internal diameter, equipped with a sintered glass porous diffuser. The chamber was mounted with two taps, one for influent wastewater and the other for the treated wastewater effluent. These taps were closed off during batch studies. The chamber was loaded with 4.5 liter samples, both in batch and continuous flow studies. The reaction chamber was vented to a fume hood to allow any ozone not dissolved to escape. A schematic of the system is shown in Figure 1.

Determination of ozone. Determinations of ozone were performed throughout the duration of the study. The first determination was to find the ozone production capacity of the generator. This value was noted in milligrams/liter/minute. The second was a study of the solubility of ozone in water for this particular system. Due to the lack of appropriate wet-test meters, the ozone concentration in the exhaust gases from the reaction chamber had to be monitored by gas traps. These traps consisted of 400 ml of a 2% potassium iodine solution in an Erlenmeyer flask. By subtracting the amount of ozone in the exhaust gases from the amount produced, the amount of ozone actually used in the wastewater treatment system could be determined.

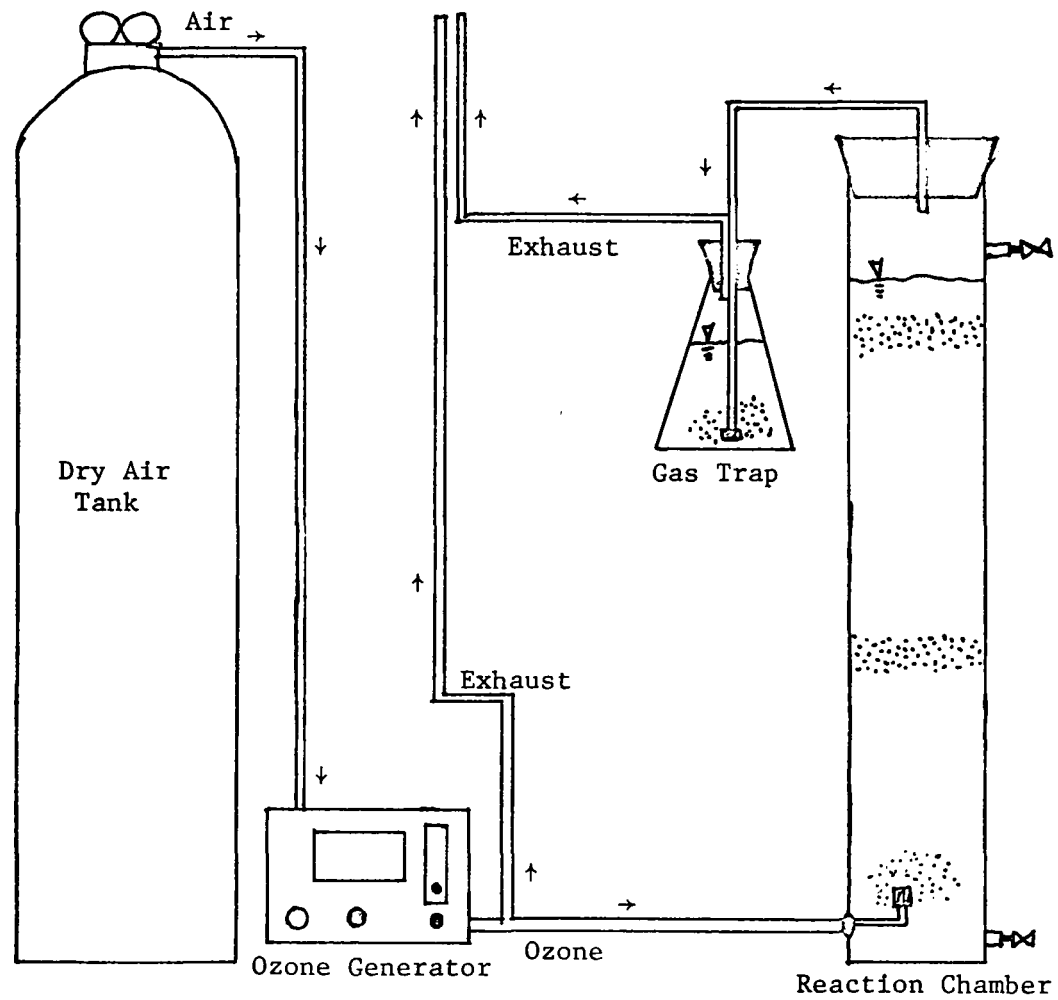


Figure 1. Schematic of Laboratory System

Experiment One: Batch Study

In this experiment, several 4.5 liter samples were ozonated for varying lengths of time. Ozone production was held at 14 mg/l/min., and contact times were 15, 30, 45, 60, 75, 90, 105, 120, and 150 minutes. The entire wastewater sample was characterized before any ozonation occurred. Each 4.5 liter sample was tested for pH and dissolved oxygen immediately before ozonation. After ozonation ended, 500 ml were withdrawn, and the dissolved oxygen content was measured. After five minutes had elapsed, the ozone residual was determined. The entire 4 liters of ozonated sample remaining were scrubbed to find this ozone residual. Two aliquots were drawn to perform the rest of the analyses and the remainder of the waste discarded. One aliquot was adjusted to pH 7.6, while the other remained at the pH attained during ozonation. Half of each aliquot was filtered, yielding 4 test samples: filtered and unfiltered ozonated wastewater, and filtered and unfiltered ozonated wastewater with pH adjusted. Each test sample was analysed for COD and TOC, and the filtered samples were analysed for true color.

Experiment Two: Continuous Flow Study

This experiment was carried out in a manner similar to the batch study except that there was a continuous flow of waste through the reaction chamber which occurred in such a way that counter-current conditions were achieved. Ozone production was held at 14 mg/l/min, and the hydraulic retention time was 30 minutes. In order to ozonate for longer periods of time, ozonated waste was

recycled back through the reaction chamber. This simulated a multi-stage injection system, chosen on the basis of Campbell's recommendations for a highly colored water, stemming from work at Loch Turret (4). Since there was often a time lapse between the wastewater draw-off from the chamber and its re-introduction, tests were run on the waste immediately after exit and before re-ozonation to note any changes that occurred in the waste during storage. In this study, ozone residuals were measured in the reaction chamber effluent, in 400 ml sample sizes, rather than in the chamber itself. In addition, a study of the BOD characteristics of the wastewater was carried out to note changes associated with the treatment process.

IV. EXPERIMENTAL RESULTS

The results of the color removal experiments and of the associated ozone determinations are presented in this section. The chapter is divided into two parts, with the first section describing the batch condition experiments and the second describing the continuous flow experiments. In each section, the experimental results are briefly discussed. The results of the preliminary study to determine the solubility of ozone in tap water for the particular system described in the previous chapter and used in this research are shown in Figure 2. As can be seen, ozone has a maximum measurable residual in this system of approximately 2.1 mg/l.

Batch Conditions

The variations of the measured parameters due to ozone contact are shown in Tables I and II. Table I shows the change in the true color of the waste due to the action of ozone upon the waste. Table II tabulates the effect of ozone upon the other measured parameters. Figure 3 shows the effect of varying the ozone contact time on the color absorption spectrum of the waste, while Figure 4 pictures a typical variation of the spectrum with pH, at one contact time. In this case, the contact time shown is one hour, and the ozone usage is 229.0 mg/l. The ozone determinations were made at ten minute intervals, and the resulting amounts of ozone used are shown in Figure 5.

As seen in Table I and Figure 4, the pH of a liquid greatly affects its color characteristics. It was for this reason that one

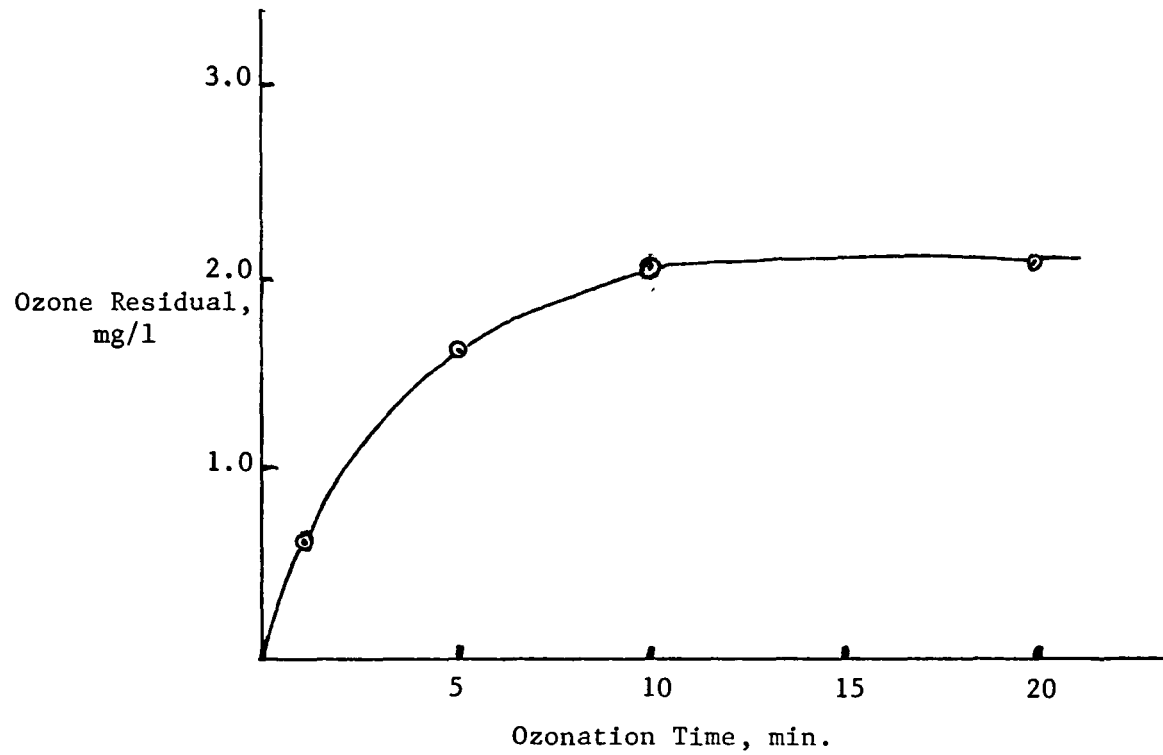


Figure 2. Measureable Residual of Ozone in Tap Water for Test System

Table I.-Effect of Ozone on True Color of Wastewater Under Batch Conditions

Ozone Used (mg/l)	pH not adjusted				pH adjusted to 7.6			
	Dominant Wavelength (m μ)	Luminance (%)	Purity (%)	Hue	Dominant Wavelength (m μ)	Luminance (%)	Purity (%)	Hue
0.0	584	32.9	62.0	Yellow-Orange	579	26.8	64.0	Yellow
69.6	580	59.5	37.0	Yellow	584	54.9	42.0	Yellow-Orange
128.9	578	69.9	29.0	Yellow	579	65.9	34.0	Yellow
180.7	581	82.3	17.0	Yellow-Orange	580	75.2	24.0	Yellow
229.0	577	86.4	12.5	Yellow	578	74.7	23.5	Yellow
278.7	583	92.7	9.0	Yellow-Orange	577	82.5	21.0	Yellow
329.6	573	90.9	8.0	Yellow	577	85.6	14.0	Yellow
361.0	579	94.9	8.0	Yellow	582	83.2	14.0	Yellow
423.2	573	93.8	1.5	Yellow	577	87.7	11.5	Yellow
508.6	565	94.7	2.0	Green-Yellow	582	87.6	8.0	Yellow-Orange

Table II.-Effect of Ozone on Wastewater Under Batch Conditions

Ozone Dosing Time (min)	Ozone Used (mg/l)	Ozone Residual (mg/l)	pH	COD (mg/l)	COD _f * (mg/l)	TOC (mg/l)	TOC _f * (mg/l)	DO (mg/l)
0	0.0	0.00	6.8	1670	1264	337	285	2.3
15	69.6	0.15	6.6	1558	1193	337	285	10.1
30	128.9	0.29	6.3	1542	1137	337	285	10.3
45	180.7	0.31	5.8	1535	1125	337	285	10.5
60	229.0	0.44	4.6	1408	1095	337	285	10.3
75	278.7	0.51	4.4	1400	1080	337	285	9.5
90	329.6	0.61	4.2	1400	1072	337	285	9.4
105	361.0	0.72	4.0	1310	1057	337	285	9.4
120	423.2	1.07	3.8	1236	993	320	270	9.4
150	508.6	1.15	3.6	1157	987	320	270	9.3

*COD_f = COD of filtered wastewater

*TOC_f = TOC of filtered wastewater

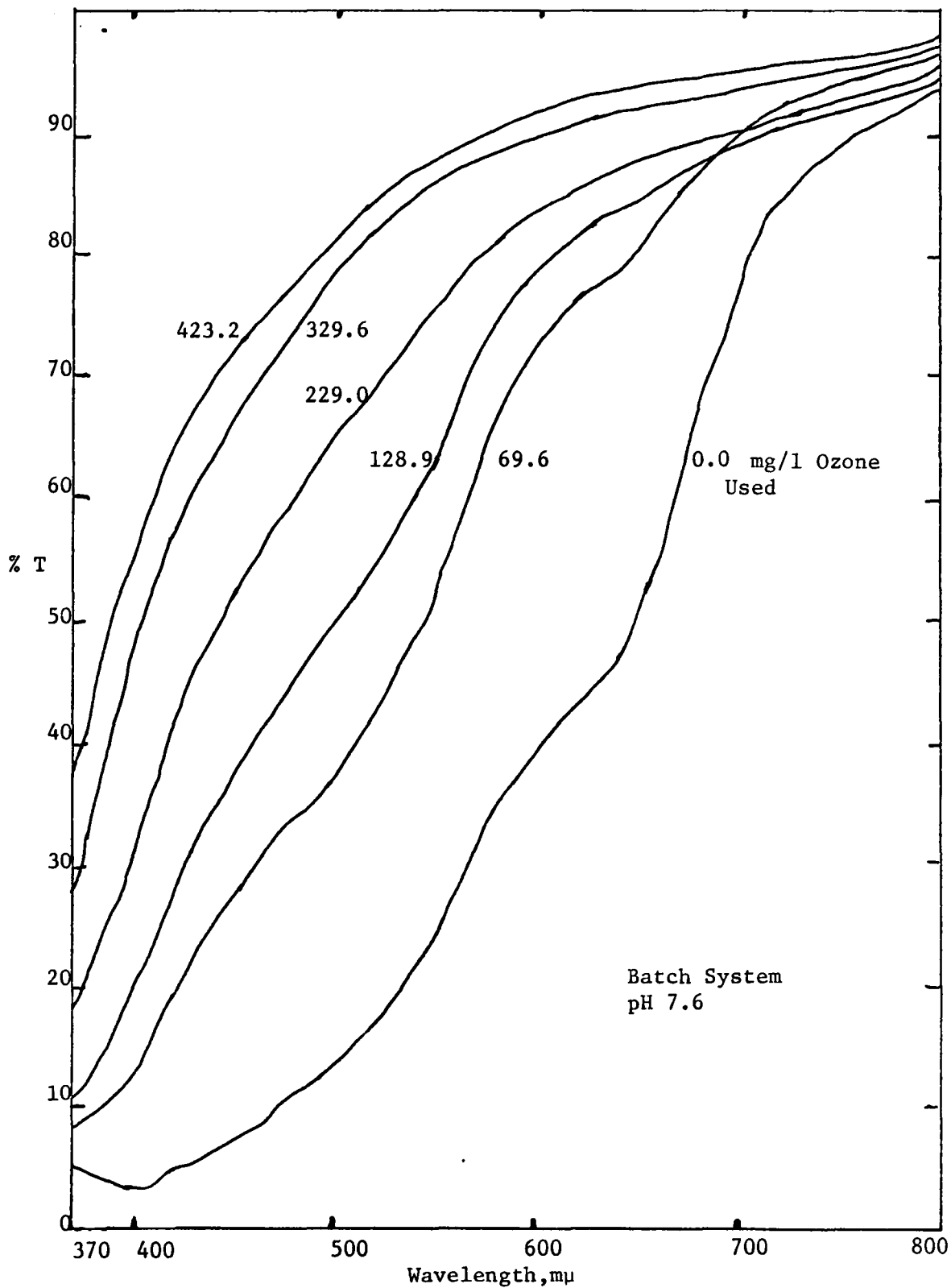


Figure 3. Effect of Ozone Contact upon Color Spectrum

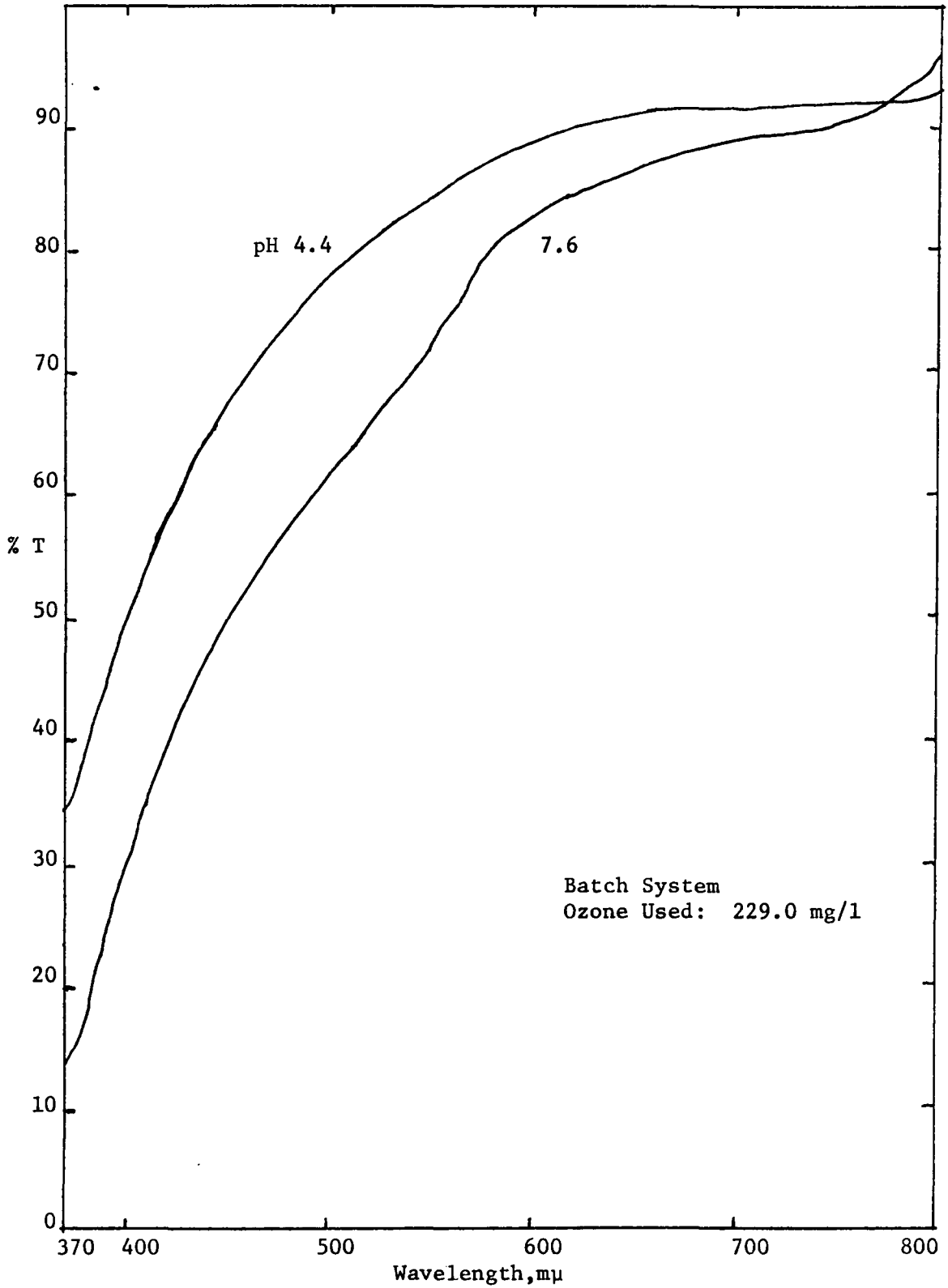


Figure 4. Effect of pH upon Color Spectrum

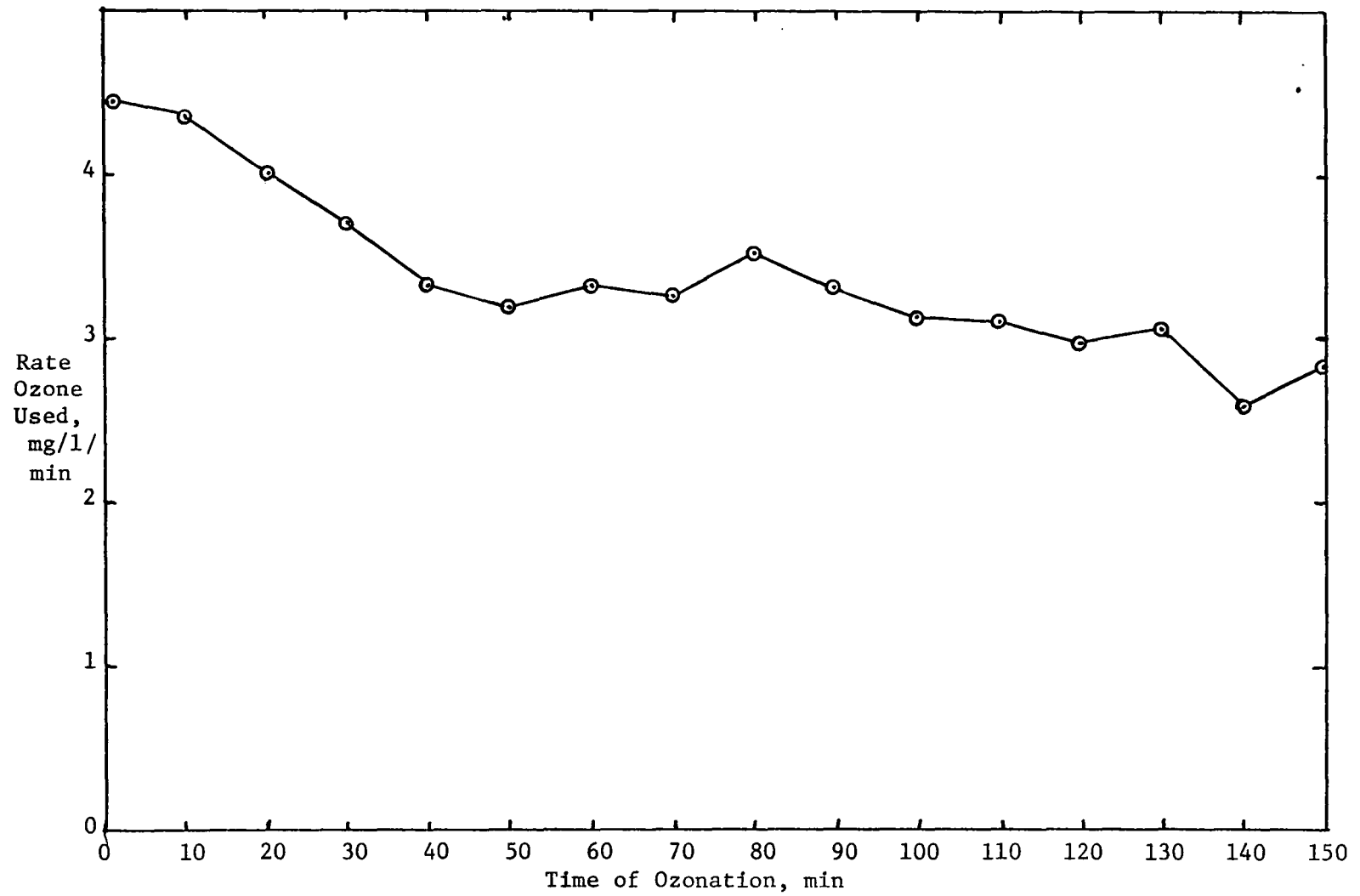


Figure 5. Ozone Usage of Wastewater in Batch System

aliquot of each sample was adjusted to pH 7.6. This allowed direct comparison of color data. The percent purity of the waste was chosen to be the parameter for comparison of color and color removal. Figure 6 shows the action of ozone in removing color and COD from the waste. As can be seen, the earlier stages of ozonation removed larger amounts of color than the later stages. However, the same result is not true with COD removal. Here, the amount of COD removed remained fairly constant with the ozone used.

Continuous Flow Conditions

The characteristics of the raw and ozonated wastewater used in the continuous flow experiments are listed in Tables III through VI. In these tables, color is reported at both the pH of the effluent and pH 7.6. Samples of the waste were analyzed immediately after ozonation and after storage. Figure 7 shows a typical change in the color spectrum of the waste after storage. This figure reveals an increase in the color of the waste after storage, indicating that color can return to the waste if not filtered immediately. Color reappearance was not noted when the waste was filtered before storage. Figure 8 shows the change in the spectrum of the waste due to varying the ozone contact time, not considering any changes resulting from storage.

As Tables III through VI show, the suspended solids concentration and turbidity increased with ozonation. This effect has been previously noted with textile wastes, and is the major reason for measuring true color rather than apparent color (25).

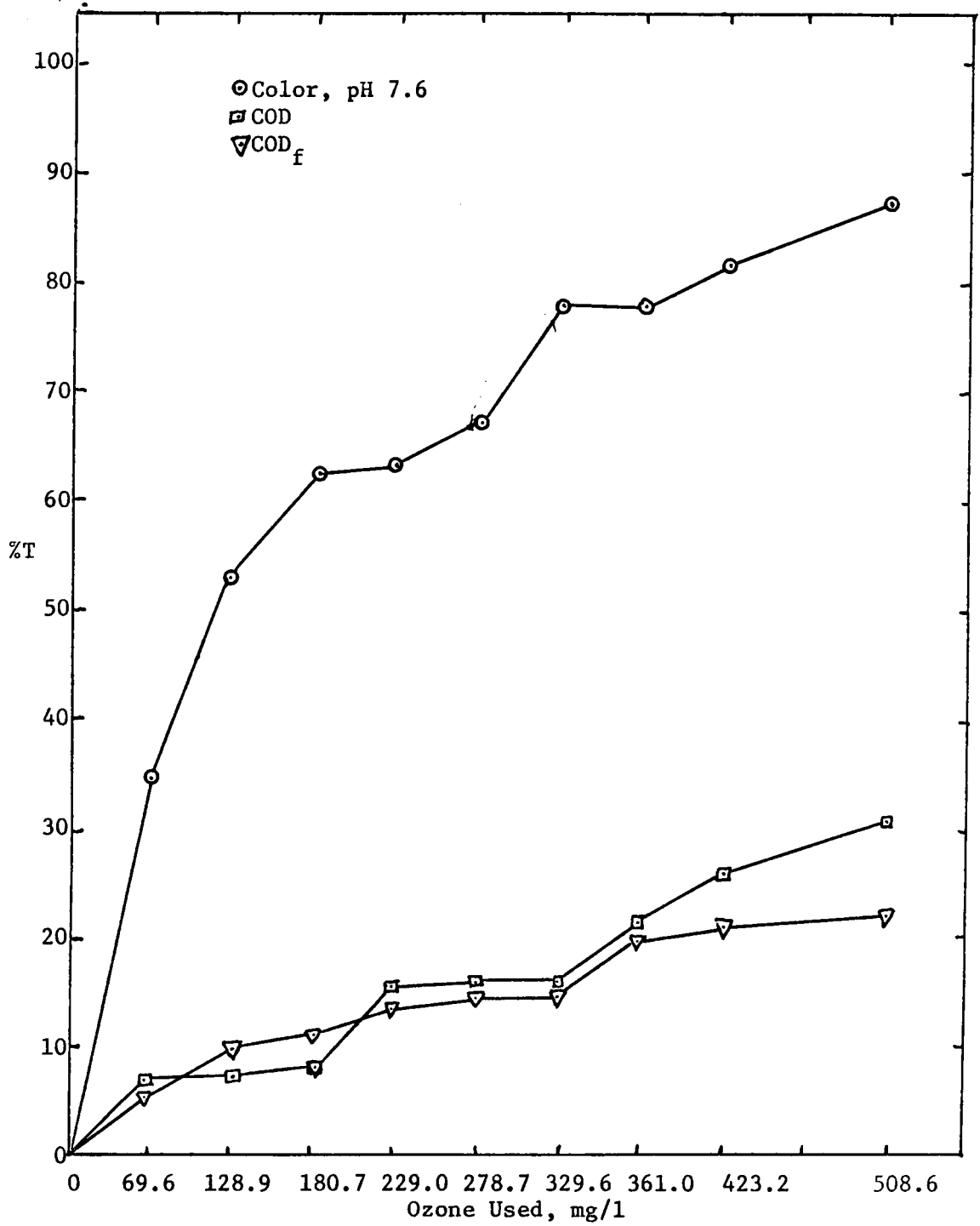


Figure 6. Variations of Batch Removal Efficiencies with Ozone Contact

Table III.-Characterization of Raw Wastewater for Continuous Flow Study

pH	6.8
Color: Hue	Yellow-Orange
Dominant wavelength, μ	585
Luminance, %	27.5
Purity, %	58.0
Total Solids, mg/l	3304
Total Volatile Solids, mg/l	962
Suspended Solids, mg/l	169
Volatile Suspended Solids, mg/l	132
C.O.D., mg/l	2014
C.O.D. _f , mg/l	1332
T.O.C., mg/l	395
T.O.C. _f , mg/l	380
B.O.D. ₅ , mg/l	695
D.O., mg/l	2.2
Turbidity, mg/l as SiO ₂	81
Color, pH 7.6:	
Hue	Yellow-Orange
Dominant wavelength, μ	585
Luminance, %	27.0
Purity, %	58.0

Table IV.-Characterization of Wastewater After Ozonation for Thirty
Minutes Under Continuous Flow Conditions

	<u>Immediate</u> 6.6	<u>Stored*</u> 6.8
pH		
Color: Hue	Yellow-Orange	Yellow-Orange
Dominant wavelength, μ	585	583
Luminance, %	55.5	62.5
Purity, %	37.0	38.0
Total Solids, mg/l	3307	3307
Total Volatile Solids, mg/l	990	990
Suspended Solids, mg/l	320	320
Volatile Suspended Solids, mg/l	260	260
C.O.D., mg/l	1750	1750
C.O.D. _f , mg/l	1260	1260
T.O.C., mg/l	395	395
T.O.C. _f , mg/l	380	380
B.O.D. ₅ , mg/l	610	610
D.O., mg/l	6.5	3.7
Turbidity, mg/l as SiO ₂	92	92
Color, pH 7.6:		
Hue	Yellow-Orange	Yellow-Orange
Dominant wavelength, μ	585	581
Luminance, %	55.6	61.6
Purity, %	37.0	39.0
Ozone Used, mg/l	66.0	66.0
Ozone Residual, mg/l	0.00	0.00

*Stored for 5 hours

Table V.-Characterization of Wastewater After Ozonation for Sixty
 . Minutes Under Continuous Flow Conditions

pH	<u>Immediate</u>	<u>Stored*</u>
	6.0	6.0
Color: Hue	Yellow-Orange	Yellow-Orange
Dominant wavelength, μ	580	580
Luminance, %	80.6	77.4
Purity, %	20.0	21.0
Total Solids, mg/l	3308	3308
Total Volatile Solids, mg/l	997	997
Suspended Solids, mg/l	400	400
Volatile Suspended Solids, mg/l	320	320
C.O.D., mg/l	1636	1631
C.O.D. _f , mg/l	1187	1182
T.O.C., mg/l	325	325
T.O.C. _f , mg/l	255	255
B.O.D. ₅ , mg/l	550	550
D.O., mg/l	7.3	3.7
Turbidity, mg/l as SiO ₂	105	105
Color, pH 7.6		
Hue	Yellow-Orange	Yellow-Orange
Dominant wavelength, μ	581	582
Luminance, %	78.5	78.2
Purity, %	21.0	22.0
Ozone Used, mg/l	117.3	117.3
Ozone Residual, mg/l	0.30	0.00

*Stored for 8 hours

Table VI.--Characterization of Wastewater After Ozonation for Ninety
Minutes Under Continuous Flow Conditions

	<u>Immediate</u>	<u>Stored*</u>
pH	4.6	5.0
Color: Hue	Yellow	Yellow
Dominant wavelength, μ	575	578
Luminance, %	91.5	85.6
Purity, %	10.5	13.0
Total Solids, mg/l	3306	3306
Total Volatile Solids, mg/l	984	984
Suspended Solids, mg/l	480	480
Volatile Suspended Solids, mg/l	370	370
C.O.D., mg/l	1518	1510
C.O.D. _f , mg/l	1107	1104
T.O.C., mg/l	305	305
T.O.C. _f , mg/l	237	237
B.O.D. ₅ , mg/l	670	670
D.O., mg/l	8.7	3.7
Turbidity, mg/l as SiO ₂	108	108
Color, pH 7.6:		
Hue	Yellow	Yellow-Orange
Dominant wavelength, μ	579	582
Luminance, %	77.9	85.7
Purity, %	18.5	19.5
Ozone Used, mg/l	148.8	148.8
Ozone Residual, mg/l	0.50	0.00

*Stored for 5 hours

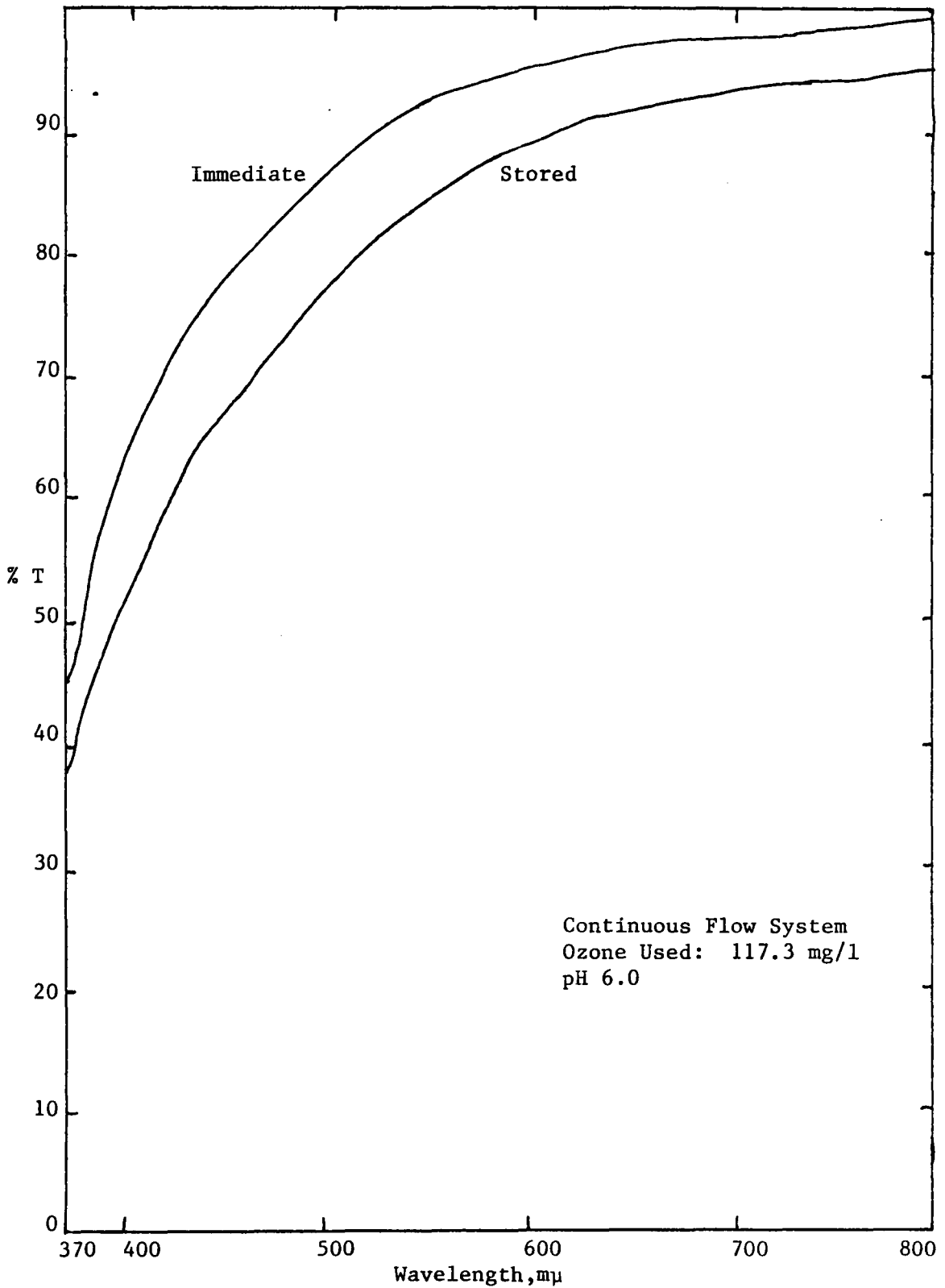


Figure 7. Effect of Storage upon Color Spectrum

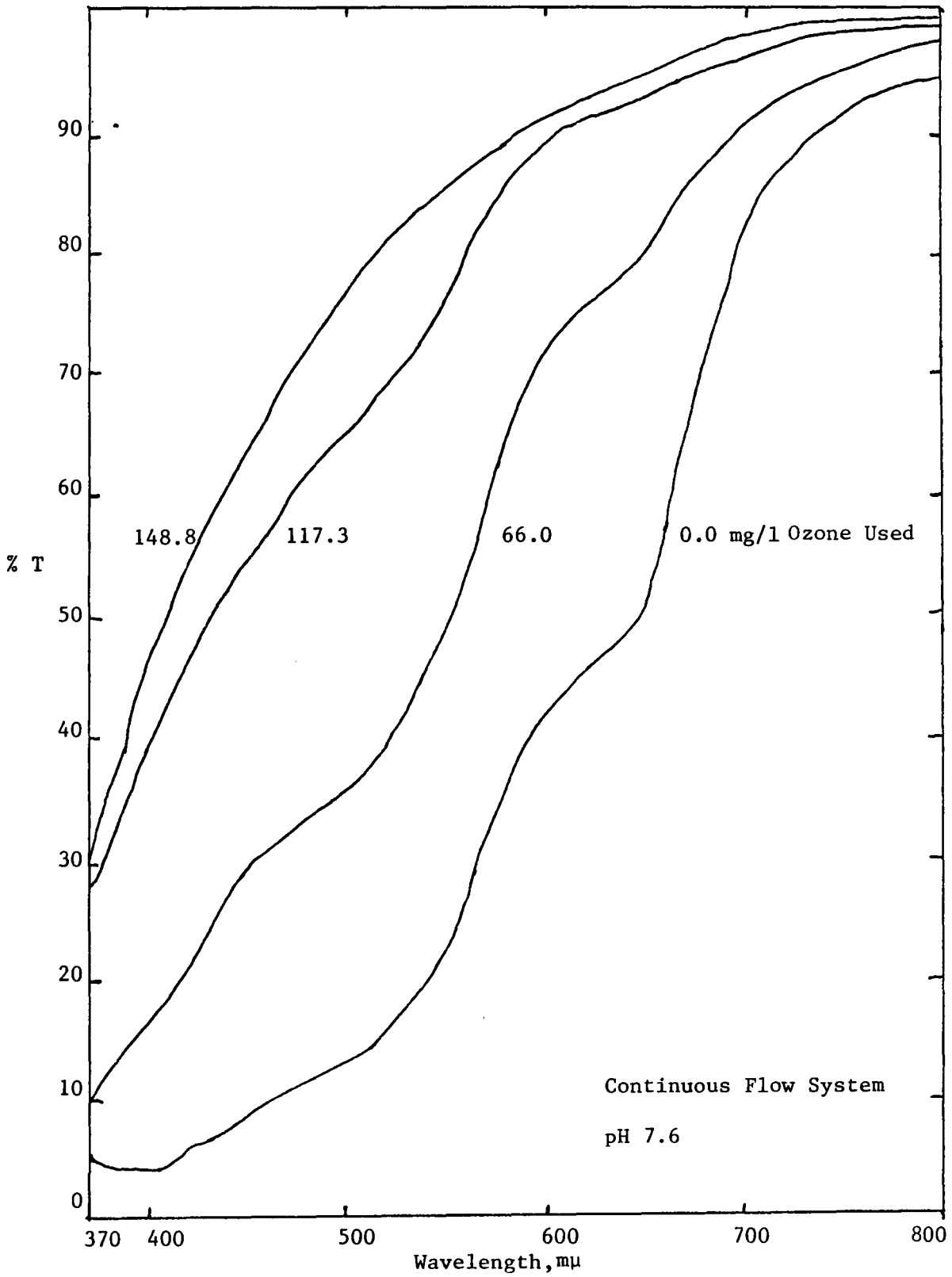


Figure 8. Effect of Ozone Contact upon Color Spectrum

Figure 9 shows the removal of filtered and unfiltered COD and TOC as a function of the ozone used, and the removal of COD in comparison with the removal of color. The COD removals remained fairly constant with the amounts of ozone used. Filtered and unfiltered TOC were not removed until large amounts of ozone were used.

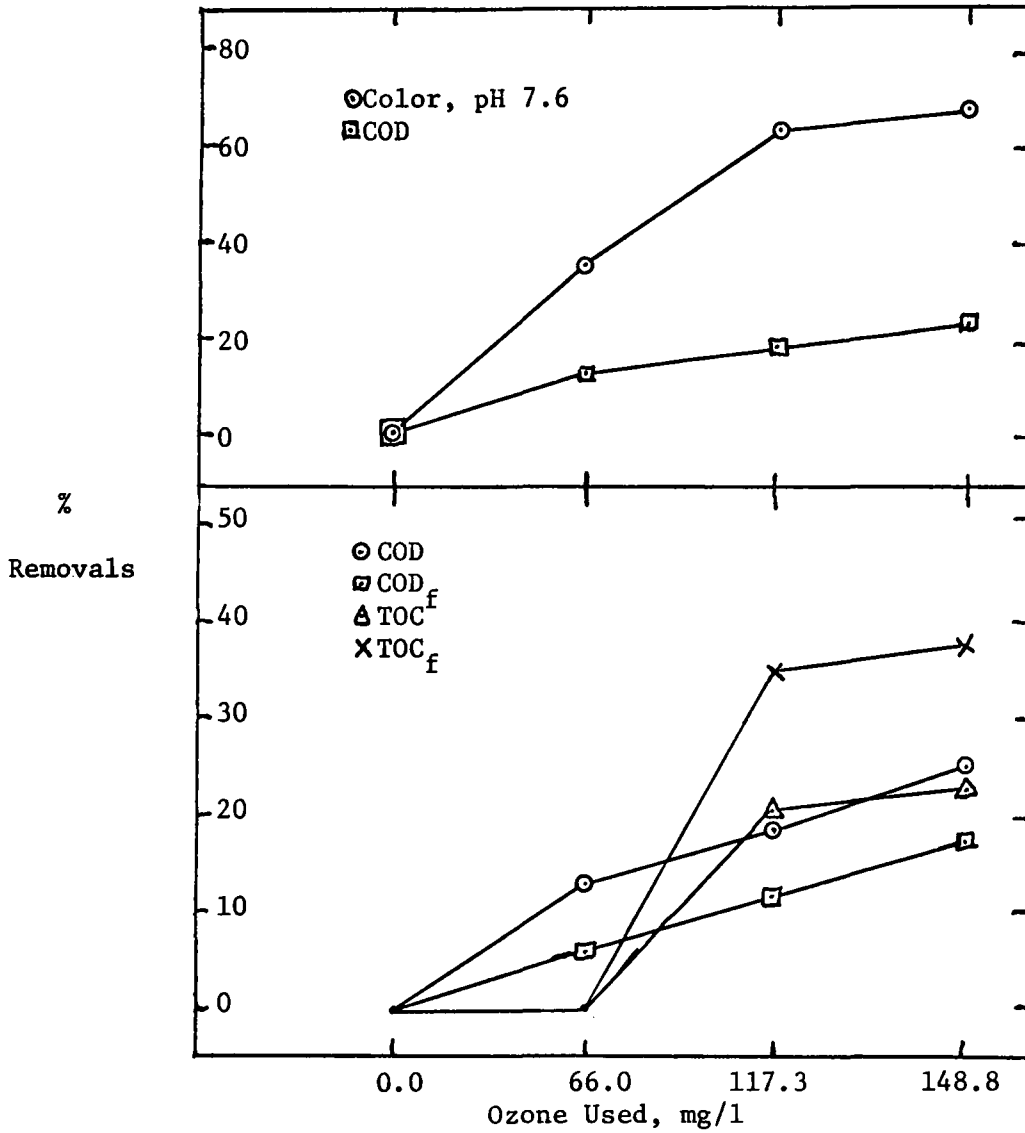


Figure 9. Variation of Continuous Flow Removal Efficiencies with Ozone Contact

V. DISCUSSION

Ozone Determination

The results of the treatment studies clearly show that the important factor in determining the effect of ozone on a waste is not the applied ozone dosage, but how much ozone is actually dissolved into the wastewater and used by the waste. The dosage required to create a particular residual is a function of the system used to apply ozone to the waste. The efficiency of the system will also affect the required dosing levels. The system used in this study had a very low efficiency of ozone use, as can be seen by comparing the amounts of ozone used with the amount applied.

The maximum measurable ozone residual for this system was found to be approximately 2.1 mg/l. This value corresponds closely with the value postulated by O'Donovan. For an ozone concentration in air of 14 mg/l, he found a normal residual ozone level in water of 2.7 mg/l (24). The difference here is due to several factors, including temperature and pressure. However, the most important probable cause for the discrepancy is the difference in the S co-efficient as previously discussed in Chapter II. O'Donovan assumed a value of 0.2 for S, which most probably is incorrect for this system. Also, the large air flow of 20 standard cubic feet per hour through the small-sized reaction chamber resulted in a self-scrubbing action, stripping the water of ozone.

The ozone residuals found in both the batch and continuous flow experiments were much lower than the amount found in tap

water. These residuals appeared before all the color in the wastewater was removed, as has been noted by Campbell (4).

Solids and Turbidity

Solids and turbidity determinations were made only on the wastewater treated under continuous flow conditions. The total solids seemed to vary slightly, but only in such a magnitude that experimental error could explain the variation. The same result is not true in the variations seen with suspended solids and turbidity. Both of these parameters increased with increasing ozone use of the wastewater. This result means the effect of ozone on the waste constituents is to make them less soluble, driving them out of solution, and into a filterable state. It is possible that the action of ozone here is largely on the positively charged portions of the constituents, with the end effect of causing colloidal particles to be restabilized. The mechanism causing this action is not yet understood. However, it has been found that ozonation of raw water containing natural organics caused the formation of negatively charged micelles, with an accompanying increase of both turbidity and suspended solids (3). This effect of ozonation would necessitate the filtration of an ozonated wastewater before discharge could be allowed.

pH

In previous studies involving ozonation of wastewaters, it has been reported that the pH of the wastewaters was driven towards

neutral (17). These changes toward neutrality occurred with original pH being both acidic and basic. However, in this study, the pH was driven further and further towards an acidic condition with continued ozonation. The batch system drove the pH down further over the comparable ozonation time, with the greatest drop in pH coming in the middle range of ozonation time employed. The continuous flow system had a continually increasing rate of pH drop. No reasons have been advanced for the effect of ozone on pH, either towards or away from neutrality.

Dissolved Oxygen

The effect of ozonation was to increase the dissolved oxygen content of the wastewater. In batch condition treatment, the dissolved oxygen was always raised above saturation. This result was not evident in continuous flow treatment, where the dissolved oxygen content was increased, but not above saturation, until after 90 minutes of ozonation. Also, the dissolved oxygen fell far below saturation after storage but always to the same level, regardless of the oxygen content at the time ozonation was completed. The super-saturation of the wastewater with oxygen after ozonation could be expected, but the drop of dissolved ozone to far below saturation could not. One possible reason for this drop would be biological action in the wastewater during storage. This effect would be highly improbable, due to the disinfectant action of ozone, but the suspended solids and turbidity of the wastewater

could yield a masking effect and thereby preserve some of the microbes which could use oxygen in their metabolism.

BOD₅

The measured BOD₅ of the wastewater followed a pattern which has been previously reported by Nebel (22). The ozone caused a decrease in BOD₅ by satisfying a portion of the oxygen demand, and then an increase by attacking refractory materials, making them biodegradable. This decrease and subsequent increase in BOD₅ occurred, but ozonation was not continued to the point where the measured BOD₅ began to decrease again.

COD and TOC Removal

The COD and COD_f of the waste was diminished slightly by the application of ozone. This result is to be expected, as the ozone demand of organic materials is extremely high. In both the batch and continuous flow treatment schemes, the removal of COD was greatly below that of color, indicating a change in chemical structure that did not materially affect the ultimate oxygen demand of the waste. Continued ozonation of the waste would most likely yield higher COD reductions. Also, in both treatment systems, COD_f removal was lower than that of total COD removal. When compared with the solids and turbidity data, this result is the opposite of what might be expected and leads to the conclusion that the action of ozone on COD is mainly on the filterable matter, not on the dissolved material.

When TOC and TOC_f are examined, there are immediate differences noted in the results of the two different systems. Under batch conditions no TOC or TOC_f removal occurred until after two hours of ozonation. However, TOC and TOC_f were removed to a very limited extent after one hour under continuous flow conditions. Also, the amount of TOC removed under continuous flow was greater than that removed in batch. This result would mean that the continuous flow system was more effective in completely oxidizing the wastewater. However, when compared with the COD data, it becomes apparent that this result is not likely. Instead, the most probable explanation is that the wastewater constituents are slightly different, and that those in the wastewater sample treated in continuous flow are more easily oxidized to completion.

Color Removal

The color of the wastewater was removed rapidly by the action of ozone. In each treatment system, the ozone attacked the color readily, removing large amounts of color in the early part of ozonation. However, the amount of color removed decreased as ozonation continued, with larger amounts of ozone becoming necessary to remove smaller amounts of color. This result would indicate that the color removed in the early stages of treatment was due to the breakdown of chromophores which are easily oxidized, while those remaining are more resistant to oxidation. This resistance may be seen by the color removal curves in Figures 6 and 9 approaching a maximum, and also in the decreasing shifts of spectrums in Figures 3 and 8.

The color was removed more easily in the continuous flow treatment system than in the batch treatment system. Approximately one-half the amount of ozone used in the batch system was required to achieve the same results under continuous flow conditions. This result could mean that the chromophores of the batch treated wastewater were more resistant to oxidation, requiring more ozone to be broken down. However, the ozone residual was greater with the batch flow conditions. This result could be related to the fact that turbulence was greater in the continuous flow system, allowing a much quicker pass-through of ozone, thus allowing less time for the ozone to dissolve into solution.

Looking at the action of ozone on the spectrum of the wastewater, the effect of ozone is greatest between the wavelengths of 400 and 650 m μ . There is almost no effect on the red end of the spectrum, at the higher wavelengths. The batch treatment system created wide variations in the dominant wavelength of the wastewater throughout treatment, while in the continuous flow treatment, the dominant wavelength remained fairly constant, although it did finally decrease. In all cases, the hue was in the yellow range, although it varied from yellow-orange to green-yellow.

The luminance of the wastewater also varied greatly. There seemed to be no direct relationship between the purity and the luminance, as the purity generally decreased while the luminance either decreased or increased.

VI. CONCLUSIONS AND RECOMMENDATIONS

There are several conclusions that can be drawn from the results of the research performed and described in this thesis.

Among them are:

1. Ozone is effective in removing color from the selected textile dye waste.
2. Filtration is necessary after ozonation, due to the tendency of ozonation to increase turbidity and suspended solids in wastewater.
3. Ozone is effective in removing COD from a wastewater, and, depending upon the constituent form, may also be effective in removing TOC.
4. BOD₅ is removed from a textile wastewater, depending on the length of ozonation. It is possible to increase the BOD₅ of a wastewater by ozonation. This result could cause further treatment to be required in order to reduce the treated effluent BOD₅.
5. Color is removed much more readily from a wastewater than is COD, due to the fact that only slight changes in molecular structure are needed to change color characteristics, while much larger structural changes are required to decrease COD.

The research raised several questions which were not answered, either due to a lack of data or because the study was not designed

to search answers in these areas. As a result, several recommendations for further research are listed as follows.

1. Further study could be performed to ascertain the mechanism by which ozone causes an increase of the turbidity and the suspended solids in a wastewater.
2. Studies could be performed to compare the treatment of raw wastewater with the treatment of filtered raw wastewater and wastewater which has been through secondary treatment to see the action of ozone on the color of the wastewater.
3. The effect of ozone on the pH of the wastewater is currently unexplained, and further research could explain how ozone causes pH changes.
4. It has been suggested that ozonation and carbon adsorption be used in conjunction with each other as wastewater treatment processes. Studies could be done to see if ozone causes materials to be more or less readily adsorbed on the carbon. However, caution would have to be exercised in a study of this sort, as mixed ozone and activated carbon sometimes has explosive tendencies.
5. As mentioned before, ozone does have a tendency to reduce and then increase BOD_5 . Further research could determine when the minimum BOD_5 is reached, in relationship to color removal, as well as when ozone begins to reduce BOD_5 again.
6. A study could be performed to find the result of ozonating

a textile dyewaste secondary effluent, to see if the amount of ozone needed to remove color would be less.

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OZONE TREATMENT OF A SELECTED
TEXTILE DYEING AND FINISHING WASTEWATER

by

Daniel Bruce Horne

(ABSTRACT)

The purpose of this investigation was to characterize the effect of ozone upon a selected textile dyeing and finishing wastewater, with primary emphasis placed on noting the effect of ozone on the color of the wastewater. The parameters measured during the study included color, chemical and five-day biochemical oxygen demand, pH, dissolved oxygen, total organic carbon, ozone residual, total and suspended solids, and turbidity.

The results of the investigation showed that color was removed to a significant degree from the selected wastewater by the action of ozone. Up to 80 percent of the original color of the wastewater was removed by ozonation. COD removals ranging from 20 to 30 percent were also measured. In addition, significant increases in the amounts of suspended solids and turbidity were noted to occur with increased ozonation.