

THE UNIVERSITY OF MANITOBA

OZONE TREATMENT OF SWINE MANURE SLURRIES

by

M. Van Den Bosch

A thesis

Submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements
for the Degree of Master of Science

Department of Agricultural Engineering
University of Manitoba
Winnipeg, Manitoba

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ABSTRACT

Ozone Treatment of Swine Manure Slurries

This investigation involved the treatment of diluted and undiluted swine manure slurries with ozone to determine its effect on the prevention of odours generated as a result of bacterial action. The ozone generator used in this study supplied 33.1 g/h of ozone with an input of 10 l/min of oxygen. Ozone was injected by means of diffusers located at the bottom of two 2.4-metre columns each containing 108 litres of swine manure slurry.

The effect of the treatment was monitored by determining the following parameters: pH, COD, volatile fatty acids, total solids, total volatile solids and total plate count. An increase in the pH of the manure slurries was experienced along with a reduction in COD. The COD of the undiluted slurry was reduced approximately 50 per cent. The total plate count was reduced 99.8 per cent in the manure slurry diluted with approximately 8 parts water compared to a reduction of 81 per cent in the undiluted slurry. Ozone treatment had no significant effect on volatile fatty acids, total solids or total volatile solids.

The results indicate a definite advantage in reducing the solids concentration in manure slurry prior to ozonation for bacterial destruction.

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The advent of modern farm mechanization has enabled the application of production line technology to the raising and managing of livestock and poultry. Modern agricultural technology has made it possible to concentrate livestock and poultry production in highly efficient large-scale operations. Examples of this type of operation are Circle 3 Custom Feeders Ltd., a 15,000 head cattle feedlot located at Carman, Manitoba and Royalean Feeders Ltd., a 300-sow (farrow-finish) hog operation located at Dugald, Manitoba.

One of the major innovations has been the introduction of liquid manure handling technology. It has enabled livestock producers to concentrate greater numbers of animals while reducing the labor involved in managing the operation, including waste disposal. Unfortunately, this advancement brought with it certain problems, not the least of which was the increased odour generated by anaerobic bacterial decomposition of the manure slurry. Although the bacterial decomposition occurs in the manure storage pits and lagoons, the full force of the odour's potency is not experienced until the waste is spread on land to be recycled. As vast open tracts of land which can be used for uninhibited manure disposal are rapidly disappearing, the successful control of odours may eventually determine whether or not the agricultural industry continues to use one of mankind's oldest waste treatment systems.

Controlling the odour generated from the manure slurry has proven to be a formidable task. Two methods of approaching the task have been tried with varying degrees of success:

- 1) Masking or destroying the odour after it has been generated;
- 2) Preventing or inhibiting the odour from being generated.

The first method has not proven very successful for the livestock industry. Although several masking agents are being marketed, their capacity to control odourous situations and their high cost have limited their use. Also odour destruction techniques such as high-temperature incineration are expensive and difficult to adapt to most livestock operations using a manure slurry handling system.

The second method, the prevention or inhibition of odour generation has proven to be more successful in controlling odour from manure slurries. The most common systems employing this method have been of the biological treatment. Cold climatic conditions, however, create many operational problems for such systems and in many cases render them ineffective for long periods of the year.

Chemical treatment systems are not as temperature-dependent as biological treatment systems. Consequently, in colder climates, chemical treatments appear more attractive although they have been limited by other dis-

advantages such as higher treatment cost and greater need for management expertise.

In this study, the treatment of swine manure slurries with ozone was investigated to determine the potential of this chemical treatment in controlling odour. Ozone has many advantages for waste treatment (Rosen, 1973), and in particular the treatment of liquid manure:

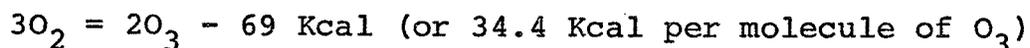
- 1) Ozone is one of the most powerful oxidizing agents;
- 2) Ozone reaction rates are rapid;
- 3) Ozone treatment is not greatly dependent on temperature as are most biological treatments;
- 4) Ozone is a highly efficient bactericide;
- 5) Ozone treatment encourages aerobic conditions by producing oxygen as a by-product;
- 6) Ozone reactions form generally non-toxic end-products.

The purpose of this study was to investigate the potential use of ozone treatment for the control of odours and to identify problems which would have to be overcome for this treatment to be used effectively.

CHAPTER 2 LITERATURE REVIEW

2.1. Nature of Ozone

The exposure of oxygen to light in the ultraviolet wavelength range or the passage of oxygen or air through an electrical discharge, causes the polymization of the oxygen molecule and as a result, ozone is produced. The following reaction applies:



More specifically, the oxygen molecules (O_2) are dissociated into atomic oxygen ($O + O$). Double and triple collisions of oxygen atoms (O) could form new molecules, some O_2 and others O_3 . Collisions between atoms (O) and molecules of oxygen (O_2) might also produce ozone (O_3). Unfortunately, due to the high atomic activity present, some ozone molecules so formed can also be broken up. By the laws of probability only a portion of the oxygen energized can be converted to ozone.

Oxygen, the source of atomic oxygen needed for ozone production, is colourless, odourless, tasteless and non-toxic with a density of 1.42904 g/l at standard temperature and pressure (0°C , 760 millimetres pressure of mercury) or 1.105 g/l when air = 1 g/l. The solubility of oxygen in distilled water is temperature-dependent and varies from 8.9 mg/l at 20°C to 12.3 mg/l at 5°C (Diaper, 1970).

Properties of ozone differ considerably from those of oxygen. Although ozone is colourless like oxygen, it has a very pungent odour similar to that of chlorine and can be dangerous to health. Odour detection, in general, is noted at 0.02 to 0.05 ppm (Evans, 1972). Irritation of the nose and throat in sensitive people has been known to start at the level of detection (0.05 ppm). Others experience dryness of the upper respiratory mucosa at 0.1 ppm and dryness of the throat at levels slightly above 0.1 ppm. Levels approaching 1.0 ppm for periods longer than 30 minutes produce headaches. Changes in visual parameters have been observed at levels of 0.2 to 0.5 ppm, while changes in pulmonary functions occur when levels range between 0.1 and 1.0 ppm. Figure 2.1.1. illustrates the various toxicity regions associated with ozone exposure.

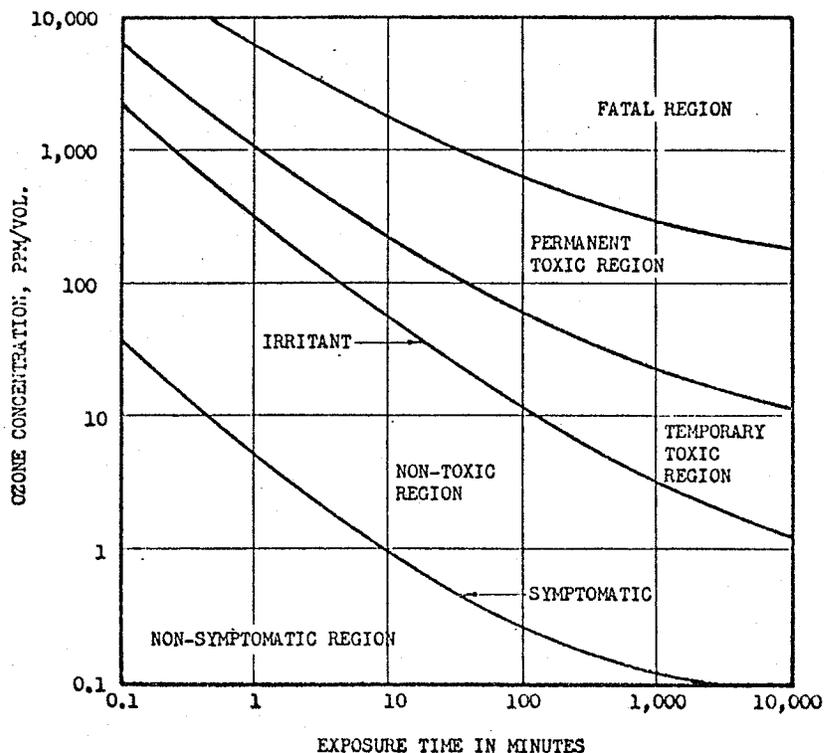


Figure 2.1.1. Ozone toxicity (Evans, 1972).

The density of ozone is 2.144 g/l at standard conditions or 1.5 times that of oxygen (Weast, 1974). Ozone is approximately ten times more soluble in water than is oxygen, but because of a much lower partial pressure, it is difficult to obtain a concentration of more than a few milligrams per litre under normal conditions. Figure 2.1.2. depicts the theoretical solubility of ozone in water.

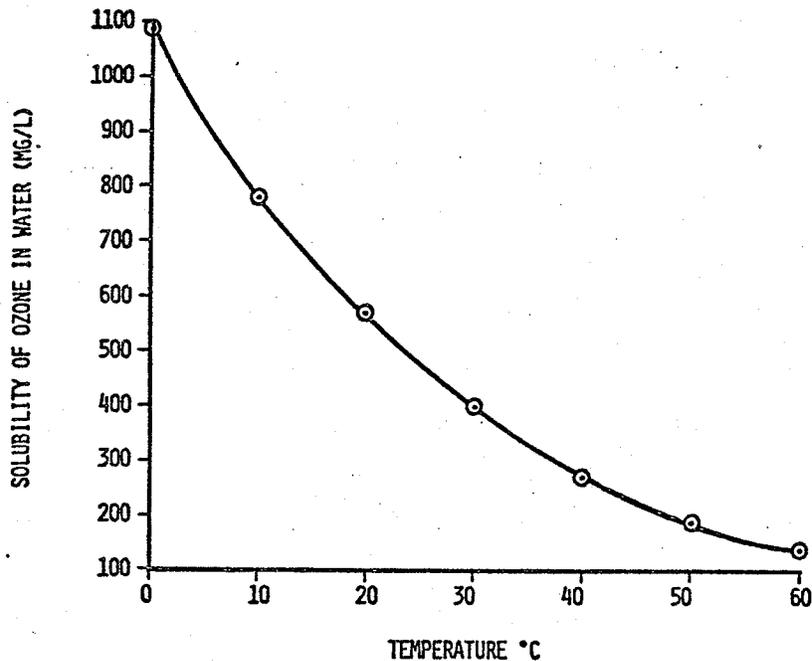


Figure 2.1.2. Solubility of ozone in water at standard pressure (Evans, 1972).

Ozone is a supporter of combustion and ozone concentrations above 30 per cent in air-oxygen mixtures are easily exploded. Explosions may be caused by trace

catalysts, organic materials, shocks, electric sparks, or sudden changes in temperature or pressure. As an oxidizing agent, ozone is the fourth most powerful, exceeded only by F_2 , F_2O and O .

Ozone is a very unstable molecule and eventually it will spontaneously turn back to oxygen. Ozone is rapidly decomposed by heat and at a temperature of $270^{\circ}C$, it is immediately converted back to oxygen. Persistence at normal ambient temperatures is, however, considerable, so long as the gas does not come into contact with substances with which it can react (Boucher, 1965).

The reactive properties of ozone which are most important in wastewater treatment are those achieved with a mixture of air. Because of the inherent instability of its molecular structure, even in low concentrations in air, ozone is capable of producing a series of virtually instantaneous reactions in either liquid or gaseous contact with oxidizable substances.

2.2. Ozone Production

There are three basic methods of producing ozone: (1) electrical discharge; (2) electrolysis of perchloric acid; and (3) ultra-violet exposure of oxygen. The first two methods will produce high concentrations of ozone, while the ultra-violet exposure method will produce ozone

in only small concentrations, approximately 0.003 g/h for each 0.01 watt (Evans, 1972). The electrical discharge method has proven to be the only practical and economic method of ozone production for large-scale utilization.

The electrical discharge method involves the passage of air (or oxygen) between electrodes, across which is maintained an alternating high voltage potential. As a result, an electrical discharge or corona occurs between the electrodes. There are three types of electrical discharge that occur between metallic electrodes exposed in a gaseous medium: glow discharge, brush discharge, and electrical arc. As the alternating potential increases across the electrodes, glow discharge will begin at a certain critical threshold potential but will pass into brush and then arc discharge. Ozone production is then jeopardized by thermal and photo-chemical manifestations. With the insertion between the electrodes of a dielectric material, stabilization of the glow discharge is obtained. The dielectric material causes the glow to spread uniformly and by virtue of its insulating properties, prevents the breakdown of the glow into brush and arc discharge.

Many variables exist in the production of ozone which are either directly or indirectly controllable. Directly controllable variables are the rate of flow of air (or oxygen) and the voltage across the electrodes. Variables which are indirectly controllable are air

humidity and air temperature. The following relationships can be used to explain the interactions between the directly controllable variables involved:

- (1) For a given total power input, total ozone production rises with increase in air flow rate, while the concentration of ozone in air and power consumption per unit of ozone, decreases;
- (2) At a given rate of air flow, total ozone production rises with increasing total power input, the concentration of ozone in air and the power consumption per unit of ozone also rising;
- (3) A given total ozone production is obtained most economically when total power input is low and the air flow rate is high;
- (4) Power consumption per unit of ozone produced depends upon the concentration of ozone in the air. It increases with the concentration and also increases, although to a lesser extent with the total ozone production.

Performance curves for a typical ozone generator are shown in Figure 2.2.1., illustrating the relationships between: air flow, total power input, power input per gram of ozone produced, ozone concentration in air, and total ozone production.

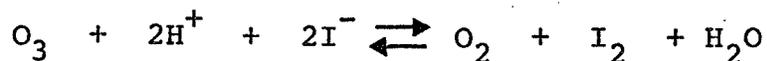
2.3. Analytical Methods for Determining Ozone Concentration

The lack of precise analytical measurement of ozone in an aqueous environment at very low level has been one of the main obstacles in conducting basic research on the application of ozonation in wastewater treatment. Several analytical methods of determining ozone in water are listed in Table 2.3.1.

Table 2.3.1. Analytical Methods for Determining Ozone in Water (Evans, 1972).

Method	Utilization of	Interferences or Limitations
Potassium iodide; alkaline, acid, and neutral conditions	$2 \text{ KI} \rightarrow \text{I}_2$	Most oxidants interfere (oxygen interferes)
Ferrous ion oxidation (Luther & Inglis)	$\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$	Results felt to be low
Manganese oxidation and orthotolidine	$\text{Mn}^{++} \rightarrow \text{Mn}^{+++}$	
Visible region spectrophotometry	Molar absorptivity of 2500 to 3000 at 260 nm	Detection limits for 1 cm cell 10^{-3}M
Oxidation of leuco crystal violet (Layton & Kinman)	Redox indicator; leuco crystal violet	Newest technique (under investigation)
Various instrumental methods using KI oxidation	$2 \text{ KI} \rightarrow \text{I}_2$	Same as KI above

Of the various methods listed in Table 2.3.1., the potassium iodide (iodometric) method is the most commonly used. It involves the oxidation of potassium iodide, by the following reaction:

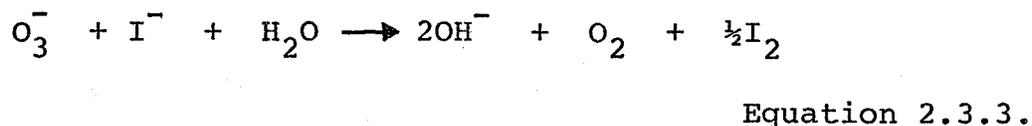


Equation 2.3.1.

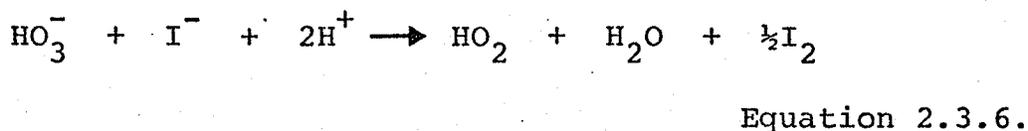
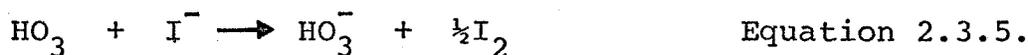
This method is limited by interferences from most oxidants. Many conflicting statements regarding the iodometric method may be found in the literature. Serious limitations have been experienced with the iodometric methods, including non-stoichiometric iodine formation under both neutral and alkaline conditions (American Chemical Society, 1959). In another study, Boelter et al, (1950) determined that high iodine production occurred in strongly acidified solutions. However, they found that by using potassium iodide absorbants in a pH range between 2.3 and 12.3, correct results were obtained for concentrations of ozone up to 20 per cent by weight if the solution was acidified with strong acid before titration with sodium thiosulfate. In a recent study, Boyd et al (1970) compared the spectrophotometric method of ozone determination using light at 254 nm with the method of oxidation of iodide in buffered neutral solutions. They observed a stoichiometry of 1.5 molecules of iodine liberated per molecule of ozone absorbed. However, the 1:1 ratio in buffered neutral solutions was also confirmed by Kopczynski and Bafalini

(1971) and Hodgenson et al (1971). Kopczynski and Bafalini employed the spectrophotometric method to determine ozone concentration. Hodgenson et al used a chemiluminescent-nitric oxide monitor; the response of which is a linear function of ozone concentration.

Shechter (1973) investigated this stoichiometric problem further and concluded that the confusion occurred due to the formation of an ozonide ion, ie. O_3^- . This is also confirmed by Parry and Hern (1973). If the reaction between ozone and iodide takes place via some intermediate form such as the ozonide ion, the stoichiometry of the reaction in neutral medium remains 1:1, in agreement with the following equations (Shechter, 1973):



However, if the same reaction takes place in an acidic medium, the ozonide ion may be transformed to HO_3^- , which may be able to oxidize additional iodide to iodine, according to the following equations:



Therefore, if the iodide solution is acidified just before titration with sodium thiosulfate, no stoichiometric error will be involved.

In conclusion, the 1:1 ratio of iodine to ozone is valid and can be employed with assurance, provided the iodine solution is acidified just prior to the determination of iodine by titration with sodium thiosulfate.

2.4. Effects of Ozone on Wastewater Characteristics

Chemical Characteristics

TOC, BOD, COD

Ozone is such a powerful oxidizing agent, that given high concentrations and long contact time it will react with almost anything. Consequently, understanding the kinetics involved aids in the determination of the required ozone treatment.

Marsh and Panula (1965) postulated that in the ozonation process, BOD reduction with ozone would have a biomolecular mechanism

$$\frac{dC_1}{dt} = K_1 C_1 C_2 \quad \text{Equation 2.4.1.}$$

where C_1 = BOD of raw sewage (mg/l)

C_2 = ozone concentration (mg/l)

K_1 = reaction constant (second order)

t = time (hr).

However, the results of their testing, indicated a pseudo-zero-order reaction existed:

$$\frac{dC_1}{dt} = \text{CONSTANT} \qquad \text{Equation 2.4.2.}$$

In other words, C_1 on the right hand side of Equation 2.4.1. is eliminated because of the fact that the concentration of BOD was large compared to the concentration of O_3 throughout the entire ozonation period. Also C_2 in Equation 2.4.1. is eliminated by the fact that O_3 concentrations in solution remained essentially constant throughout the test period and large enough relative to the rate of consumption of O_3 .

In a pilot plant study (Evans, 1972), ozone treatment of wastewater was studied in combination with other treatment systems. Typical COD reduction curves for two plant feeds are given in Figure 2.4.1. The log of COD is plotted versus reaction time with ozone for an independent physical/chemical treatment (IPC) and a potential biological treatment process - UNOX. Two observations were made.

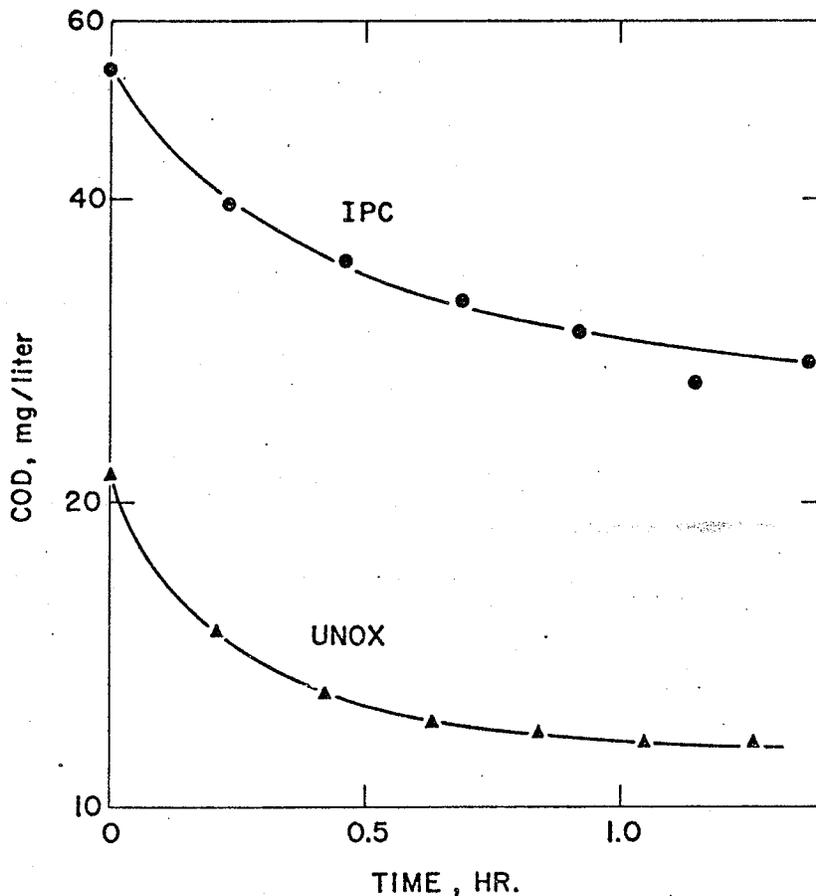


Figure 2.4.1. Typical COD reduction curves for IPC and UNOX. Pretreated feeds: Log COD versus reaction time (Evans, 1972).

The initial reaction is quite rapid, but as the reaction continues it slows down so drastically that one may suspect that it has neared completion.

Figure 2.4.2. illustrates the extended COD reduction curves as a function of ozone reaction time. The data used in this figure represent several runs on UNOX treated effluent and include end points from the post-ozonation experiment. The convex shape of the curves

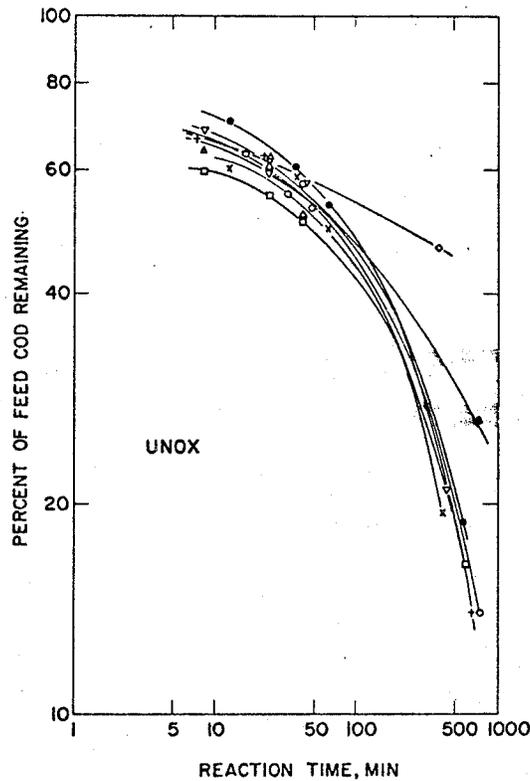


Figure 2.4.2. Extended COD reduction curves for UNOX pretreated feeds including end points from post-ozonation experiment (Evans, 1972).

illustrates that practically all of the COD is eventually oxidized by ozone. Consequently, there appears to be no fraction of the COD that is refractory to ozone treatment. However, economic practicability of further reduction becomes questionable since the reaction time is extended after 50 to 70% reduction.

In a study on ozonation of wastewater in a continuous counter-current column, Huibers et al (1969) found that the ozone efficiency decreased with decreasing TOC and COD levels of the secondary effluent, thus indicating that the most readily bio-oxidizable organic compounds in the effluent also consume ozone most efficiently. For example it was much more difficult to reduce the COD from 25 to 15 mg/l than ~~from~~ 65 to 55 mg/l.

Nitrogen

In a pilot plant study, Boucher et al (1968) found that nitrite in wastewater is oxidized by ozone but ammonia and nitrate were unaffected. However, results of bench-scale tests by Thirumurthi (1968) on ozonation of wastewater indicated ammonia nitrogen is oxidized by ozone to nitrate nitrogen.

Pilot-plant studies by Kirk et al (Evans, 1972) demonstrated that during one-hour ozone treatment periods, nitrification was only significant with high pH wastewater feeds. In another ozonation study, Huiber et al (Evans, 1972) found that the ammonia-nitrogen content of wastewater effluent was not affected by ozonation. In this study, a solution of ammonium sulfate equivalent to a nitrogen content of 28 mg/l was treated with ozone in a column reactor. After running two six-hour tests the

ammonium-nitrogen content of the treated sample varied between 24 and 29 mg/l indicating that ozone did not react appreciably with ammonia.

No explanation can be given for the differing results obtained by Thirumurthi (1968), however, the fact that these results were obtained from a crude bench-scale study must be considered. The results obtained by other researchers originated from pilot-plant studies, and presumably their results can be considered more reliable.

Physical Characteristics

Turbidity

Ozone treatment of wastewater greatly reduces the turbidity. Kirk et al (Evans, 1972) found that the turbidity was reduced about 70 per cent with the product water ranging generally between one and four Jackson Turbidity Units (J.T.U.).

Turbidity of secondary effluent is a composite of suspended solids and the dispersed colloidal matter. Ozone is an allotropic form of oxygen and often reacts as a positive charge. The colloids are negatively charged spheres which are attracted by the ozone and broken down by chemical oxidation. Results of pilot studies by Nebel

et al (1973) have shown an average turbidity reduction of 70 per cent with ozone treatment.

Suspended Solids

Suspended solids are removed by ozone-induced frothing. If ozone is applied properly to a secondary effluent, it can be used to remove suspended solids by a flotation process that utilizes skimming devices to remove solids as froth (Nebel et al, 1973).

Biological Characteristics

Although ozone is an extremely powerful oxidizing agent, its mechanism of disinfection has never been clearly understood. Scott and Lesher (1958) experimenting with Escherichia coli, postulated that the primary attack of ozone was on the cell wall, -- probably by reaction with the double bond of lipids, and that cell lysis depended on the extent of that reaction.

Bringman (1955) felt that the mode of action of chlorine differed from that of ozone; chlorine selectively destroyed certain enzymes, whereas ozone acted as a general protoplasmic oxidant. Barron (1954) hypothesized that the primary bactericidal action of ozone was the oxidation of sulfhydryl groups on enzymes.

Murray et al (1965) recognized that the outermost layer of gram negative organisms is a lipoprotein followed by a lipopolysaccharide layer. Therefore, these layers would be the first subject to attack by ozone resulting in a change in cell permeability eventually leading to lysis. Smith (1969) stated that Escherichia coli and Streptococcus fecalis experienced a 99% kill after being ozonated for 60 seconds. Boucher et al (1968) conducted experiments on micro straining and ozonation of wastewater effluent and found that by using an ozone dose of 10 to 20 mg/l almost all of the organisms were killed although a sterile effluent was never obtained. All the Salmonella and viruses naturally present were killed by ozone except in the instance when there was a single survivor. Some coliform organisms and Escherichia coli survived and numbers were generally higher when the ozone dose could not be maintained at the 20 mg/l level.

Nebel et al (1973) investigated the effect of ozonation of bacteria and viruses in effluent from an extended aeration pilot plant at Fort Southworth in the Metropolitan Sewer District of Louisville, Kentucky. Using an average applied dosage of 15.2 mg/l for an average contact time of 22 minutes, fecal coliform reductions of greater than 99% were achieved, resulting in a mean fecal coliform concentration of 103 cells/100 ml, a mean total

coliform concentration of 500 cells/100 ml, and a mean fecal streptococci concentration of 9 cells/100 ml in the final effluent.

The effect of ozone on viruses was also studied, using F₂ bacteriophage as the model virus. Virtually 100% inactivation efficiency was achieved after a contact time of five minutes at a total ozone dosage of 15 mg/l and a residual of 0.05 mg/l. It was observed that the rate of inactivation was greater for F₂ bacteriophage than bacteria (refer to Figure 2.4.3.).

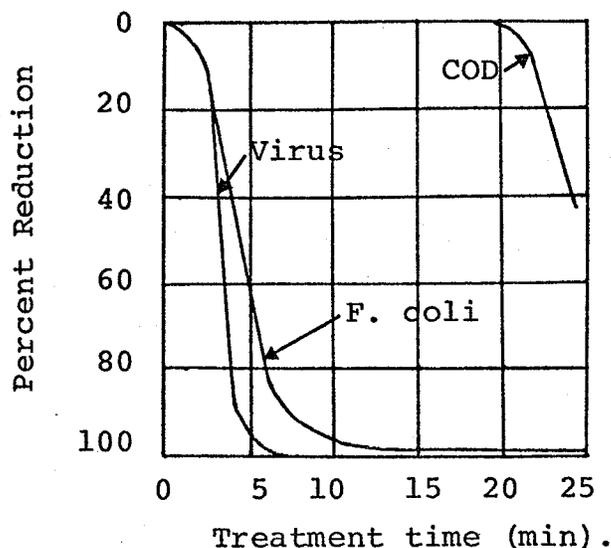


Figure 2.4.3. Comparison of kills of bacteria and viruses (Nebel et al, 1973).

CHAPTER 3. EXPERIMENTAL PROCEDURE

The testing program for this study consisted of measuring the effects of ozonation on swine manure. Both diluted and undiluted swine manure slurries were subjected to ozonation using batch reactors. The ozone application rate was determined by pretest calibration of the ozone generator.

The following waste parameter tests were performed on samples taken periodically during the treatment runs:

- 1) pH
- 2) chemical oxygen demand
- 3) total solids and total volatile solids
- 4) volatile fatty acids
- 5) total plate count.

3.1. Ozonation Equipment

The equipment used in this study includes both commercially available equipment and laboratory fabricated units. The treatment system has been divided into three sections for discussion purposes:

- 1) Description of O₂ supply and flow regulation;
- 2) Ozonator;
- 3) Reactor columns and diffuser.

3.1.1. Description of O₂ Supply and Flow Regulation

Air contains approximately 20 per cent oxygen by volume (Weast, 1973). Consequently, the output of an ozone generator unit is increased significantly (approximately 100%) when pure oxygen is used rather than air. Therefore, oxygen rather than dehydrated air was used in the generation of ozone for this study. Oxygen was supplied in large pressurized cylinders with sufficient capacity for one complete test period.

Since the amount of ozone produced in the generator is highly dependent on the amount of oxygen flowing through the corona discharge gap, it is essential that the flow be accurately controlled. To ensure steady-state flow characteristics during the test period, a two-stage pressure compensating flow regulator was used. The regulator, a Linde Model R501 with rotometer, is shown in Figure 3.1.1. It has a range of 0-15 l/min, therefore a flow of 10 l/min is well within its optimum operating range (Holmon, 1971).

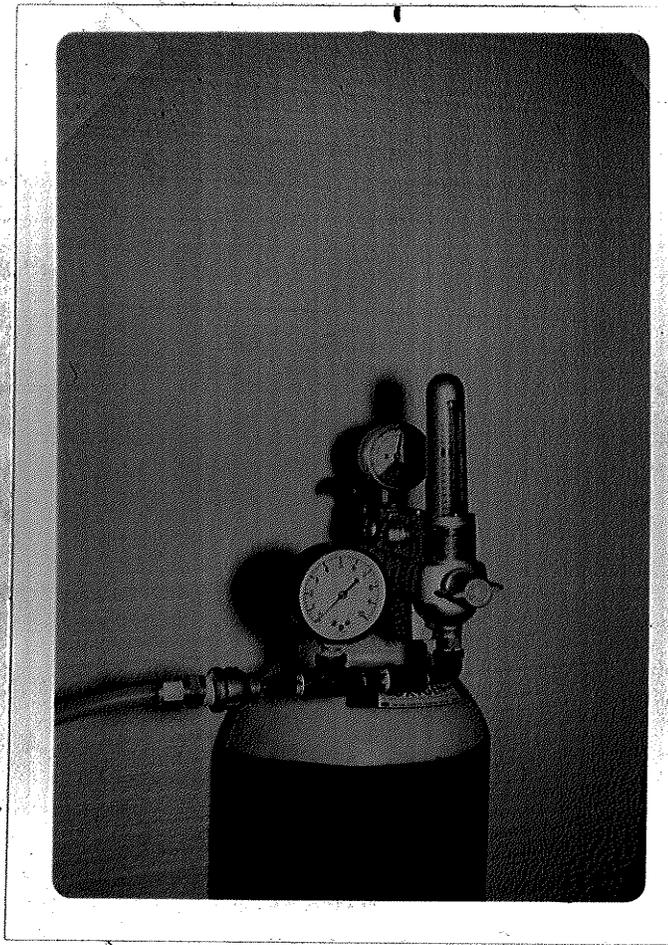


Figure 3.1.1.1. Two-stage pressure-compensating flow regulator with rotometer.

3.1.2. Ozonator

The ozone generator used in this study was an Ozonair R-X-G-12 manufactured by Canatraco Ltd. (Figure 3.1.2.1.). The unit had a minimum and maximum air throughput of 240 l/h and 2400 l/h respectively. Although the unit came equipped with a rotometer, the oxygen input line was modified to by-pass it since the rotometer on the regulator was sufficient to gauge the flow.

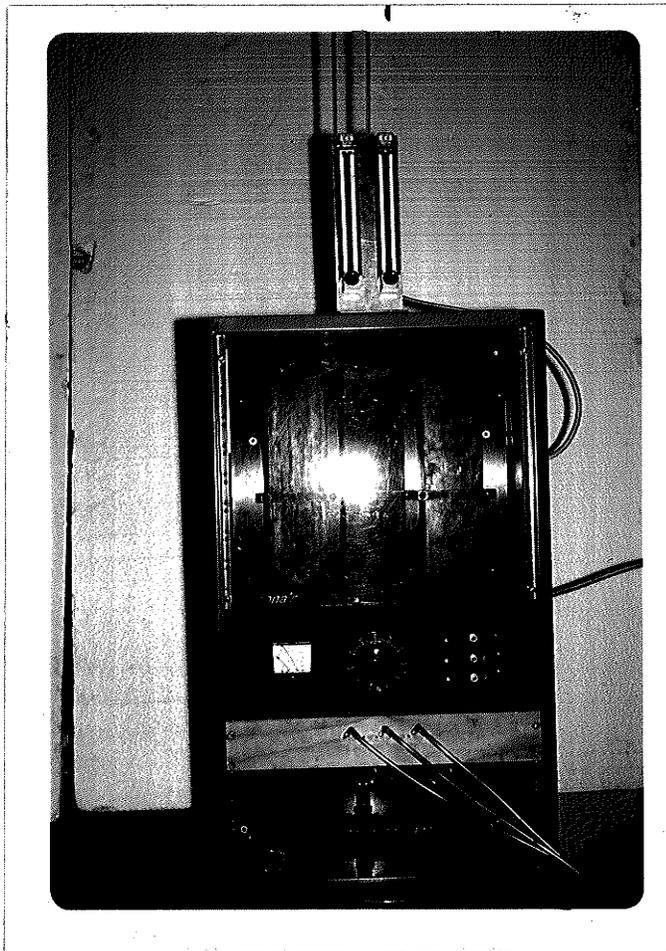


Figure 3.1.2.1. Ozonair R-X-G-12 used in treatment study.

The unit is of the Otto plate type with three vertical reactor columns arranged in series. The suggested ozone output with an oxygen feed is 24 g/h based on an ozone concentration of 1.7 per cent by weight and an oxygen flow rate of 16.5 l/min. However, ozone concentrations of up to eight per cent by weight in oxygen or higher can be obtained by varying gas flow rate, primary voltage, and cooling medium temperature.

3.1.3. Reactor Columns and Diffuser

Two reactor columns were used in this study, each operating independently from the other (Figure 3.1.3.1.). The columns were constructed from 2.4 m lengths of polyvinyl chloride (PVC) tubing with an inside diameter of 25.4 cm. The column cap and base were fabricated from 1.9 cm acrylic sheet. A circular groove, approximately 25.4 cm in diameter was cut into each section. A bead of silicon rubber base glue was placed in the groove to act as a seal. Tie rods were used to hold the ends together and form a pressure seal.

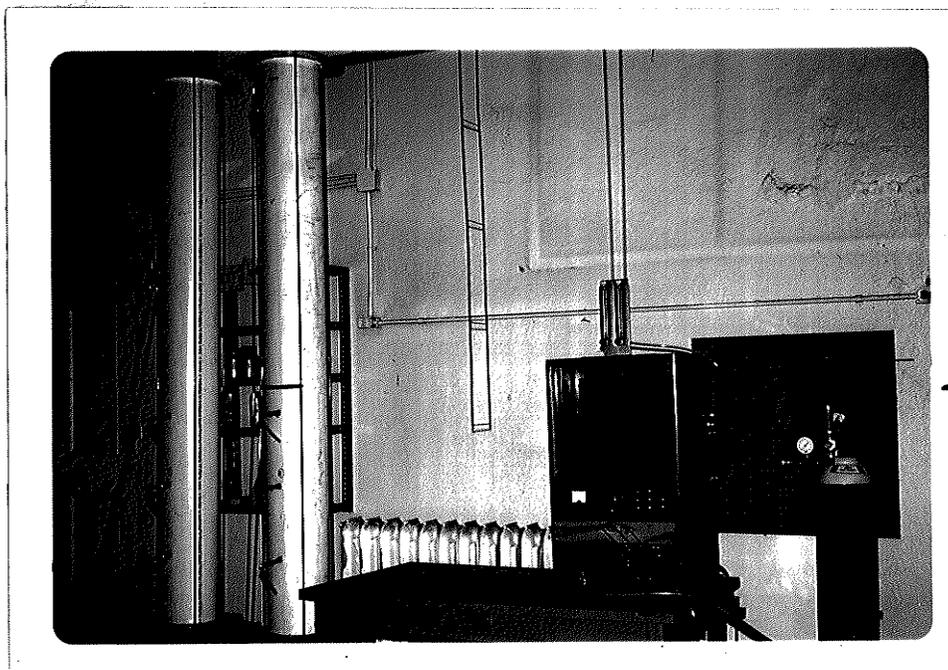


Figure 3.1.3.1. Reactor columns.

Since the ozone generator was to supply both columns, the ozonized oxygen stream had to be divided equally. This was accomplished by installing a "Y" connector in the gas line after it left the ozonator. The two leading ends of the "Y" connector were attached to separate rotometers, equipped with needle valves. By varying the needle valve setting and observing the flow rates of the rotometers it was possible to regulate the amount of gas supplied to each contact column. Due to the highly corrosive nature of ozone, a Brookings Model 150 "Showrate" rotometer with stainless steel ball and teflon packing was used. The ozonized oxygen was fed into the reactor column from the base through three porous stone diffusers. The diffusers were placed in a triangular pattern, equidistant from each other.

Three sampling ports were provided on each column at the 0.3-, 0.6- and 0.9-m levels from the base (Figure 3.1.3.2.). A 6.4 cm loading port was installed in the column cap. Also attached to the cap was an exhaust line which was used to lead waste gases and foam outside the test lab to collection containers.



Figure 3.1.3.2. Column sampling ports at 0.3, 0.6, and 0.9 m levels.

3.2. Ozone Generator Calibration

In order to fully evaluate the effect of ozone on swine manure, it was essential that the ozone production rate be known. Bearing in mind the instability of ozone, it was determined that the most practical method of measuring the ozone supplied would be to calibrate the generator at the steady-state conditions which would be duplicated during the waste treatment study.

A set of steady-state conditions were determined after taking into consideration the following factors: oxygen supply, maximum and minimum air-flow rates recommended for the ozone generator to be used, capacity of the diffuser system in the contact columns, and output efficiency as determined by the voltage setting. Steady-state conditions were established by selecting an oxygen flow rate of 10 l/min and a primary coil voltage of 1000 volts. The arrangement of the test apparatus is illustrated in Figure 3.2.1. Oxygen was supplied from pressurized oxygen cylinders. A pressure-compensating two-stage regulator equipped with a rotometer was used to meter the oxygen supply. Three ozone collection bottles, containing a potassium iodide solution as outlined in Standard Methods for the Examination of Water and Wastewater (1971), hereinafter referred to as Standard Methods, and arranged in series, were used to ensure that all the ozone generated was trapped. All gas lines carrying ozone were constructed of glass tubing except for the joints which were constructed of tygon tubing.

Six calibration test runs were conducted. The duration period for each run was five minutes. Each run was preceded by a ten-minute warm-up period, thus ensuring that steady-state conditions had been reached. A constant coolant water temperature of 25°C was noted during each

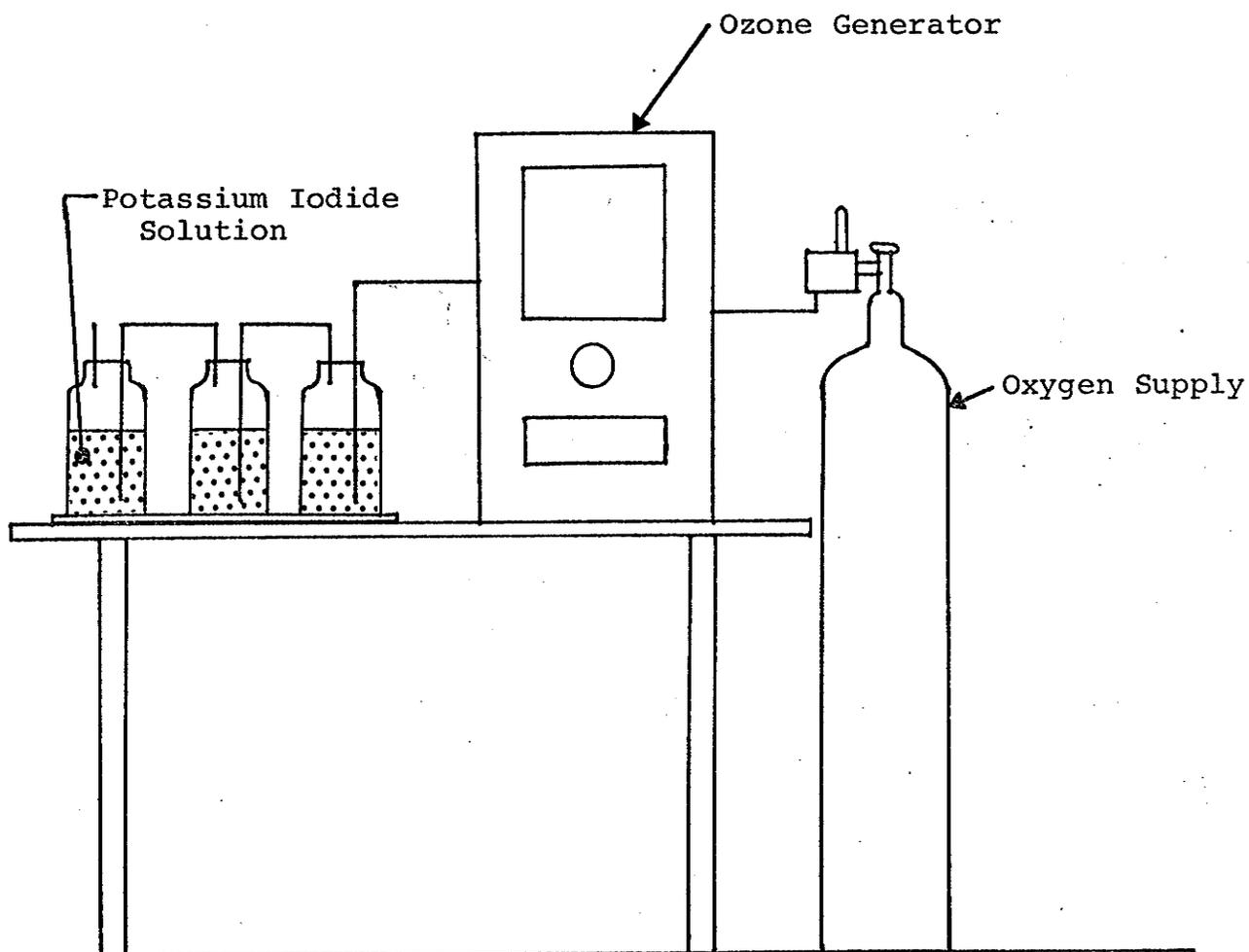


Figure 3.2.1. Calibration Apparatus for Ozone Generator.

test run. The result of the calibration test was a measured ozone generator output of $33.1 + 1.13$ g/h based on a 95% confidence interval (Appendix A). This corresponded with an ozone concentration of 5.5 per cent by weight in the ozonized gas stream.

3.3. Batch Reactor Runs

Batch reactor runs were conducted using swine manure taken from the manure storage pits at the Glenlea Research Station located 21 km south of the University of Manitoba. The effect of ozone treatment was measured on both diluted and undiluted swine manure slurries. For the diluted test, the manure slurry was diluted with tap water in a ratio of 1:7. The swine manure used in the undiluted slurry treatment, was taken from the manure storage pit approximately two days before that used in the diluted slurry treatment.

3.3.1. Pretreatment and Loading

In order that a waste of approximately uniform consistency could be available for the ozone treatment study, pretreatment of the swine manure slurry was necessary. A recirculating pumping system was used to pre-mix the manure slurry in the manure pit located under the barn.

The manure slurry was then passed through a Johnson hydra-sieve (Figure 3.3.1.1.).



Figure 3.3.1.1. Hydra-sieve used for solids separation of swine waste.

Figure 3.3.1.2. illustrates the removal of large solids and hog-bristles (hair) with the hydra-sieve.

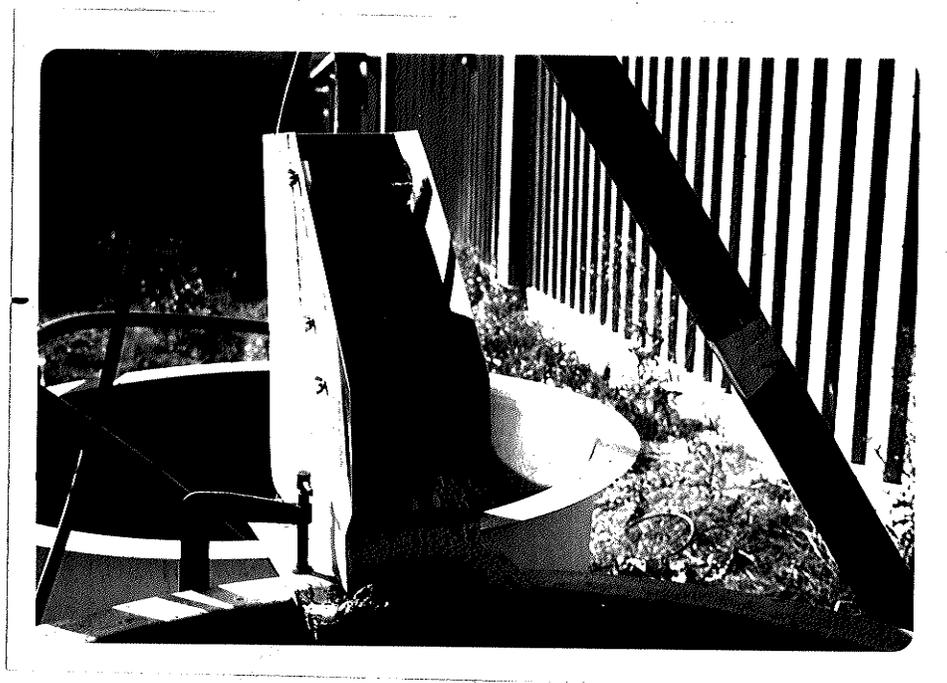


Figure 3.3.1.2. Solids being removed from swine manure.

Effluent passing through the hydra-sieve (Figure 3.3.1.3.) was collected and transferred to large flexible plastic containers for transport to the laboratory for the test. The pretreated swine manure slurry was removed from the containers and poured into a large plastic bucket (Figure 3.3.1.4.). This allowed the manure slurry, stored in the smaller transporting containers, to be mixed prior to loading the columns. A small transfer pump was used to convey the manure slurry to the top of the columns.

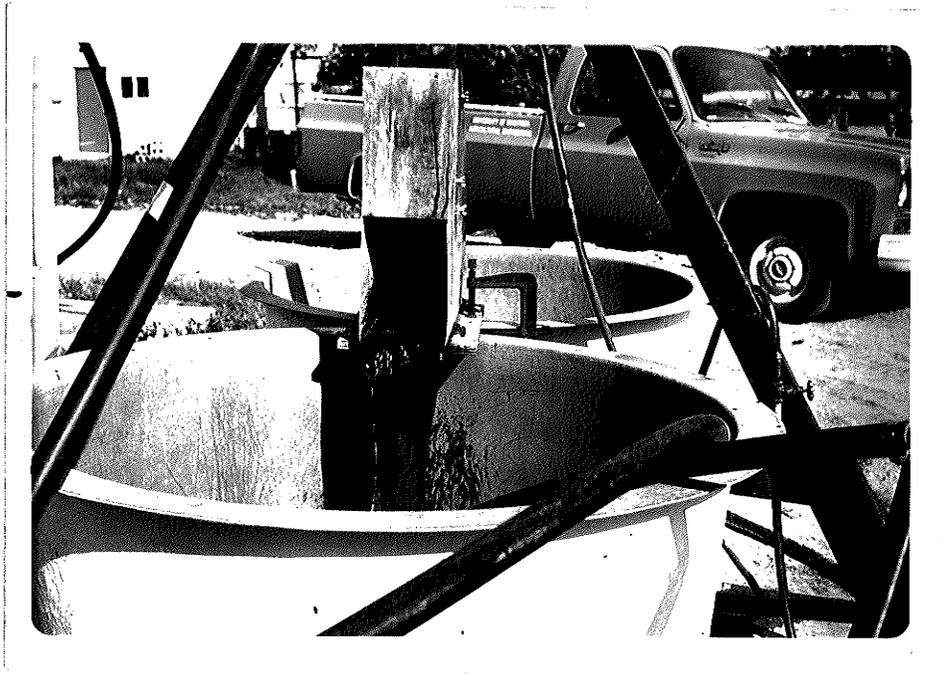


Figure 3.3.1.3. Pretreated effluent leaving hydra-sieve.



Figure 3.3.1.4. Effluent transfer system.

The columns were each loaded with 108 l of swine manure slurry to a liquid depth of 2.1 m, allowing a free column head of 0.3 m. The head space was necessary to ensure that foaming action would not create a pumping effect on the waste and physically draw it out of the column.

3.3.2. Ozonation Procedure

The procedure for the ozone treatment test consisted of two phases:

- 1) start-up;
- 2) ozone application.

During the start-up phase the ozonator's coolant water was turned on and allowed to stabilize. The oxygen supply was turned on for approximately five minutes prior to the activation of the ozone generator. This was done to remove all the moisture that might have condensed in the gas lines and to thoroughly mix the waste in the column prior to starting the ozone application. While the oxygen was flowing, all joints in the air lines and column fixtures were checked for air leaks.

The ozone application phase, consisted of ten hours of uninterrupted ozone application at a rate of 16.6 g/h per column. Foam generated in the column and carried out with the exhausted oxygen was transferred to

collection containers located outside the laboratory by flexible plastic tubes.

3.3.3. Sampling and Sample Storage

During ozone treatment, samples of waste were removed from the columns at periodic intervals. Samples were taken from a sampling port located 0.9 m from the base of the column. Separate samples were taken for chemical and bacteriological analysis. Sample volumes of 100 ml and 500 ml were taken for bacteriological and chemical analysis, respectively. All samples were refrigerated immediately after being taken.

A total of five samples was taken from each column during each test. The first sample was taken after the waste in the columns had been subjected to the mixing action of the oxygen flow for five minutes and just prior to ozonation commencing. Each test lasted ten hours with the four remaining samples being taken at time intervals of 2.5 h.

3.4. Analytical Procedures

The analytical program for this study consisted of measuring ozone residual for the calibration of the ozone generator and performing the following control parameter tests:

- a) pH;
- b) Chemical oxygen demand (COD);
- c) Total solids (TS) and total volatile solids (TVS);
- d) Volatile fatty acid content;
- e) Total plate count.

3.4.1. Ozone Residual

Ozone residual determinations were performed in accordance with the iodometric method for the determination of ozone in air as outlined in Standard Methods. Three ozone collection bottles were used in series to ensure that all the ozone was trapped. When preparing a sample from the first ozone collection bottle for titration with sodium thiosulfate, it was necessary to dilute a 10-ml aliquot of the potassium iodide solution to 400 ml with distilled water.

3.4.2. Control Parameter Tests

The control parameter tests performed in this study were as follows:

- 1) pH - measured electrochemically with a Fisher Accumet Model 230 pH meter;
- 2) Chemical oxygen demand - in accordance with the procedures outlined in Standard Methods;

- 3) (a) Total solids - in accordance with the procedures outlined in Standard Methods, except for the use of a sample size of 50 ml and a drying time of 16 h;
- (b) Total volatile solids - in accordance with the procedures outlined in Standard Methods except for a drying time of 4 h;
- 4) Volatile fatty acid content - ~~in accordance~~ with the procedures outlined by Hach Chemical Corporation (1971). Two replicate analysis were performed on each sample. The concentrations were measured spectrophotometrically at a wave length of 495 nm using a Bauch and Lomb Spectronic 70. A calibration curve was prepared from acetic acid solution of known concentrations (Figure 3.4.2.1.);
- 5) Total plate count - standard plate counts were performed in accordance with Standard Methods using an incubation temperature of $35 \pm 0.5^{\circ}\text{C}$ for $48 \pm 3\text{h}$.

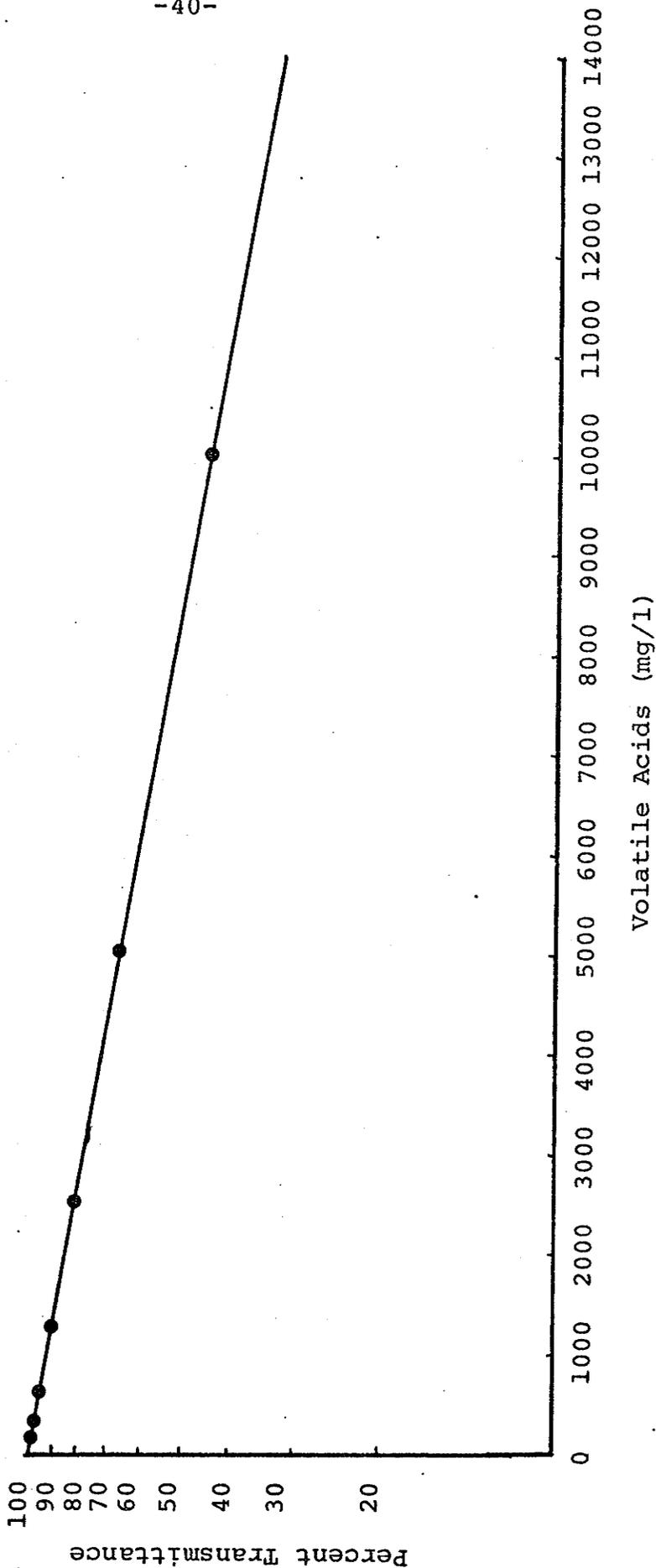


Figure 3.4.2.1. Calibration Curve for Volatile Fatty Acids Content prepared by using acetic acid solutions of known concentrations.

CHAPTER 4. RESULTS AND DISCUSSION

During the study swine manure of two consistencies was subjected to ozone treatment, specifically an undiluted manure slurry and a slurry diluted in a ratio of 1:7 with tap water. However, after comparing the ratio of total solids content of both the diluted and undiluted raw manure slurries, it was observed that the prescribed dilution ratio of 1:7 had been exceeded. The dilution ratio was calculated as being approximately 1:8 (Table 4.0.1.).

Since the dilution water that was added to the reactor columns was carefully measured, it was felt that the additional water must have been added to the swine waste slurry while it was in the storage pits. After an investigation the additional dilution water was traced to a leaking watering bowl in the swine barn.

Table 4.0.1. Comparison of total solids content in diluted and undiluted manure slurries.

Parameter	Undiluted Run	Diluted Run	Ratio
Total Solids (mg/l)	20866	2496	1:8.36
	<u>20916</u>	<u>2726</u>	<u>1:7.67</u>
Average	20891	2611	1:8

4.1. Effect on pH

During ozone treatment, both the diluted and undiluted swine manure slurries experienced an increase in pH, away from neutrality. The largest increase in pH occurred in the undiluted slurry during the first five hours of treatment (Figure 4.1.1.). The general shift in pH away from neutrality was unexpected, since Kirk et al (Evans, 1972) found that during ozone treatment of various wastes of differing pH, whether acidic or basic, the pH of the treated waste tended to move toward neutrality. However, Kirk et al also found that most of the pH change took place in the early stages of treatment and that the pH change was greater for the higher COD wastewaters. These findings are confirmed in this study even though the direction of change (ie. away from neutrality) differs from that experienced by Kirk et al.

In their study, Kirk et al made no provisions for controlling the pH throughout the reaction period. Therefore in examining the effects of pH on COD reduction, they could only use the feedwater pH as an independent variable. After experimenting, they found that the higher the pH of the feed, the higher the COD removal realized during a given ozonation period.

In general, the above mentioned relationship is borne out by the results of this study. The effects of pH

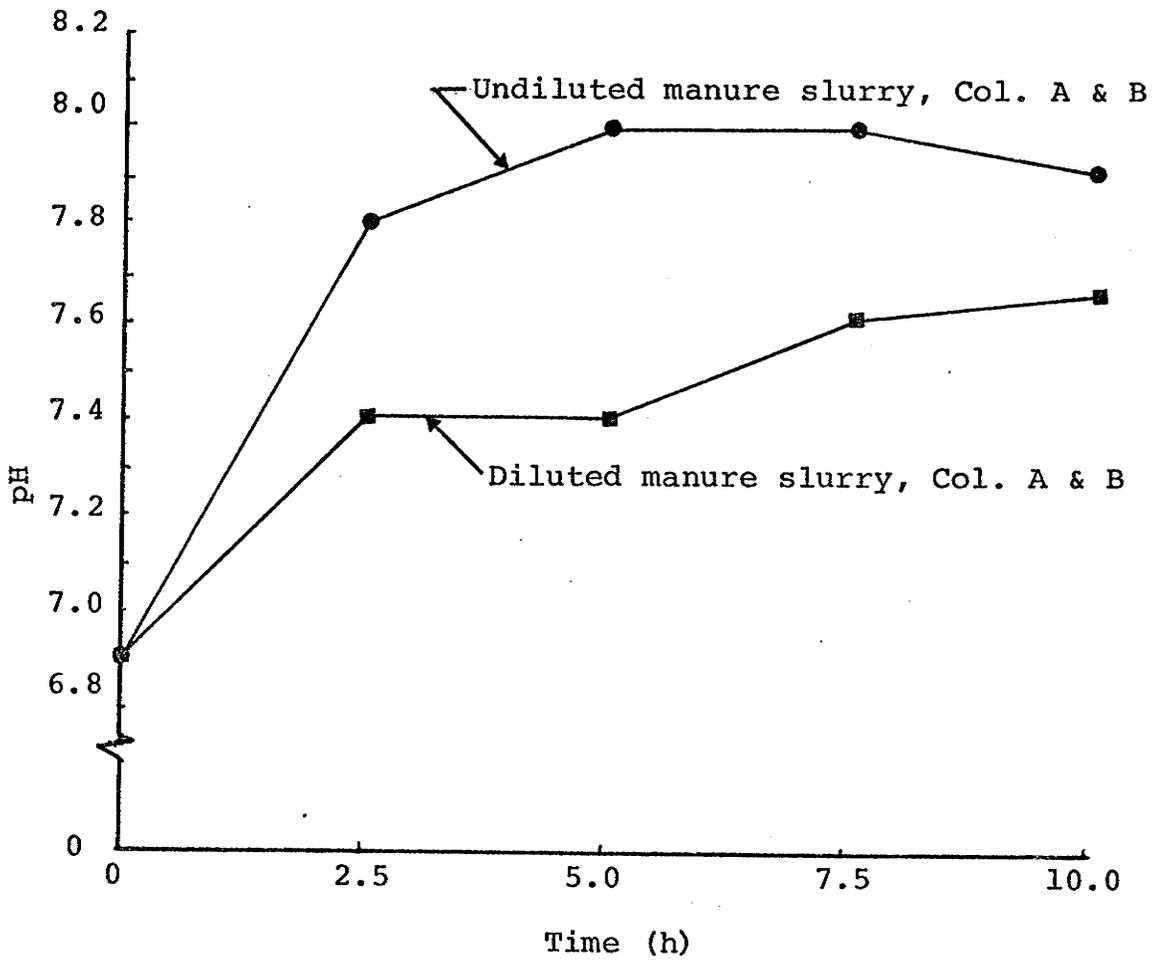


Figure 4.1.1. Change in pH of swine manure slurries vs time period of ozone treatment.

on the per cent COD removed by ozonation is summarized in Figure 4.1.2. It should be noted however, that each data point plotted, reflects the relative change occurring from the start of the treatment run. They are not changes experienced over the length of a 10 hr treatment run at the respective pH levels.

4.2. Effect on COD

The effects of ozonation on the COD of diluted and undiluted swine manure slurries are illustrated in Figure 4.2.1. Ozonation was found to have a much greater effect on the waste with a higher COD, reducing it at a much faster rate. The limited effect of ozonation on the diluted slurry is surprising, however, when considering the waste had an initial COD of 1510 mg/l and experienced only a 17.5 per cent reduction, equivalent to a reduction of 260 mg/l. The COD reduction of the undiluted slurry was more significant. A COD reduction of 1350 mg/l or 48 per cent was realized.

After averaging the COD values from the two reactor columns, a least-squares linear regression was performed on the data and the results are illustrated in Figure 4.2.2. The following equations can be used to describe the relationship between COD reduction and ozone treatment time (t):

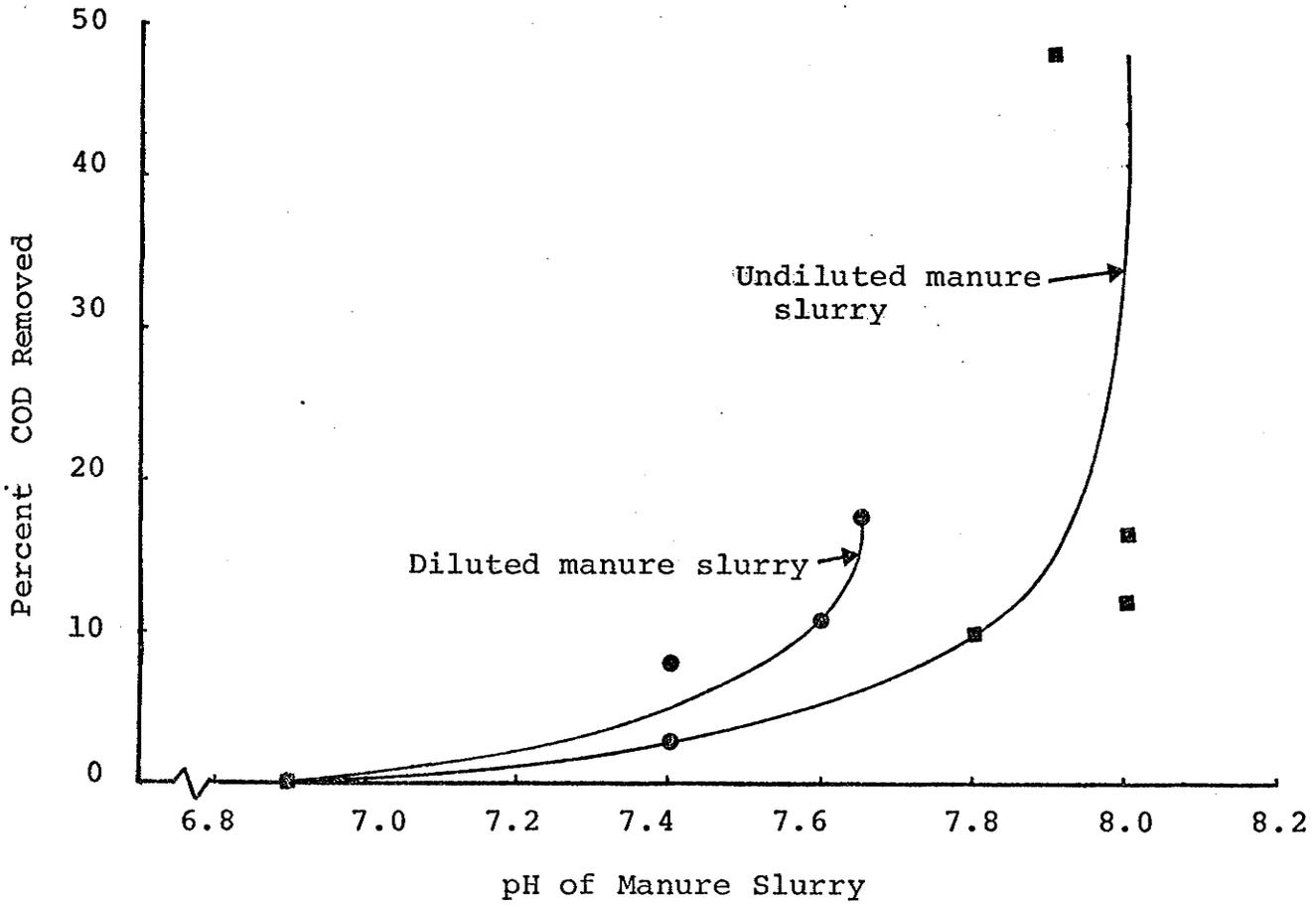


Figure 4.1.2. Effect of pH on COD Reductions.

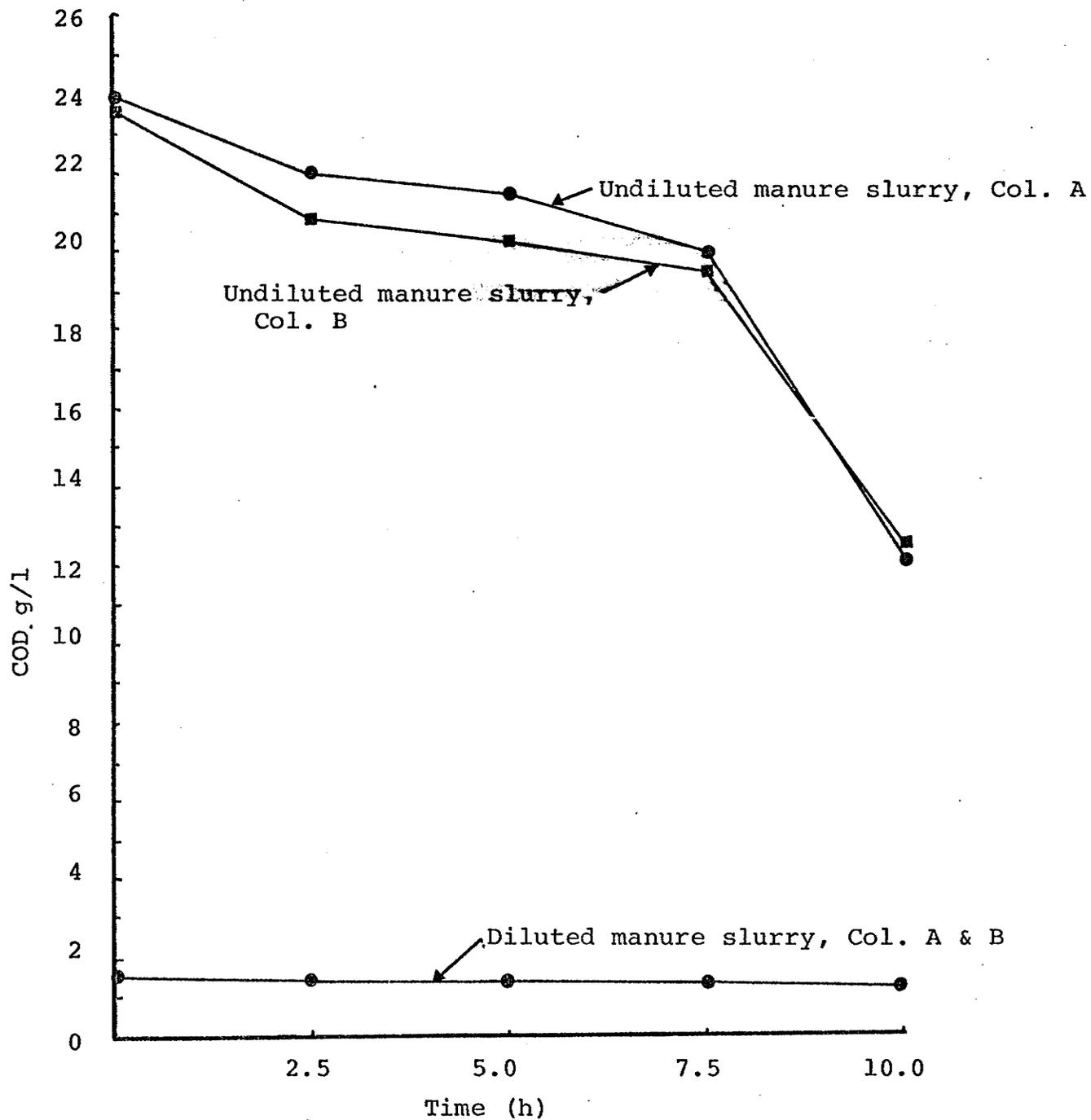


Figure 4.2.1. COD reduction in diluted and undiluted liquid swine manure by ozone treatment.

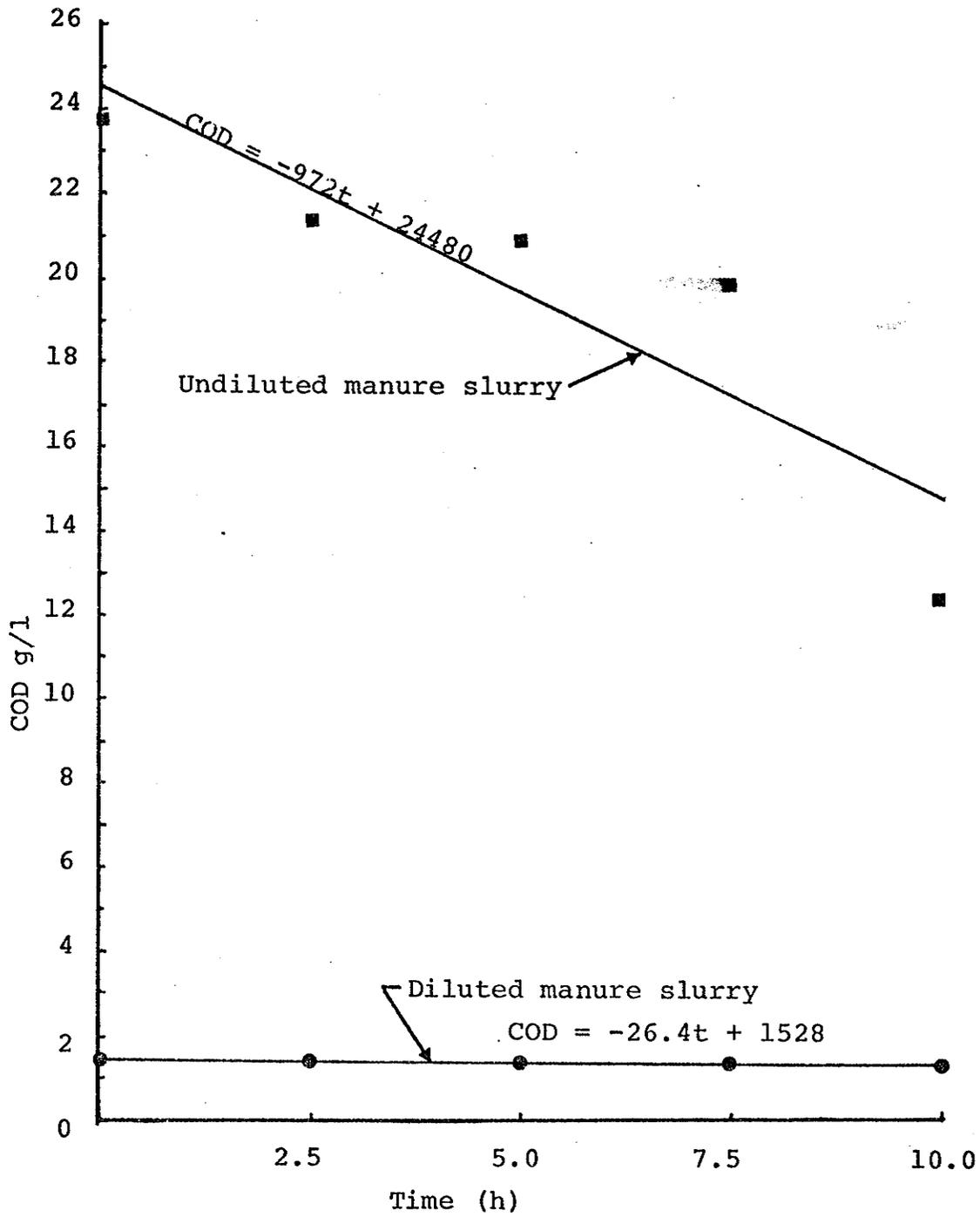


Figure 4.2.2. Relationship between COD reduction to ozone treatment time.

Undiluted Waste

$$\begin{array}{ll} \text{COD (mg/l) remaining} = -972 t \text{ (h)} + 24480 & \text{Equation 4.2.1.} \\ & (r = 0.892) \end{array}$$

Diluted Waste

$$\begin{array}{ll} \text{COD (mg/l) remaining} = -26.4 t \text{ (h)} + 1528 & \text{Equation 4.2.2.} \\ & (r = 0.985) \end{array}$$

By differentiating the foregoing equations, the COD reduction rates can be obtained. These reduction rates can best be described by the following zero-order reaction:

$$\frac{d(\text{COD})}{dt} = \text{CONSTANT}$$

The existence of the zero-order reduction rate for COD would indicate that the diffusion of ozone through the liquid film surrounding the organic matter was rate-controlling since it is not dependent on the concentration of ozone in solution.

The zero-order reduction rate for COD is supported by the findings of Marsh and Panula (1965) regarding BOD reduction with ozone. In their study, domestic sewage contained in a 208-l contact column was ozonated using a Welsbach T-23 ozonator with an air-oxygen flow rate of 1.416 l min. The average BOD of the raw sewage used was 300 mg/l. Analysis for the determination of BOD using two four-ml dilutions indicated negative rate constants of 0.933 and 1.146 mg/l BOD/min respectively.

In the oxidation of organic material by ozone, only one atom of oxygen from the O_3 molecule is considered highly reactive. As a result, six grams of ozone should be consumed in the oxidation of one gram of COD with four grams of molecular oxygen as a by-product. The results of this study demonstrate that the weight ratio of O_3 per g COD removed ranges from approximately 0.1 g O_3 per g COD (ie. 331 g O_3 per 2450 g COD) up to 6 g O_3 per COD (ie. 331 g O_3 per 56 g COD) for undiluted and diluted manure slurries, respectively.

This indicates that the ozone efficiency in reducing COD dropped as the manure slurry becomes more dilute. This is probably accounted for by the presence of a greater total amount of easily oxidizable organics in the undiluted slurry. Since less than the expected 6 g O_3 per g COD removed are consumed in the ozonation of the undiluted manure slurry, auto-oxidation (Evans, 1972) would appear to be involved in the reaction mechanism. These findings are in keeping with the results of a study by Kirk et al (Evans, 1972) in which less than expected 6.0 g O_3 per COD removed were consumed in the first stage of a five-stage reactor. The ozone consumption varied from 2.15 to 5.04 g O_3 per g COD removed in stages one and five respectively.

4.3. Effect on Total Solids (TS) and Total Volatile Solids (TVS)

In general ozonation was found to have little effect on the total solids content or the total volatile solids content as illustrated in Figure 4.3.1. The diluted swine manure slurry exhibited a slight reduction in total solids and total volatile solids. A linear regression analysis of the data of diluted manure slurry indicates negative reduction rates for total solids and total volatile solids of 14.64 mg/l/h and 31.24 mg/l/h respectively.

Part of the solids reduction may have been caused by solids being carried out of the column with the foam and exhausted air stream. Nebel et al (1973) also experienced solids removal by frothing during ozone treatment of municipal secondary effluents.

Low initial solids content values were experienced with the undiluted manure slurry. Although the undiluted slurry was mixed for five minutes prior to the commencement of ozonation, the low initial solids content values may have resulted from insufficient premixing. Visual observations of the diluted manure slurry, indicated that ozonation had a significant effect on increasing the settling rate of solids. Unfortunately tests on the solids settling rates, which could confirm this observation, were not performed.

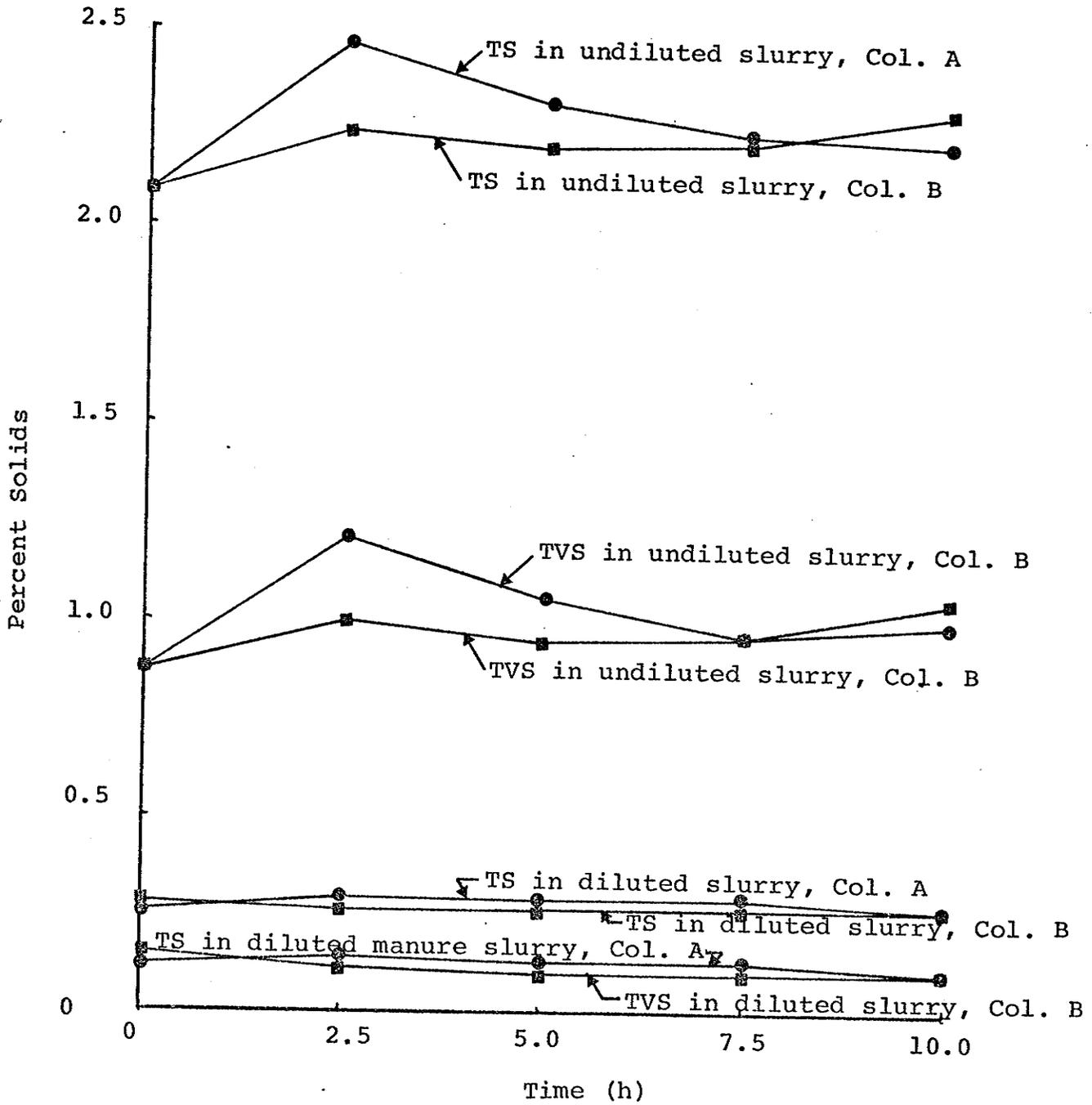


Figure 4.3.1. Effect of ozone treatment on total solids (TS) and total volatile solids (TVS) in swine manure slurries.

4.4. Effect on Volatile Fatty Acid Content

Ozonation had no significant effect on the volatile fatty acid content of either the diluted, or undiluted swine manure slurries in these tests as illustrated in Figure 4.4.1. However, the number of replicates tested in this analysis was insufficient to rule out the possibility of any relationship.

4.5. Bacteriological Effects

The changes in the bacteriological quality of swine manure slurries subjected to ozonation, as measured by the total plate count, are illustrated in Figure 4.5.1. The reduction in total plate count of the diluted manure slurry, during the ozone treatment was more rapid and pronounced than that of the undiluted slurry. A reduction of 99.8 per cent was realized in the diluted wastewater while an 81 per cent reduction was obtained in the undiluted wastewater.

A least-squares linear regression was performed on the data and the results are illustrated in Figure 4.5.2. The two following equations can be used to describe the relationships between the number of bacteria and the ozone treatment time (t):

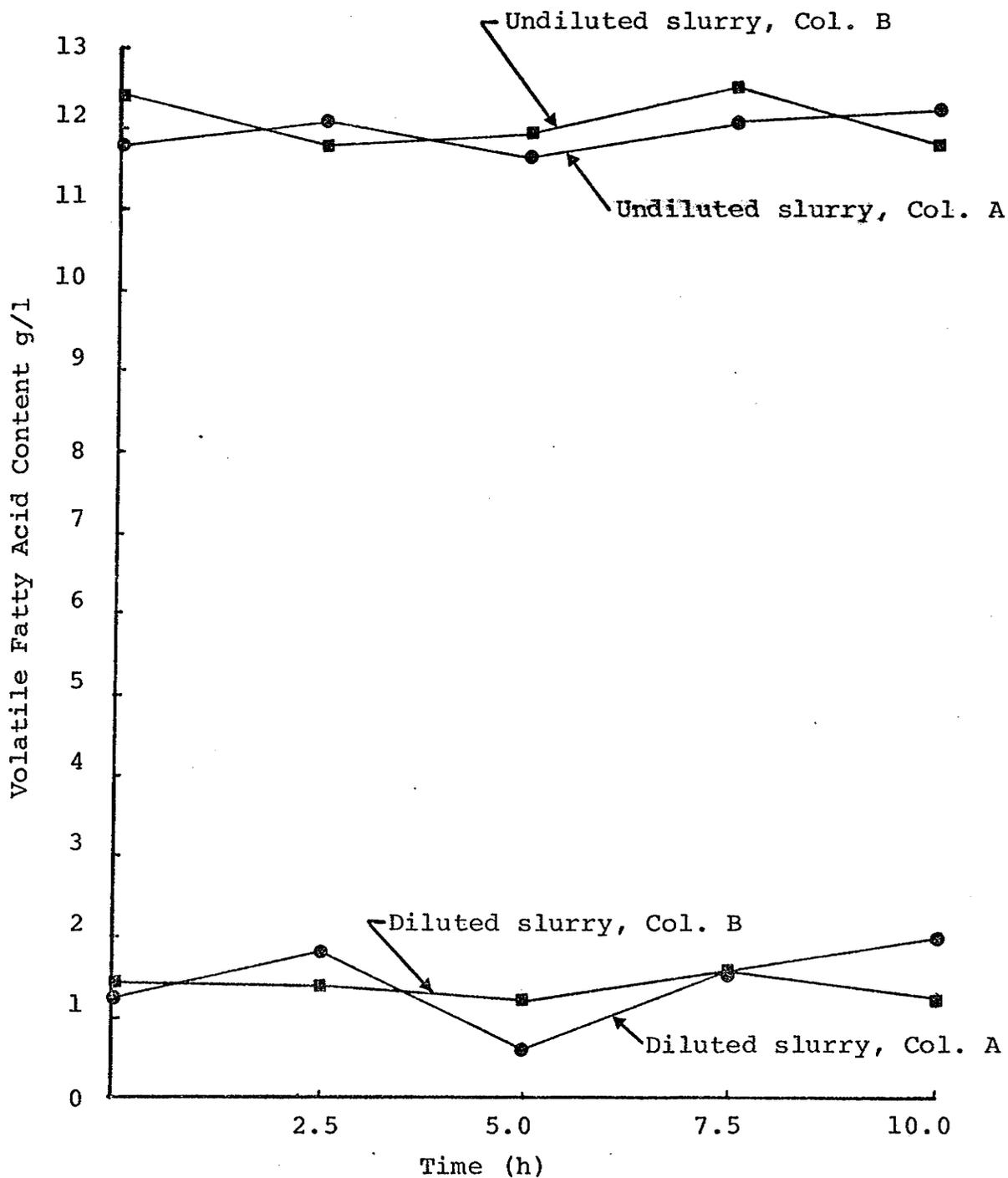


Figure 4.4.1. Volatile fatty acid content of diluted and undiluted manure slurries vs ozone treatment time.

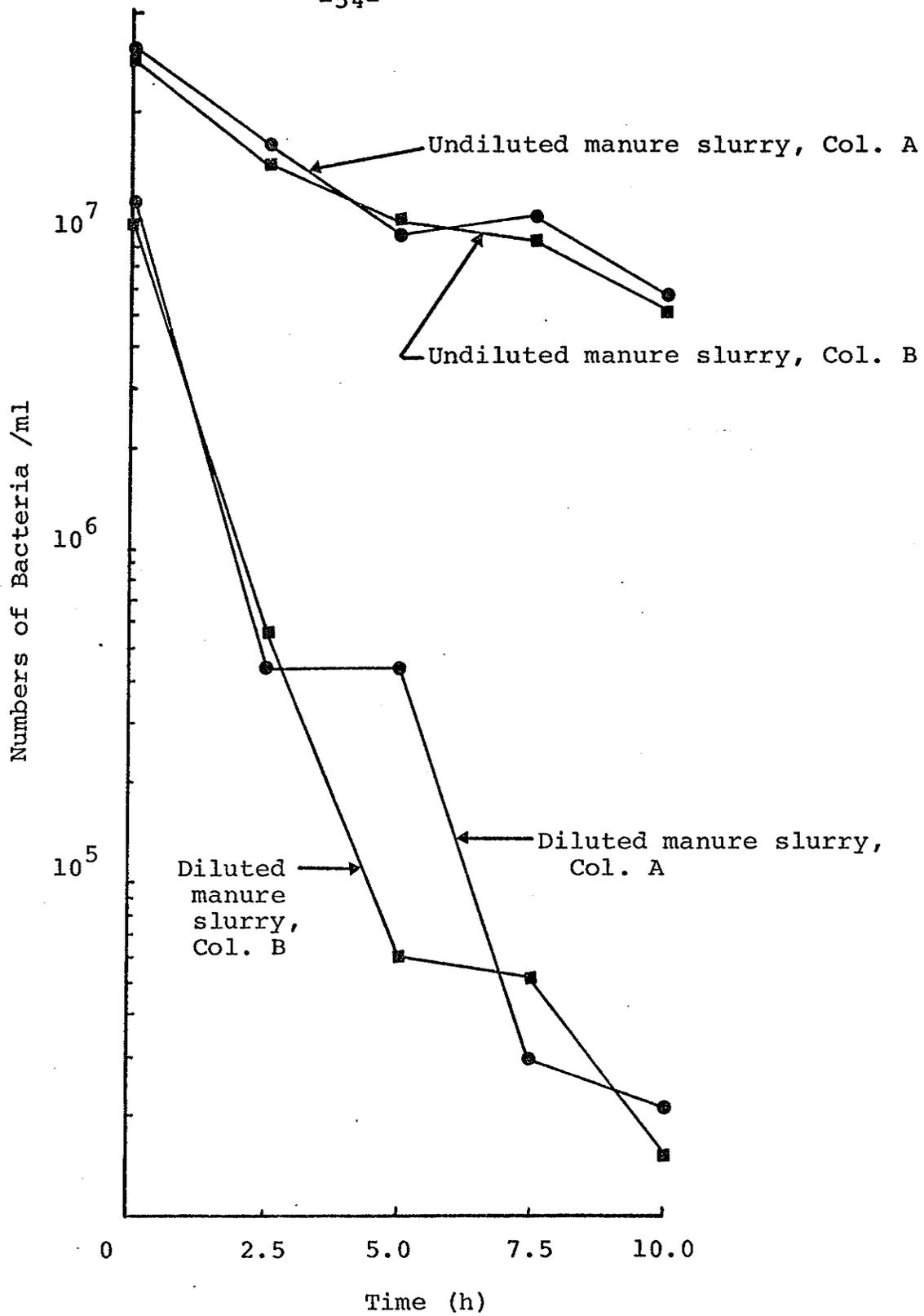


Figure 4.5.1. Effect of ozone treatment on the standard plate count of diluted and undiluted swine manure slurries.

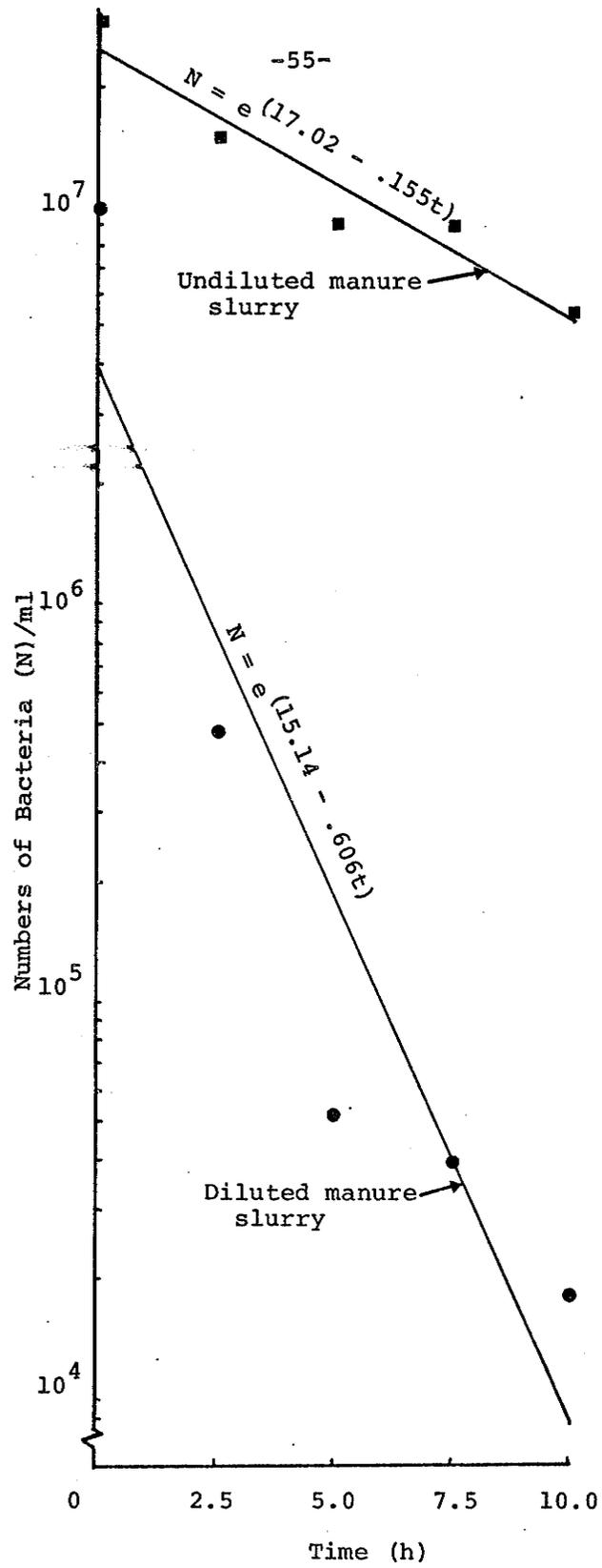


Figure 4.5.2. Relationship between bacterial kill and ozone treatment time.

Undiluted Waste

$$N = e^{(17.02 - .155t)}$$

Equation 4.5.1.

(r = 0.958)

Diluted Waste

$$N = e^{(15.14 - .606t)}$$

Equation 4.5.2.

(r = 0.933)

where N = number of organisms/ml

and t = time (h.)

From Equations 4.5.1. and 4.5.2. it is apparent that the bacterial kill follows a logarithmic function. Consequently, sterilization will only be achieved with an extremely long contact time. Therefore, the practical application of ozonation as a sterilization process for swine manure slurries is highly questionable due to economic considerations of extended treatments.

By plotting both the reduction in COD and the bacterial kill on a percentage basis, versus ozone treatment time, the relationship between bacterial kill and manure slurries with varying oxygen demands is illustrated. In Figure 4.5.3. the more rapid bacterial kill of the diluted manure slurry, having a lower COD than the undiluted slurry, is illustrated. However, this should not be interpreted as meaning that as the COD of a manure slurry is reduced during ozonation, the rate of bacterial kill increases.

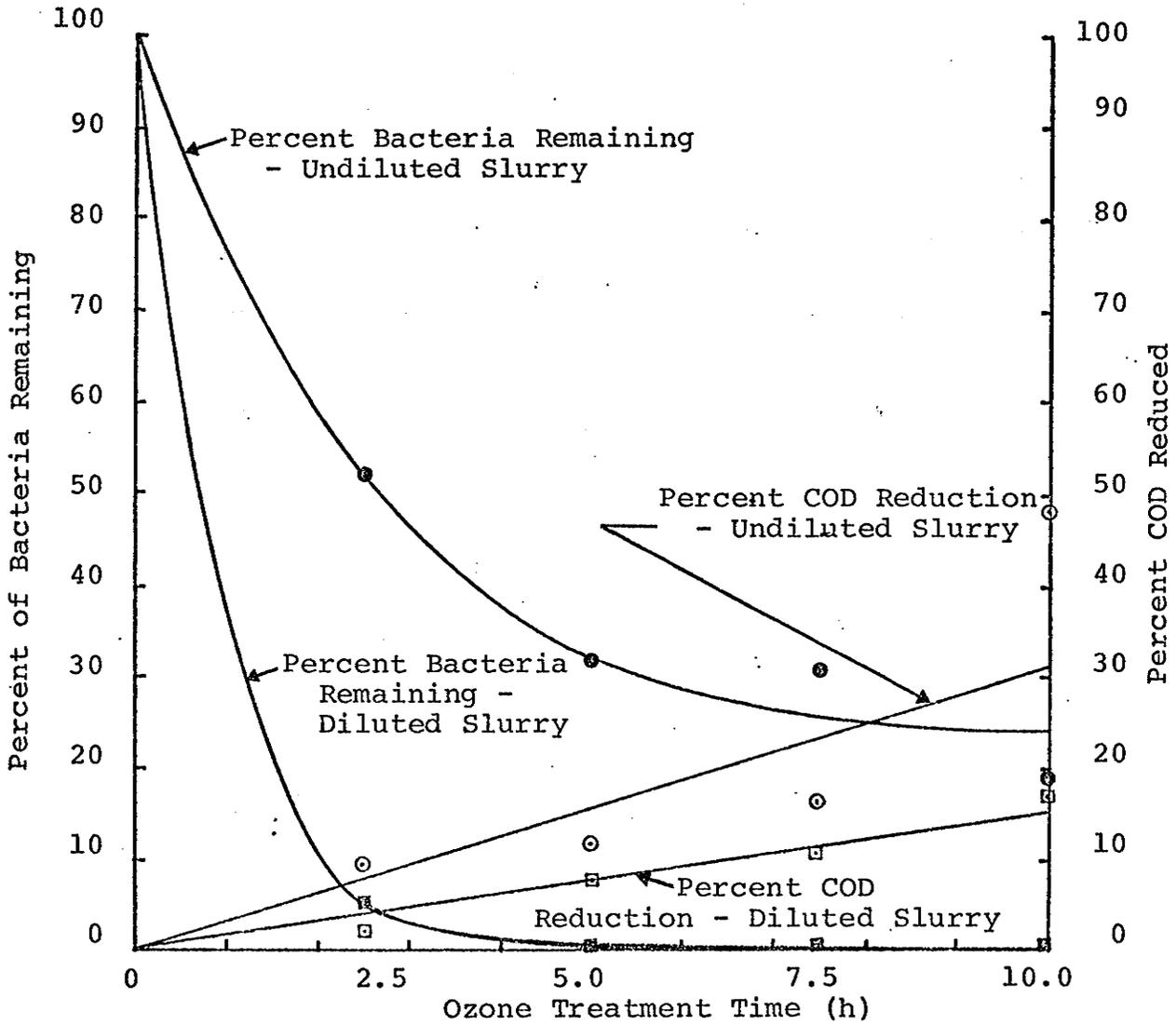


Figure 4.5.3. Relationship of bacterial kill to COD reduction of swine manure slurries.

The effect of a more dilute manure slurry is to increase the susceptibility of organisms to ozone attack, by reducing the amount of protective organic material in which they can hide. The rate of bacterial kill drops rapidly when only the bacteria which are protected by organic matter remain, since ozone must then attack the organic material and the organisms simultaneously.

4.6. Effect on Color

No significant color reduction was observed in the undiluted manure slurry, although a color change from charcoal black to dark bluish green was noted. A color reduction was observed in the diluted manure slurry. Samples of the ozonated manure slurry are illustrated in Figure 4.6.1. The samples, as shown from left to right, were ozonated for time periods of 0, 5, and 10 h.

4.7. Specific Observations on Process Performance

From the data presented in Section 4.2 it is apparent the ozone is the powerful oxidizing agent it is reported to be. Also, ozone proved itself as a highly efficient bactericide. Unfortunately, a trade-off exists between ozone's oxidizing and bactericidal qualities. Since the primary reason for employing ozone treatment was to control or eliminate bacterial activity which generates



Figure 4.6.1. Samples of diluted swine manure slurry subjected to ozonation for 0, 5, and 10 h (l to r).

odour, the bactericidal effect must be maximized at the expense of ozone's oxidizing capacity. To accomplish this selective use, the COD load and therefore the organic solids content of the manure slurry must be reduced. Therefore in a full-scale operational system a much more effective pretreatment for solids removal is required.

Ozonation also caused changes to the odour from the treated slurries. The permeating nature of the odour was reduced in both of the treated slurries, with a tallowy

odour being exhibited by the diluted slurry. Therefore in terms of odour reduction, ozonation is effective on diluted slurries and would probably be equally effective on non-diluted slurries which undergo effective pretreatment for solids removal.

During ozonation foaming occurred in both the diluted and undiluted slurry. The rate of foaming slowed substantially during both treatment periods, but never stopped. Therefore, in any full-scale treatment system, special provisions will be required to deal with the foaming problem.

CHAPTER 5. CONCLUSIONS

The conclusions based on the findings of this investigation concerning ozonation of swine manure slurries are:

- (1) Ozonation increases the pH of manure slurries;
- (2) During ozonation the per cent COD removed corresponds to increase in the pH of manure slurries;
- (3) Manure slurries with a high initial COD level exhibit more rapid COD reduction rates than slurries which have a low initial COD level;
- (4) The COD reduction rate is constant for any particular slurry. Diffusion of ozone through the liquid film surrounding the organic matter appears to be the rate-controlling factor;
- (5) Ozonation does not appear to have a substantial effect on volatile fatty acid content, total solids content, or total volatile solids content of manure slurries;
- (6) The bacterial kill rate in ozonated slurries follows a logarithmic function. The maximum bacterial kill achieved was 99.8 per cent with the diluted manure slurry;

- (7) Pretreatment for organic solids removal is required to maximize bacterial kill;
- (8) Ozonation of diluted manure slurries provides substantial color reduction.
- (9) Ozone treatment, with its strong bactericidal quality, is effective in controlling the odours from diluted swine manure slurries; however, odourant data was not used to establish a numerical measure of this control.

CHAPTER 6.

RECOMMENDATIONS FOR FURTHER STUDY

The findings obtained from this study indicate a need for additional research into more effective solids separation techniques. The importance of effective solids removal from manure slurries prior to ozonation cannot be overstated, since it has a definite effect on the bacterial kill rate.

Additional research work is required on the design of a continuous-flow ozone treatment system. Particular attention should be given to the design of the ozone injection equipment since efficient ozone transfer is essential.

Further investigation into the auto-oxidation of COD during ozonation should be considered. This may provide the key to a very effective and efficient treatment process.

REFERENCES

- A.P.H.A., A.W.W.A., W.P.C.F., 1971, Standard Methods for the Examination of Water and Wastewater, 13th Edition.
- Barron, E.S., 1954. "The Role of Free Radicals of Oxygen in Reactions Produced by Ionizing Radiation", *Radiation Research*, Vol. 1, p. 109.
- Boelter, E.D., G.L. Putnam, and E.I. Lash, 1950. "Iodometric Determination of Ozone of High Concentrations", *Analytical Chem.* Vol. 22, No. 12, p. 1533.
- Boucher, P.L., M.R. Lowndes, G.A. Truesdale, E. Windle Taylor, N.P. Burman and S.B. Poynter. 1968. "Use of Ozone in the Reclamation of Water from Sewage Effluent", *Institute of Public Health Engineers Journal*, Vol. 67, p. 75.
- Boucher, P.L., 1965. "Microstraining, Micronzone and Demicelisation Applied to Public and Industrial Water Supply", *Water Treatment Symposium*, Adelaide, South Australia.
- Boyd, A.W., C. Willis and R. Cyr, 1970. "New Determinations of Stoichiometry of the Iodometric Method for Ozone Analysis at pH 7.0", *Analytical Chem.* Vol. 42, p. 670.

- Bringman, G., 1955. "Determination of the Lethal Activity of Chlorine and Ozone on E. coli", Water Poll. Abs., Vol. 28, p. 12.
- Diaper, E.W.J., 1970. "Ozone in Water Treatment", Western Canada Water and Sewage Conference.
- Evans, F.L. (Ed.), 1972. Ozone in Water and Wastewater Treatment, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan.
- Hach "Colorimeter" Methods Manual, 1971. 7th Edition
Hach Chemical Corporation Arnes, Iowa, p. 124-125.
- Hodgenson, J.A., R.E. Baumgardner, B.E. Martin and K.A. Rehme, 1971. "Stoichiometry in the Neutral Iodometric Procedure for Ozone by Gas-Phase Titration with Nitric Oxide", Analytical Chem. Vol. 4, No. 8, p. 1123.
- Holman, J.P., 1971. Experimental Methods for Engineers, 2nd Edition, p. 230, McGraw-Hill Book Company, New York.
- Huibers, D.Th.A., R. McNabney and A. Halfon, 1969. "Ozone Treatment of Secondary Effluent from Wastewater Treatment Plants", Report No. TWRC-4, Federal Water Pollution Control Administration U.S. Department of the Interior, Cincinnati, Ohio.
- Kopczynski, S.L. and J.J. Bufalmi, 1971. "Some Observations on Stoichiometry of Iodometric Analysis of Ozone at pH 7.0", Analytical Chem. Vol. 43, No. 8, p. 1126.

Marsh, G.R. and G.F. Panula, 1965. "Ozonation in the BOD Reduction of Raw Domestic Sewage", Water and Sewage Works, Vol. 112, No. 10, p. 372.

Murray, R.G.E., P. Steed and H.E. Elson, 1965. "Location of Mucopeptide of Selections of the Cell Wall of E. coli and Other Gram-Negative Bacteria", Canadian Journal of Microbiology, Vol. 11, p. 547.

Nebel, C., R.D. Gottschling, R.L. Hutchison, T.J. McBride, D.M. Taylor, J.P. Pavoni, M.E. Tittlebaum, H.E. Spencer and M. Fleischmans, 1973. "Ozone Disinfection of Industrial-Municipal Secondary Effluents", Journal W.P.C.F., Vol. 45, No. 12, p. 2493.

Parry, E.P. and D.H. Hern, 1973. "Stoichiometry of Ozone Iodide Reaction: Significance of Iodate Formation", Environmental Sci. Technol. Vol. 7, p. 65.

Rosen, H.M., 1973. "Use of Ozone and Oxygen in Advanced Wastewater Treatment", Journal W.P.C.F., Vol. 45, No. 12, p. 2521.

Scott, D.B.M. and E.C. Leshner, 1963. "Effect of Ozone on Survival and Permeability of E. coli", Journal of Bacteriol., Vol. 85, p. 567.

Shecter, Hans, 1973. "Spectrophotometric Method for Determination of Ozone in Aqueous Solutions", Water Research, Vol. 7, p. 729-739.

Smith, D.K., 1969. "Disinfection and Sterilization of Polluted Water with Ozone", Report AM-6704, Ontario Research Foundation, Sheridan Park, Ontario, Canada.

Thirumurthi, D., 1968. "Ozone in Water Treatment and Wastewater Renovation", Water and Solid Waste, R-106 to R-114.

Weast, R.C. (Ed.), 1974. "Handbook of Chemistry and Physics, 54th Edition, Chemical Rubber Company, Cleveland, Ohio.

Wei, Y.K. and R.J. Cvetanovic, 1963. "Study of Vapour Phase Reactions of Ozone with Olefins in the Presence and Absence of Molecular Oxygen", Canadian Journal Chem., Vol. 41, p. 913.

APPENDIX A

Run	Ozone Output	g/h
1	32.9	
2	32.9	
3	33.3	
4	33.1	
5	32.9	
6	33.5	

Mean

$$\bar{x} = 33.1 \text{ g/h}$$

Standard Deviation

$$s = 0.253$$

95% Confidence Interval

(t distribution)

$$\bar{x} \pm t_{\alpha/2} s / \sqrt{n}$$

$$\alpha = 0.5$$

$$33.1 \pm 1.13 \text{ g/h}$$

$$t = 2.776$$