THE TREATMENT OF A MUNITIONS MANUFACTURING WASTE WITH LIME, CHLORINE AND PERMANGANATE

by

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INTRODUCTION

The purpose of the study reported in this thesis was to investigate the chemical-physical treatability of the wastewater resulting from a TNT manufacturing process. The chemical-physical methods used in this investigation included excess lime coagulation and chemical oxidation employing either chlorine or potassium permanganate as oxidizing agents. In addition a process using excess lime combined with an oxidizing agent was also investigated.

The waste from the Radford Army Ammunition Plant (RAAP) trinitrotoluene (TNT) manufacturing process was selected for study. This material may be characterized as high in solids, nitrates, and sulfates, low in pH, and high in temperature immediately before discharge. The wastewater contains not only TNT, but various other aromatic compounds which have not yet been identified.

Aromatic organic compounds have been successfully removed from water supplies and wastewaters by the use of oxidizing agents, carbon absorption, biological degradation, and chemical precipitation. Data previously presented by Nay (10) confirmed the use of lime as a possible method of treating this TNT waste. However, no information was available on the use of oxidizing agents as a possible method of treatment of the TNT waste from the new counter flow process now being used at the Radford Arsenal. It is known, however, that some tests were conducted using permanganate alone and that the preliminary results obtained were not overly promising (5).

During this investigation, the use of excess lime coagulation and oxidizing agents both separately and in combination was assessed in the treatability of the selected TNT waste. Removal of the aromatic compound was established through the use of short term batch studies. These studies were intended to ascertain the optimum means of using these processes for physical-chemical removal of the aromatic compounds from the TNT waste and to establish whether these methods may provide an economically feasible method of treatment.

LITERATURE REVIEW

The use of coagulants and oxidizing agents in the treatment of industrial and municipal waters and wastewaters is not a new concept. It is, however, necessary to determine their effectiveness as tools in the treatment of new wastes which are the unwanted by-product of our advancing technology.

Lime, chlorine, and permanganate have played an important part in the treatment of many contaminated waters. They have been used to remove colloidal matter, color, taste, odor, and organic matter. However, very little work has been reported on the use of these compounds in the treatment of the waste from the new counter-flow TNT manufacturing process. In view of the possible application of these processes a need exists to investigate the use of these compounds in the treatment of the waste from this industrial process.

Lime Treatment

The use of lime in the treatment of waters which contain undesirable compounds is well established. It may be used in a water softening process, in a coagulation process for the removal of inorganic and organic colloids, and as an adsorbent for the removal of color from a textile dye waste (7, 20).

Lime is the common name usually used to designate the compound calcium hydroxide ($Ca(OH)_2$). The main source for the production of lime is limestone ($CaCO_3$), which is crushed and heated in a kiln. When $CaCO_3$ is heated, the following reaction occurs:

$$CaCO_3 \xrightarrow[\text{heat}]{\Delta} CaO + CO_2$$

The products of the reaction are carbon dioxide and calcium oxide, which is known as quicklime. Quicklime is very difficult to handle because of its affinity for water. For this reason, water is usually added to the calcium oxide in a process known as slaking to form calcium hydroxide or slaked lime. Slaked lime is normally the form used in treatment processes (7).

The use of coagulants to destabilize colloidal systems is one of the most effective methods of water treatment. However, the use of lime as a primary coagulant is rare in comparison to its use as a secondary coagulant and coagulant aid (11). Lime is widely used in conjunction with iron and aluminum salts to maintain pH control, assist in charge neutralization, and to promote floc formation. In some cases, the use of lime as a primary coagulant to destabilize specific colloidal systems has been very effective where other coagulants have proved uneconomical or ineffective. An example of this effectiveness is in the removal of colloidal color from textile finishing and pulp and paper mill wastewaters (20).

There are four accepted ways of destabilizing a colloidal system (7, 14, 20). These include:

1. Adsorption and charge neutralization brought

about by the addition of a hydrolyzable metal ion as a cationic polyelectrolyte. This process lowers the zeta potential largely because of formation of charged hydrous oxide species which adsorb on colloids in the system.

2. Double layer compression, which is the lowering of the zeta potential by employing a strong electrolyte. This process allows the short range Van der Waals forces of attraction to become effective in bringing the colloidal particles together.
3. Enmeshment in a precipitate caused by an excessive dosage of coagulants in which the colloid particles are trapped in the settling floc. This process is frequently termed "sweep coagulation."
4. Adsorption and interparticle bridging involving the use of long chain polymers. These polymers contain two or more groups which interact with sites on adjacent colloidal particles thereby producing a larger floc.

Absorption and enmeshment are of particular interest when using excess lime coagulation as the method of treatment. When lime is introduced in excess quantities to a system resulting in the rise of pH to above 9.3, an insoluble calcium hydroxide floc is formed (11, 14). This floc provides a sweeping action in the system, collecting the colloidal particles as the floc settles. The insoluble floc thus has the ability to adsorb or trap the color present within the system as reported by Wilbourn (20). Wilbourn found that the excess lime treatment of a textile finishing waste resulted in the removal of about 94 per cent of the color from the dye waste.

The large lime quantities necessary to promote sweep floc conditions make regeneration of the spent lime feasible. Thermal regeneration of lime is the most common method of lime recovery. The organic material that has been trapped by the lime floc is burned away leaving the inorganic compound, calcium oxide. However, special consideration must be taken when regenerating lime which has been used to remove explosive compounds (15). Reuse of the lime without regeneration has also been found effective in some cases. This application usually involves mixing of new lime with lime removed from the settling basin, thus lowering the cost of the operation.

Chemical Oxidation Processes

Oxidation is defined as any process which increases the proportion of oxygen or acid-forming elements or radicals in a compound (18). Simplifying, one can say that oxidation is a loss of electrons, and an oxidizing agent is any substance that can add electrons. The best known oxidizing agents are oxygen, the halogens, ozone, potassium permanganate, and hydrogen peroxide. While these compounds are only a few of the available oxidizing agents, they are the most important in water treatment (14). The complete oxidation of an organic compound produces carbon dioxide and water. The process by which this occurs is known, especially for the simple hydrocarbons (8).

Chlorine Oxidation

Chlorine is a member of the halogen (salt-forming) group of elements. It is a greenish-yellow gas, combining directly with nearly all elements. Most of the chlorine produced is in the form of chlorinated compounds which are used for sanitation, pulp bleaching, disinfectants, and textile processing (14, 18).

Chlorine is used in water supplies as a disinfectant and for taste and odor control. Depending on the size of the treatment facilities, chlorine is usually used in the form of chlorine gas at large treatment facilities, and as calcium hypochlorite at smaller treatment plants. When mixed with water, the following reactions take place:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$Ca(OCl)_2 + 2H^+ \longrightarrow 2\ HOCl + Ca^{++}$$

The hypochlorus acid which is formed is a much stronger oxidant than is molecular oxygen in air (2, 14).

In a recent study conducted by the Manufacturing Chemists Association (19), nitrobenzene was shown very unreactive to chlorination due to the electron-attracting and ringdeactivating effects of the nitro groups. These studies, however, were conducted in dilute aqueous solutions, and no determinations were made involving the nitro-benzene compounds in solutions containing large concentrations of chlorine. It was discovered that phenols did react readily with chlorine. This reactivity was attributed to the ring-activating, electron-releasing properties of the hydroxide functional group. The reaction produced chlorophenols by stepwise substitution at the 2, 4, and 6 positions on the aromatic ring. Ring oxidation followed the formation of 2, 4, 6 trichlorophenol, but no determination of the oxidation products was made. Although chlorine is accepted as an effective oxidizing agent, very little is known about final products of chlorine oxidation.

Potassium Permanganate Oxidation

Potassium permanganate ($KMnO_4$) has long been known to be an effective compound in the oxidation of iron and manganese, but it was not until fairly recently that it was used as an oxidizing agent for the removal of organic compounds. Recent studies have shown that potassium permanganate is effective in the control of taste and odor problems created by algae and in the breakdown of organic refractories and aromatic hydrocarbons.

A field study conducted by Cherry (3) using potassium permanganate to control a taste and odor problem caused by algae in a reservoir produced effective results. The addition of permanganate was made at the intakes and no other chemicals were added until after the primary mixer and the clarifiers had been passed. After the addition of the potassium permanganate, the water had a deep reddish-purple color, fading to a brown or pink color as the water progressed through the system. The color caused by the permanganate was removed by the addition to the water of activated carbon before passing to the filters. Later it was found that the color caused by the permanganate could be eliminated by reducing the dosage to a level wherein the color disappeared before final filtration (4, 21). The odor was drastically reduced with a permanganate dosage of 7 to 10 ppm. This method proved more economical than activated carbon treatment to reduce taste and odor.

Spicher and Skrinde (16, 17) conducted studies on the reaction of permanganate with organic refractories and aromatic compounds. They found the reaction kinetics to be first order and the rate to be dependent on such variables as temperature, pH, organic concentration, and type of organic present. Using peak height analysis developed by Wright, they were able to determine the concentration of permanganate in solution versus the amount that was originally added. By plotting the curve on semi-log paper, a determination of a formula was made for oxidation of organics by permanganate. The equation is as follows:

$$y = kx^{0.3}$$

where:

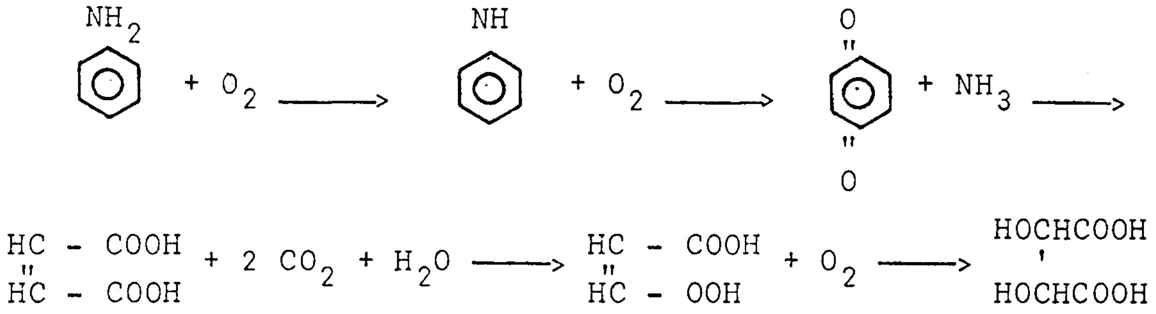
y = permanganate utilized (or organic

material oxidized)

x = permanganate added

k = constant, depending on the condition of the reaction

In reactions between permanganate and ring compounds, the double bond appeared to be destroyed, breaking the ring. No end products of the reaction were determined, but a theory was developed for the oxidation of anilines as follows:



Nitrobenzene, a ring compound similar to trinitrotoluene, can be reduced to aniline in the presence of zinc and hydrochloric acid (8). Whether the same reaction mechanism is true for trinitrotoluene is not known, for no reference could be found involving this type of reaction.

Manufacture of TNT

Information involving previous experimental methods of treating the wastewater from the TNT manufacturing process is not readily available through normal channels of communication used by the engineering profession. Security requirements invoked by the Department of Defense limit the amount of material available for publication, especially that material dealing with the recently developed counter-current continuous flow process now being used at the Radford Army Arsenal Plant. An unclassified review of the TNT manufacturing process has been presented by Nay (10), and this review is the source of the following discussion.

TNT is an abbreviation for trinitrotoluene. It is an aromatic hydrocarbon resulting from the nitration of toluene, a methylated benzene compound. The toluene ($CH_3C_6H_5$) is nitrated in three steps to form 2-, 4-, 6-, trinitrotoluene ($CH_3C_6H_2(NO_2)_3$), otherwise known as alpha trinitrotoluene (α-TNT). Nitric acid is the nitrating agent and sulfuric acid is used as the catalyst. After the nitrating process is completed, the molten crude TNT must be purified to remove the unstable TNT isomers caused by incomplete nitration of the toluene or improper structuring of the nitrated toluene. The purification involves washing the molten, crude TNT with sodium sulfite (trade name, sellite). The sellite dissolves the unstable TNT isomers which can then be flushed away leaving the α-TNT, which is insoluble in sellite. Other compounds which are removed in the washing process include hexanitrodibenzl, tetranitromethane, cyanic acid, trinitrobenzoic acid, dinitrocresol, phenol, and various nitrotoluene sulfonic acids.

The wastewater from the TNT manufacturing process is called "yellow water" and "red water." The yellow water results from washing crude TNT before purification with sellite.

This washing removes excess acids. The resulting yellow water contains nitric acid, sulfuric acid, and trace quantities of nitrobodies. Yellow water at RAAP is presently being neutralized with sodium hydroxide and then discharged into New River after dilution. Red water is the wastewater solution resulting from the sellite purification. In the past, the most widely accepted complex associated with red water has been hexanitrodibenzyl; however, recently this has been proven to be untrue. Red water from RAAP is presently being shipped to a pulp mill where it is used to break down the wood pulp into fibers (5).

A. B. Centaur Co. and Canadian Industries Ltd. designed the manufacturing process for TNT, which was put into operation at RAAP in 1967. It is a continuous nitration process that utilizes counter-current flow in the nitrating process and in the purification process. The main differences between the waste produced by the batch process and the counter-current continuous flow process is that the red water is not combined with the yellow water in the continuous flow process and the cooling water flows in a separate piping system and is not mixed directly into the manufacturing process. The production of 100 lbs. of TNT requires 47 lbs. toluene, 210 lbs. sulfuric acid, 125 lbs. nitric acid, 6 lbs. sodium sulfite, 1 lb. soda ash, and 650 lbs. water. The resulting waste volume is about 100 gallons per 100 lbs. of TNT produced.

TNT Wastewater Characterization

Waste from the TNT manufacturing process is highly variable as to the concentration of each of the major constituents. Table 1 shows two characteristic samples of TNT waste. Sample 1 is the characterization of a 24-hour composite sample (taken June 13-20, 1969) made by the U.S. Army Environmental Hygiene Agency (Survey No. 24-011-69/70) as reported by Nay (10). Sample 2 is the characterization of a grab sample (taken April 26, 1970) by Nay. The wastewater does show certain general characteristics which include low pH, high temperature, high solids, nitrates, sulfates and color and various forms of the TNT isomers. The above analyses were conducted on the yellow water which has a reported average flow at RAAP of 0.23 million gallons per day (10). The waste is stored for approximately three days for equalization purposes, then neutralized with sodium hydroxide and diluted before discharge in the New River. The system was originally designed for lime neutralization, but equipment was not available to remove the sludge that settled in the neutralization basins (5).

Recent studies by the U. S. Army have shown that most of the TNT in the wastewater either reacts with other compounds in the waste stream or decomposes between the time it enters the equilization basin and the time it leaves. The compounds that the TNT does form are complex and have not yet

TABLE 1

TNT WASTE CHARACTERIZATION

(After Nay (10))

Concentration, mg./l. (except pH and temperature)

Parameter	Sample 1	Sample 2
TNT	20.3	145
pH	2.5	2.05
COD	64	274
TOC	59	-
nitrate as N	213	53
sulfate as SO_4	1821	842
color as standard color	161	228
total solids	2792	1160
volatile solids	1377	960
suspended solids	619	224
temperature	95°F	-

been identified. One major problem associated with these compounds is the dramatic increase in the color of the wastewater after discharge. Investigators have shown that the color developed by the TNT wastewater after discharge is a function of pH, sunlight and heat (10).

Treatment of TNT Wastewaters

The first extensive studies on the treatability of TNT manufacturing wastes were made by Schott, Ruchhoft, and Megregian in 1943 (12). These studies were conducted on the strong red water resulting from the batch method of TNT production. The investigation of the treatability of TNT waste included biological and chemical-physical treatment methods.

The TNT waste was found to be highly resistant to biological treatment due to the toxicity of waste. Nay (10) later demonstrated that while the red water was biologically untreatable, the yellow water could be treated by biological means with a removal efficiency of up to 84 percent at an α-TNT loading of 5 mg./l.

Treatment by physical-chemical methods included study of neutralization, chemical precipitation, fractionation, solvent extraction, ozonation, electrolytic reduction, activated carbon, chlorination, and bromination. These methods of treatment appeared either unsuccessful or uneconomical with the possible exceptions of the chlorine and bromine processes. The chlorine dosage necessary to achieve good color reduction of a waste sample that was diluted by a factor of 50 to 1 was 19 mg./l. of Cl_2 (9, 12).

Edwards and Ingram (6) performed further studies on the use of chlorine as a possible method of treating TNT waste. Using platinum cobalt as a color standard, they were able to reduce the color of the red water from 299,000 to 8,000 color units by using 15,000 to 25,000 ppm of chlorine at pH 1. By diluting samples to equal or less than 5,600 color units, they found a dosage of 2,200 ppm of calcium hypochloride would remove all the color. However, the color partially returned when the pH was increased.

Preliminary studies conducted by Nay (10) on the use of activated carbon and excess lime flocculation showed very promising results. The activated carbon was able to remove both color and TNT from the wastewater. A later study conducted by Schulte (15) showed that TNT removal by activated carbon was optimized when the waste was highly acidic, low in color, and when the carbon treatment was by the packed bed method.

Nay also reported three batch studies using excess-lime flocculation as a means of removing TNT from wastewater. The results from these studies showed a 66 percent removal of the TNT from the waste. The major drawback to this method of treatment was the increased color development due to the pH increase. The color in this scheme increased up to 60 times the original color. Nay also reported a 70 percent decrease in the color developed by lime coagulation followed by reacidification.

The new counter-current flow system has significantly altered the characteristics of the wastewater from the TNT manufacturing process at the Radford Arsenal. This alteration of the wastewater characteristics enhances the possibility of successful treatment by physical and chemical means. The purpose of this thesis is to determine if lime, chlorine and potassium permanaganate are feasible methods of treating the TNT manufacturing wastewater.

MATERIALS AND METHODS

During this investigation, tests were performed to determine the removal of TNT and color by the use of excess lime coagulation and oxidizing agents, chlorine and potassium permanganate. The purpose of this chapter is to describe the experimental techniques and procedures used in the research.

Color Analysis

The color of the waste was determined photometrically with the results being reported as "standard color unit," one color unit being the color produced by 1.0 mg./l. platinum in the compound potassium chloroplatinate.

Standard color units developed by the potassium chloroplatinate were of similar hue to that of the wastewater and the color complex developed in analysis for TNT by the Silas-Mason test. The dominant wave lengths were determined by the procedure described in Standard Methods (1) in the Industrial Wastewater section (Procedure A. Spectrophotometric Method, ten ordinate modification).

The dominant wavelength analyses were performed with a Beckman model B Spectrophotometer using cuvettes with 1 cm. light path. The variation in dominant wave lengths for various solutions was 7 mμ and followed closely those determined by Schulte (15) and Nay (10).

A standard curve (Figure 1) was developed by using a

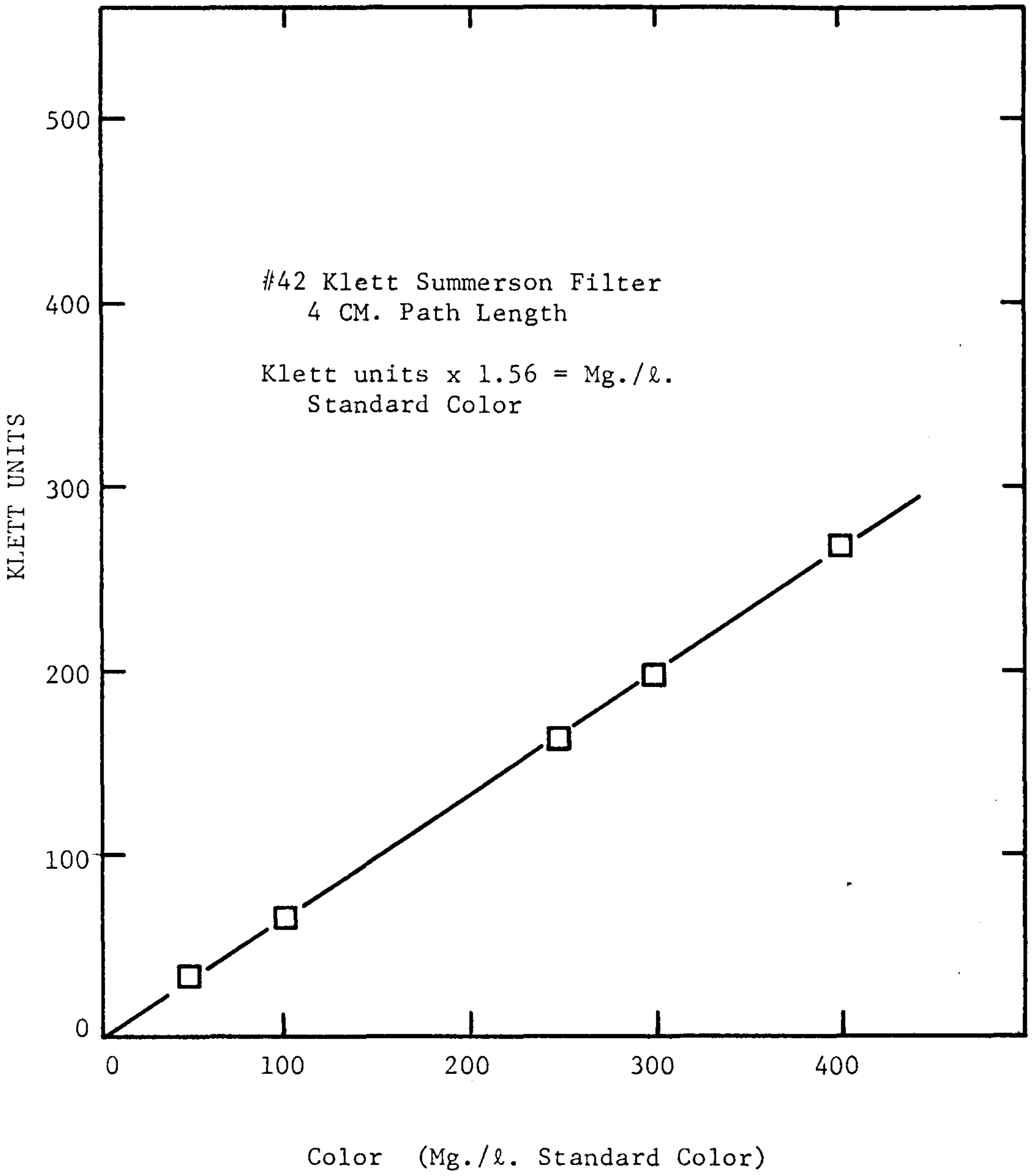


Figure 1. Standard Curve for Color

photometric colorimeter (Klett-Summerson Photoelectric Colorimeter, Model 9003) with a 4 cm. light path and a #42 blue filter. The absorbance recorded in terms of Klett units was determined for different concentrations of the color standard, potassium chloroplatinate.

TNT Analysis

The Silas-Mason test was used to determine the concentration of TNT in the waste. This test was developed by the personnel at the Radford Army Ammunition Plant to provide a quick method of determining the TNT concentration in the wastewater. The test involves a colormetric analysis of color development due to the addition of 2-diethylaminoethanol to the TNT waste. The color development was found to follow Beer's Law for concentrations of up to 50 mg./l. α-TNT.

The 2-diethylaminoethanol is believed to form color complexes with all nitroaromatic compounds found in the TNT waste. However, analytical data derived when the Silas-Mason Test is used for TNT analyses can be described in terms of α-TNT when α-TNT is used in preparing the standard curve. Therefore, data reported as "concentration of α-TNT" for the wastes should be interpreted to mean the concentration of all nitroaromatic compounds in the waste (15). This approach appears logical in view of the fact that all the nitroaromatic compounds in TNT waste appear to be toxic to the organisms of receiving waters. It has not been stated, however, that the reagent when added to the sample raises or decreases the pH of the samples to 11.1 ± .1.

The Silas-Mason Test procedures which follow are taken from the work of Schulte (15):

A. Filter the sample through Whatman No. 40 filter paper in a Buchner funnel.

B. Dilute an aliquot of the filtrate with distilled water to produce a concentration of TNT less than 50 mg./l.

C. Transfer 25 ml. of diluted sample into a small beaker. Add 5 ml. of 2-diethylaminoethanol.

D. Prepare a reagent blank with 25 ml. distilled water and 5 ml. diethylaminoethanol.

E. Heat the sample and the blank over a steam bath for 12-15 minutes.

F. Transfer the blank and the sample to 50 ml. volumetric flasks and dilute to 50 ml.

G. Filter the sample through a membrane filter, 0.45μ.

H. If the untreated sample contains color, prepare a color blank by diluting 25 ml. to 50 ml., but add no diethylaminoethanol.

I. Determine the absorbance of the sample and color blank (if used) with a Klett-Summerson Photoelectric Colorimeter using either the 2 or 4 cm. path length and a blue filter, #42.

The TNT concentration is determined by subtracting the absorbance (Klett units) of the color blank from the absorbance of the sample and expressing the difference as the concentration of TNT determined from a standard curve. The concentration must be multiplied by the dilution factor to determine the TNT concentration of the sample. The absorbance of the color blank can be subtracted from that of the sample because the color complex developed with diethylaminoethanol and the color of the waste itself have the same hue. Thus, they exhibit maximum absorbance at the same wavelength.

The TNT standard curve (Figure 2) was prepared from a solution containing 1-20 mg./l. α-TNT prepared by diluting a 50 mg./l. stock solution. The stock solution was prepared by diluting 10 mg. α-TNT (previously dissolved in approximately 20 ml. acetone) to 200 ml. with distilled water. Each standard was analysed by the Silas-Mason Test. No correction for inherent color was necessary because the α-TNT solutions were colorless.

Other Analytical Procedures

pH

All pH determinations were made with a Leeds & Northrup pH meter. The meter was standardized with a standard pH buffer solution prepared by Fisher Scientific Company. The pH meter probe was placed into the jars utilized in the jar test to monitor the lime dosing and neutralization process. This

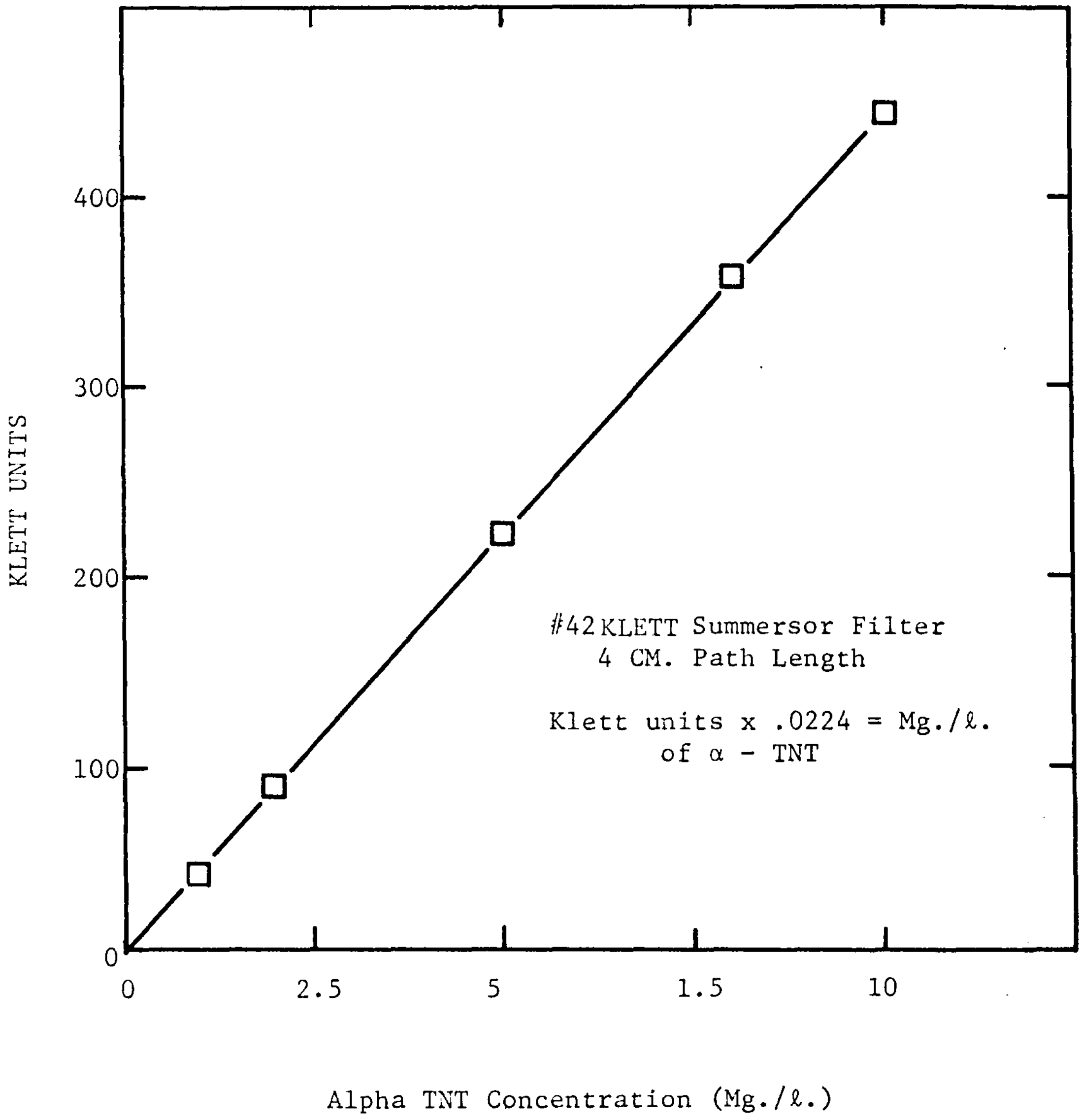


Figure 2. Standard Curve for Alpha TNT

procedure was necessary to achieve the desired pH because of the inaccuracy obtained in using data fromthe titration curve.

Solids

Total, suspended, and volatile solids were performed on all raw waste samples according to methods outlined in *Standard Methods*. Total solids were determined by evaporating a 100 ml. sample. The evaporated samples were then ignited in a 600°C. oven for twenty (20) minutes to determine the volatile solids. Suspended and volatile suspended solids were determined by vacuum filtering a 100 ml. sample through a Gooch crucible containing a glass-fiber filter. The Gooch crucible was dried at 103°C. to determine suspended solids and then ignited at 600°C. for twenty (20) minutes for the volatile suspended solid determination.

Sample collection and storage

The samples were collected in a five (5) gallon carboy at the Radford Army Ammunition Plant and transported to the Sanitary Engineering Laboratory at Virginia Tech. The samples were then mixed to provide uniform characteristics. The carboys were used as storage containers and were kept at room temperature away from any strong light sources. All tests were performed within five (5) days of sample collection.

Batch Studies with Lime

A commercial grade of calcium hydroxide was used during this investigation. The calcium hydroxide was first dissolved with distilled water before being added to the TNT waste samples. The samples were stirred at 100 R.P.M. in square jars on a Phipps and Bird Stirring Apparatus until the lime was completely mixed with the waste. The coagulation and flocculation process were visually controlled so as to maintain the floc in suspension for a one hour period. This required different paddle speeds for different dosages, since the lime floc became heavier as the dosage was increased.

A standard titration curve was developed for the TNT wastewater using lime as a titrant. This curve proved unsatisfactory in determining the lime dosage required to achieve specified pH's between the pH range of 4 to 11.

The pH of the samples was varied to determine the effectiveness of lime for the removal of nitroaromatic compounds at different pH levels. After flocculation at each pH, the lime floc was allowed to settle and the supernatant was carefully removed from the jars by volumetric pipets to prevent agitation of the settled floc. The pipeted samples were then filtered through Whatman #40 filter paper utilizing a vacuum of approximately 28 mm mercury. The filtered samples were tested for TNT concentration by the procedure previously described.

All tests involving the use of lime in combination with an oxidant were conducted by the procedure previously described, except that the time the lime·floc was maintained in suspension was varied with the experiment.

Activated Carbon Studies

A short term batch study was conducted using 12 x 40 Mesh Activated Carbon (Westvaco Nuchar, type WV-G) to determine the effectiveness of activated carbon to remove color from the lime treated wastewater. The wastewater samples were adjusted to pH 12 by lime addition and after the floc settled the supernatant was removed. One sample was adjusted to pH 7. The activated carbon was added to both samples, in varying dosages and flash mixed for three hours. The samples were then filtered and color determinations were made by the method previously described.

Chlorine Oxidation Studies

The source of chlorine used in this research was high test hypochlorite (HTH), manufactured by the Olin Chemical Corporation. A selected quantity of this calcium salt was added to distilled water and completely dissolved before addition to the TNT waste. Tests were then run involving the use of chlorine at different concentrations in conjunction with lime for the removal of color and nitroaromatic compounds.

The samples were adjusted to the desired pH by lime and then chlorine was added by pipeting. The chlorine contact time varied from six (6) hours for determination of the optimum pH for chlorine dosage, to twelve (12) hours for tests involving color reduction by chlorine. Color and TNT concentration were then determined by the methods previously described to determine the pH at which optimum color and α-TNT removal occurs as well as the extent to which removal of these compounds was achieved.

Potassium Permanganate Oxidation Studies

The potassium permanganate was prepared by adding the crystalline form of the reagent grade chemical to distilled water. Tests were then conducted to determine the effectiveness of permanganate for the removal of color and α-TNT.

Four different tests were conducted using permanganate. The first test involved the addition of increasing concentration of permanganate to the raw waste to determine color and α-TNT reductions at the different potassium permanganate concentrations. A six-hour contact period was utilized. The samples were first flash mixed for ten minutes and then allowed to stand for the rest of the contact period.

The second test involved the use of zinc sulfate which reacts with some types of nitroaromatic compounds to form aniline--which is known to be oxidizable by potassium permanganate. The zinc sulfate was added in increasing dosages to the raw waste and flash mixed for three hours. The permanganate was then added to the waste and flash mixed for ten minutes. Color and α-TNT reduction were determined after a six-hour contact period by methods previously described.

The third and the fourth tests involved the use of lime and permanganate with and without zinc sulfate at specified pH's. Color and α-TNT concentrations were then analyzed to determine the effectiveness of these methods of treatment.

Appropriate mixing times for the tests utilizing potassium permanganate were determined by the disappearance of the color originally imparted to the waste by the addition of the potassium permanganate.

EXPERIMENTAL RESULTS

The investigation of α-TNT removal by lime and the oxidizing agents chlorine and potassium permanganate was conducted in two phases. The first phase concerned the use of lime alone as a primary coagulant for the removal of TNT from the wastewater. The second phase dealt with the use of lime in combination with an oxidizing agent for the removal of color and TNT from the TNT manufacturing wastewater. These studies involved the use of laboratory "jar tests" which were conducted in a manner similar to the existing treatment facilities presently used by the Radford Army Ammunition Plant.

Raw Waste Characteristics

In order to achieve a satisfactory understanding of various available methods of treating TNT waste, characteristics of each waste sample utilized in the laboratory studies should be known. Making correlations between different waste samples and treatment methods is impossible without some knowledge of the raw waste characteristics, because the stronger the waste (color and α-TNT concentration), the more difficult it becomes to treat. Characteristics of the three raw wastewater samples used in this research are presented in Table 2.

Lime Studies

The purpose of this portion of the investigation was to determine the removal of TNT from the wastewater Sample

TABLE 2

CHARACTERISTICS OF RAW WASTE SAMPLES

Sample Number	pH	TNT mg./l.	Standard Color mg./l.	Total Solids mg./l.
1	1.1	46.5	194	7902
2	0.9	48.7	212	8300
3	1.2	62.0	350	4820

No. 1, utilizing lime as a primary coagulant. All the tests involving the use of lime as a coagulant produced a heavy floc which settled rapidly. Floc formations occurred at pH 2 through 12. The floc that formed at the lower pH levels was considered to be caused by a reaction between the wastewater and the lime.

A titration curve (Figure 3) using lime as the titrant was developed for the TNT wastewater. Relationships between pH, color, and lime dosage are presented in Figures 4 and 5. The results obtained from using different lime dosages for the removal of TNT are shown in Figures 6 and 7. Some TNT removal did occur at the lower pH levels, but significant TNT removal did not occur until the formation of the insoluble calcium hydroxide floc at pH 9 and above. Further tests were conducted at a pH 12.0 to substantiate those findings in Figure 6, and the results varied less than 4 percent from the original test. Although TNT removal was substantial, the color increase caused by the elevated pH levels was undesirable. Neutralization of the waste sample after lime treatment provided some color reduction, but still left the waste unsuitable for discharge.

One short term batch study involving the use of activated carbon for the removal of color was conducted. The activated carbon was introduced into the neutralized and nonneutralized waste that had been treated with excess lime. The result obtained from the use of activated carbon for color

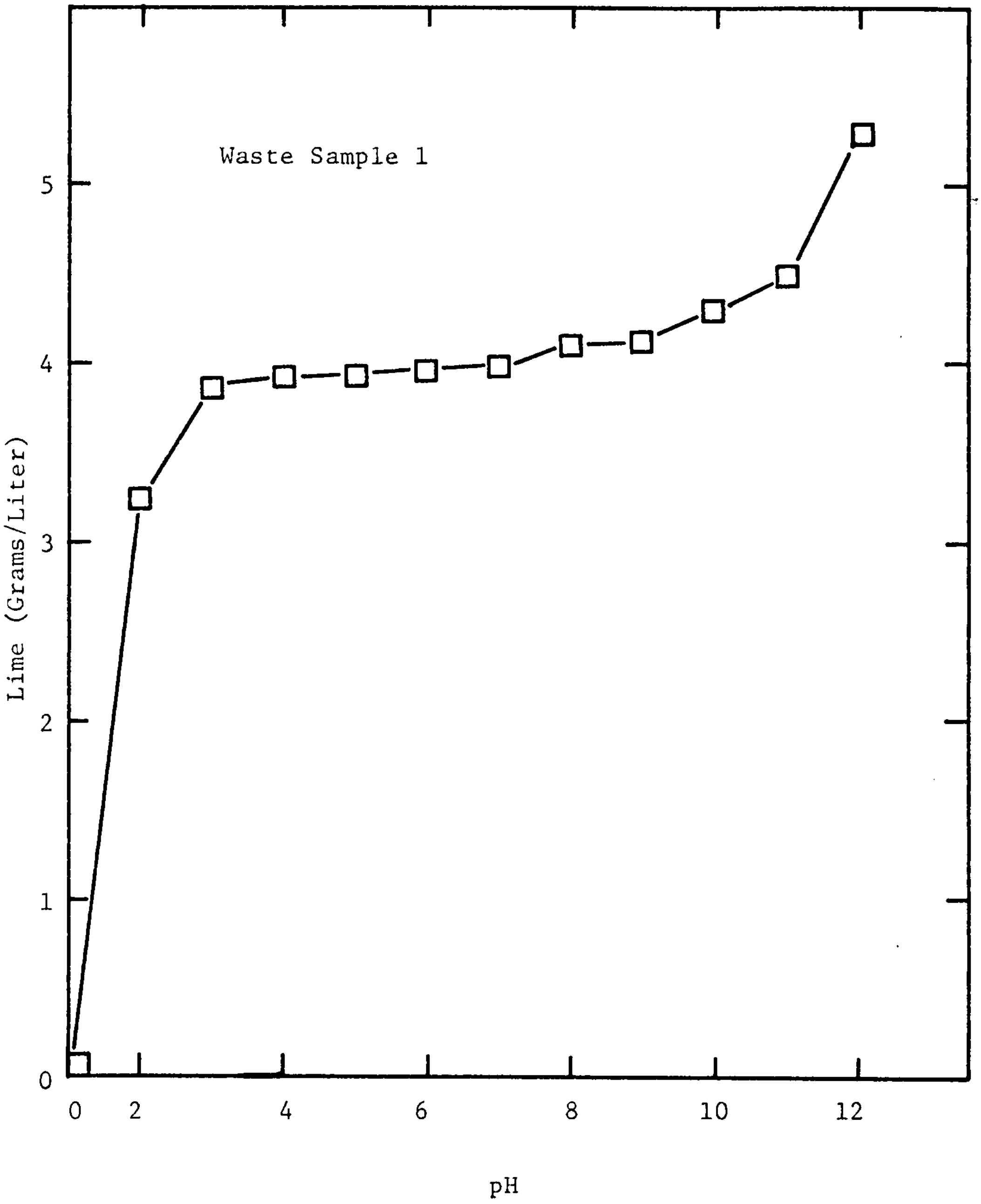


Figure 3. Titration Curve For TNT Wastewater Utilizing Lime as a Titrant

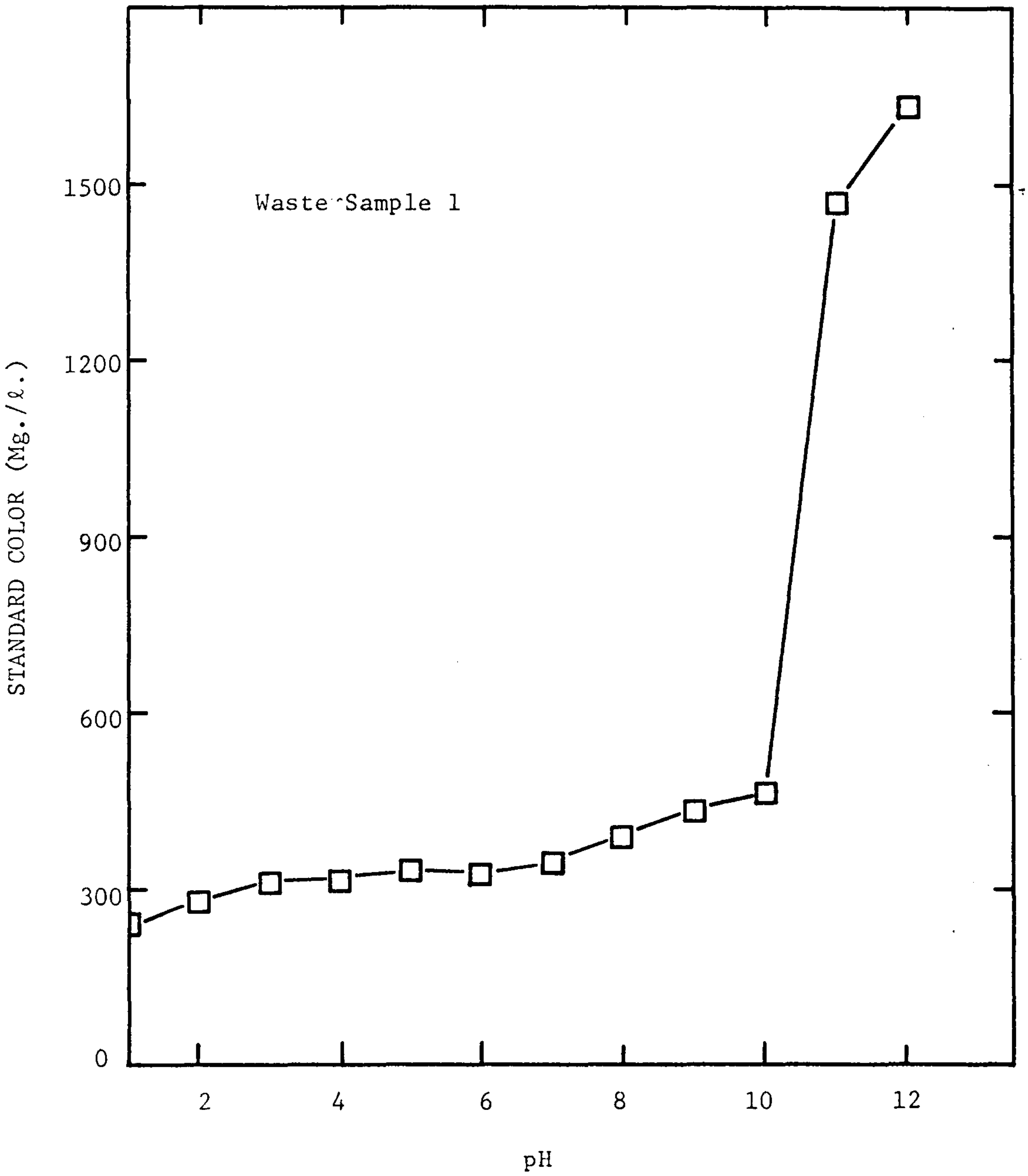


Figure 4. Color Developed By TNT Wastewater at Different pH Levels.

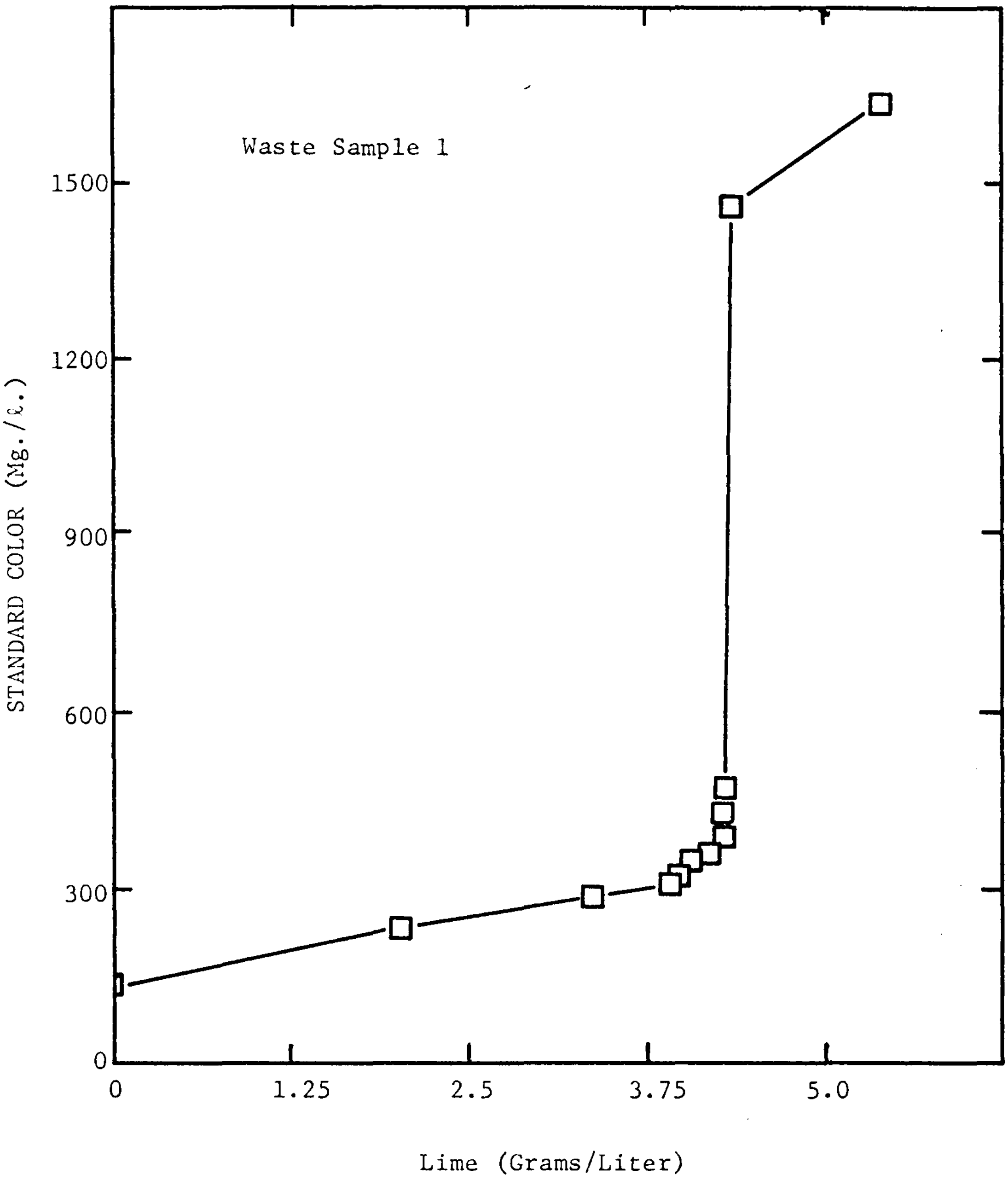


Figure 5. Color Developed By TNT Wastewater At Different Lime Concentrations

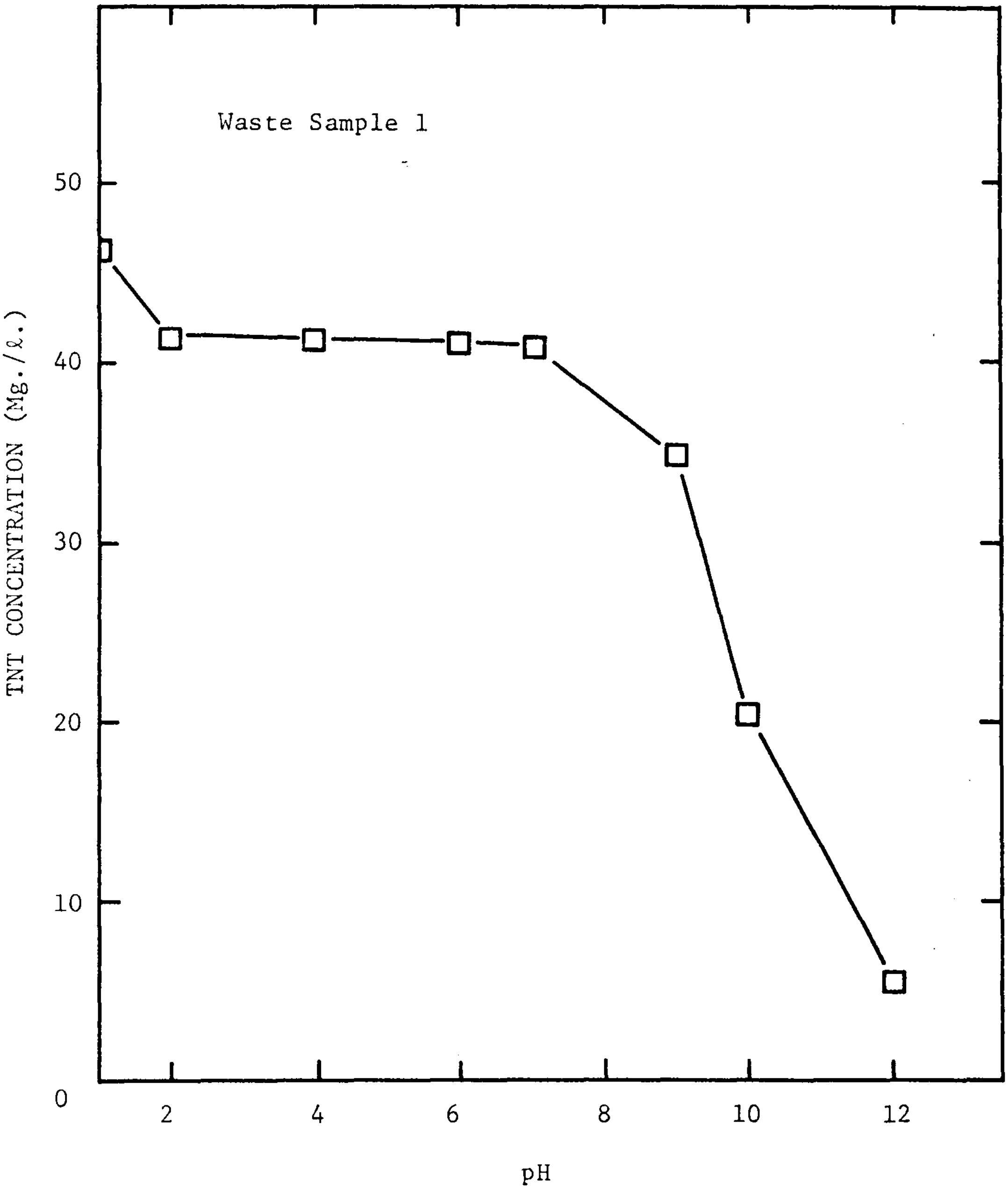


Figure 6. Removal of TNT By Lime At Different pH Levels

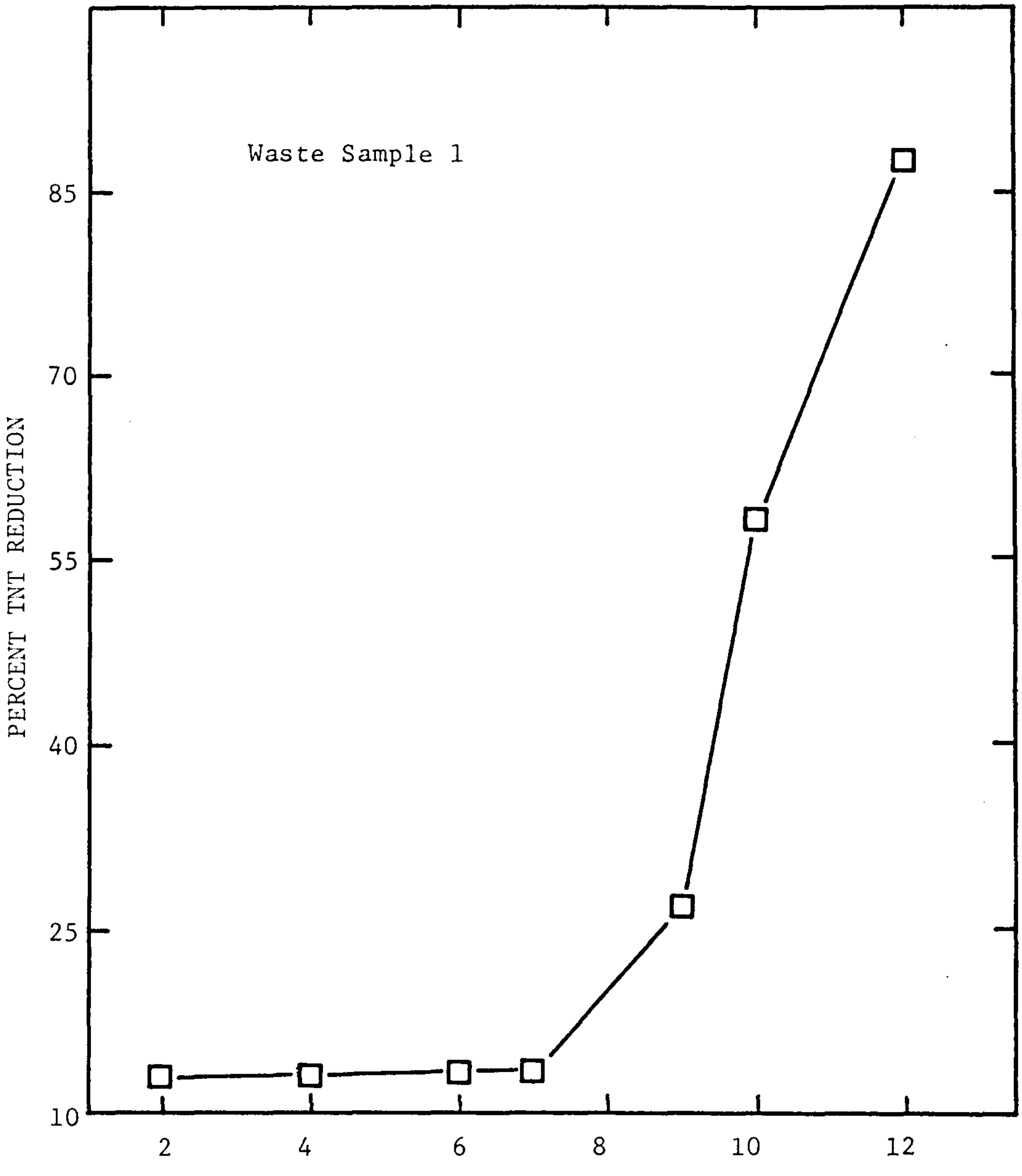


Figure 7. Percent TNT Removal By Lime At Different pH Levels

reduction is presented in Figure 8, which indicates the effectiveness of this material as an adsorbent for residual color following lime treatment of the TNT wastewater.

Combined Chlorine and Lime Studies

The purpose of this portion of the investigation was to determine the effectiveness of chlorine in conjunction with lime for the removal of TNT and color from the TNT wastewater Sample No. 2. The pH of the samples was adjusted to 2, 4, 6, 8, 10 and 12 in this study. A dosage of 250 mg./l. of High Test Hypochlorite was added to samples at each of the above pH levels and mixed for a six hour contact period. Lime was then added to the samples to raise the pH to 12. The floc was settled and determinations of TNT and color (Figures 9-11) were obtained utilizing procedures previously described. Maximum color and TNT removal occurred with chlorine addition at pH 6, resulting in a reduction in TNT concentration of 86.5 percent and in a standard color concentration reduction of 35 percent. Hypochlorous acid is the most effective oxidant formed upon the addition of HTH to water. When the pH is between 5 and 7, hypochlorous acid is the predominate form and would account for the maximum TNT and color removal obtained with HTH addition at pH 6.

A second test utilizing a dosage of 1,000 mg./l. of HTH was run to determine the effectiveness of chlorine to remove the color developed by lime addition. The samples were

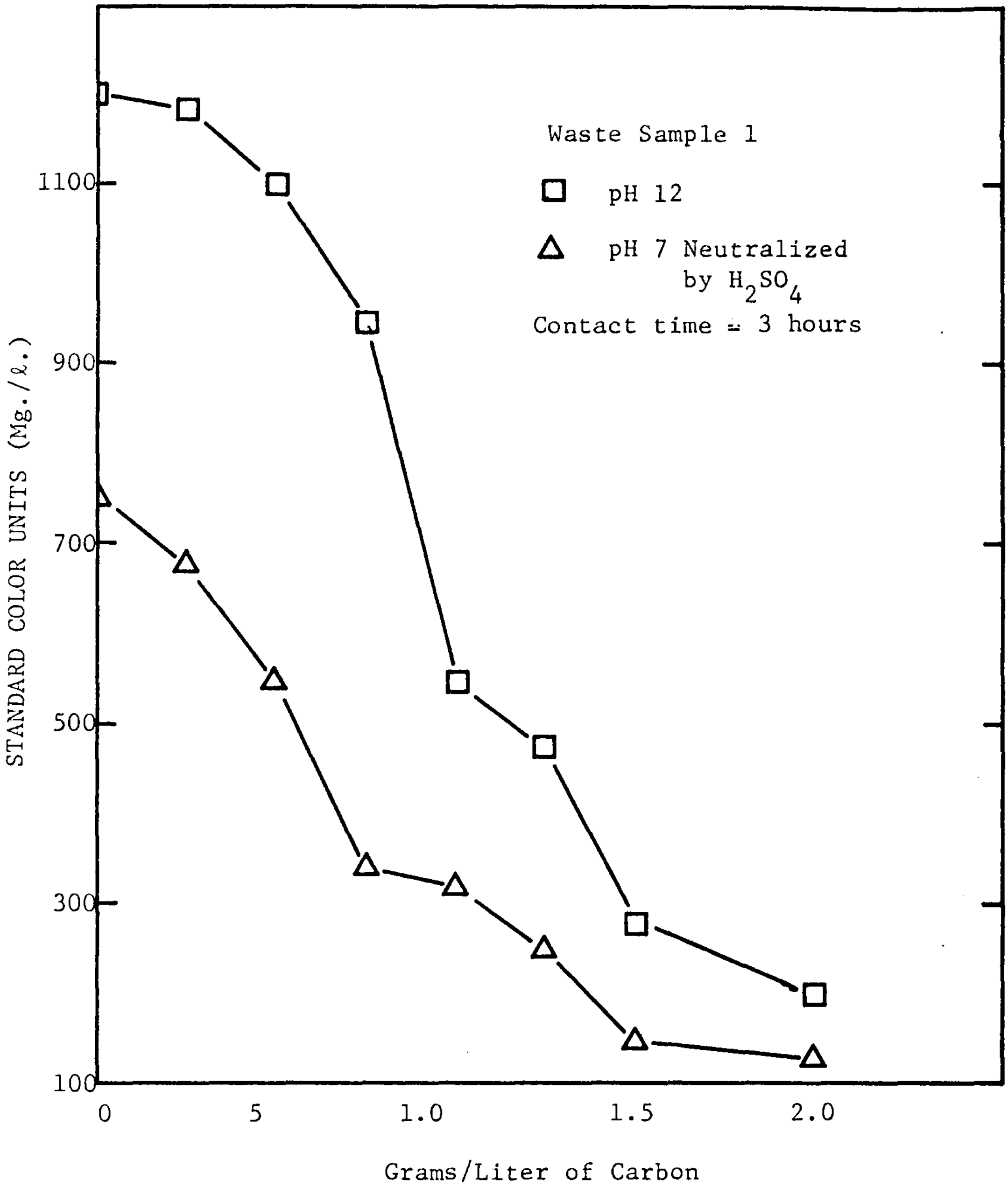


Figure 8. Removal of Color by Activated Carbon After Lime Treatment

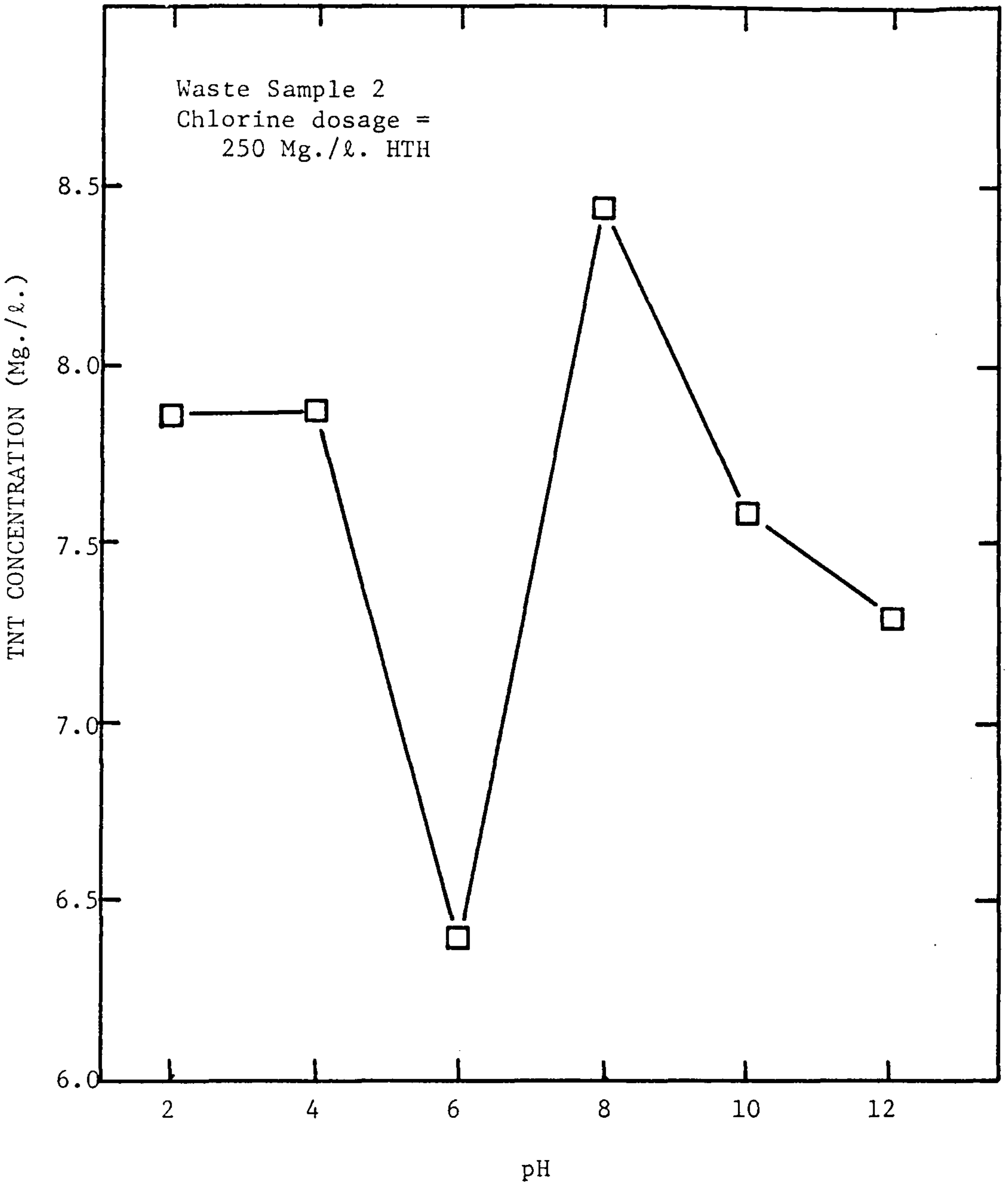


Figure 9. TNT Removal With Lime Addition to pH 12. Addition of Chlorine at the Indicated pH Levels

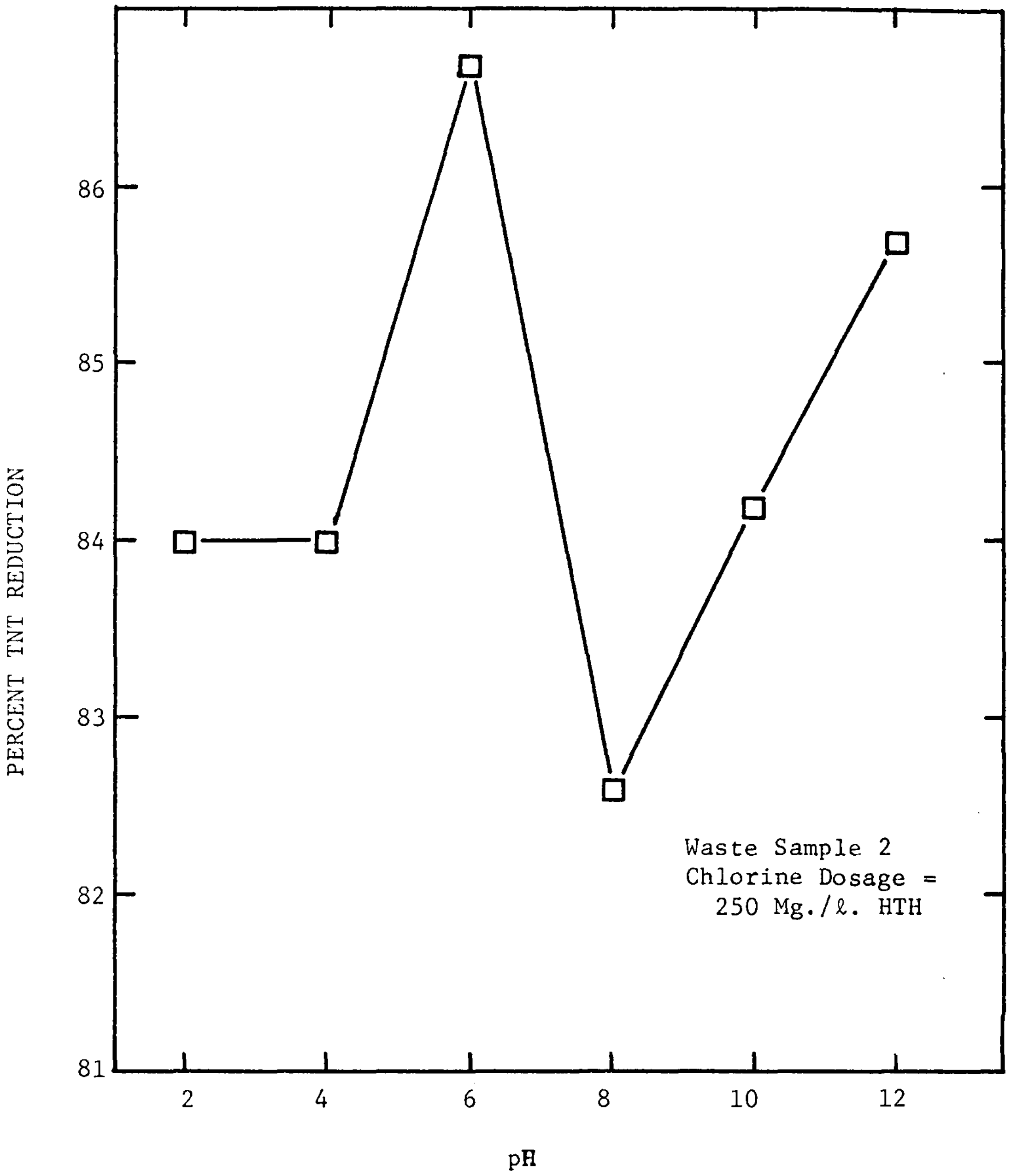


Figure 10. Percent TNT Removal with Lime Addition to pH 12. Chlorine Addition at the Indicated pH Levels

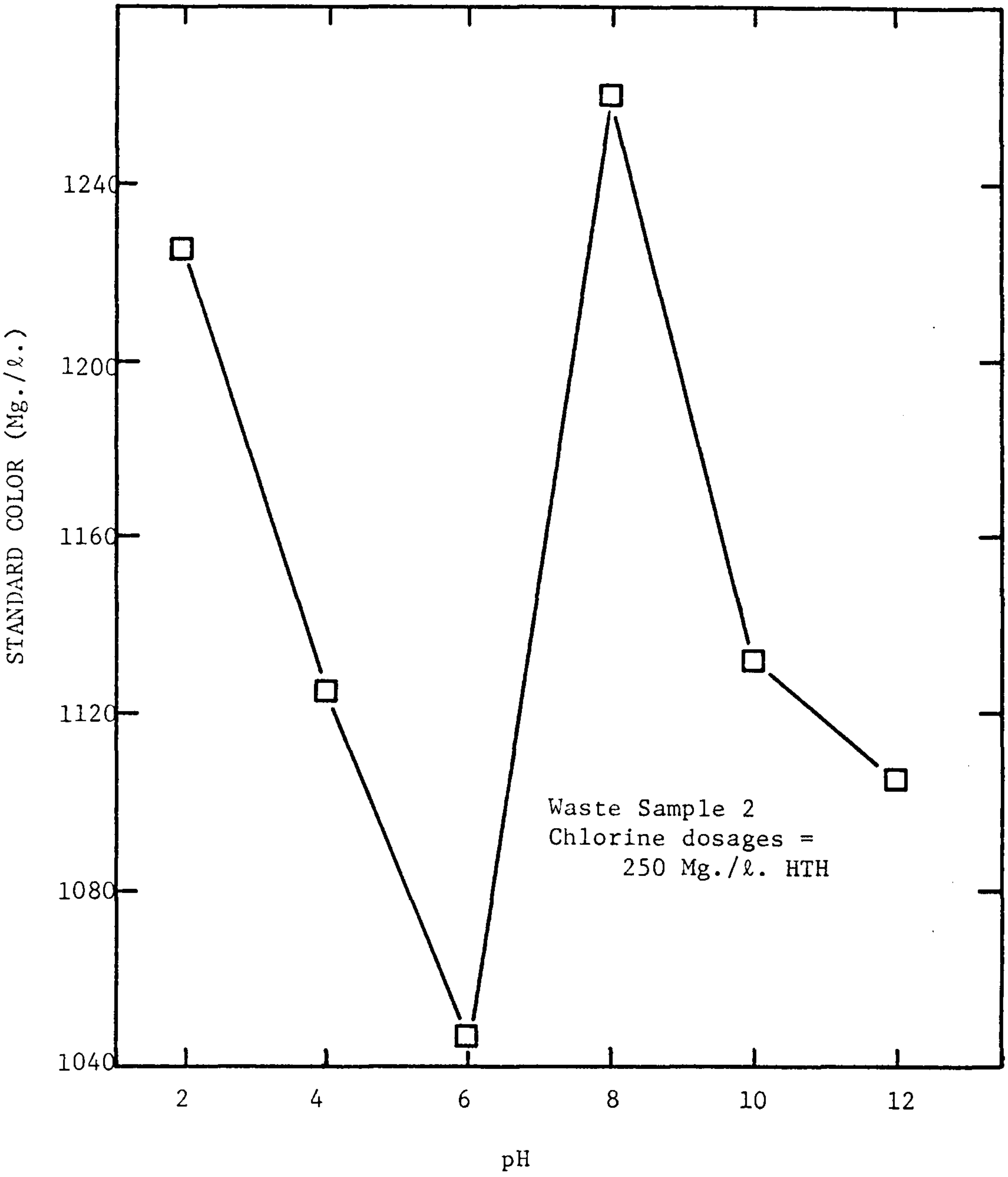


Figure 11. Color at pH 12 With Chlorine Addition at Indicated pH Levels

raised to pH 2, 4, 6, 8, 10, and 12 with lime and the chlorine was added to the waste at these designated pH levels. A six hour contact period was utilized. The color reduction (Figures 12 and 13) occurring at all pH levels was significant, with a color reduction of 78 percent at pH 12. A distinct chlorine odor remained after the six hour contact period which meant that either the reaction between the waste and the chlorine was not completed, or a dosage of 1,000 mg./l. HTH was in excess of the amount needed to react with the nitroaromatic compounds in the waste.

A third test was conducted with a chlorine dosage of 750 mg./l. HTH and a contact period of twelve hours. The chlorine was added as before and color and TNT reduction results are shown in Figures 14 through 16. Maximum TNT removal occurred with chlorine addition at pH 12. It is noted, however, that if the sample treated with chlorine at pH 6 had been further treated by excess lime to pH 12, the TNT removal obtainable would probably be greater than the 88 percent achieved by chlorine addition at pH 12. The chlorine odor of the waste sample treated with 750 mg./l. HTH for a twelve hour contact period was far less than the samples resulting from use of a concentration of 1,000 mg./l. HTH.

Potassium Permanganate and Lime Studies

The purpose of this phase of the investigation was to determine the ability of potassium permanganate to remove color

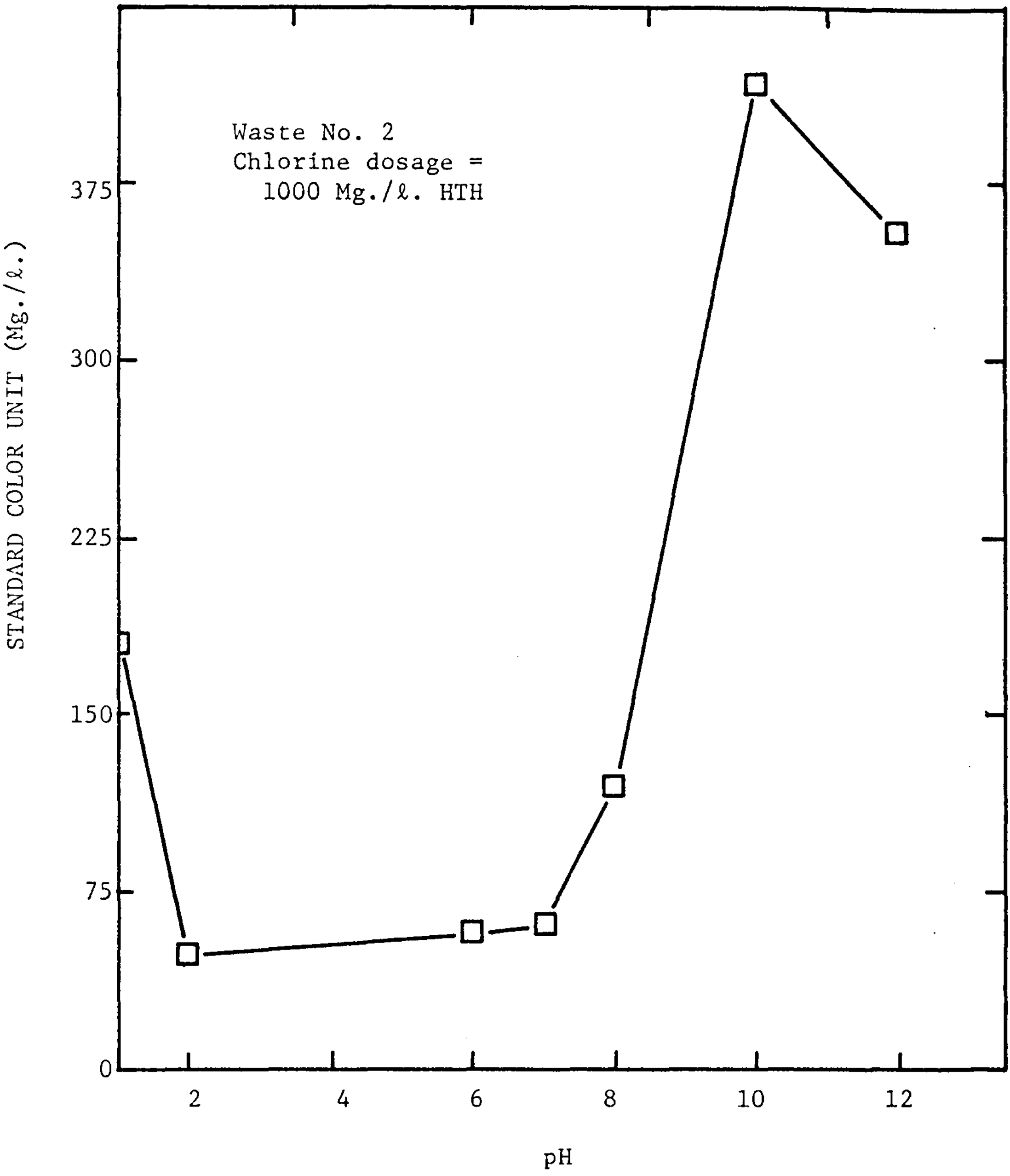


Figure 12. Use of Chlorine at Different pH Levels For Color Reduction

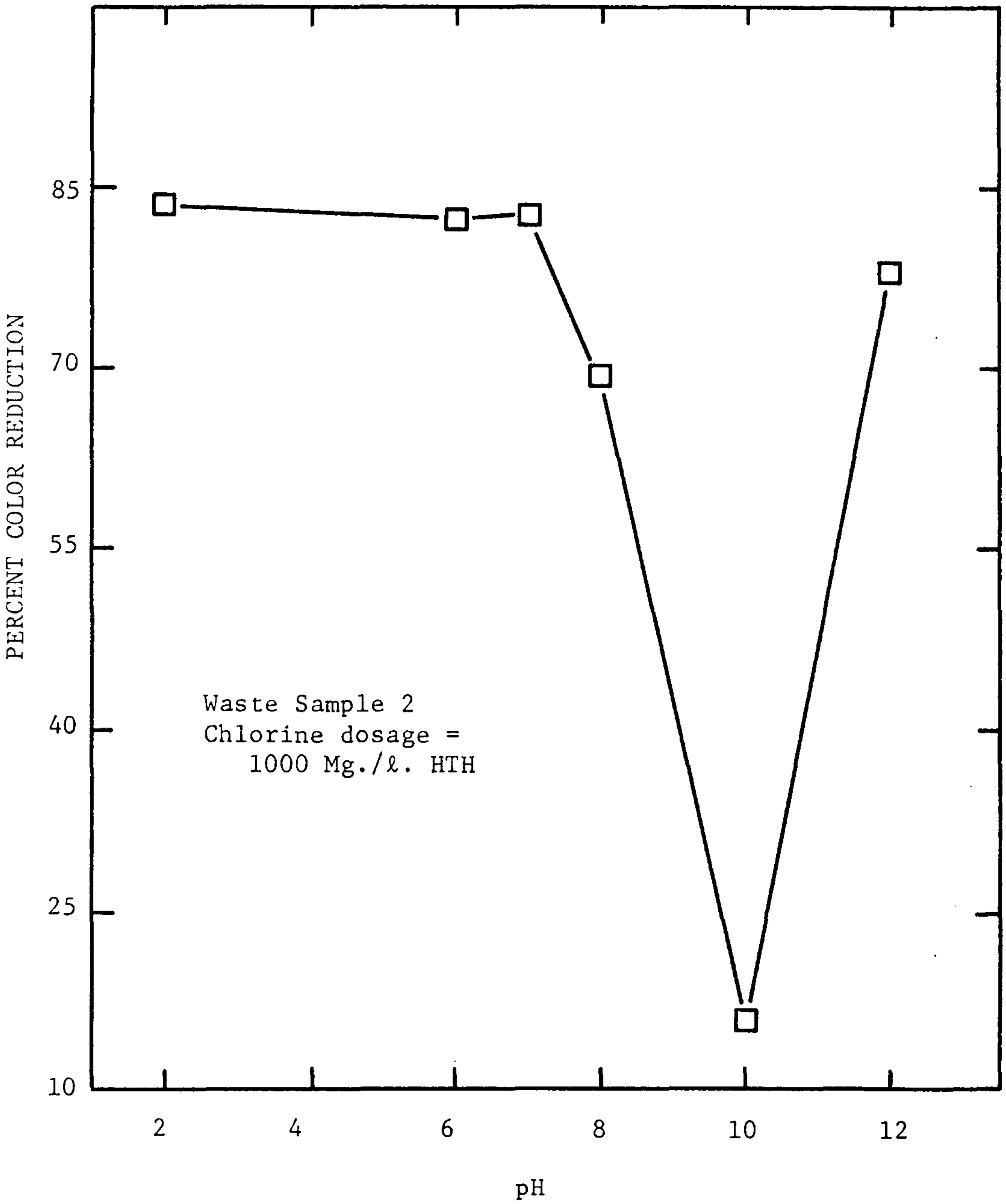


Figure 13. Percent Color Reduction Using Chlorine At The Indicated pH Levels

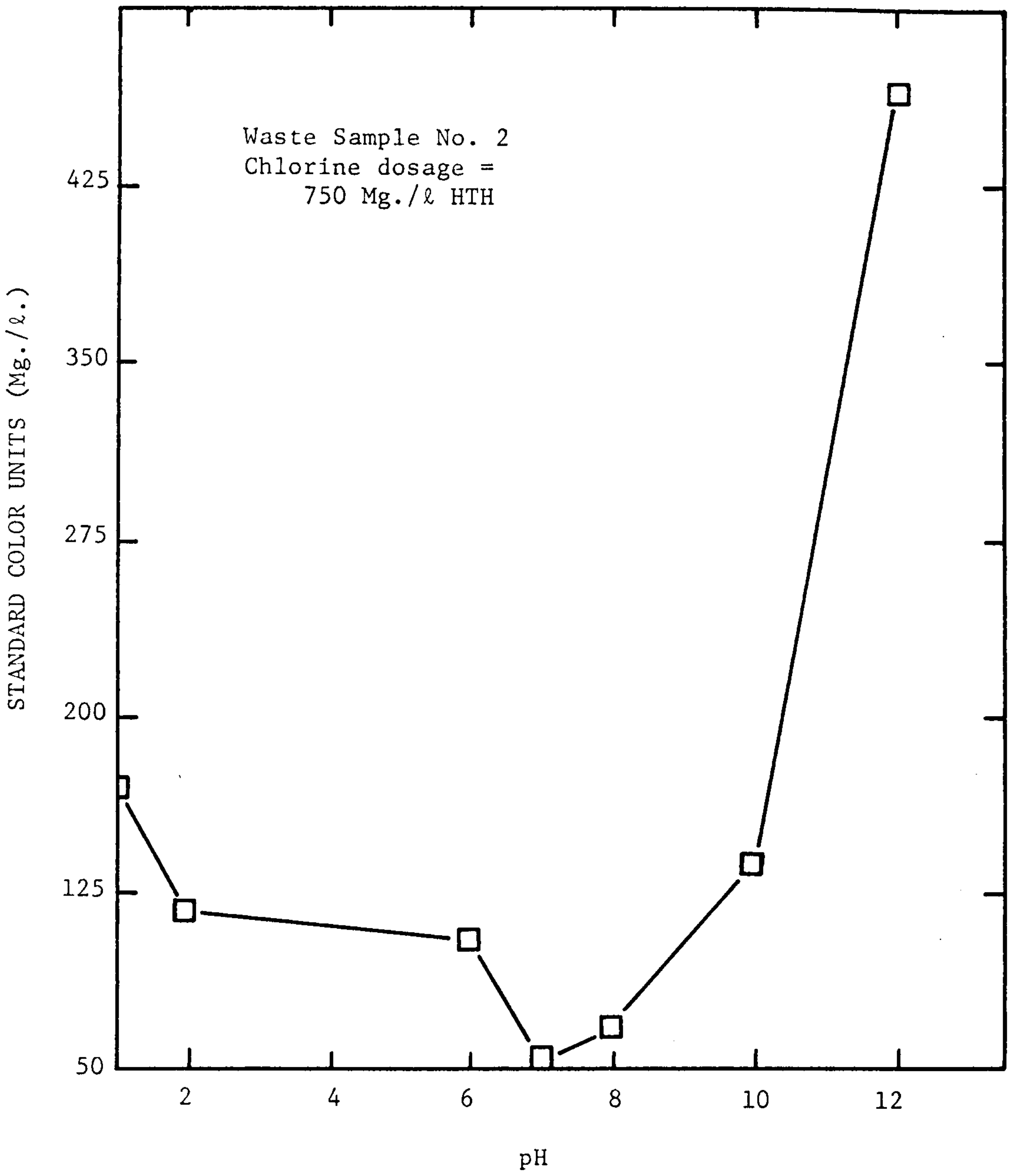


Figure 14. Use of Chlorine at Different pH Levels For Color Reduction

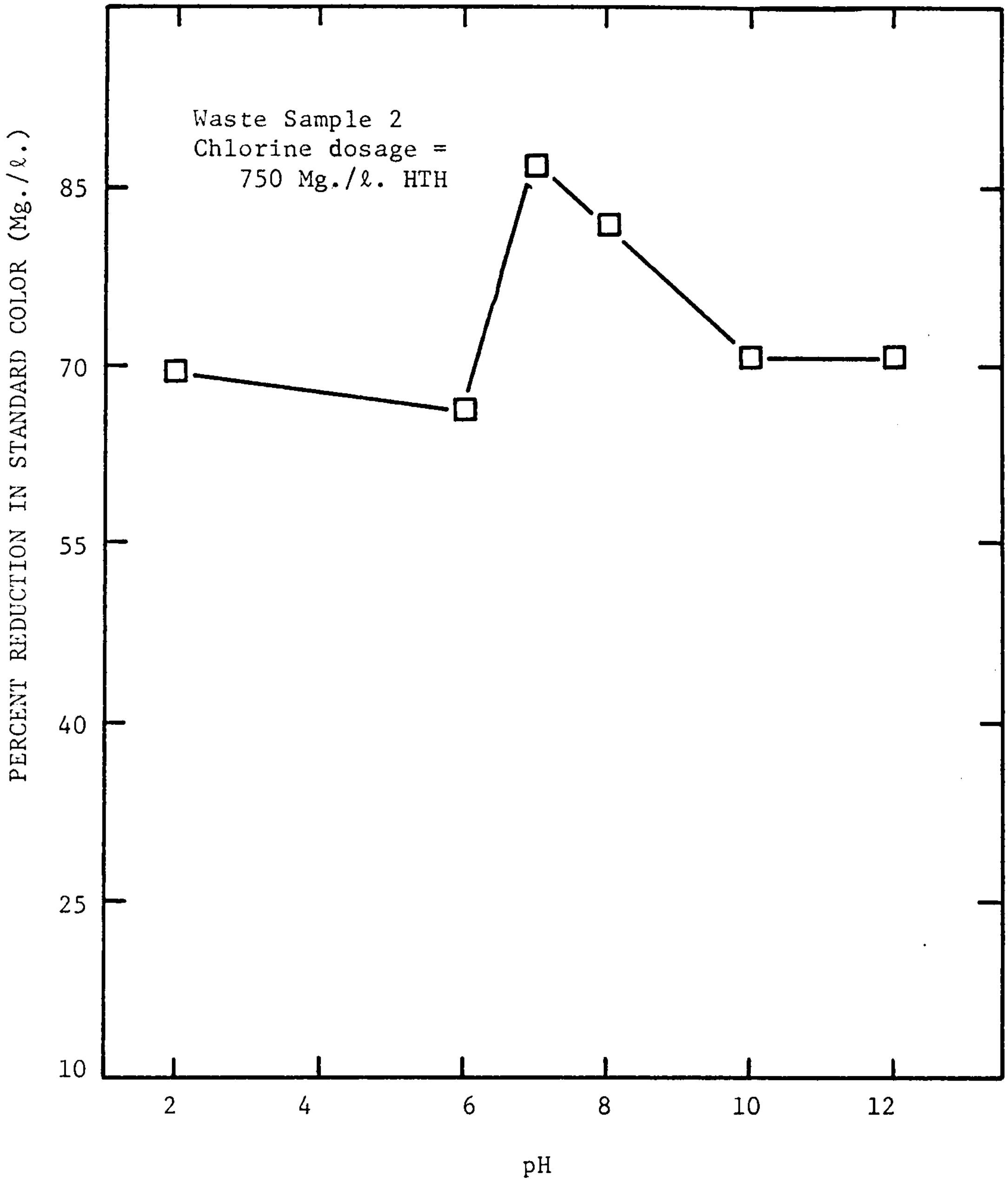


Figure 15. Percent Color Reduction After Addition of Chlorine at Indicated pH Levels

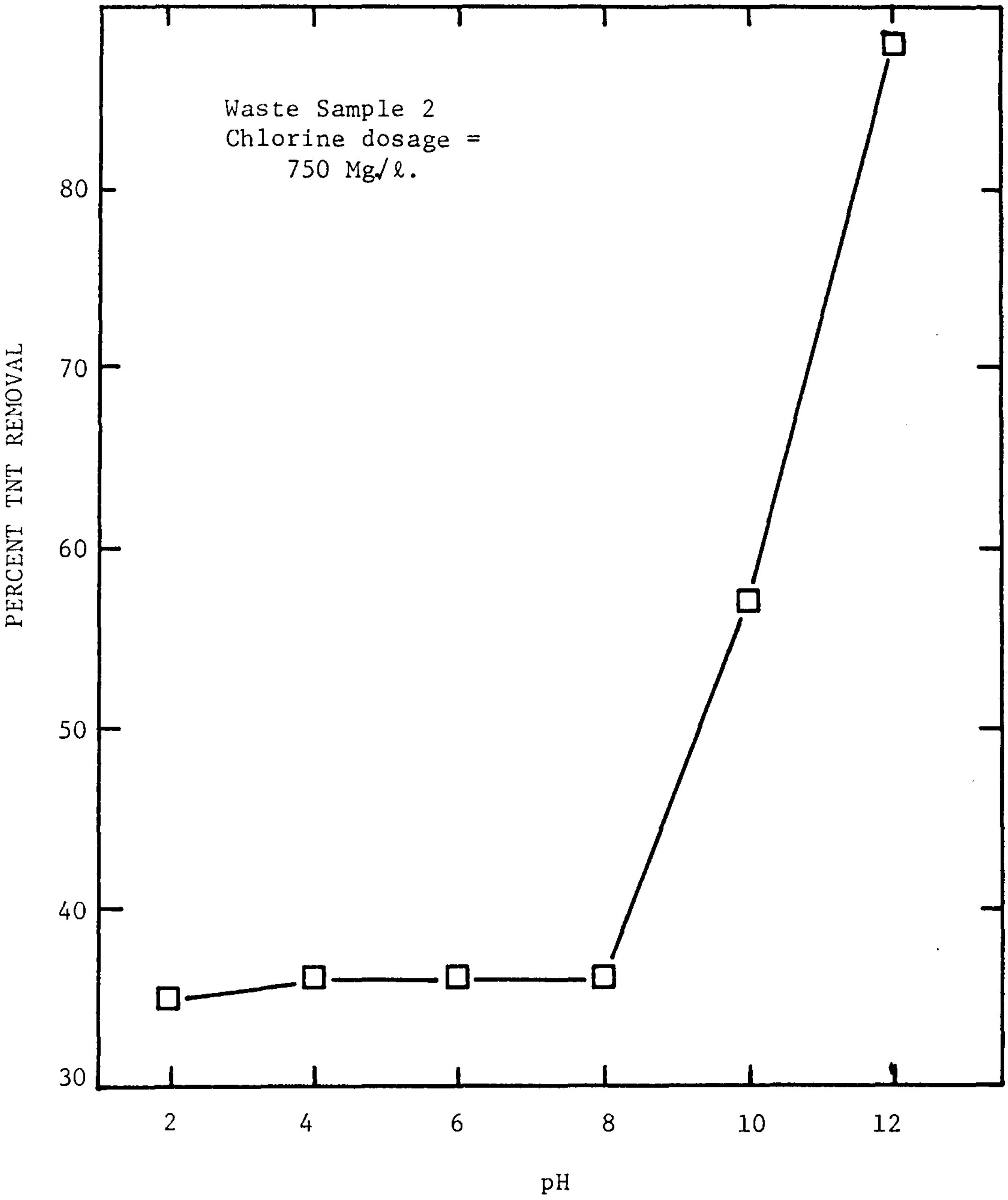


Figure 16. Percent TNT Reduction With Chlorine Addition At The Indicated pH Levels

and TNT from the TNT manufacturing wastewater Sample No. 3. The potassium permanganate dosage was varied from 35 to 120 mg./l. The results obtained for color and TNT removal are shown in Figures 17-20. A manganese floc appeared in the samples with a potassium permanganate concentration of over 60 mg./l. and appeared to interfere with the apparent removal of the TNT. Further tests were conducted utilizing lime to adjust the pH to 2, 4, 6, 8, 10, and 12. A potassium permanganate dosage of 85 mg./l. was initially added to the waste samples at the pH levels designated above. The color imparted to the waste by the potassium permanganate remained after forty-eight hours in all samples except the sample at pH 2, and interfered with the colormetric analysis of the TNT concentration. A smaller dosage of 50 mg./l. potassium permanganate was utilized and proved satisfactory. The removal of color and TNT at each of the designated pH levels is presented in Figures 21 through 23. The pH of each sample was then adjusted to 12, and the color and TNT removal are represented in Figures 24 through 26. The use of lime slowed the reaction of the potassium permanganate with the nitroaromatic compounds between pH 4 and 10, but the reaction time at pH 2 and 12 was fairly close to that of the samples which contained no lime.

Zinc Sulfate, Potassium Permanganate and Lime Studies

The purpose of this investigation was to determine if zinc sulfate would react with the compounds in the TNT

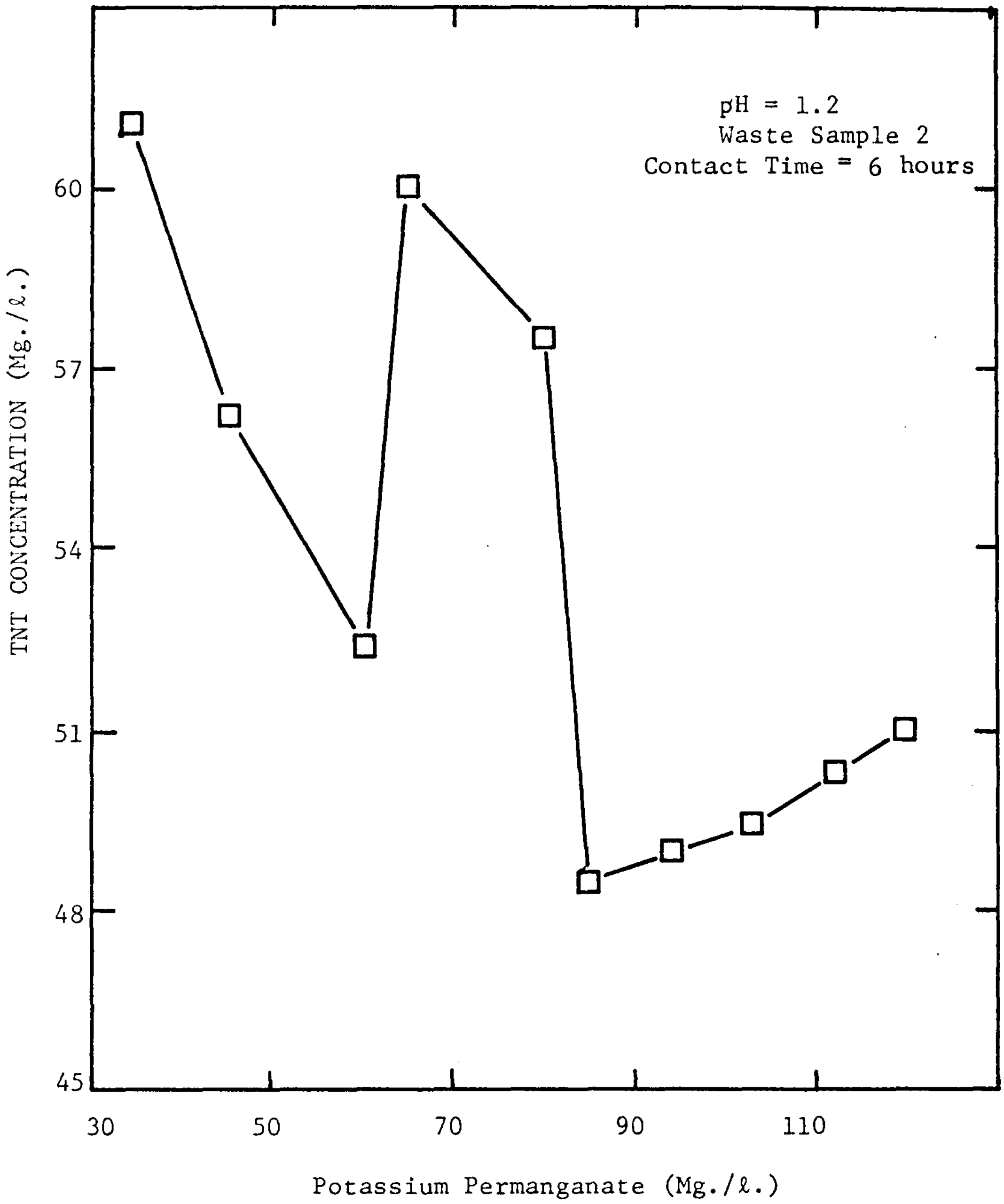


Figure 17. TNT Removal By Potassium Permanganate Addition

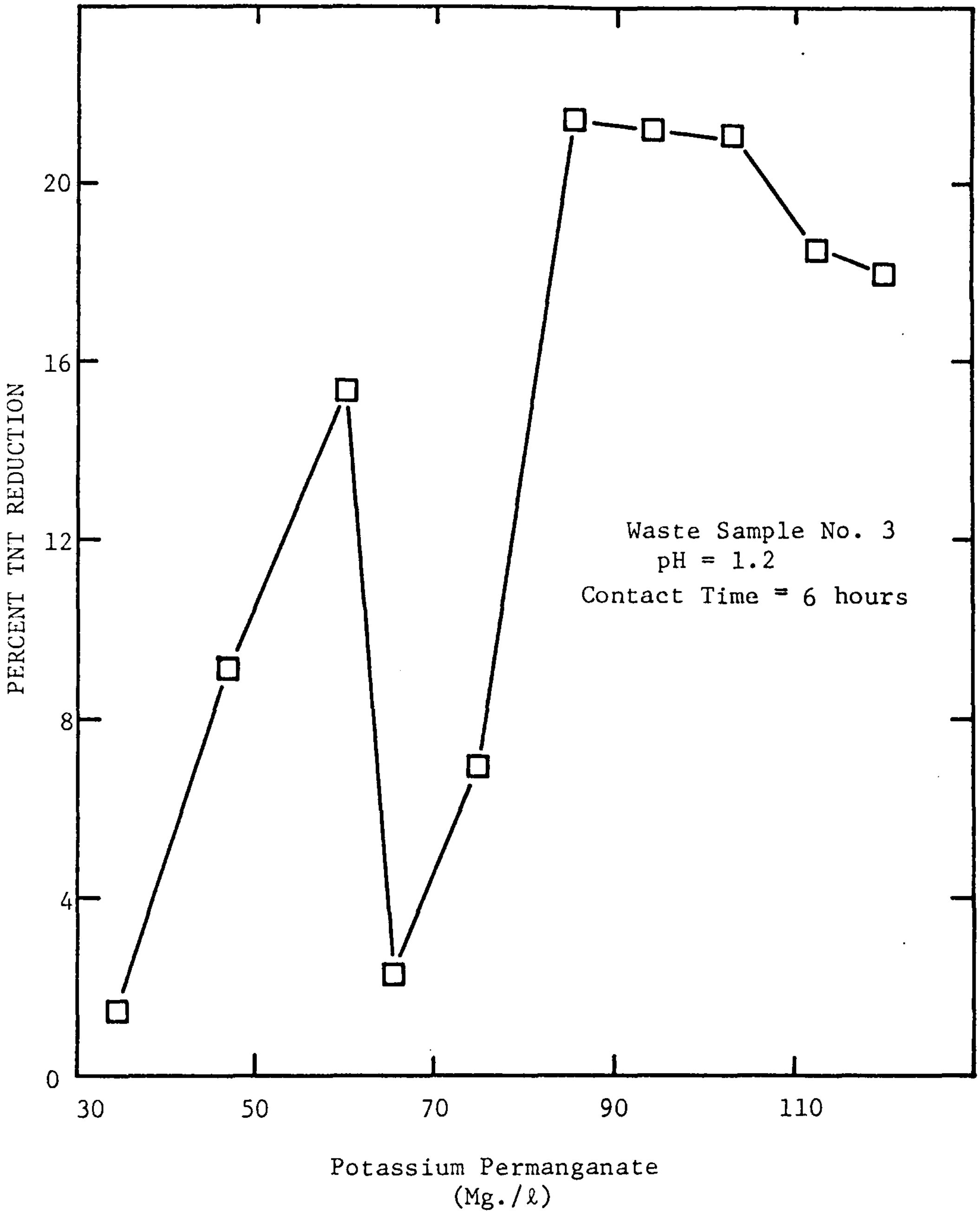


Figure 18. Percent TNT Removal By Potassium Permanganate Addition

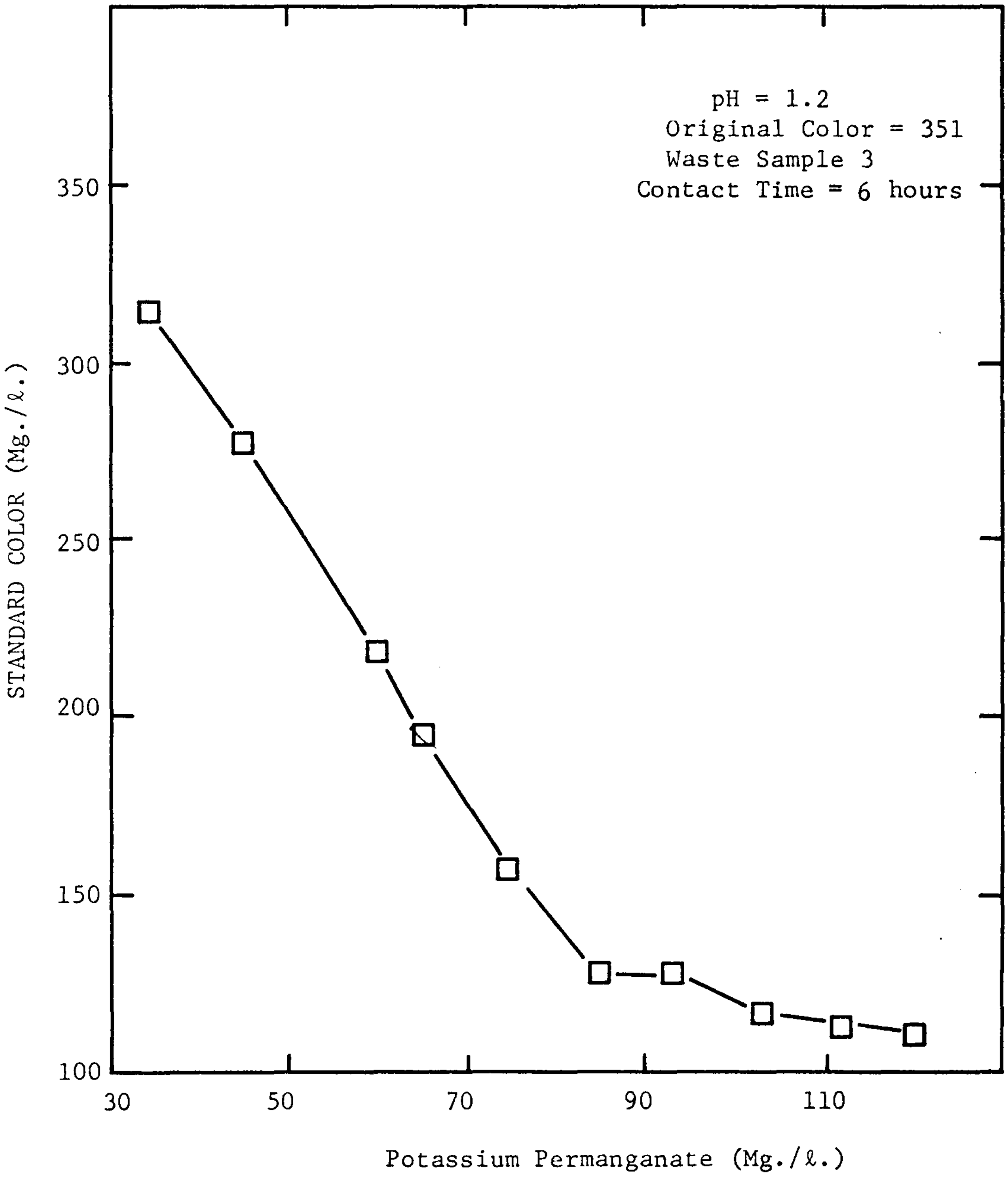


Figure 19, Color Removal By Potassium Permanganate Addition

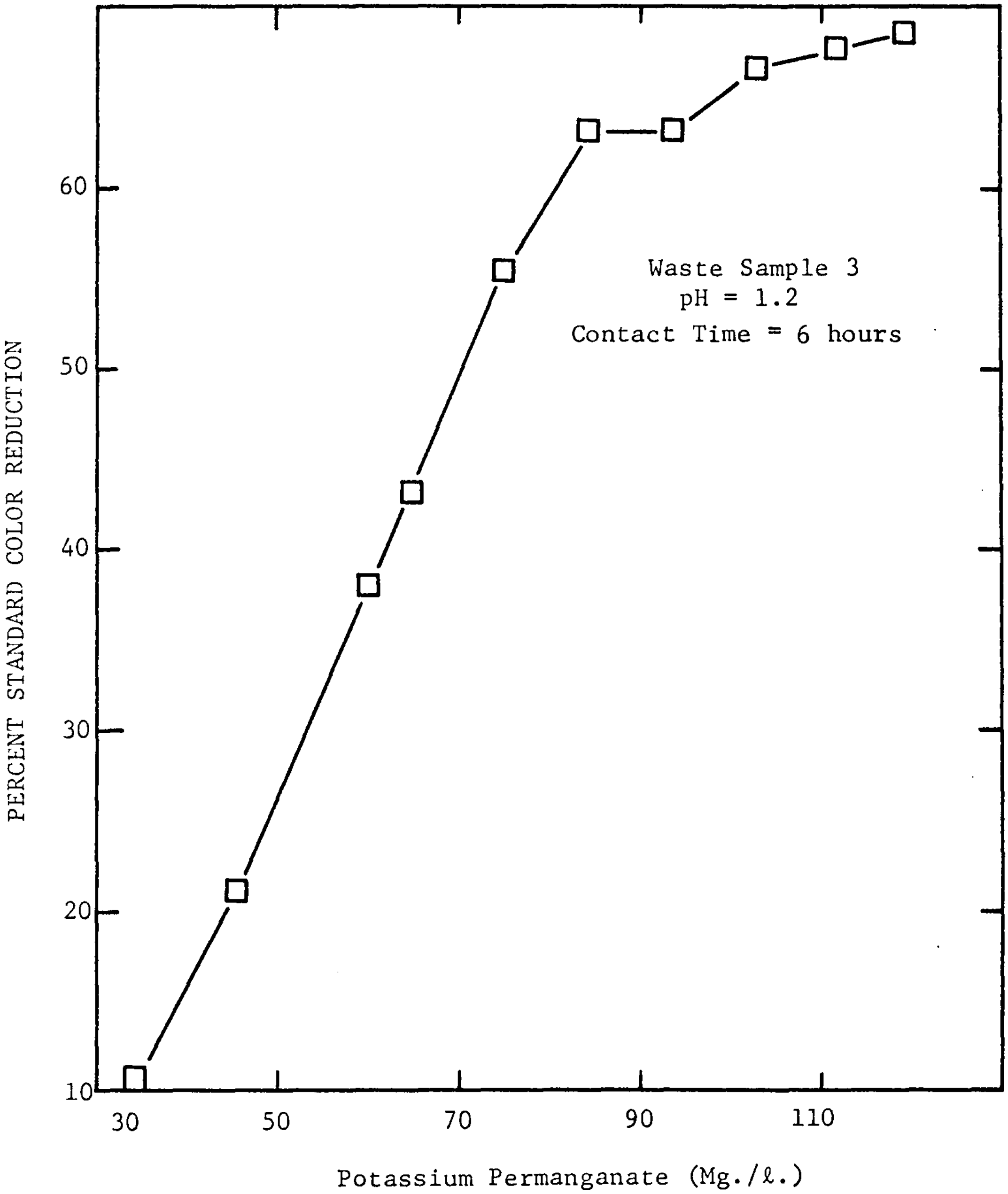


Figure 20. Percent Color Removal By Potassium Permanganate Addition

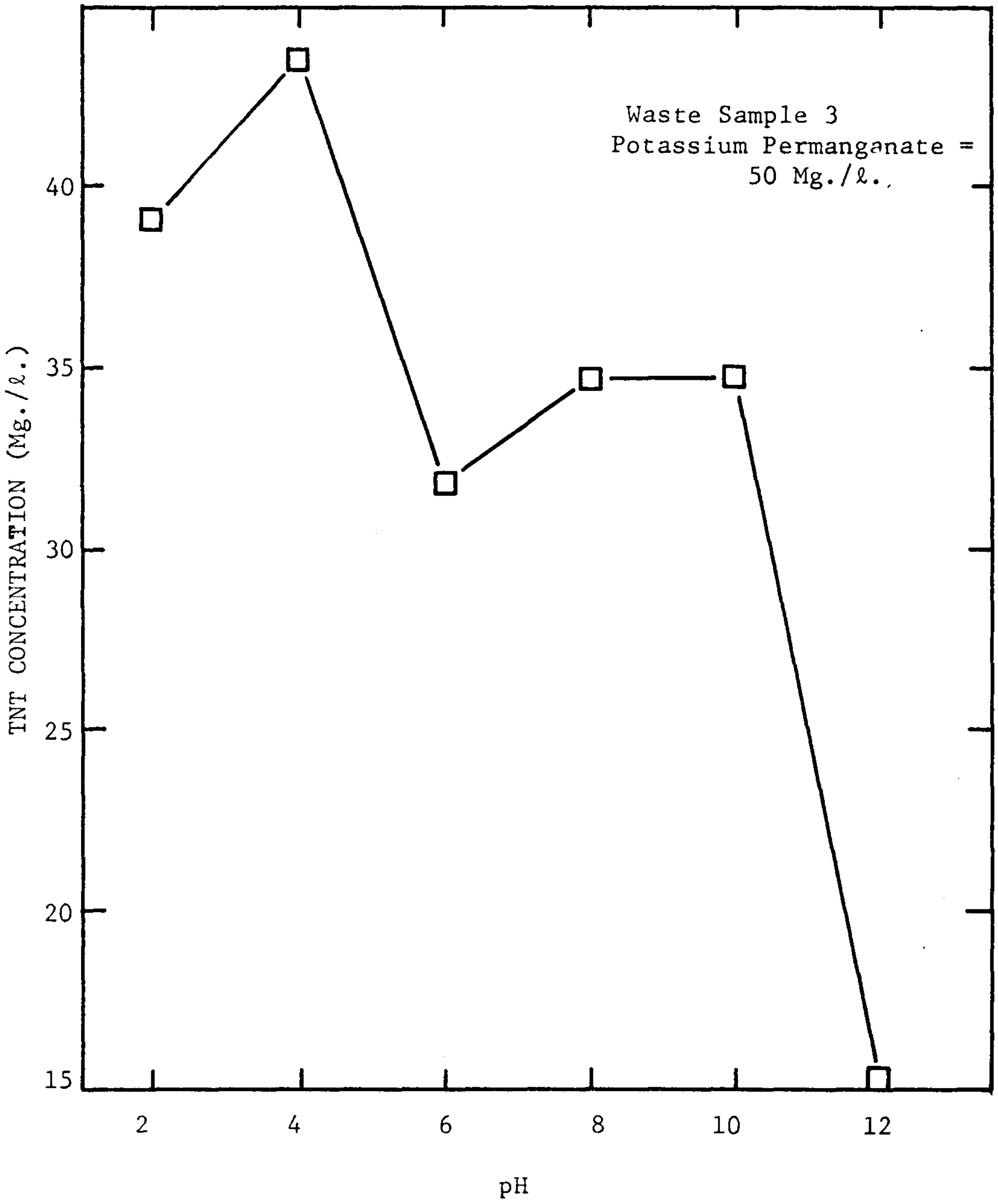


Figure 21. TNT Concentration With Potassium Permanganate Addition At Indicated pH Levels

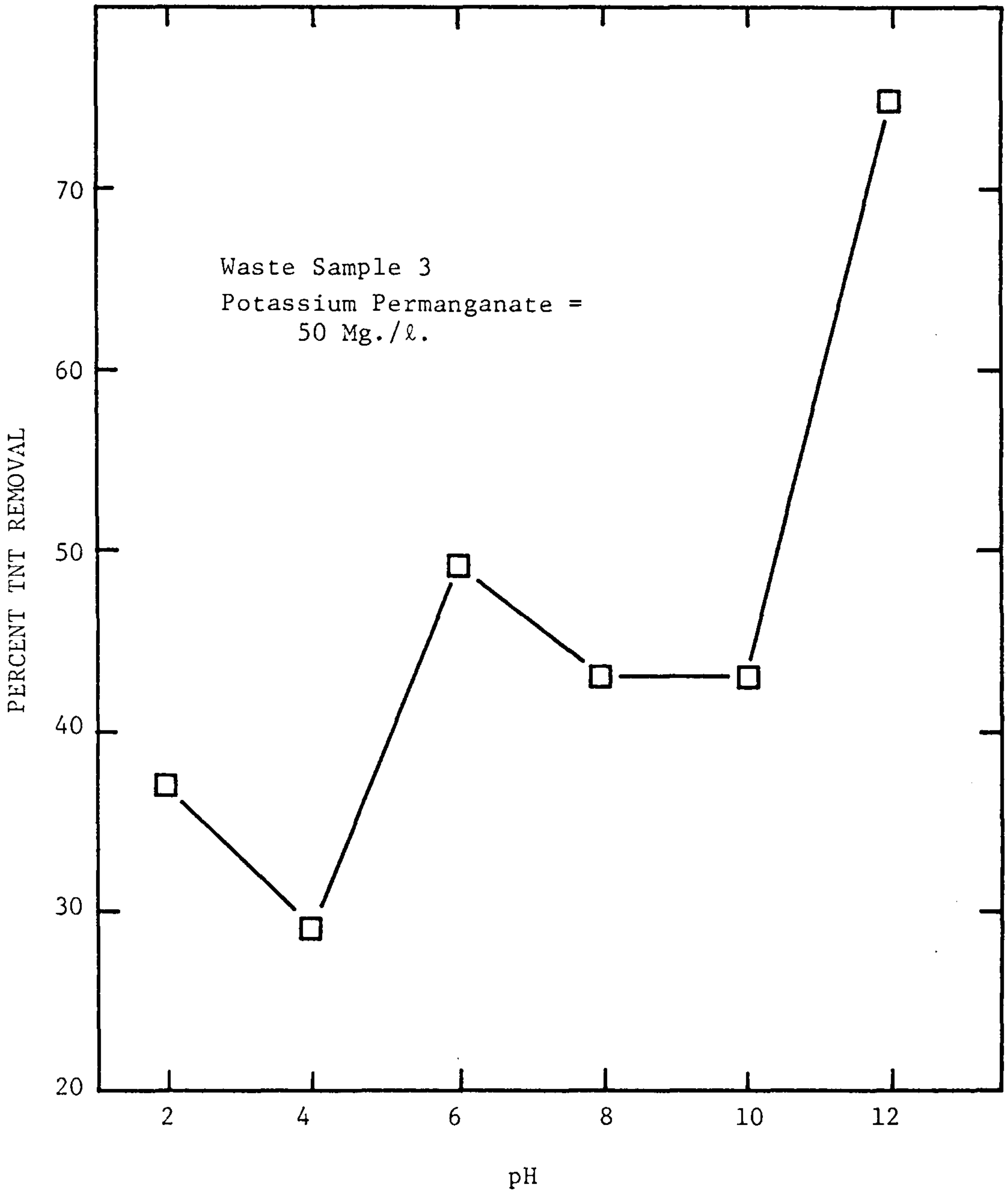


Figure 22. Percent TNT Removal By Potassium Permanganate Addition at the Indicated pH Levels

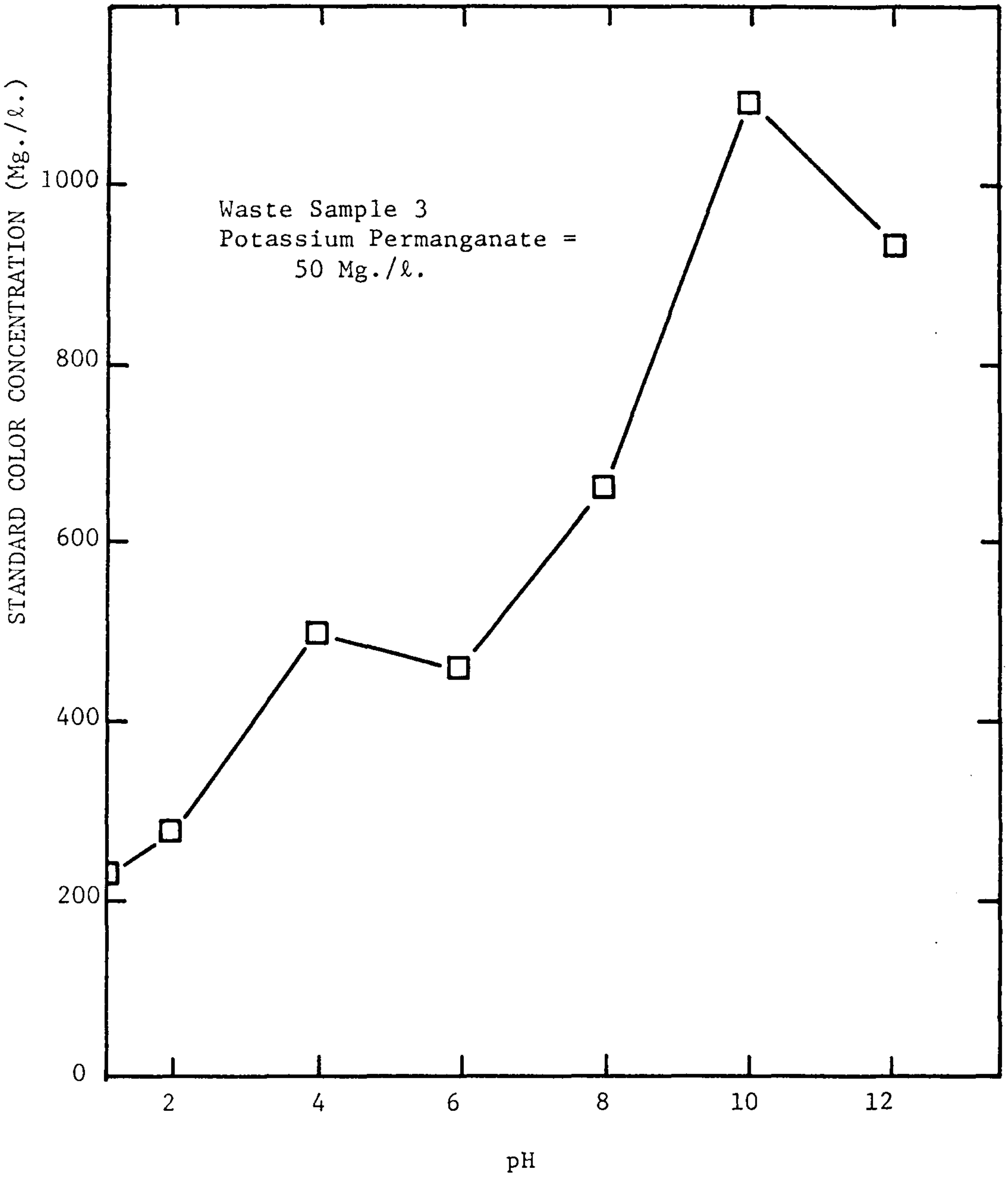


Figure 23. Standard Color of TNT Wastewater With Potassium Permanganate Addition at the Indicated pH Levels

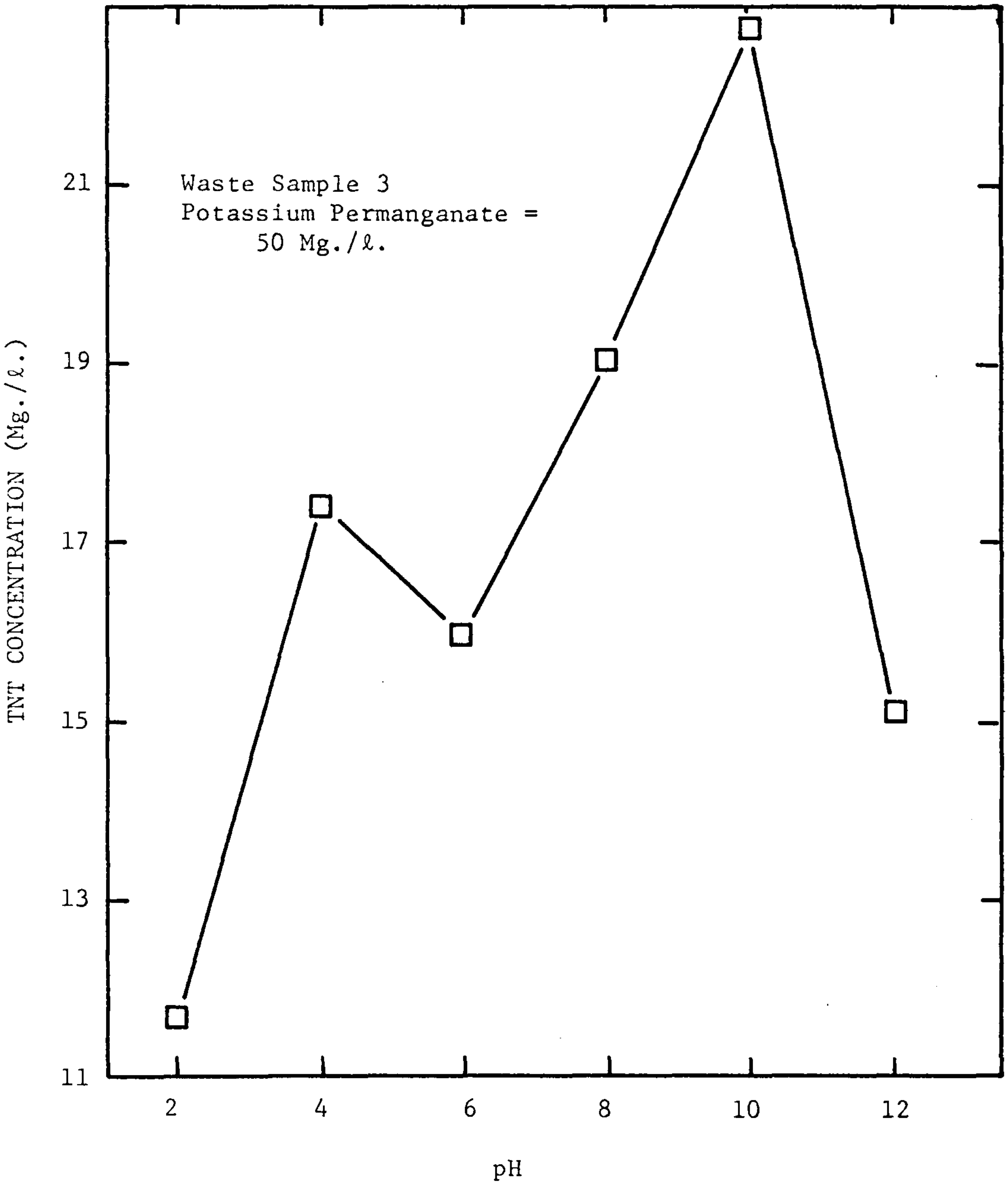


Figure 24. TNT Concentration With Permanganate Added at the Indicated pH Levels.
All Samples then Raised to pH 12 by Lime Addition

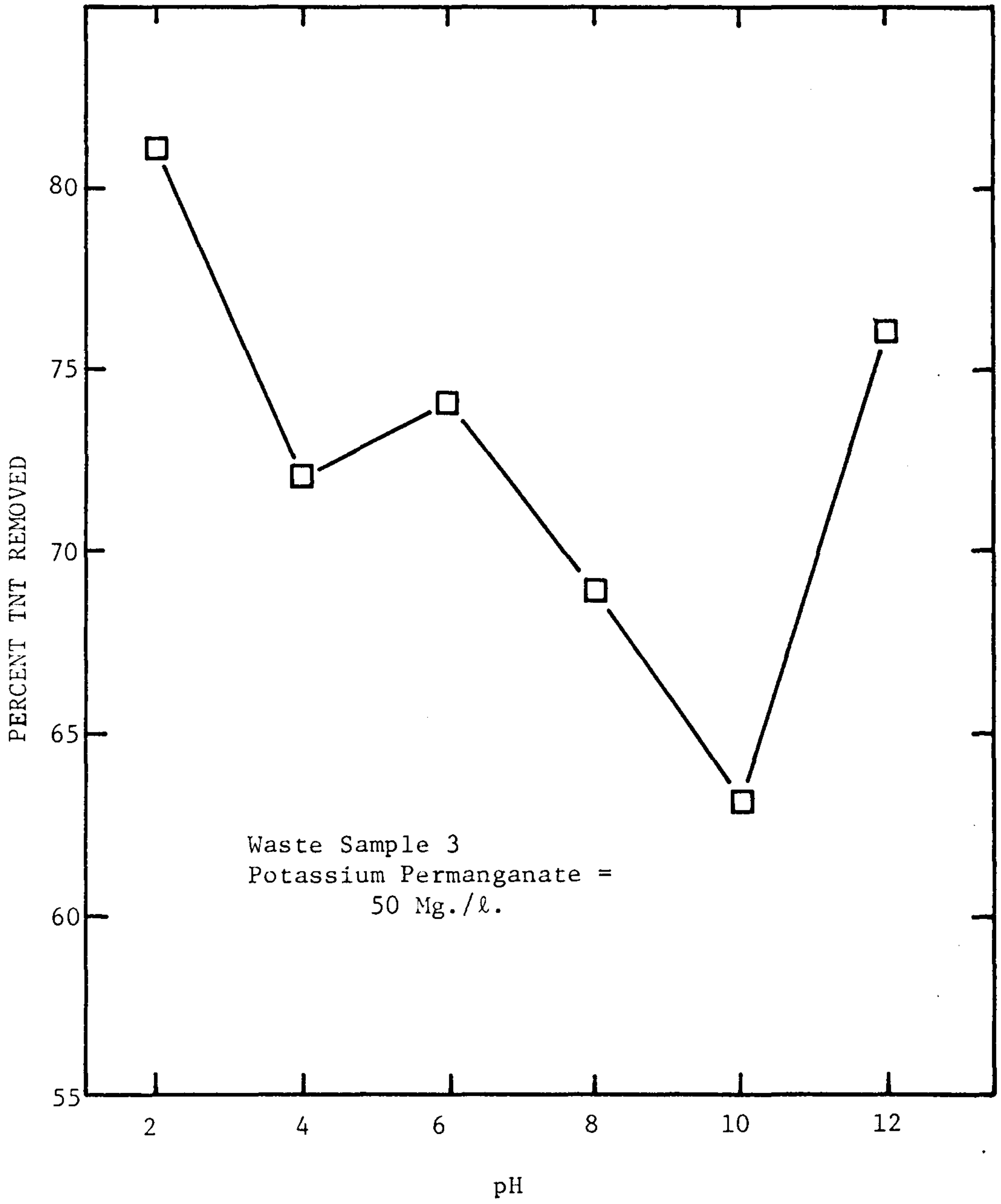


Figure 25. Percent TNT Removal With Potassium Permanganate Addition at Indicated pH Levels. All Samples Then Raised to pH 12 by Lime Addition

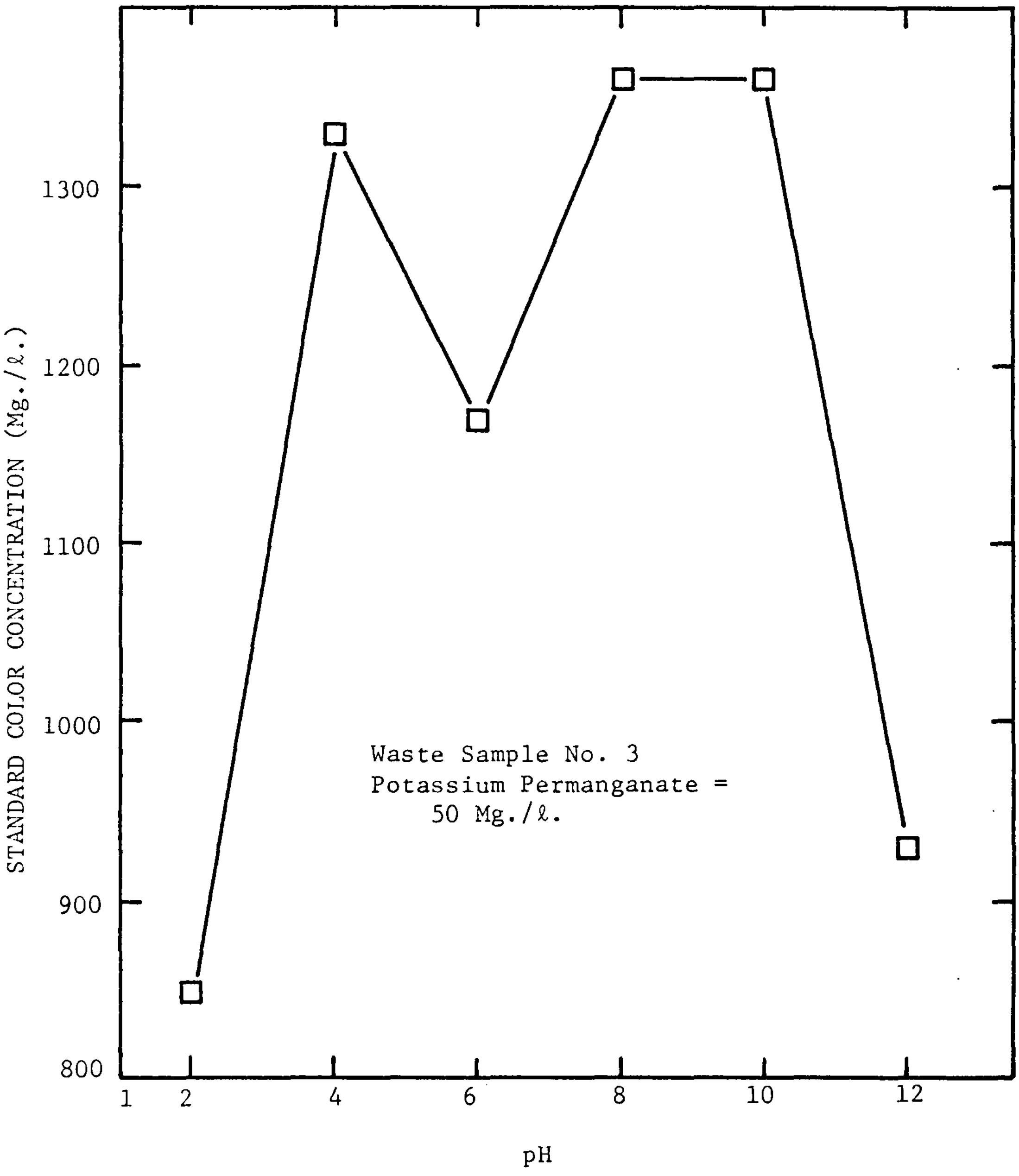


Figure 26. Standard Color With Potassium Permanganate Addition at Indicated pH Levels. All Samples Then Raised to pH 12 by Lime Addition.

wastewater to form new compounds that were more easily oxidized by permanganate. Zinc sulfate was first added to the raw wastewater in varying dosages and flash mixed for three hours. A potassium permanganate dosage of 85 mg./l. was then added to each of the samples for a six hour contact period. The results of this test are presented in Figure 27.

The samples were then raised to pH 12 by lime addition. Color and TNT concentrations were determined (Figures 28 and 29 to see whether the zinc sulfate addition improved the removal of TNT from the wastewater. The results obtained were marginally superior to those using potassium permanganate without zinc sulfate. Tests were then conducted to determine the dependency of TNT removal on pH. The samples were adjusted to pH 2, 4, 6, 8, 10, and 12 with lime addition after the waste samples had been treated with 80 mg./l. of zinc sulfate for a three hour contact period. The samples were then treated with 50 mg./l. of potassium permanganate. The results are presented in Figures 30, 31, and 32. The pH of the samples was then raised to 12 to determine the most effective pH range for potassium permanganate addition (Figures 33 through 35). The removal of TNT was slightly higher using zinc sulfate with potassium permanganate than using potassium permanganate alone, with maximum removal occurring at pH 2 in both cases.

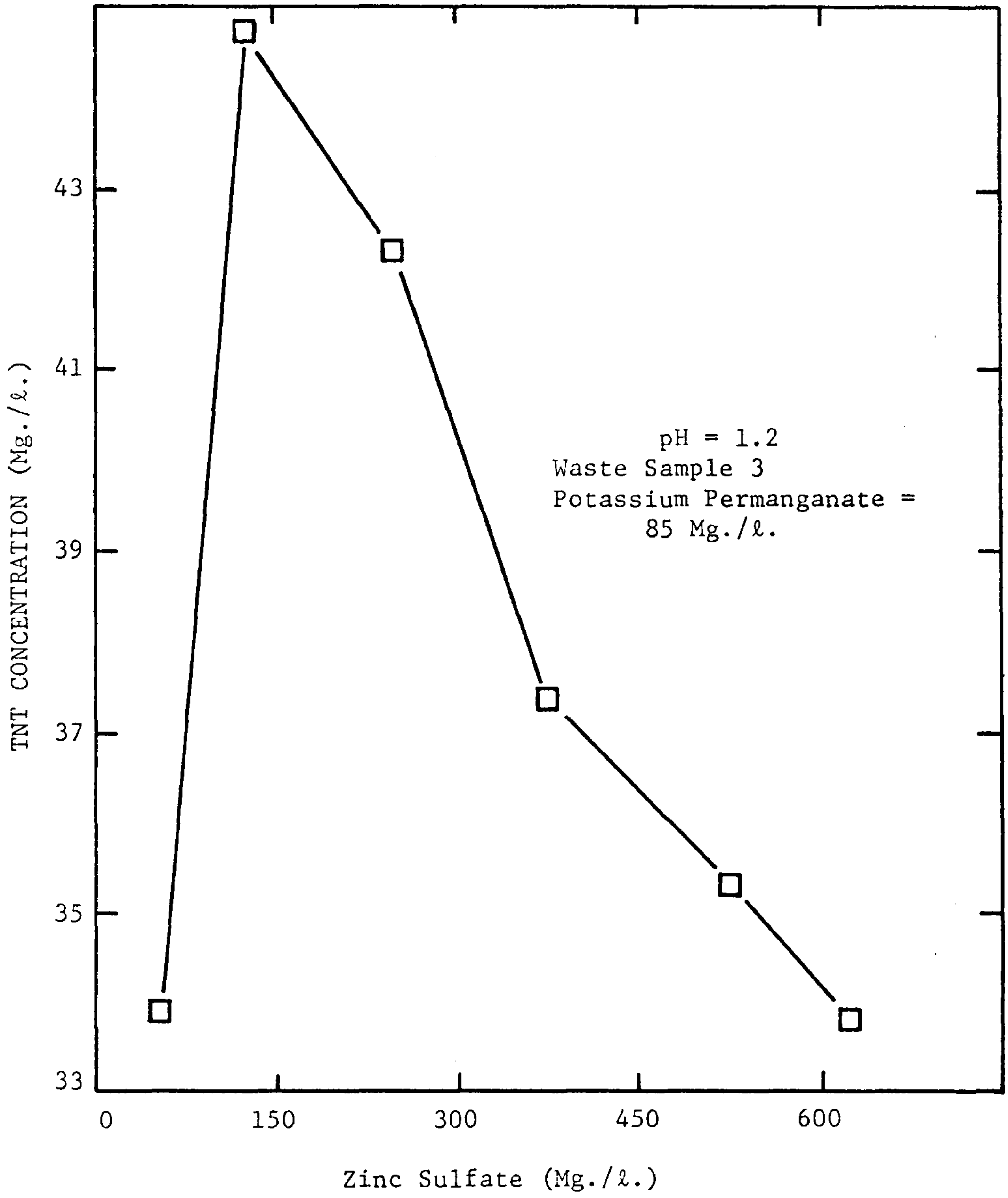


Figure 27. Zinc Sulfate and Potassium Permanganate Addition at pH 1.2 For The Removal of TNT

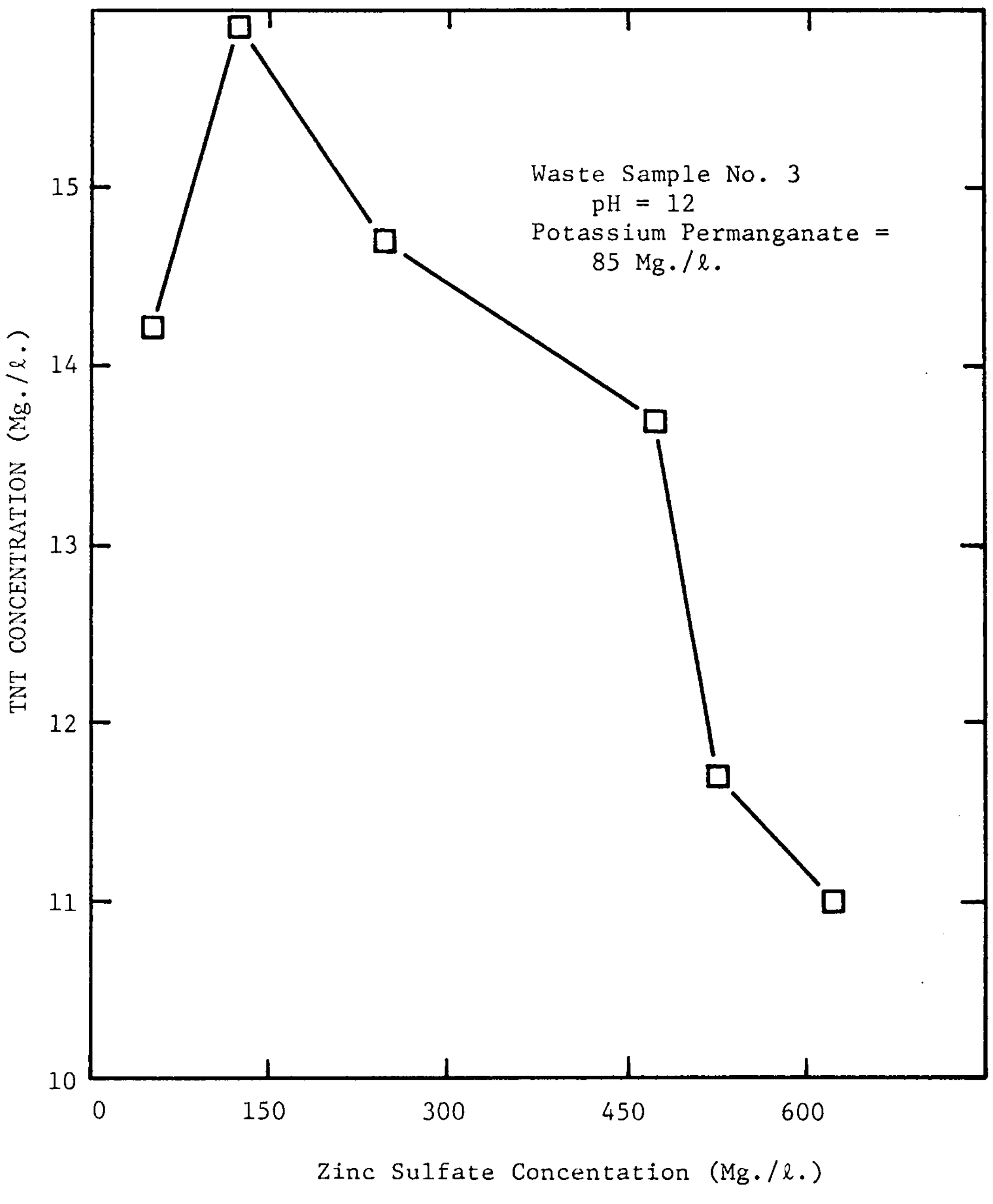


Figure 28. Zinc Sulfate and Potassium Permanganate Addition at pH 1.2 With Lime Addition to pH 12 For the Removal of TNT.

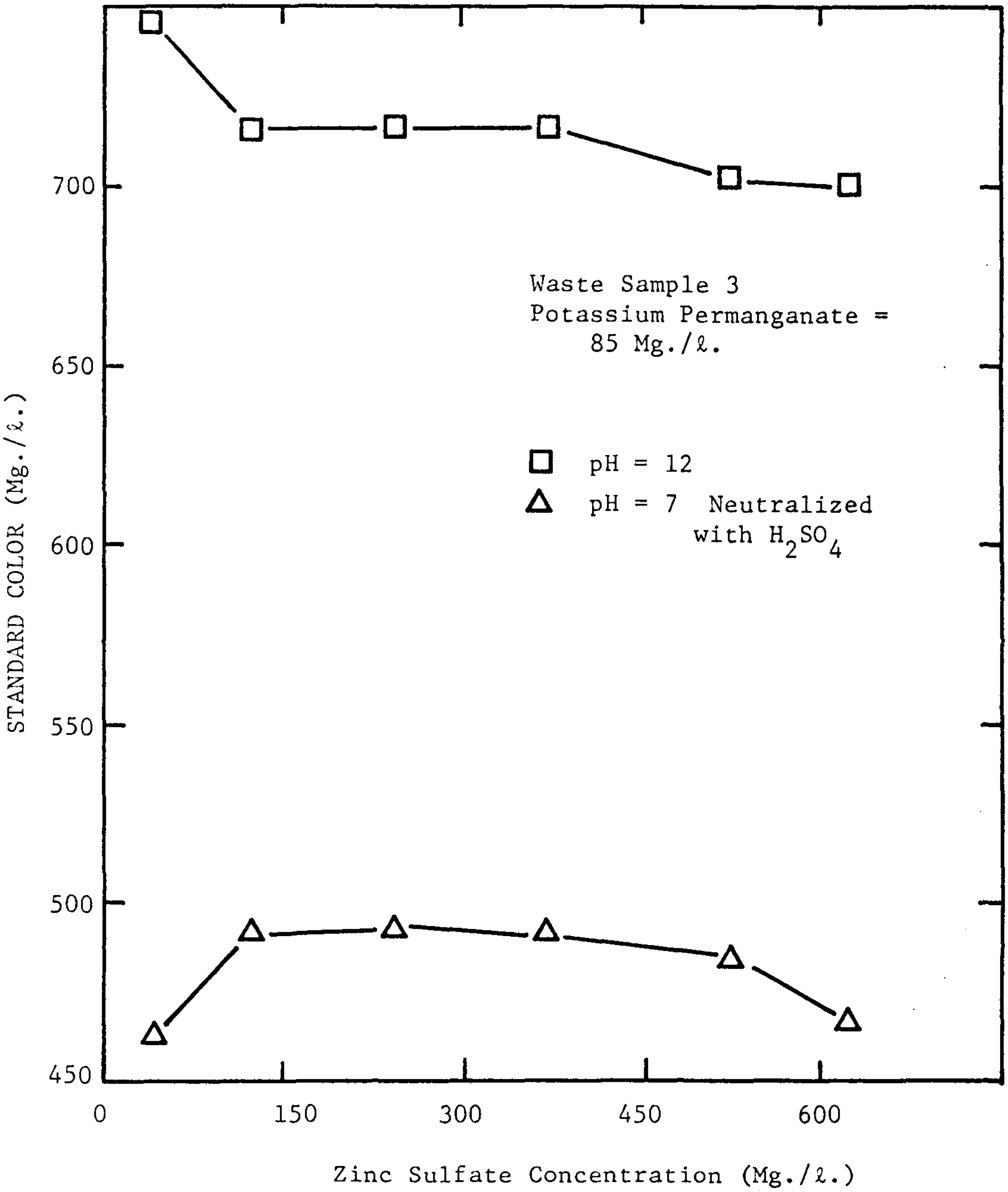


Figure 29. Color Concentration After Addition of Zinc Sulfate and Potassium Permanganate at pH 1.2. Raised to pH 12 By Lime Addition.

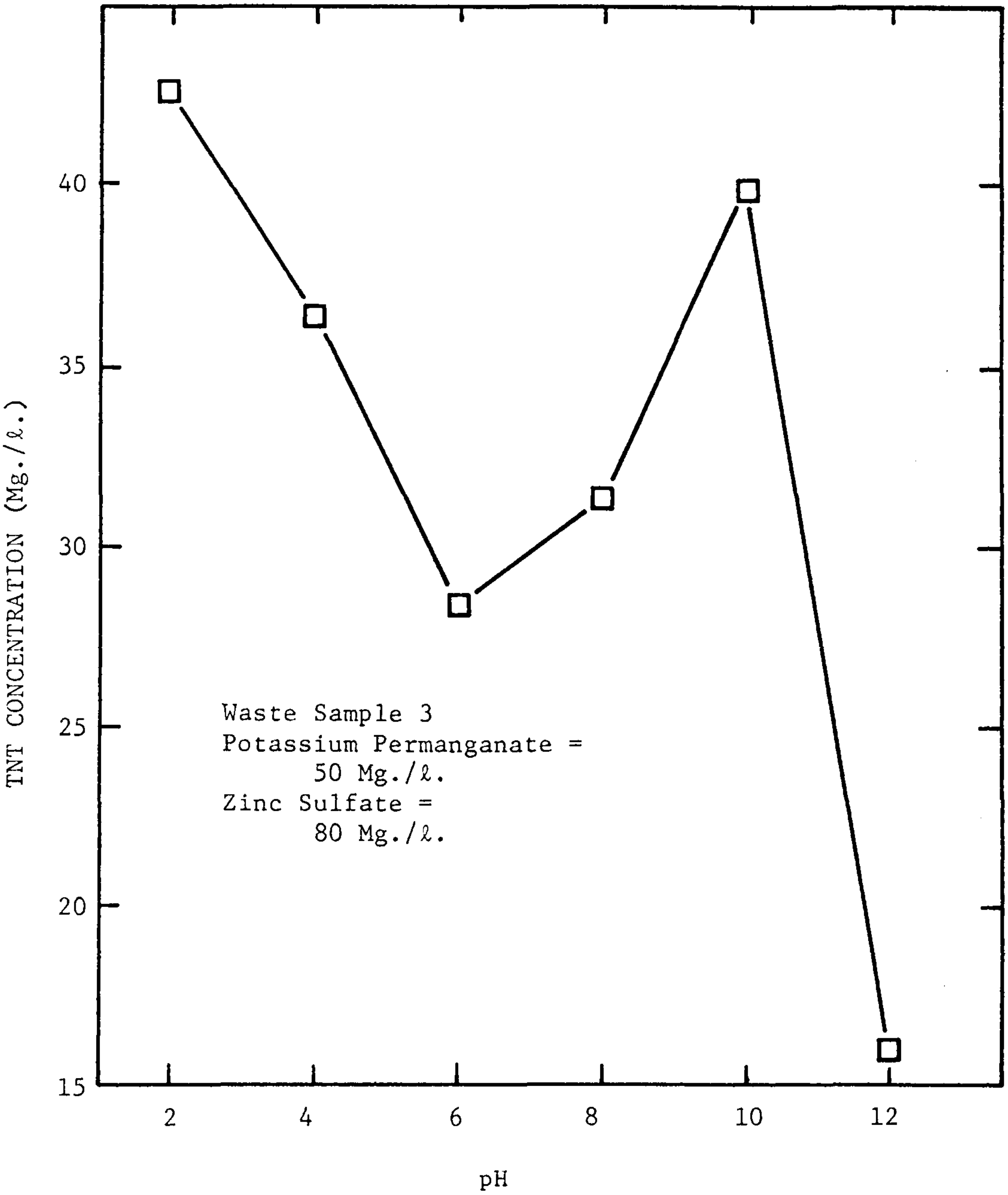


Figure 30. TNT Removal Using Zinc Sulfate Addition at pH 1.2 and Potassium Permanganate Addition at the Indicated pH Levels.

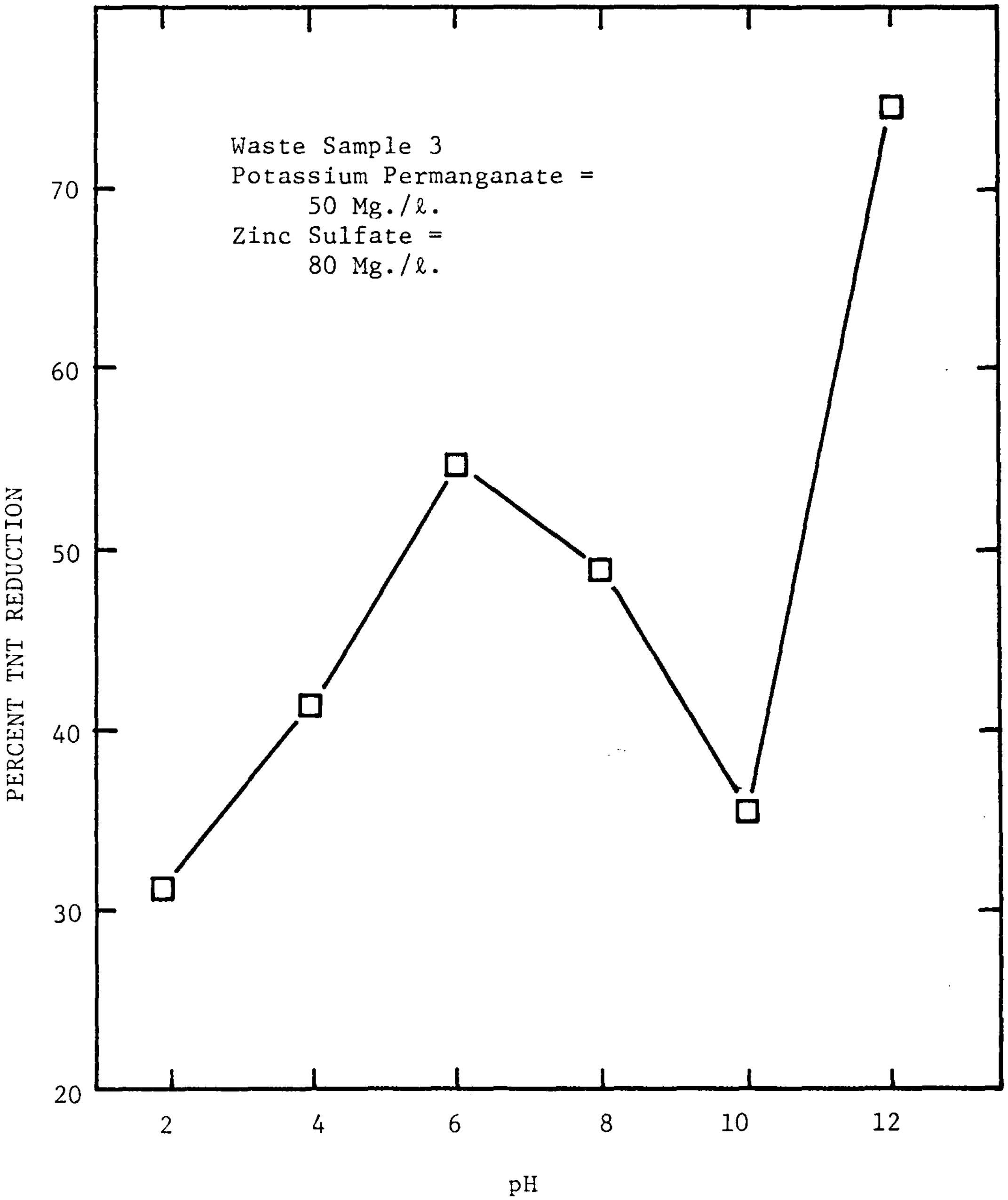


Figure 31. Percent TNT Removal Using Zinc Sulfate Addition at pH 1.2 And Potassium Permanganate Addition at the Indicated pH Levels.

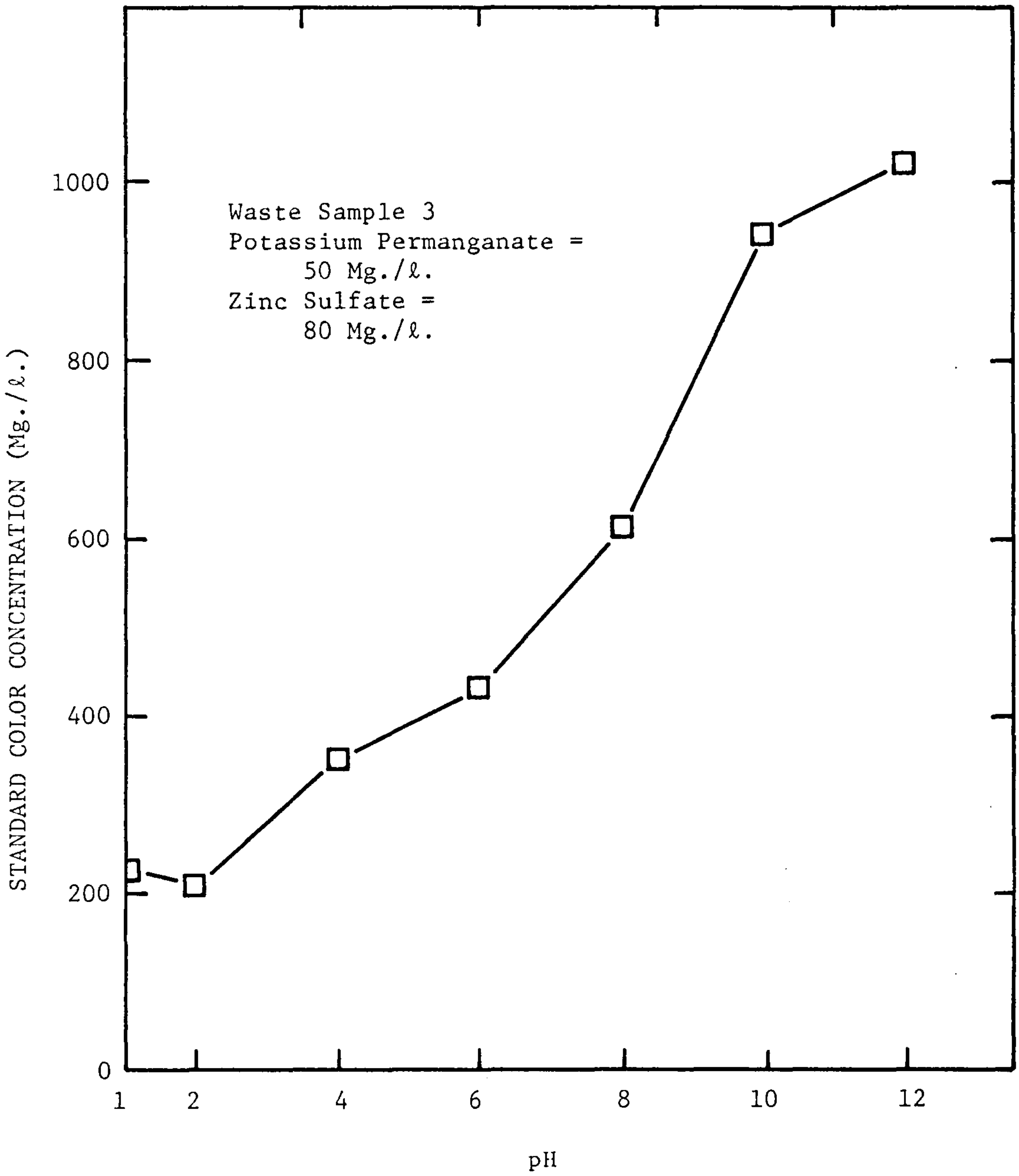


Figure 32. Color Concentration After Addition of Zinc Sulfate at pH 1.2 and Potassium Permanganate at the Indicated pH Levels.

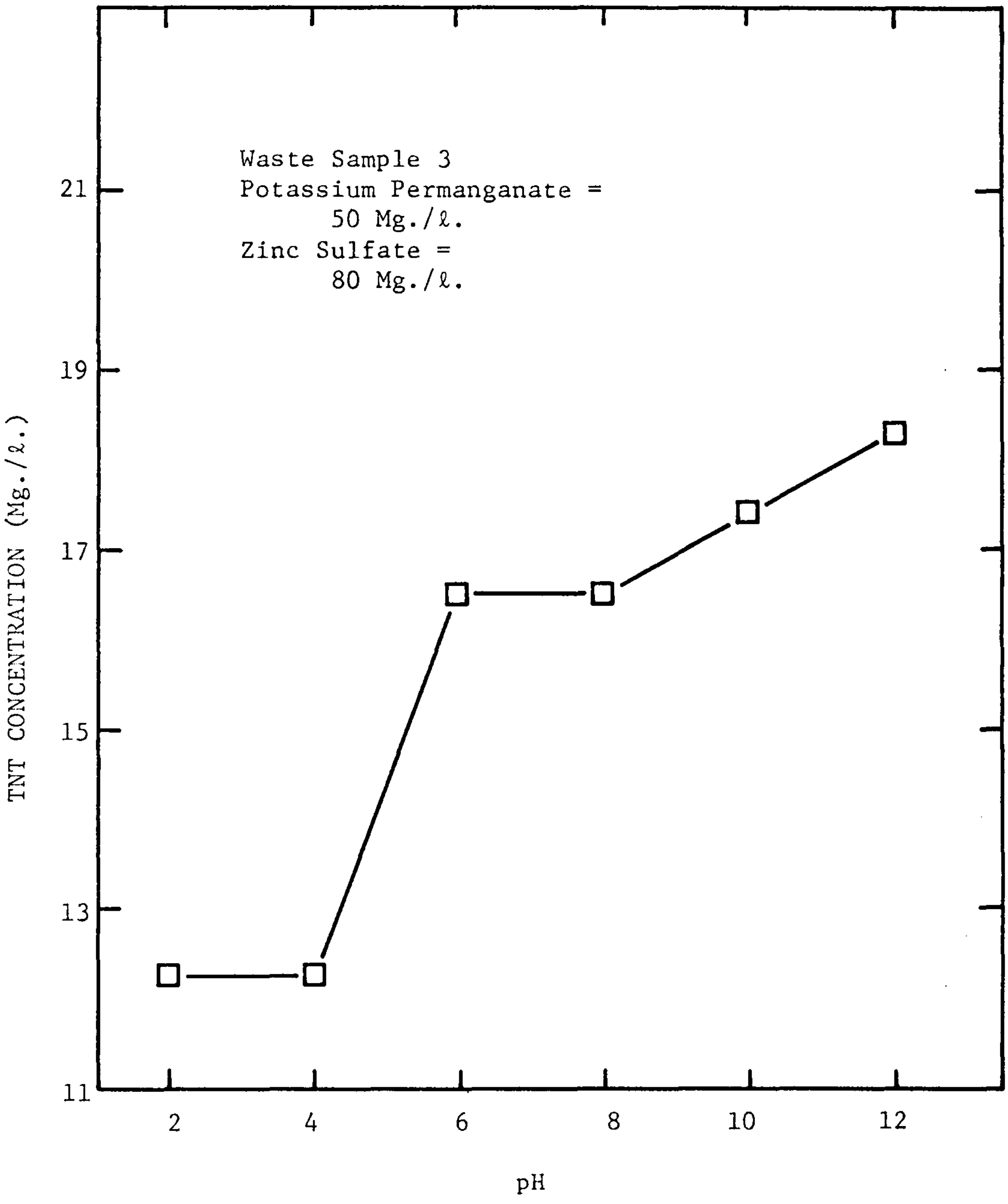


Figure 33. TNT Concentration Using Zinc Sulfate Addition at pH 1.2 and Potassium Permanganate Addition at the Indicated pH Levels. All Sample Raised to pH 12 By Lime Addition.

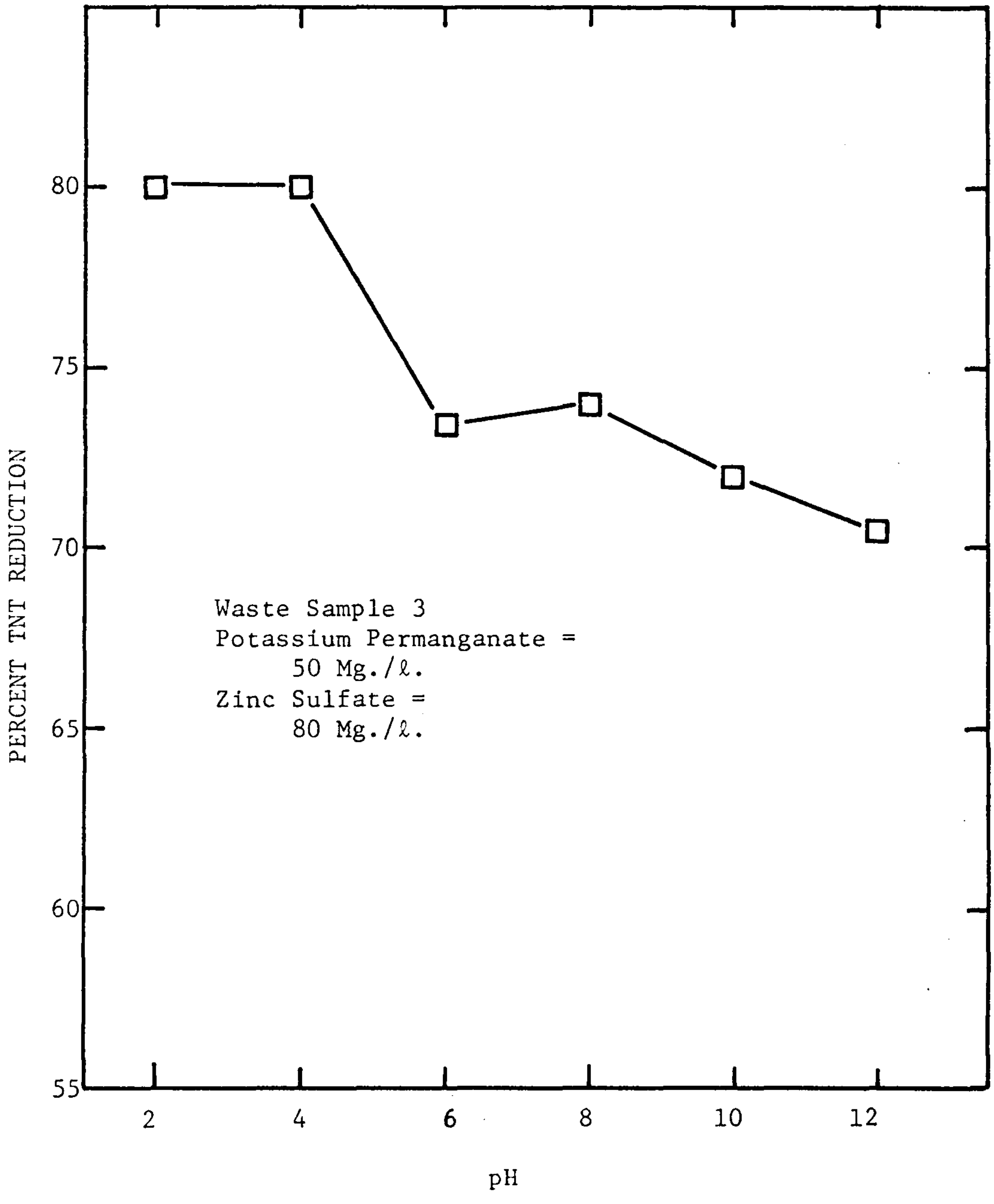


Figure 34. Percent TNT Removal Using Zinc Sulfate Addition at pH 1.2 and Potassium Permanganate Addition at the Indicated pH Levels. All Sample Raised to pH 12 By Lime Addition.

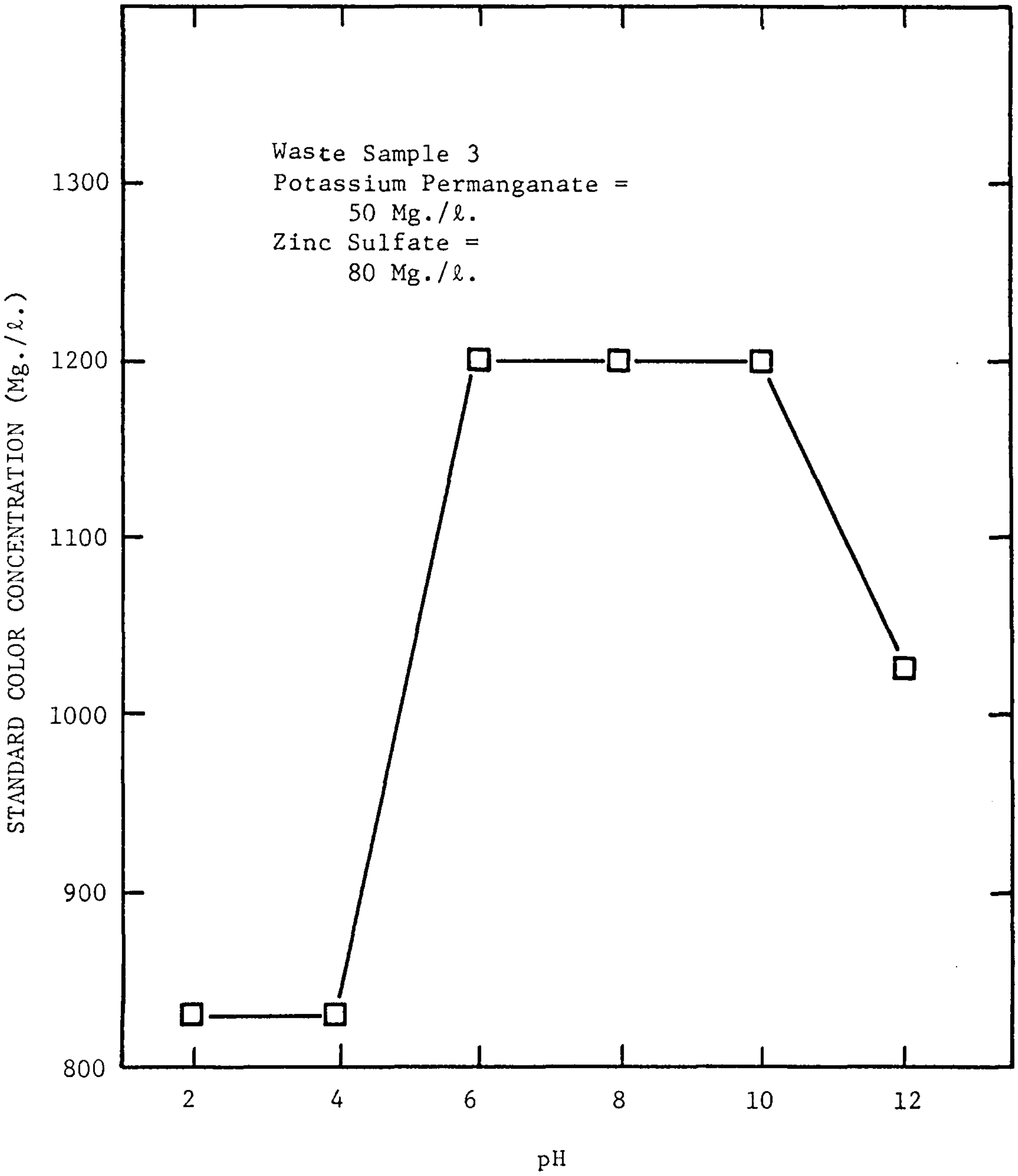


Figure 35. Standard Color at pH 12 After Zinc Sulfate Addition at pH 1.2 and Potassium Permanganate Addition at the Indicated pH Levels.

DISCUSSION

The following sections are devoted to a discussion of the results obtained from using lime, chlorine, and potassium permanganate for the removal of color and TNT from the TNT manufacturing process.

Lime

Excess lime treatment is an effective method of removing the nitroaromatic compounds associated with the TNT manufacturing wastewater. However, the use of excess lime treatment causes color development and with it an undesirably large increase in the color of the wastewater. Reacidification of the lime treated wastewater resulted in partial color removal, but was not satisfactory in providing an acceptable effluent for discharge.

Floc formation occurred at all pH levels when lime was added to the wastewater. The floc formation at the lower pH levels was believed to be caused by a reaction between the lime and the wastewater. Approximately 13 percent of TNT was removed at pH 2 through 7. This removal can be attributed to a reaction between the lime and wastewater. Increased TNT removal occurred at pH 9 and reached a maximum removal of 87 percent at pH 12. The TNT removal in this pH range can be attributed to sweeping action of the insoluble calcium hydroxide floc which is formed at higher pH levels.

Although color was increased by lime addition to the wastewater, it was noted that at pH levels above 7, the floc appeared to have the same color intensity as that of the supernatant, with maximum coloration of the floc occurring at pH 12. The color adsorption by the lime floc may explain the result obtained by Nay (10) in his experiments involving the use of lime and sodium hydroxide for waste neutralization. He noted that lime caused a more immediate color development than soda ash, but over a period of five days the color intensity of waste treated by soda ash was 3.5 times that treated by lime at pH 9. A tentative conclusion can be drawn from these results. The lime reacts faster with the TNT wastewater than the sodium hydroxide and the lime floc which is formed absorbs a color concentration equal to the difference of the color concentration of the lime neutralized wastewater and that of the sodium hydroxide neutralized wastewater when the color concentration becomes stationary.

Chlorine and Lime

Chlorine has been shown to be an effective oxidant for the removal of color and TNT from the TNT manufacturing wastewater. Reductions in TNT concentrations of up to 86 percent were obtainable when chlorine was used in conjunction with lime. The color development usually incurred by lime addition was reduced 70 percent by the chlorine.

The pH at which the chlorine was added to the waste samples had a significant effect on the removal of color and TNT. Optimum pH range for chlorine addition was pH 6 to 7. This result can be attributed to the compounds that high test hypochlorite forms when mixed with water. Hypochlorous acid, the most effective oxidant compound formed on the addition of HTH to water, is the predominant form when the system pH is below 7.

TNT removal varied only slightly with changes in chlorine concentration above a chlorine concentration of 250 mg./l. HTH at pH 12. However, it may be noted that residual color was greatly dependent on chlorine dosage. The color at pH 12, with a chlorine dosage of 1,000 mg./l. HTH was approximately one-third of the color developed when only 250 mg./l. HTH was used. At pH 7 and below, the chlorine accounted for a 30 percent removal of TNT, independent of the TNT removed by lime treatment. Color was also reduced sufficiently in this pH range.

The main problem with using chlorine is the possibility of substitution reactions occurring between the aromatic compounds and chlorine. The formation of chlorinated hydrocarbons may prove more detrimental to the receiving waters than the original compounds contained in the TNT wastewater. Bioassay tests would be necessary to define the extent of this problem.

Potassium Permanganate and Lime

Potassium permanganate has been shown to be an effective oxidant for the removal of color and TNT from the TNT manufacturing wastewater. Reductions in TNT concentration to 81 percent were obtainable when potassium permanganate was used in conjunction with lime.

When potassium permanganate is added to raw wastewater in increasing dosages, a break point similar to that associated with chlorine is formed. The break point was distinguished by a floc formation and occurred at a potassium permanganate dosage of 65 mg./l. Concentrations above 65 mg./l. potassium permanganate greatly increased the removal of TNT. A maximum TNT removal of 35 percent was obtainable with a potassium permanganate dosage of 85 mg./l.

The use of lime in conjunction with potassium permanganate slowed the reaction of the permanganate with the nitroaromatic compounds between pH 4 and 10. The reaction times at pH 2 and 12 were noted to be fairly close to those of the samples which contained no lime and also proved to be the pH levels at which TNT removal was optimized. These results may possibly be explained by the effects of extreme pH conditions on the organic compounds in the wastewater. Since lime is known to interfere with permanganate oxidation, minimum oxidation should have occurred with potassium permanganate addition at pH 12. The high pH levels, however, are known to alter the organic compounds in the wastewater. This change either makes oxidation of altered compounds easier or the compounds undergo a reaction in the presence of permanganate at high pH levels, which in turn forms new compounds that will not react with the Silas Mason reagents.

Zinc Sulfate Addition

The use of zinc sulfate to convert the compounds in TNT wastewater to forms which are more easily oxidized by potassium permanganate appears promising. Using raw wastewater samples, TNT removals of 48 percent were obtainable. This level represents a 13 percent increase over the amount of TNT removed by potassium permanganate alone. Color reduction was also improved when zinc sulfate was added to the wastewater before potassium permanganate addition.

The use of lime in conjunction with zinc sulfate and potassium permanganate produced TNT removals up to 82 percent. The lime was found to slow the reaction between potassium permanganate and the organic compound in the wastewater as was stated earlier. The results obtained using potassium permanganate addition at different pH levels with prior zinc sulfate addition proved more predictable than those obtained without zinc sulfate addition. The compounds in the waste apparently react with the zinc sulfate to produce compounds which are not greatly affected by pH changes.

A ratio of zinc sulfate to potassium permanganate of 1 to 1.5 appears optimum for TNT and color removal from the raw wastewater. This result would call for a zinc sulfate dosage of 55 mg./l. and a potassium permanganate dosage of 85 mg./l. for wastewater Sample No. 3. Optimum pH for addition of the chemicals is at the raw wastewater pH. This addition prevents the interference caused by lime and helps stabilize the wastewater, preventing it from undergoing radical physical changes during lime treatment.

SUMMARY AND CONCLUSIONS

Treatment with lime, chlorine, and potassium permanganate is effective for the removal of TNT and color from the Radford Army Ammunitions Plant wastewater. The following statements summarize the experimental results derived from this investigation:

1. The TNT and color concentration affected the treatability of the waste.
2. Excess lime treatment is an effective method of removing TNT from the wastewater. Percent TNT removal was, however, found to decrease with increasing TNT and color concentration of the raw wastewater.
3. Excess lime treatment caused a substantial increase in the color of the waste. Reacidification partially removed the color developed by excess lime treatment.
4. Chlorine was an effective oxidant for the removal of color and TNT when applied in large quantities.
5. Optimum pH for chlorine addition, to achieve maximum color and TNT removal was pH 6. The formation of the hypochlorous acid at pH 6 accounts for the increased removal of TNT and color.

6. Chlorination of lime treated wastewater reduced the color caused by the lime addition and improved TNT removal.
7. Potassium permanganate was effective in removing TNT and color from the raw wastewater.
8. Potassium permanganate oxidizing power was reduced in the presence of lime. Addition of the permanganate to the raw waste before lime treatment improved removal of color and TNT from the wastewater.
9. Addition of zinc sulfate to the raw wastewater marginally improved the percent removal of TNT and color by potassium permanganate.
10. Zinc sulfate appeared to help stabilize the wastewater, reducing some of the reactions that occurred with lime addition.

REFERENCES CITED

1. American Public Health Association, Standard Methods for the Examination of Water and Wastewater. 13th edition, American Public Health Association, New York (1971).

2. Caldwell, D. M., "Effect of Water Quality Parameters and Chemical Oxidants on Oxidative Precipitation of Iron and Manganese," Masters Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia (1970).

3. Cherry, A. K., "$KMNO_4$ Improves Water Quality," Journal of the American Water Works Association, 109, 7 (1962), pp. 266-268.

4. Cherry, A. K., "Use of Potassium Permanganate in Water Treatment," Journal of the American Water Works Association, 54, 4 (1962), pp. 417-424.

5. Cours, K., Radford Army Ammunition Plant, Radford, Virginia, Private Communication (July, 1972).

6. Edwards, G. P. and Ingram, W. T., "The Removal of Color from TNT Waste," Proceedings of the American Society of Civil Engineers, Sanitary Engineering Division, No. 645 (March, 1955).

7. Fair, M. F., Geyer, J. C., and Okun, D. A., Water and Wastewater Engineering, John Wiley and Sons, Inc., New York, New York (1968).

8. Hart, H. and Schuetz, R. D., Organic Chemistry, 4th edition, Houghton Mifflin Company, Boston, Massachusetts (1972).

9. Hartman, B. J., "Lime Treatment of Waste from a Small Arms Ammunition Plant," Sewage Works Engineering, 4, (1944), pp. 178-180.

10. Nay, M. W., "A Biodegradability and Treatability Study of TNT Manufacturing Wastes With Activated Sludge Systems." Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia (1971).

11. Nemerow, L. N., Liquid Waste of Industry, Theories, Practices and Treatment, Addison-Wesley Publishing Company, Reading, Massachusetts (1971).

12. Ruchhoft, C. C., LeBosquet, M., and Meckler, W. G., "TNT Wastes From Shell-Loading Plants," *Industrial and Engineering Chemistry*, *37*, 10 (1945), pp. 937-943.

13. Ruchhoft, C. C., Schott, S., and Megregian, S., "TNT Wastes," *Industrial and Engineering Chemistry*, *35*, 10 (1943), pp. 1122-1127.

14. Sawyer, C. N. and McCarty, P. L., *Chemistry for Sanitary Engineers*, 2nd edition, McGraw-Hill Book Company, New York, New York (1967).

15. Schulte, G. R., "Thre Treatability of a Munitions-Manufacturing Waste with Activated Carbon," Masters Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia (1972).

16. Spichers, R. G. and Skrinde, R. T., "Effect of Potassium Permanganate on Pure Organic Compounds," *Journal of the American Water Works Association*, *57*, 4 (1965), pp. 472-484.

17. Spichers, R. G. and Skrinde, R. T., "Potassium Permanganate Oxidation of Organic Contaminants in Water Supplies," *Journal of the American Water Works Association*, *55*, 9 (1963), pp. 1156-1194.

18. The Chemical Rubber Company, "Handbook of Chemistry and Physics," 51st edition, The Chemical Rubber Company, Cleveland, Ohio (1970).

19. The Manufacturing Chemists Association, *The Effect of Chlorination on Selected Organic Chemicals*, EPA Project No. 1202EXG, U.S. Government Printing Office, Washington, D. C. (1972).

20. Wilbourn, E. G., "Treatment of Textile Waste Utilizing a Lime-Polyelectrolyte System," Masters Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia (1970).

21. William, M., "A Tough Taste and Odor Problem!" *Journal of the American Water Works Association*, *116*, 1 (1963), p. 36.

THE TREATMENT OF A MUNITIONS MANUFACTURING WASTE WITH LIME, CHLORINE, AND PERMANGANATE

by

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(ABSTRACT)

Lime, chlorine, and potassium permanganate have long been important chemicals in the treatment of municipal and industrial wastewater. Their effectiveness in treating munitions manufacturing wastes was determined in a laboratory study using bench scale coagulation tests designed to simulate the facilities presently used to treat the wastewater. The wastewater from the new counter-current flow TNT manufacturing process at the Radford Army Arsenal Plant, Radford, Virginia, was found to be treatable by excess lime addition alone or in combination with the oxidants chlorine and potassium permanganate.

The excess lime treatment removed 86 percent of the Silas-Mason reactable substances but created a color problem. The oxidants were employed to remove the color developed by the lime addition. Optimum color removal occurred if the chlorine was added to the waste at pH 6. The potassium permanganate treatment system was limited by the color imparted to the waste and by the slow reaction of the permanganate with the organic compounds in the presence of lime. Optimum color and TNT removal was obtained by adding the potassium

permanganate at pH 2. A TNT removal of 81 percent was obtainable with a permanganate concentration of 50 mg./l. followed by excess lime treatment. Zinc sulfate addition marginally improved system performance.