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ABSTRACT

APPLICATION OF COAGULATION AND OZONATION TO CONTROL HAZARDOUS WASTES

Atakan ÖNGEN

The main scope of the study is to determine an appropriate control system in order to reduce pollution potential of a hazardous waste generated by a pesticide industry. In order to achieve that goal, both chemical treatment and ozonation applied on this hazardous waste which has been listed in EPA hazardous waste lists. During the study, ozone has been applied for both detoxification and monitoring its impact on chemical treatment.

The hazardous waste investigated during the study, is a liquid-formed toxic waste, which also has the properties of both flammability and reactivity with water. The waste is derived from the combination of both cleaning of the reactors that are used for formulation of liquid and powdered pesticides and laundry wastewater.

In the study, three different characterized samples were monitored and two different experimental procedures were followed to monitor which system reached maximum removal efficiency. In the first experimental procedure, chemical treatment and ozone application processes have been performed to the samples, respectively. For chemical treatment lime, $FeCl_3$ and alum are used as coagulants and NaOH and H_2SO_4 are used as helping agents. Non-ionic polyelectrolyte has also been used to achieve sufficient settling during jar tests. Ozone generator, used in the study, reaches the optimum operating efficiency by 5 lt/min oxygen flow rate. Ozone generation starts after 4-min delay time and the ozone was injected with a teflon pipe into the circulated wastewater in reactor.

To monitor detoxification ability of O_3, acute fish toxicity test has been run for both raw and treated wastewater. In the study, toxicity characteristic of hazardous waste derived from pesticide industry has been evaluated according to acute fish toxicity test. Screening and toxicity methodology is used to determine the lethal concentration (LC_{50}) and toxicity unit ($TU_{(a)}$). Using this method LC_{50} and $TU_{(a)}$ determined 17 as concentration percentage of the wastewater and 6, respectively.

Key words : Ozone, detoxification, coagulation.

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ÖZET

KOAGÜLASYON VE OZON UYGULANARAK ZARARLI ATIKLARIN KONTROLÜ

Çalışmanın öncelikli amacı, in-situ, on-site koşullar göz önünde bulundurularak, pestisit endüstrisinden kaynaklanan, zehirli etkiye sahip bir zararlı atık için uygun kontrol mekanizmasının saptanmasıdır. Söz konusu atık EPA zararlı atık listelerinde yer almaktadır. Bu atığa uygun bir yönetim mekanizması belirlemek amacıyla, kimyasal arıtma ve ozonlama prosesleri uygulanmıştır. Çalışma süresince, ozon hematığın zehirlilik özelliğini giderebilmek hem de kimyasal arıtma üzerindeki etkilerini gözlemleyebilmek amacıyla uygulanmıştır.

Çalışma süresince incelenen zararlı atık, sıvı formda, zehirli, tutuşabilir olduğu gibi suyla reaktif olabilme özelliğine de sahiptir. Atık, reaktörlerin yıkanması sonucu çıkan proses sıvıları ve çamaşırhane sularının birleşmesinden oluşmaktadır.

Çalışma esnasında, farklı karakteristiklere sahip üç örnek üzerinde gözlemleme yapılmıştır. Bu gözlemleme için iki farklı deneysel akım şeması belirlenmiş ve her bir numune için uygulanarak en iyi verime hangi düzende ulaşılabildiği araştırılmıştır. Deneysel akımların ilkinde, sırasıyla kimyasal arıtma ve ozonlama işlemleri tatbik edilmiştir. Kimyasal arıtma esnasında kireç, alum ve $FeCl_3$ koagülant olarak denenmiş ve pH ayarları NaOH ve H_2SO_4 ile yapılmıştır. Yeterli çökelmeyi sağlayabilmek amacıyla yardımcı kimyasal olarak non-iyonik polielektrolit kullanılmıştır.

Deneysel çalışmalarda kullanılan ozon cihazının optimum çalıştığı oksijen akım hızı 5 lt/dak. dır. Cihaz ozon üretmeye çalıştırıldıktan 4 dakika sonra başlamakta ve üretilen ozon bir pompa vasıtası ile reaktör teflon boru sisteminde döndürülen atıksuya boru enjeksiyonu ile uygulanmaktadır.

Ozonun detoksifikasyon özelliğini izleyebilmek amacıyla akut balık zehirlilik deneyi sürdürülmüştür. Çalışma esnasında, üzerinde araştırma yapılan numunenin zehirlilik özelliği sürdürülen standart balık zehirlilik deneyine göre değerlendirilmiştir. Böylece öldürücü konsantrasyon (LC_{50}) ve zehirlilik seyrelme faktörü ($TU_{(a)}$) değerleri saptanmıştır. LC_{50} değeri atıksuyun konsantrasyon yüzdesi biçiminde 17 olarak, $TU_{(a)}$ ise 6 olarak bulunmuştur.

Anahtar Kelimeler : Ozon, detoksifikasyon, koagulasyon.

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1. INTRODUCTION

1.1. Aim and Scope

During the past decade, the public has become increasingly aware of one of the major impacts of industrial development. Concurrently, awareness has been growing that certain disposal methods used for such waste may pose risks to human health and the quality of the environment. Several countries have made great efforts to develop effective technologies and administrative procedures for hazardous waste management.

Waste is frequently a complex mixture that makes the collection of data on waste composition difficult and often very costly to obtain.

Hazardous waste is potentially damaging to the environment and therefore, needs control. Most of it, however, is derived from industries among the most important to the growth and maintenance of a modern industrial society, such as iron and steel and chemical industries.

If, in addition to materials that are toxic, flammable, corrosive, etc., the definition of "hazardous" includes materials with a high water pollution potential which requires special controls. Thus, environmental protection and economic development must be finely judged in order to achieve a balance.

To perform the experimental procedures in the study, a hazardous waste, which is derived from a pesticide industry, was investigated. The solvent power of both halogenated and non-halogenated organic solvents is used in industry. Whichever method is employed, a sump residue accumulates with use. The residue is either allowed build up until an unacceptable level of contamination is reached and the dirty solvent removed for disposal or recovery or the residue is continuously removed by recycling via an on-line purification plant. Wash-down wastes are also dangerous after contamination with a range of solvents.

The main scope of the study is to create a management system for a specific, highly toxic hazardous waste derived from a pesticide industry. In order to reach that scope during the study, both chemical treatment and chemical oxidation processes were performed in different orders to monitor and decide the most suitable treatment system for this listed hazardous waste. Toxicity tests were also applied after deciding an effective treatment system order.

In the study, ozonation efficiency both before and after chemical treatment and detoxification of ozone were investigated. To reach that goal, first literature searches about hazardous wastes, toxicity and chemical oxidation by ozone were completed. Experimental approach was detailed and procedures were explained. Calculation method for ozone was also mentioned and all results were shown in tables and figures.

In results and evaluations section results were given in figures in order to evaluate and discuss the results determined.

2. HAZARDOUS WASTE MANAGEMENT

2.1. Conception of Hazardous Waste

There has been a rapid increase in the generation of the hazardous both organic and inorganic wastes per year since the industrial facilities started to grow up. Industries have produced a wide variety of products that have improved our standard of living and generally increased human life expectancy. However, associated with these benefits is the risk of accidents that can endanger human health and the environment. The magnitude of the problem was so clear that in order to consider these potential risks and try to determine adequate management facilities, the concept of hazardous waste has been adopted since 1970s.

Risk of accidents that can be dangerous for both human health and the environment, toxic effects of the many chemicals on human, the lack of knowledge about the adverse effects of those chemicals to the media, the rapid increase in the production of organic chemicals as well as increased demand for valuable heavy metals are believed to be the main reasons for the adoption of hazardous waste conception.

2.2. Definition of the Problem

2.2.1. Definitions

Waste is something that the owner no longer wants at a given place and time and which has no current or perceived market value. Hazardous waste is waste that has physical chemical or biological characteristics that require special handling and disposal procedures to avoid risk to health and/or other adverse environmental effects.

In the United States, hazardous waste has been defined by Resource Conservation Recovery Act (RCRA) legislation as "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical or infectious characteristics may cause or significantly contribute to, an increase in mortality or an increase in serious irreversible or incapacitating reversible illness or pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported or disposed of or otherwise managed." [1] While the definition refers to "solids" it has been interpreted to include semi-solids, liquids, and contained gases as well.

The U.S. Environmental Protection Agency (EPA) has defined a waste to be hazardous under the legislation if it meats one or more of the following conditions:

- Exhibits characteristics of flammability, corrosivity, reactivity, and/or toxicity
- Is a nonspecific source waste (generic waste from industrial processes)
- Is a specific source waste (from specific industries)
- Is a specific commercial chemical product or intermediate
- Is a mixture containing a listed hazardous waste
- Is a substance that is not excluded from regulation under the RCRA

Statutory definitions of hazardous waste used by various nations reflects not only the nature of the environmental problems they were designed to cover, but also the social, political and economic conditions of the nations concerned. When attempting to define hazardous waste, concern is essentially with waste, which presents either of the following:

- Short-term acute hazards. Such as acute toxicity by ingestion, inhalation, or skin absorption corrosivity or other skin or eye contact hazards or the risk of fire or explosion;
- Long-term environmental hazards, including chronic toxicity upon repeated exposure, carcinogenicity (which may in some cases result from acute exposure but with a long latent period), resistance to detoxification processes such as biodegradation, the potential to pollute underground or surface waters, or aesthetically objectionable properties such as offensive odors.

Wastes with these properties may arise as by-products, side-products, process residues, spent reaction media, contaminated plant or equipment, etc., from manufacturing operations and as consumer discards of manufactured products.

2.3. Criteria for Identifying Hazardous Waste

Waste has the potential to be hazardous by virtue of the following:

- Substances present in the waste
- Their concentration
- Their chemical reactivity
- Physical form in which the substance are present
- Quantity and recurrent rate of arising of potentially hazardous material
- Mobility and persistence of the potentially hazardous materials in which they are placed
- Targets available in that environment and their vulnerability to the potentially hazardous materials
- Possibility of remedial measures and their costs

The shot-term acute and longer-term environmentally hazardous properties of a waste are a function of the chemical species present. In some cases, wastes have well-defined dangerous properties and are unequivocally hazardous; such wastes generally result from the use of commonly encountered chemical compounds. The majority of wastes considered, however, are likely to be complex mixtures which do not readily lend themselves to chemical characterization.

Within the context of waste management, the hazard characteristics of a waste are more relevant than knowledge of its precise chemical composition, which in many cases will be impractical to obtain.

2.3.1. Composition

Concerning the composition of the waste, individual components of a waste should be known before a complete assessment of its hazard potential is made. This knowledge however, is often very difficult and may be impossible in practical terms, particularly for solid wastes. To demand, either directly or by implication, that all waste be analyzed for all potentially hazardous species is quite impractical.

Nevertheless, good information on waste composition is needed, and in many cases broad compositional data will be adequate.

2.3.2. Physical Form

The physical form of the waste (solid, semi-solid, sludge, liquid, etc.) is relevant to a consideration of both potential acute or longer-term environmental hazards. In general, liquid or sludge waste is more liable to cause water pollution problems than is solid waste. Small particle size by itself may confer hazard on a material that is nonhazardous in larger pieces; many finely divided metals are acutely hazardous while the massive material is harmless. Solids formed by cooling from the molten state may often have their potential hazard much reduced.

2.3.3. Quantity

The quantity of the waste and its recurrent rate of arising are important. The handling and disposal of a few hundred kilograms of a particular waste as an isolated arising may demand a totally different solution to the disposal of similar material arising on a regular basis in quantities that may be orders of magnitude greater or smaller.
The potential for environmental damage at a waste disposal site is clearly related not only to the concentration of the substance released but also to the total quantity released at a given time.

2.3.4. Acute Hazard

The acute hazard posed by the waste may be expressed in terms of oral, inhalation or dermal toxicity, flashpoint, explosivity, concentration of known corrosive species, etc. Physical characteristics, such as vapor pressure and boiling point, may be important. To avoid dangerous interactions with co-deposited materials, highly reactive materials (e.g. powerful oxidants) should also be considered. However, unless toxicity tests are performed on the waste itself, acute hazards posed by the waste can only be predicted by the hazards of its components.

2.3.5. Long-term Hazard

Finally, the long-term hazard posed by the waste will depend upon the chosen disposal route. For example, such properties as volatility, water solubility in organic chemicals will influence the mobility of wastes deposited in landfill. The persistence

of a particular material will depend upon its vulnerability to various natural breakdown mechanisms : microbiological, photochemical, oxidation/reduction, etc. The toxicity of a deposited material and its metabolites and organoleptic factors, such as taste and smell, are all-relevant.

2.4. Exclusive and Inclusive Lists of Hazardous Waste

2.4.1. The Exclusive List

One alternative approach to the problem of adequately defining what constitutes a hazardous wastes which present no significant short-term environmental hazards and to define hazardous waste by exclusion (as any wastes not listed). This approach has been used successfully. In the United Kingdom, for example, it was formerly used to define those wastes for which notification of intent to deposit was a statutory requirement under the Deposit of Poisonous Waste Act [2]. Of noteworthy importance is the extra environmental safeguard incorporated in this case, whereby exclusion from the notification procedure was subject to the listed waste meeting certain qualitative criteria in terms of its composition. These criteria were that the waste should not contain any hazardous quantity or concentration of any poisonous, noxious or polluting substance.

While one advantage of the exclusive list approach is that it is relatively simple to ensure that the listed materials are not hazardous, materials not listed and, therefore, by inference hazardous may well be only marginally so. In addition, when reliance is placed upon qualitative, subjective criteria, different interpretations will inevitably be possible. Thus, waste producers, waste disposers and regulatory authorities are denied the certainty they need.

2.4.2. The Inclusive List

More widely employed for regulatory purposes are listing of hazardous waste, either with or without accompanying criteria. This inclusive list approach is currently employed in Belgium, Denmark, France, Germany, Netherlands, Sweden, the United Kingdom and the United States. The lists comprise wastes from certain industries, wastes containing specific components or specific waste streams identified by the processes from which they originate.

The inclusive list offers a greater degree of certainty but suffers from the disadvantage that omissions may well be significantly hazardous. The greater the degree of specificity, the more an all-embracing, inclusive list approaches encyclopedic proportions. Any list, inclusive or exclusive, may itself use terms that are difficult to define in a waste management context, such as solvent, pharmaceutical, toxic or phenol, etc.

Despite individual differences in approach, international agreement is substantial on those components of a waste, which cause it to be classified as hazardous.

Hazardous waste can be solid, liquid or gas. The characterization of a hazardous waste can range from a simple review of a list. The EPA has listed specific hazardous waste according to the following criteria:

F Series : Hazardous waste from nonspecific sources(e.g., halogenated solvents used in degreasing and spent electroplating bath solution)
K Series : Hazardous waste from specific sources (e.g., API separator sludge and tank bottoms from leaded petroleum refining)
P Series : Acutely hazardous waste of specific commercial chemical products, including discarded products, off-specification products, containers, and spill residuals.
U Series : Toxic hazardous wastes which are commercial chemical products, including discarded products, off-specification products, containers, and spill residuals.

The complexity of characterizing a waste to determine whether it is hazardous increases significantly when the source and/or nature is unknown. The only methods available are to sample and perform chemical analysis to determine the nature of the material [3].

2.5. Characteristics of Hazardous Waste

In establishing these criteria for the treatment of any identification of a hazardous waste four characteristics selected:

- Flammability
- Corrosivity
- Reactivity
- Toxicity characteristic

2.5.1. Flammability

Flammability is the characteristic used to define as hazardous those wastes that could cause a fire during transport, storage, or disposal. Examples of ignitable wastes include waste oil and used solvents.

1. It is a liquid, other than an aqueous solution containing less than 24 percent alcohol by volume. And has a flash point less than 60^{o} C (140^{0} F), as determined by a Pensky- Martens Closed Cup Tester (using the test method specified in the ASTM standard D-93-79 or D-93-80) or by a Setaflash Closed Cup Tester (using the test method specified in the ASTM standard D-3278-78)

2. It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or spontaneous chemicals changes and when ignited, burns so vigorously and persistently that it creates a hazard.

3. It is an ignitable compressed gas as defined in 49 Code of Federal Regulations 173.300 DOT regulations.

4. It is an oxidizer as defined in 49 Code of Federal Regulations 173.151 DOT regulations.

A waste that exhibits flammability but is not listed as a hazardous waste in Subpart D of RCRA has the EPA hazardous waste number D001 [3]

2.5.2. Corrosivity

Corrosivity, as indicated by pH, was chosen as an identifying characteristic of a hazardous waste because wastes with high or low pH can react dangerously with other wastes or cause toxic contaminants to migrate from certain wastes. Examples of corrosive wastes include acid wastes and used pickle liquor from steel manufacture. Steel corrosion is a prime indicator of a hazardous waste, since wastes capable of corroding steel can escape from drum and liberate other wastes.

1. It is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.5, as determined by a pH meter using an EPA test method
2. It is a liquid and corrodes steel (SAE 1020) at a rate greater than 6.35 mm (0.250 inch) Per year at a test temperature of 50^{o} C (130^{0} F), as determined by the test method specified in National association of Corrosion Engineers Standard TM-01-69 and standardized in "Test Methods for the Evaluation of the Solid Waste, Physical/Chemical Methods."

A waste that exhibits corrosivity but is not listed as a hazardous waste in Subpart D has the EPA hazardous waste number D002 [3]

2.5.3. Reactivity

Reactivity was chosen as an identifying characteristic of a hazardous waste because unstable wastes can pose an explosive problem at any stage of the waste management cycle. Examples of reactive wastes include water from TNT operations and used cyanide solvents.

1. It is normally unstable and readily undergoes violent change without detonating.
2. It reacts violently with water.
3. It forms potentially explosive mixtures with water.
4. When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.
5. It is a cyanide- or sulfide-bearing waste that, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.
6. It is capable of detonation or explosive reaction if subjected to a strong initiating source or if heated under confinement.

7. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.
8. It is a forbidden explosive as defined in 49 Code of Federal Regulations 173.51, a Class A explosive as defined in the 49 Code of Federal Regulations 173.53, or a Class B explosive as defined in 49 Code of Federal Regulations 173.88 DOT regulations.

A waste that exhibits reactivity but is not listed as a hazardous waste in Subpart D has the EPA hazardous waste number D003 [3]

2.5.4. Toxicity

A toxic waste on contact with a living organism is capable of killing, injuring, or otherwise impairing that organism. These poisonous substances are hazard in that there is risk depending upon the exposure and the manner in which such a waste is handled.

The toxicity characteristic leaching procedure (TCLP) test is designed to identify wastes likely to leach hazardous concentrations of particular toxic constituents into the ground water as result of improper management. During the TCLP, constituents are extracted from the waste to simulate the leaching actions that occur in landfills. If the concentration of the constituent exceeds the regulatory limit, the waste is classified as hazardous.

The TCLP test replaced the EP toxicity test in September 1990 and added 25 organic compounds to the eight metals and six pesticides that were subject to the EP toxicity [4]

2.6. Wastes Hazardous in Only Part of the Management Cycle

The management cycle for any particular hazardous waste comprises its generation, transport, storage, treatment (where appropriate) and final disposal. These options are called Treatment, Storage, Disposal facilities (TSD Facilities) by EPA. The aim was to estimate the total quantity of hazardous waste managed by TSD facilities and to identify hazardous waste management process, their commercial availability and the general waste type managed at each facility [4]. Clearly many hazardous waste

characteristics, such as corrosivity, flammability and toxicity, will cause potential problems at all these stages.

By contrast, many wastes, which offer no significant short-term handling hazard, may cause severe disposal problems based on their physical or chemical properties. Certain halogenated hydrocarbon solvents, for example, are non-flammable and of a low order of acute toxicity where no recovery options exist and landfill is considered unsuitable because of the potential threat to water supplies, a thermal destruction route will be sought.

Such wastes, however, should only be considered for incineration in specialized plants equipped with gas scrubbing facilities to remove the hydrogen chloride generated. Many oily wastes cannot be economically recovered or incinerated because of their high water and/or solids content, but they are low order of toxicity and present no handling hazard.

Certain wastes, which present an inhalation hazard, only present a hazard at the point of arising. Once securely bagged, transport and disposal are straight forward, although the disposal method selected should guarantee that the sealed bags are unlikely to be disturbed.

3. TOXICOLOGY

3.1. The Concept of Toxicology

Pharmacology is the study of the nature, properties, and effects that chemical substances have on biological systems. Hence, in its entirety, pharmacology embraces the study of all substances known to affect living processes, whether beneficially or detrimentally. For academic purposes, pharmacology is divided into several branches. One such branch relates to the specific study of adverse health effects caused by poisonous or toxic substances; it is called toxicology.

Toxicology is the science that deals with the effects of poisons upon living organisms. A poison or toxicant is a substance that, above a certain level of exposure or dose, has detrimental effects on tissues, organs, or biological processes. Among the important aspects of toxicology are the relationship demonstrated presence of a chemical or its metabolites in the body and observed symptoms of poisoning, mechanisms by which toxicants are transformed to other species by biochemical processes, the processes by which toxicants and their metabolites are eliminated from an organism, and treatment of poisoning with antidotes.

USEPA characterizes RCRA hazardous waste by means of a property called extraction-procedure toxicity (EP toxicity) [5]. This property relates only the following toxic metals and pesticides: arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, endrin, lindane, methoxychlor, toxaphane, 2, 4 – dichlorophenoxyacetic acid, and [2-(2, 4, 5-tri-chlorophenoxy) propionic acid]. A hazardous waste exhibits the characteristic of EP toxicity if a sample of the waste is found to contain any of these contaminants at a concentration equal to or greater than the respective values noted in Table 3-1. Hazardous wastes that exhibit the characteristics of EP toxicity are assigned an EPA hazardous waste number from D004 to D020, as tabulated [5]

Table 3-1 Toxicity characteristics, Maximum Concentration of Contaminants

EPA Hazardous Waste Number	Contaminant	Max. Concentration, (mg/l)
D004	Arsenic*	5.0
D005	Barium	100.0
D006	Cadmium*	1.0
D007	Chromium	5.0
D008	Lead*	5.0
D009	Mercury*	0.2
D010	Selenium	1.0
D011	Silver*	5.0
D012	Endrin*	0.02
D013	Lindane*	0.4
D014	Methoxychlor*	10.0
D015	Toxaphane*	0.5
D016	2,4-D*	10.0
D017	2,4,5,-TP(Silvex)*	1.0
D018	Benzene	0.5
D019	Carbon tetrachloride	0.5
D020	Chlordane	0.03

* Formerly EP toxicity contaminants
Source: U.S. Environmental Protection Agency

3.2. How Toxic Substances Enter the Body

There are many routes by which a substance may enter the body, mainly such as inhalation, skin absorption, and ingestion.

3.2.1. Ingestion

Ingestion refers to the swallowing of a substance through the mouth and into the stomach, and generally followed by its entrance into the small intestine. Ingested toxic substances either directly damage the tissues of the mouth or digestive tract at the site of contact, are metabolized to toxic or non-toxic substances, or are absorbed through the intestinal walls to enter the blood system. In the latter case, the circulatory system then disseminates the substances to various body organs and tissues.

3.2.2. Absorption

Absorption through the skin is a second route by which a substance may enter the body. Skin is the largest single organ of the body. It often serves as an organ of defense by preventing the direct entry of a substance into the body or its parts, except for the eyes and lungs. But the skin may also act as a portal of entry for some chemical substances. In these instances, the skin acts like a permeable membrane.

Generally, liquids absorb most easily, since their concentration is high at a particular point of contact; capillary action aids in their penetration. Some toxic substances, like hydrofluoric acid, absorb through the skin and damage near by bone matter. But, more commonly, substances affect a specific site of action or the body as whole.

3.2.3. Inhalation

It is a third route by which a substance may enter the body. The internal surface of our lungs is so rich in blood vessels that actually cover an average surface area of approximately 75 m^2 [5]
Thus, a substance inhaled into the lungs is readily absorbed into the bloodstream. This means that the body's response action from inhalation is often relatively swift.

3.3. Classification Of Toxic Effects

When a substance is toxic, it may cause local damage at the site of contact or at a site of action (that is, at certain tissues or organs), or it may adversely affect the entire organisms in some way. These various ways by which a substance may cause biological damage are often used as a broad basis for the classification of toxic effects. In particular, these adverse effects are often called local and systemic effects. Damage caused by a substance at the site of its contact is a local effect but an adverse health effect that is experienced at a site of action is a systemic effect. For instance, when mercury absorbs through the skin, it may damage the kidneys, or affect the central nervous system; these are examples of systemic effects.

Toxic effects are also classified according to the time needed for a substance to cause an injury or disease. The following types are commonly noted: acute, short term, chronic and latent. A toxic substance may produce only one or more than one of these effects.

3.3.1. Acute Effect

An acute effect is generally regarded as a severe injury caused by a single, relatively short exposure to a substance. For instance, inhalation of hydrogen chloride for only a few seconds may cause lung damage; this is an acute injury.

3.3.2. Short-term Effect

An individual may also expose to a substance repeatedly over a relatively short term, say consecutive daily exposures over a few days or weeks, before an adverse health effect is noted. Such an injury is called a short-term effect. An example of a short-term effect is illustrated by exposure of skin tissue to certain harsh cleaning agents. While a single handling of such cleaners may not seemingly affect skin tissue, repeated handling may cause dermatitis; this is a short time injury. Some substances having a relatively low acute toxicity may have significant potential for producing harmful effects by repeated exposures.

3.3.3. Chronic Effect

A chronic effect is an injury or disease that manifests itself after a relatively long period of time has elapsed since initial exposure to the substance causing the ailment. For example, liver angiosarcoma may develop in an individual years after inhalation of vinyl chloride [5]. This development of cancer is an example of a chronic effect.

3.3.4. Latent Effect

It is an injury or disease that remains undeveloped until an incubation period has elapsed. For example, benzene induces aplastic anemia in humans, but the affliction may not become noticeable until ten years after the initial exposure to benzene [5]

A toxic substance that enters the body by inhalation may act as either an asphyxiant or an irritant. An asphyxiant is a chemical substance that causes a loss of consciousness as the result of an insufficient amount of oxygen in the blood. Simple asphyxiant, like nitrogen and hydrogen, are immediately harmful only to the extent that they displace oxygen.

A mixture of inhalation asphyxiants with oxygen or air may have an anaesthetizing effect on the body. Anaesthetized individuals may be either conscious or unconscious, but they experience a partial or total loss of the sense of pain. Such substances are called anesthetics, especially when they are intentionally administered for performing surgery [5].

An irritant is a chemical substance that injures the tissues of the respiratory system and lungs, thereby causing inflammation of the respiratory passages.

3.4. Factors of Affecting Toxicity

The human body is a very complex and delicately balanced system. Each cell in the body, the basic unit of life, takes in nutrients, resist biological attackers, reproduce, and produces the substances that the host organism needs to survive. Many chemical reactions occur within cells that are responsible for life itself. But when toxins are absorbed across the cellular membrane, they may upset this delicate chemistry. In turn, these cells may malfunction, causing the organism to experience impaired health, disease, or death.

Fortunately, the body possesses natural mechanisms for protecting itself against the adverse action of foreign substances. One such mechanism is provided by the body's immunological system, which is often capable of defending individual cells against toxic invaders. Another mechanism is provided by the normal action of specific organs that possess the capability of converting harmful substances into harmless ones or into substances that are more rapidly excreted than the original toxin. As the result of such biochemistry, foreign substances may be modified in chemical structure, temporarily stored in specified organs, and/or directly eliminated.

Certain organs play particularly important roles in ridding the body of foreign substances. Metabolic and excretory processes often work in unison in this manner to keep bodies free of unwanted substances.

3.4.1. Quantity of Substances

Poisons cause adverse health effects in relatively small amounts, typically 3g or less [5]. Toxicologists refer to the amount of the substance at issue as the dose. Some substances are so poisonous that extremely minute doses cause death. There are relatively few substances that exhibit this unusually high degree of toxicity.

Nearly all foreign substances adversely affect the body at some dose. We are mainly concerned here only with those substances that cause disease or death when taken in relatively small amounts. The effect that a substance has on the body often changes with its dose.

3.4.2. Length of Exposure

A factor closely related to the dose is the length of exposure. For example, the mixture of toxic substances found in tobacco smoke; these combined toxins are the main cause of throat and lung cancer [5].

The length of exposure is often an important factor when considering the adverse health effects caused by exposure to toxic substances in the work environment.

The length of exposure can also be a factor affecting toxicity in a comparatively beneficial way. Sometimes the body acclimates somehow to repeated exposure to certain toxic substance; that is, while adverse health effects are noted at the time of an initial exposure, such effects are not always repeated upon subsequent exposures to the same dose of the same substance.

3.5. Rate and Extent to Which the Substance Is Absorbed Into the Bloodstream

Most adverse health effects are experienced only after sufficient time has elapsed for the substance to absorb into the bloodstream. There are seven ways by which this may occur:

- Intravenous
- Inhalation
- Intraperitoneal
- Intramuscular
- Subcutaneous
- Oral
- Cutaneous

The fastest of these means for entry of liquid poisons into the bloodstream is intravenous, that is, injection directly into a vein; for gaseous poisons, the fastest route of entry is inhalation.

Some time usually elapses before substances taken orally are assimilated into the bloodstream. This is a fortunate circumstance in the case of poisons, since it provides the opportunity to administer an antidote, to induce vomiting, or to take some other

action appropriate to saving a life. The time elapse relates with the fact that the intestine, the organ that connects the stomach to the large intestine.

3.5.1. Physical and Chemical Nature of the Substance

This factor is closely related to the previous one. For instance, the compounds of chromium, all of which are toxic. Several chromium compounds manifest this toxicity more noticeably, however, because they enter the body more easily than others do. The water solubility of substances also affects the toxicity of ingested substances.

Finally, different oxidation states may have a bearing as a substance's toxicity.

3.5.2. Age and Health of Afflicted Individual

The degree to which a toxic substance affects individuals may depend on their age and general state of health. In general, youngsters and the elderly are much more susceptible and less tolerant to toxins than the middle-aged. Similarly, individuals already weakened from disease are likely to be more susceptible to poisons than healthy people. This individual sensitivity is typical of individuals who suffer from heart and respiratory ailments; they cannot tolerate moderate concentrations of air pollutants while healthy people are often simultaneously oblivious to their presence.

3.6. Measurement Of Toxicity

In general toxicological studies, animal are exposed to a given dose of a substance and monitored to establish a defined effect. Then the results of such studies are extrapolated to humans. This method is generally credible for establishing acute or short-term effects.

However, chronic toxicological studies on animals are not always relevant when applied to humans, since the physiology of humans is not always like that of animals. This fact is particularly important as it affects studies on potentially carcinogenic substances. Toxicologists regard a substance as a suspect human carcinogen when laboratory studies on animals establish that the substance induces cancer in more than one species or sex in animals, or when they show that the substance increases the incidence of site-specific malignant tumors in a single species or sex, and when there is a statistically significant dose-response relationship in more than one

exposed group. When it is established coincidentally that a substance induces cancer in humans, the substance is called a human carcinogen.

The following four means are commonly employed to quantify acute toxicity:

1. Lethal Dose (%50 kill, LD_{50}): The LD_{50} is the amount of a material that, when administrated to the laboratory animals, kills half of them. It is expressed in grams of the substance administrated per body weight of the animal expressed in kilograms (mg/kg). When extrapolated to humans, the lethal dose for an average person who weight w kilograms is $LD_{50} * w$
2. Lethal Concentration (%50 kill, LC_{50}): The LC_{50} is the concentration of a material, normally expressed as parts Per million (ppm) by volume, that, when administrated to laboratory animals, kills half of them during the period of exposure.
3. Threshold Limit Value (TLV): The TLV is the upper limit of a toxin concentration to which an average healthy person may be repeatedly exposed on an all day, everyday basis without suffering adverse health effects. For gaseous substances in air, the TLV is usually expressed as parts Per million (ppm); for fumes or mists in air, it is expressed in milligrams Per cubic meter (mg/m^3). The American Conference of Governmental Industrial Hygienists (ACGIH) sets values of the TLV [6]. In the workplace, employees often measure a similar factor called the weighted average threshold limit value (TVA-TLV). This is the average concentration to which most workers can be exposed during a 40-hour week 8-hour day without developing adverse health effects.
4. Immediately Dangerous to Life and Health (IDLH) Level: An IDLH level represents a maximum concentration from which one could escape within 30 minutes without experiencing any escape-impairing symptoms or any irreversible adverse health effect.
5. Toxic Units (TU) : The toxic units approach has become accepted for utilizing the toxicity test results. Both federal and state standards and/or criteria have been or are being formulated on the toxic unit basis. In the toxic unit approach, a TU concentration is established for the protection of aquatic life

   Toxic Unit Acute ($TU_{(a)}$) is the reciprocal of the effluent dilution that caused the acute effect by the end of the acute exposure period.

   $$TU_{(a)} = 100/ LC_{50}$$

A number of terms are utilized in expressing toxicity test results. Acute toxicity is toxicity which is severe enough to produce a response rapidly (typically a response observed in 48 or 96 hours). Acute means short and does not necessarily imply mortality. LC_{50} is the concentration of effluent in dilution water that causes mortality to 50 percent of the test population.

Toxicity testing has been widely validated in recent years. Even though organisms vary in sensitivity to effluent toxicity, the EPA has documented that toxicity of effluents correlate well with toxicity measurements in the receiving waters when effluent dilution is measured.

3.7. Dose – Response Relationship

Dose is defined as the degree of exposure of an organism to a toxicant, commonly in units of mass of toxicant per unit of body mass of the organism. The observed effect of the toxicant is the response. A plot of the percentage of organisms that exhibit a particular response as a function of dose is a dose-response curve. As shown in Figure 3-1 such plots are S-shaped. The statistical estimate of the dose that would cause death in 50 percent of the subject is the inflection point of the dose-response curve and is designated as LD_{50} (Lethal Dose). As illustrated in Figure 3-1 the LD_{50} values and the slope of the dose-response curves may differ substantially.

Most subjects respond to toxicants at doses corresponding to the mid-range of the dose-response curve and are called normals. A response to a very low level of toxicant is known as hypersensitivity whereas response to only extremely high levels is called hyposensitivity. In some cases hypersensitivity develops as an extreme reaction to a toxicant after one or more doses of it. Hypersensitivity usually involves an allergic reaction, which is an exaggerated response of the body's immune system. For example, some individuals develop such a reaction to formaldehyde [6].

Figure 3.1 Dose – Response Relationship

3.8. The Relationship of Toxicology To Hazardous Waste Management

A toxic waste, when it contacts a living organism, can kill, injure, or otherwise impair the organism. These poisonous substances are thus hazards, depending on the exposure and handling of the waste.

Acute toxic wastes may injure humans or other mammals when inhaled or ingested or on contact with the skin. LD_{50} toxicity measurements have been standardized on the basis of whether the contact is by ingestion, inhalation, or skin and are generally accepted by the scientific community as reliable.

Long-term exposure, or chronic toxicity, measurements are not nearly as standardized as acute toxicity measurements. The inability to maintain humans and other mammals under long-termed controlled test conditions makes reliable chronic measurements virtually impossible. Testing of short-lived laboratory animals is often used to developed information on chronic toxicity. Based on life expectancy, these laboratory animal data are then studied for possible relationships to humans and other mammals.

Toxic properties are also evident in irritants that that produces roughened, reddened or inflamed skin. Proper management of such wastes is necessary to minimize human contact wherever possible, and medically recognized producers should be followed if such contact occurs.

Bioaccumulation of less then toxic levels of waste can, on chronic exposure, exceed the threshold level and create a hazard to human health. Some toxic substances can be concentrated in a single organism and passed through the food chain. Proper management of such wastes is necessary to avoid their release into environment.

Some hazardous wastes can alter the genetic base of humans and other mammals, which could have long-term adverse effects on human health and the environment.

Figure 3.2 presents a model of the threshold theory. This theory holds that exposure to low concentrations of chemical substances is not harmful to human health until some threshold exposure level has been exceeded [1].

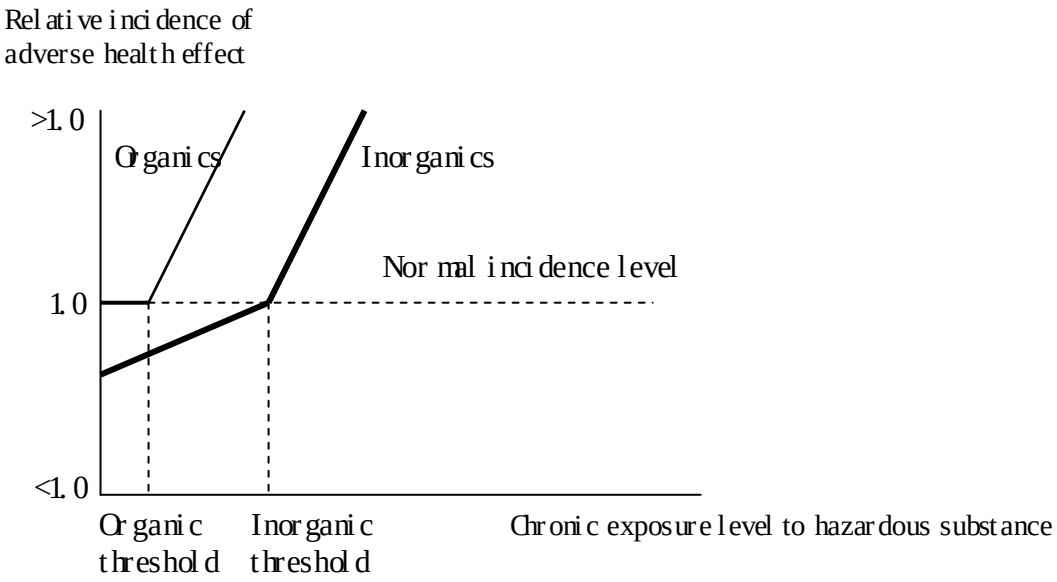


Figure 3.2. Threshold theory of long-term exposure to toxic substances

4. CHEMICAL OXIDATION OF HAZARDOUS WASTES

4.1. Chemical Oxidation

The objective of chemical oxidation in water and wastewater treatment is to transform undesirable chemical constituents to a more oxidized state which reduces the pollution potential. It is often unnecessary to carry the oxidation of a compound to completion since, depending on the oxidant and oxidizing conditions, the intermediate oxidation products which may be formed will be of much lower toxicity or less objectionable characteristics than the original materials. Complete oxidation may not only be impracticable from a treatment standpoint, but also represents a non-justified economical outlay. Subsequently, chemical oxidation might be considered as a selective modification or elimination of objectionable or toxic substances, including [7];

1. Inorganic constituents, such as Mn^{++}, Fe^{++}, S^{-}, SO_3^{--}
2. Organic compounds, such as phenols, amines, humic acids, other taste, odor, or color producing or toxic compounds, bacteria and algae.

The desirable characteristics of a chemical oxidant are that it be readily and economically available and that it not generate secondary pollutants into the wastewater. The significant considerations an oxidizing agent and process include:

1. Integration with other existing or proposed unit treatment operations;
2. The treatment effectiveness;
3. The nature of the oxidation reactions;
4. The capital and operating economics;
5. Storage and handling considerations.

Generally, the chemical oxidants, which have been found most suitable for the oxidation of industrial wastewaters, include ozone, hydrogen peroxide, potassium permanganate, chlorine or hyperchlorite, and chlorine dioxide.

Generally, the effectiveness and economics of a specific oxidant depend on:

1. The concentration of reactants in the waste water;
2. The initial temperature and changes of temperature upon reaction;
3. Waste characteristics;
4. Influences of impurities.

Since ozonation and chlorination offer the most effective means of waste water oxidation and since the laboratory techniques for these compounds are similar to using other constituents, these oxidants are commonly applied.

4.2. Ozone as a Chemical Oxidant

Ozonation consists of treatment with ozone (O_3), an extremely reactive gas.
In gaseous form, ozone is colorless (but blue in high layer thickness), whereas liquid ozone is almost non-transparent and bluish-black and its crystals are violet blue. It has a characteristic odor, reminiscent of phosphorus and sulphur dioxide. Olfactory organs are extremely sensitive to ozone; it can be detected by humans at a dilution of one to half a million in air. The lower limit of detection of ozone by smelling lies at a concentration corresponding to a partial pressure of 0.1 to 1 Pa. Ozone can be detected by humans at a concentration of 0.01 mg/kg in the presence of nitrogen oxide; with pure ozone, this limit is raised to 0.02 to 0.005 mg/kg [8].

Ozone cannot be shipped or stored, and must be generated on site immediately prior to its application.

Ozone is a very powerful oxidizing agent. Organic chemists have long made use of the ability of ozone to cleave carbon-carbon bonds in synthetic and structure-determination procedure. The liquid even the gas, if it is not at low pressure or diluted with an inert gas such as nitrogen, may decompose explosively in a strongly exothermic reaction:

$$2\,O_3 \longrightarrow 3\,O_2 \qquad \Delta H = -284\ kJ \quad [9]$$

Thermodynamic properties of ozone are shown in Table 4.1.

Table 4.1. Thermodynamic properties of Ozone

Molecular Weight	48g
Boiling Point at normal atm. Pressure	(-119+-0.3) ^{o}C
Critical Temperature	(-12.1+-0.1) ^{o}C
Critical Pressure	55.30*10^{5} Pa
Enthalpy at –298 ^{o}K(1.013*10^{5})	(34220+-240) kcal
Air relevant reactive density	1.657
Density at normal conditions	2.143 kgNm^{-3}

Some of the chemical properties displayed by ozone may be described by its decomposition reactions which are thought to proceed as [10]:

$$O_3 + H_2O \longrightarrow HO_3^+ + OH$$
$$HO_3^+ + OH \longrightarrow 2HO_2$$
$$O_3 + HO_2 \longrightarrow HO + 2O_2$$
$$HO + HO_2 \longrightarrow H_2O + O_2$$

The free radicals formed, HO_2 and HO, have great oxidizing powers and are probably the active form in the disinfection process. These free radicals also possess the oxidizing power to react with other impurities in aqueous solutions.

0There are abundant literature references to the mechanisms and products of ozonation of a variety of organic compounds. References to reactions of inorganic chemicals with ozone are fewer, but not scare.

In addition to high chemical reactivity, ozone has powerful antibacterial and antiviral properties. The disinfecting and oxidizing powers of ozone have been responsible for virtually all of the large-scale applications of ozone date. Ozone is widely used in Europe for application, at doses of a few ppm, to millions of gallons per day of aqueous streams. This technology is therefore highly developed and can be readily adapted to treatment of selected industrial waste streams.

Ozone is a powerful oxidizing agent, as illustrated by the following redox potentials:

$$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O \qquad E_0 = 2.07 \text{ V}$$

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O \qquad E_0 = 1.07 \text{ V}$$

$$1/2Cl_2 + e^- \longrightarrow Cl^- \qquad E_0 = 1.36 \text{ V}$$

It is sufficiently strong to break many carbon-carbon bonds and even to cleave aromatic ring systems. Complete oxidation of an organic species to CO_2, H_2O, etc., is not improbable if ozone is sufficiently high.

The reactions of ozone as a chemical oxidant appear to involve at least two distinct mechanisms. One mechanism considers an electrophilic attack by ozone while the other mechanism involves an ozone-initiated oxidation whereby ozone serves as the reaction initiator and oxygen is the principal reactant. The reactions of ozone with tertiary amines, phosphines, arsines, sulfides and sulfoxides are examples of the electrophilic attacks as shown for the oxidation of dialkyl sulfide below [6]:

$$R_2S + O_3 \longrightarrow R_2SO + O_2 \longrightarrow R_2SO_2 + O$$

Examples of ozone-initiated reactions are the oxidative reactions of ozone and aldehydes, ketones, alcohols, ethers, and saturated hydrocarbon groupings. It is postulated in these reactions that ozone serves as a radical reagent by mobilizing an additional number of oxygen molecules.

Since ozone reacts to certain bonds, which are susceptible to cleavage, the products of oxidation may not simply carbon dioxide and water, but intermediates formed by the mechanism.

4.3. Effectiveness of Ozonation

Wastewater treatment by ozonation may be influenced by many considerations, including [6]:

1. The nature and concentration of wastewater constituents will determine the amenability of ozonation.
2. The wastewater pH and temperature will control the efficiency of ozone reactivity. Ozone is more stable at acidic pH levels, probably because of the

catalytic decomposition of ozone by hydroxide ions. Additionally, the pH may influence the reactivity of certain constituents with ozone. The temperature influences ozone solubility and stability, namely, higher wastewater temperatures result in decreased ozone stability.

3. The ozone application rate and contact time, which is required by a specific wastewater, is determined by the nature of the waste, the extent of chemical oxidation required, and the efficiency of the ozone-wastewater contactor.
4. The mechanism of contact of ozone with wastewater is a direct function of economics and will subsequently dictate the extent and efficiency of ozonation

Because of its many years of use in Europe to disinfect water supplies and its high oxidizing potential, ozone has received much attention as an alternative to chlorine. Ozone equals chlorine in ability to kill bacteria and may be superior in ability to inactivate viruses. Also, ozone reduces wastewater color and odor, does not produce dissolved solids, is not affected by pH, and provides an oxygenated effluent.

There are results available from numerous pilot plant studies and a few full-scale operations that use ozone for disinfections. For best results, filtration or other tertiary treatment processes should precede the ozonation process since oxidizable organics may consume ozone faster than the rate of disinfection. The design engineer should seek current performance data.

Since ozone is a relatively unstable gas and breaks down into elemental oxygen relatively quickly, it is generated on site with an ozonator that applies an electrical charge across air or oxygen. Automatic devices are available to control voltage, frequency, gas flow, and moisture.

Wastewater ozonation may be accomplished by the using of mechanical mixing, countercurrent or concurrent flow columns, diffusers, or injectors. Dosage requirements and contact time will vary with the wastewater characteristics, but common ranges are 1 to 10 mg/l and less than 15 min, respectively [3]

4.4. Environmental Impacts of Using Ozone

Unlike the other chemical disinfecting agents, ozone will mainly exert beneficial impacts on the environment. It has been reported that ozone residuals can be acutely toxic to aquatic life. However, because ozone dissipates rapidly, ozone residuals will normally not be found by the time the effluent is discharged into the receiving water. Several investigators have reported that ozonation can produce some toxic mutagenic and/or carcinogenic compounds. These compounds are usually unstable, however, and are present only for a matter of minutes in the ozonated water. Thus, these compounds will normally not be present by the time the effluent reaches the receiving water. It is observed that ozonation destroys certain harmful refractory organic substances such as humic acid and malathion. Whether toxic intermediates are formed during ozonation depends on the ozone dose, the contact time, and the precursor compounds. It has been reported that ozone treatment before chlorination for disinfection purposes reduces the likelihood of trihalomethane formation [10].

An additional benefit associated with the use of ozone for disinfection is that the dissolved oxygen concentration of the effluent will be elevated to near saturation levels as ozone rapidly decomposes after application to oxygen. This may eliminate the need of reaeration of the effluent to meet required dissolved oxygen water quality standards. Further, because ozone decomposes rapidly, no chemical residual that may require removal, as is the case with chlorine residuals, persists in the treated effluent.

4.5. Experimental Procedures and Equipment Required for Ozonation

4.5.1. Analytical Methods for Ozone Detection

The most common method of measuring ozone in water at low concentrations is by the oxidation of potassium iodide in acidic solutions by:

$$O_3 + 2H^+ + 2I^- \longrightarrow O_2 + I_2 + H_2O$$

Investigators have encountered serious problems with this method including non-stoichiometric iodine formation at neutral and alkaline conditions. Other work has inferred high iodine formation in acidic solutions. A summary of analytical methods for oxidant detection in water is shown in Table 4.2 [6]

Table 4.2 Analytical Summary For Ozone Measurement

Analytical Method	Method of Oxidation	Interference or Limitations
Potassium Iodide; alkaline, and neutral conditions	$2KI \longrightarrow I_2$	Most oxidants including oxygen
Ferrous ion oxidation	$Fe^{2+} \longrightarrow Fe^{3+}$	Results believed to be low
Manganese oxidation and orthotolidine	$Mn^{2+} \longrightarrow Mn^{3+}$	
Visible Region Spectrophotography	Molar absorptivity of 2,500 to 3,000 at 260 mμ	Detection limits for 1 cm cell 10^{-3} M
Leuco Crystal Violet	Redox indicator: Leuco Crystal Violet	Newest technique (under investigation)
Instrumental methods Using KI oxidation	$2KI \longrightarrow I_2$	Same as KI above

The newest technique for ozone measurement called leuco crystal violet test involves a colorimetric measure of the oxidation of leuco crystal violet at a wavelength of 592 mμ in acidic solutions. The color is very stable and has actually been monitored for 44 days.

The equipment and associated apparatus required for batch and continuous ozonation are depicted in Figure 4.1 and Figure 4.2 and are the same for either treatment mode except for the ozone-wastewater contactor. Ozone may be generated from the laboratory by a small ozonator. The apparatus required for both batch and continuous experimentation includes the following items.

Figure 4.1. The equipment and associated apparatus required for batch and continuous ozonation

Figure 4.2. The equipment and associated apparatus required for batch and continuous ozonation

4.5.2. General Equipment

1. Four, 1-liter sealed glass containers for containing the analytical solution utilized for measuring ozone concentrations before and after wastewater contact.
2. Two standard wet test meters for measuring the flow of ozone gas before and after wastewater contact. One meter could be arranged to serve both purposes, but the switching of valves at the critical times is difficult.
3. Two rotameters for controlling and adjusting gas flowrates. The rotameters built into most commercial generators are not reliable for accurate measurement.
4. A commercial ozonator.
5. An oxygen cylinder with the appropriate metering valves and a pressure regulator.
6. Miscellaneous tubing and glassware as required. The tubing should be glass, if possible, although Teflon and Tygon, in that order, could be used as conveyances for the ozone gas. Of the three materials, Tygon is the least acceptable.

4.5.3. Batch Reactor Equipment and Procedure

1. One 3-liter glass reactor. One liter of volume is the minimum acceptable volume with the 3-liter volume being preferable.
2. One glass-fritted diffuser. The diffuser should not be the common aquarium type due to the presence of unstable, oxidizable adhesives used in many cheaper aquarium stones.
3. One 2-way glass valve for withdrawing periodic samples from the reactor.

The batch procedure for ozonation wastewater consists of measuring the ozone concentration in the ozone and oxygen gas stream from the ozonator and then monitoring the residual ozone in the gas stream after contacting a known quantity of wastewater with a measured quantity of gas. Subsequently, the amount of ozone, which was used to oxidize a measured reduction in wastewater contaminants, such as COD, phenol or color, can be determined. Different contact times and ozone loadings can be examined under various operating variables, such as pH and temperature. The procedures for the batch tests follow; [6]

1. Connect the oxygen cylinder to the ozonator.
2. Fill the batch ozone reagent reactors with one liter of potassium iodide solution at 20 g/l concentration. Two contactors are operated in series on the exit gas stream to insure that all off the ozone is captured for subsequent analysis.
3. Fill the contactor with 3 liters of waste water, which have been analyzed, for the specific constituents under study, such as COD, BOD or phenol.
4. Adjust the ozonator gas flow to the desired flow rate with the primary rotameter. Vent the gas stream to the atmosphere during this period.
5. Using the primary stopcock, divert the gas flow through the primary reagent reactors. Pass exactly 3 liters of gas, using the wet test meter as an indicator, through the primary reagent reactor.
6. When exactly 3 liters have passed through the reagent, divert the gas stream through the waste sample.
7. Ozonate the waste sample for the desired contact time (5 min. to 5 hours), and pass the gas stream to the secondary reagent reactors.
8. At the end of the contact time, cut off the gas flow to the reactor with the primary stopcock and remove the primary and secondary reagent solutions for titration with standard 0.1 N $Na_2S_2O_3$ solution. Record the secondary wet test meter readings to obtain the total gas flow through the system during the oxidation test. Measure the residual COD or other pertinent constituents of the waste sample.
9. Repeat steps 2 through 8, varying the contact time and the quantity of ozone applied. The amount of ozone can be controlled by employing a higher gas flow rate or by increasing the ozone concentration in the gas, using a higher voltage on the ozonator. Generally, the gas flow is used to control the amount of applied ozone. However, by varying the gas rate through the system, it is possible that the bubble size and degree of turbulence may also varied thereby changing the actual conditions of the test. Other conditions, such as pH, and temperature, can be evaluated at a constant ozone concentration.

4.5.4 Continuous-Flow Reactor Equipment and Procedure

1. One 6-foot, 3-inch diameter glass column. The column is operated counter-currently with the ozone entering from the bottom and the waste water from the top. For pilot and finalized design investigations, a contactor such as illustrated in Figure 4.1 should be used.
2. One glass-fritted diffuser as described above.

After conclusion of the batch tests, the continuous-flow reactor can be used to determine optimum conditions under counter-flow, continuous operation as will be experienced in the field. Operation of the continuos column as shown in Figures 4.1 was developed by a manufacturer and was employed with a 2 gpm pilot system for color reduction in a waste containing approximately 5,000 to 6,000 mg/l APHA units of color. The procedures for the continuos study are described as follows:

1. Estimate the desired contact time by pumping the waste water into the top of the column at the calculated flow rate.
2. Measure the ozone concentration in the gas flow as described under the batch procedure.
3. Divert the gas flow into the reactor column in which waste is being fed at the desired flow rate. Vent the exit gas from the column to the atmosphere
4. After one detention time necessary to attain steady-state conditions, divert the gas using the stopcock, through the secondary reagent contactors and the wet test meter for measurement of the ozone concentration and the gas flow rate. The contactor is generally operated at 6 to 9 pH
5. Continue the tests until the reagent in the first contactor indicates saturation. It is desirable to have sufficient reagent life for at least one detention time.
6. Shut off the influent gas flow and the waste flow simultaneously. Measure the volume of waste water pumped during the test run and record the volume of gas passed through the sample. Analyze the wastewater sample for the specific constituents and measure the reagent solutions for ozone levels.
7. Repeat Steps 1 through 6 at various operating conditions. It may be desirable to examine the effects of contactor depth and bubble size on ozone efficiency in the event that a pilot contactor is not available.

4.6. Calculation of Ozone

Creating the data format that presents operating conditions, observed data, the results of titration of the potassium iodide solution with a 0.1 N $Na_2S_2O_3$ solution, removal of desired constituents is the first step for calculation of ozone. The influent gas sample is the gas stream coming directly from the ozonator.

Calculation Of Ozone Quantities:

	A	B	C
	Influent Ozone Gas	Bottle No. 1	Bottle No. 2
1. ml of 0.1 N $Na_2S_2O_3$	**A1**	**B1**	**C1**
2. Total mg of O_3	**A2**	**B2**	**C2**
3. Liters of Gas	**A3**	**B3**	**C3**
4. mg of O_3 per liter of Gas	**A4**	**B4**	**C4**
5. mg of O_3 Applied	**A5**	**B5**	**C5**

The quantity of ozone in each sample can be determined by multiplying A1 by 2,4 (1 ml of 0.1 N $Na_2S_2O_3$ is equivalent to 2,4 mg O_3) [6]

- Influent Ozone Gas = A1 * 2,4 = mg O_3
- Concentration of Ozone = A2 / A3 = mg O_3 / liter influent gas
- Total Ozone Applied = A4 (mg O_3 / liter) * B3 (liters) = mg O_3
- Calculation of Efficiency of Ozone Utilization
  1) Total Ozone Remaining (TOR) = B2 + C2 = mg O_3
  2) Total Ozone Applied (TOA) = A4 (mg O_3 / liter) * B3 (liters) = mg O_3
  3) Percent Ozone Utilization = (TOA - TOR) / TOA = percent
- Calculation of the concentration of ozone used in the waste water
  1) mg Ozone Used = TOA - TOR
  2) Total waste water volume = X l
  3) Concentration of Ozone Used = TOA - TOR / X = mg/l

5. EXPERIMENTAL STUDY

5.1. Definition of the Pesticide Industry

With the development of civilization, so has man gradually realized the extent to which pests harm his crops, annoy him and transmit diseases, both human and those of domestic animals. The use of chemicals to kill pests is not a new concept. The use of chemicals has continued, and, during the early part of the twentieth century, large quantities of such compounds were used to control insect pests. Later it is recognized that chemicals are highly dangerous for our environment if used uncontrolled. Some of those chemicals have been banned or restricted in some countries of the world because of its toxicity. [12]

The samples analyzed in the study, which were solvent originated, were taken from a pesticide industry in Tekirdağ with a large production capacity. Commercial names of those pesticides produced are;

1. Herbicide
2. Insecticide
3. Fungicide
4. Plant Regulator

Trifluranyl, propanyl and isooctyl ester are some of the chemicals that are used to produce liquid herbicide. The main process category of the industry can be defined as;

Synthesis + Formulation + Packaging

The firm is active 5-6 days a week with a single shifting system. It involves 10 managers, 120 workers (including seasonal workers). In the area there are raw material depots, boiler chamber, quality control and research laboratory, social foundations and a wastewater treatment system.

It is observed that the industry uses the treated water coming from wastewater treatment system to water its huge garden in the area. The existing wastewater treatment system is shown in Figure 5.1

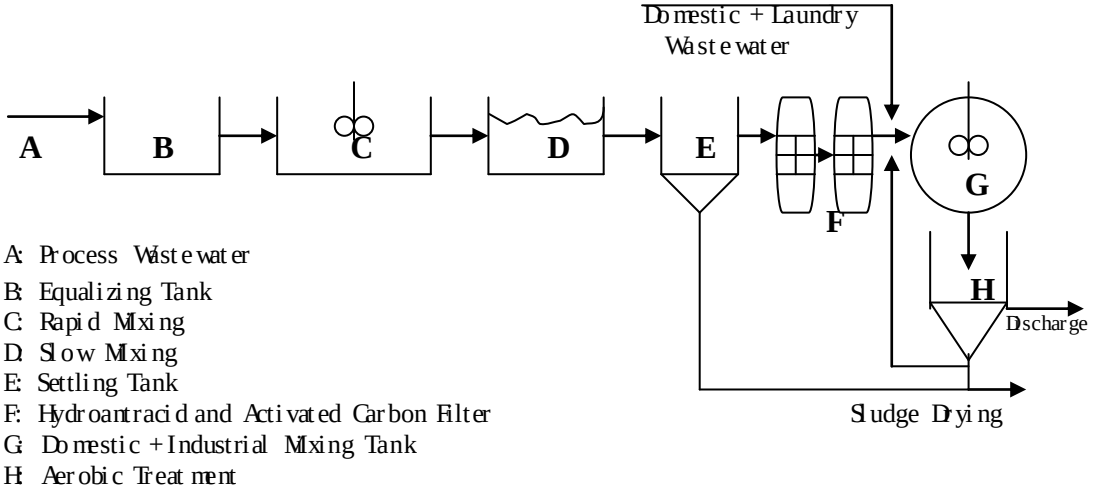


Figure 5.1 Existing wastewater treatment plant

Process and domestic wastewater are 2 major wastewater in industry. Pesticide-contaminated wastewaters are mainly originated from wastewaters water-based and solvent-based formulations. These wastewaters also include waste rinse water, waste cleaning solvents and stormwater run off from pesticide spillage and fallout of pesticide dust in open process area.

In the industry, both the chemicals used in research laboratory and solvents used to clean the tanks directed to the wastewater treatment process in liquid form. This mixture had to be considered as a hazardous waste because of its contents, which are mentioned in characterization of sample section. The waste collected in stabilization tank handled as hazardous waste in the lists that are regulated by EPA.

As shown in Figure 5.1 domestic and laundry wastewaters also joint to the treatment system after Hydroantracid and Activated Carbon Filters.

The solvent originated waste treated in wastewater treatment system involves laundry service, domestic and process wastewaters.

Average quantity of domestic and laundry service wastewaters is determined approximately 10-25 m^3/day according to the maximum and minimum number of the workers in the industry.

It is also determined that average quantity of process waste water is approximately 2-2,5 m^3/day in the industry.

5.2. Experimental Approach

The samples analyzed in the study, which were solvent originated, is produced by cleaning step of the reactors that are used for pesticide production.

During the studies, the effect of ozone on chemical treatment was also investigated. Both before and after chemical treatment processes ozone was applied and the results were discussed.

During the chemical treatment experiments $FeCl_3$, lime and $Al_2(SO_4)_3$ are used to determine the optimum coagulant. At the same time NaOH, H_2SO_4 and lime are used to adjust the pH to the desired range. To obtain the sufficient flocculation during the jar tests non-ionic polyelectrolyte is also used.

Chemical precipitation in wastewater treatment involves the addition of the chemicals to alter the physical state of dissolved and suspended solids and to facilitate their removal by sedimentation. In some cases alteration is slight, and removal is entrapment within a voluminous precipitate consisting primarily of the coagulant itself. Another result of chemical addition is a net increase in the dissolved constituents in the wastewater. Chemical processes, in conjunction with various physical operations, have been developed for the complete secondary treatment of untreated wastewater, including the removal of either phosphorus or nitrogen or both.

Experiments revealed that lime is not an effective coagulant if used alone for this hazardous waste but an effective helper if used to adjust the pH.

Deciding the most suitable treatment system, bioassay tests were performed to investigate detoxification efficiency of ozone and $TU_{(a)}$ determined. The experiments performed were shown in Figure 5.2

Toxicity test have been used to assess the suitability of environmental conditions for aquatic life and to establish acceptable receiving water concentrations for conventional parameters. It is also used to study the effect of water quality

parameters on wastewater toxicity. And to assess the toxicity of wastewater to a variety of fresh, marine and estuarine test species.

To observe the effect of ozone gas on detoxification acute fish toxicity test was applied. An additional benefit associated with the use of ozone for disinfection is that the dissolved oxygen concentration of the effluent will be elevated to near saturation levels as ozone rapidly decomposes after application to oxygen. Ozone is also a very effective virucide and is generally believed to be more effective than chlorine.

Some conventional parameters, such as COD, TSS, oil & grease, pH were also measured to monitor the removal efficiency of both ozonation and chemical treatment and results were all tabled.

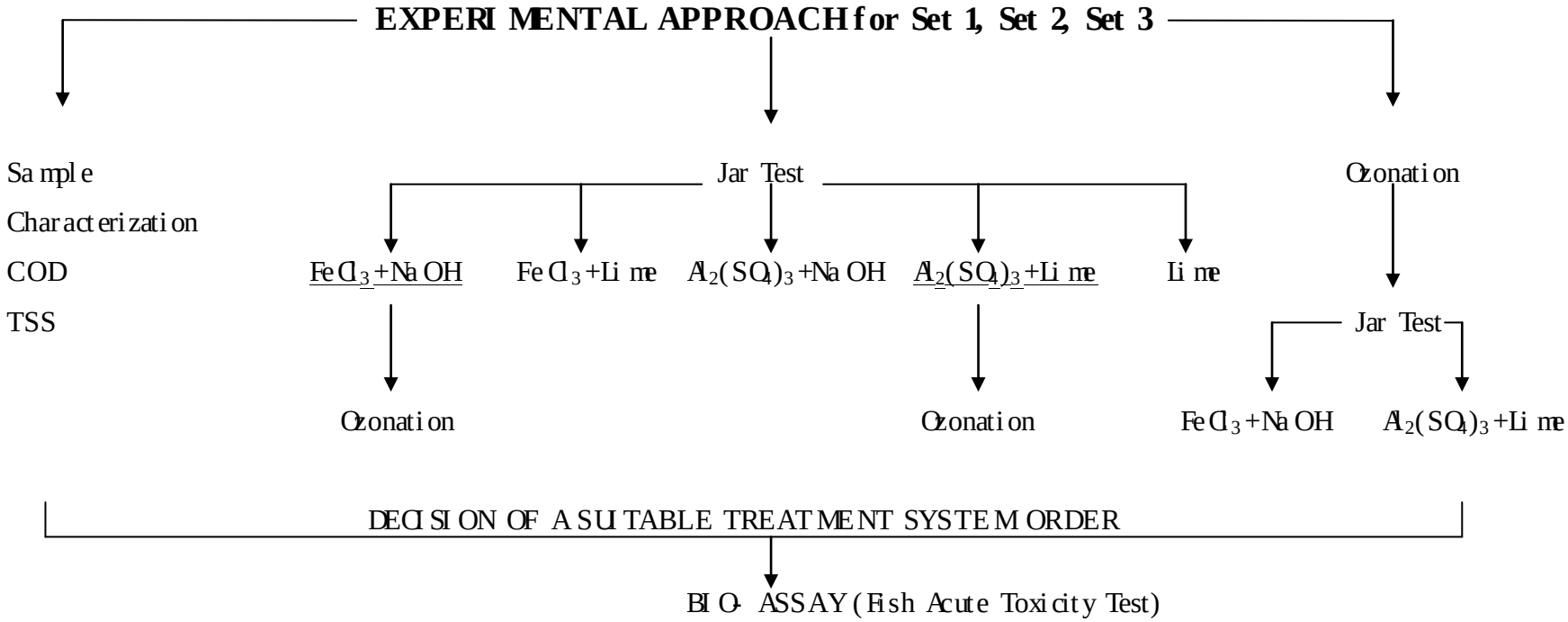
5.3. Determination of Samples

Experiments were performed on three different samples taken from the wastewater treatment of pesticide industry on different dates. To determine the problem and confirm that the waste investigated was a hazardous waste, the lists that are regulated by EPA were checked and the results are shown in Table 5.1.

Table 5.1 Listing of Samples – Set 1, Set 2, Set 3

	Turkish Hazardous Materials Legislation		EPA Legislations		SIC Code
	Ek-3	Ek-5			
Numbers and Codes	A651	Y4 Y9 Y10	F003 F004 F005	K043 K099	287 Agricultural chemicals

Related to the composition of the waste the singular produced chemicals, such as 2,4 DCP, cyclohexanone and Xsilene, are also listed as U081, D016, U057 respectively.



- Hazardous waste formed three samples with different characterization were taken from the inlet of the waste water treatment system
- After each step COD, TSS, pH and oil &grease analyzes were performed
- The chemicals after + is used to adjust the pH to desired range

Figure 5.2 Schematic Diagram of Experimental Approach

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Explanations of the codes involved in EPA Regulations that are shown in Table 5.1 are given below:

EPA Hazardous Waste Number – F004:

The following spent non-halogenated solvents: cresols and cresylic acid, and nitrobenzene; all solvent mixtures/blends containing before use, a total of a 10 percent or more (by volume) of one or more of the above halogenated solvents or those solvents listed in F001, F002, F005; and still bottoms from the recovery of these spent solvent mixtures.

Hazard Code: (I, T)
NOTE: (T) Hazard Code should be used to specify mixtures containing toxic constituents.

EPA Hazardous Waste Number – F004:

The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol, pyridine benzene, 2-ethohxyethanol, and 2-nitropropane; all spent solvent mixtures / blends containing, before use, a total of a 10 percent or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, F004; and still bottoms from the recovery of these spent solvent mixtures.

Hazard Code: (I, T)
NOTE: (I, T) Hazard Code should be used to specify mixtures containing ignitable and toxic constituents.

EPA Hazardous Waste Number – K043:

2, 6- Dichlorophenol waste from the production of 2, 4- D
Hazard Code: (T)

EPA Hazardous Waste Number – K043:

Untreated waste water from the production of 2, 4-D
Hazard Code: (T) [12]

5.4. Characterization of Samples

It is considered when the characterization of samples was determined that the composition of the waste changed every time. In Table 5.2 many of the parameters were shown in a range because of the change in the characterization of the waste according to both production sort and quantity of the pesticide industry. Chemicals used in production steps and the solvents used for cleaning step are all capable of increasing the conventional parameters measured during the study.

Range cells that are given in Table 5.2 were all determined after serial measurements of related parameters and the average of those results were shown in the cells called measured.

The characterization of samples are shown in Table 5.2

Table 5.2 Characterization of samples

Parameters	Set 1		Set 2		Set 3	
	Range	Measured	Range	Measured	Range	Measured
PH	6-8	7,3	6-8	7,8	6-8	8
COD (mg/l)	9000-12000	9500	20000-30000	25000	24000-32000	29000
S. COD (mg/l)	5000-9000	7500	12000-18000	16450	15000-20000	18500
Oil &Grease (mg/l)	-	400	-	585	-	650
TSS	200-250	230	200-250	220	420-480	450
Fish Toxicity	-	HT	-	HT	-	HT
2,4 D acid (mg/l)	0-750	-	-	-	-	-
Carbaryl (mg/l)	1-2	-	-	-	-	-

HT: Highly Toxic DF: Dilution Factor
Local industrial standards for Fish Toxicity: DF10

5.5. Material, Method and Equipment Used During the Study

During the study a half batch ozone generator marked as Ozone Air RXO-15 with 28 g/min flowrate capacity was used. It utilizes 9000 V electric to generate ozone gas. The ozonator has a mechanism that lets the machine get the air either from oxygen generator or directly from air. It reaches the optimum operating efficiency by 5

lt/min oxygen flow rate. Ozone generation starts after 4-min delay time and the ozone was injected with a teflon pipe into the circulated wastewater.

Ozonation mechanism is shown in Figure 5.3. and Figure 5.4.

CE-95 model, STA-RITE marked pump used to obtain an effective contact between ozone gas and wastewater. While the pump circulates the wastewater in the steel reactor with 10 l capacity, ozone gas is injected to this circulated wastewater. Thus, ozone is utilized as it decomposes rapidly in the wastewater.

To measure the off gas two traps (500 ml) were used. These traps were filled with 20 g/l KI solution prepared according to the Standard Methods. For efficient chemical treatment, initially; it is desired to determine the optimum condition, namely, coagulant and operating conditions, for maximum removal or coagulation of the desired wastewater constituents. Generally, the selected coagulant is added to the wastewater under specified conditions, such as dosage, pH, or temperature, and then the mixture is rapidly mixed followed by the addition of a coagulant aid and gentle flocculation. After determining the best coagulant and the optimum conditions of applications, other design parameters, such as settling properties and sludge production should be determined.

During the study, experiments such as COD, TSS, Oil & Grease were performed according to Standard Methods (APHA 1990).

Bioassay (Acute Fish Toxicity Test) was performed as mentioned in Metcalf & Eddy, "Wastewater Engineering" [10].

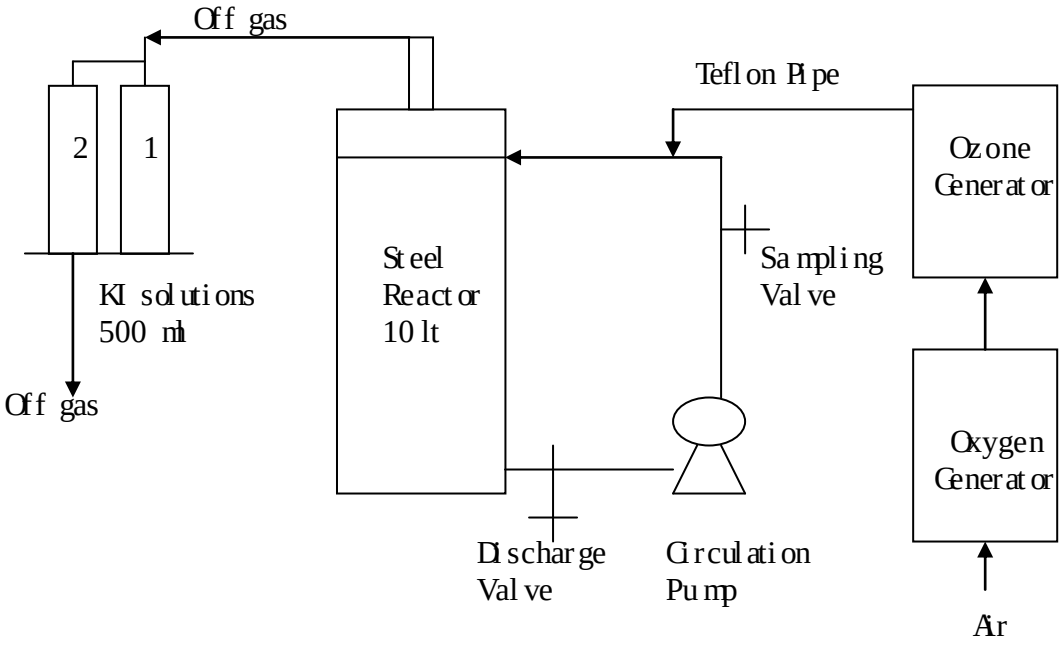


Figure 5.3. Ozonation Mechanism

Figure 5.4. Ozonator used for ozone generation

Measurement of Ozone Gas in Gas Flow

The commercial production capacity of ozone generator is 28 g/hour. It is expected that the ozone generated per minute should be 466 mg. To calibrate the machine, ozone gas flowrate is measured by preparing KI (20g/l) solution.

According to this experiment ozone gas flowrate is measured as 477 mg/min.

Ozone gas concentration in generated gas flow was calculated as follows;

45 min application;

mg O_3 = (477 mg/l / 5l/min) * 45 min * 5l/min = 21465 mg
ozone gas concentration
95,4 mg/l

60 min application;

mg O_3 = (477 mg/l / 5l/min) * 60 min * 5l/min = 28620 mg
ozone gas concentration
95,4 mg/l

90 min application;

mg O_3 = (477 mg/l / 5l/min) * 90 min * 5l/min = 42930 mg
ozone gas concentration
95,4 mg/l

5.6. Experimental Results

In this section results of all experiments were given and were discussed. For each set both ozonation and chemical treatment was performed. $FeCl_3$, $Al_2(SO_4)_3$ and lime were used as coagulant and H_2SO_4, NaOH and lime were used to adjust pH to desired range.

According to the results, chemical treatment experiments with lime, $Al_2(SO_4)_3$ + NaOH, $FeCl_3$ + lime were not successful to obtain a sufficient COD removal efficiency. So that none of those results about these experiments were given in this section.

Deciding the best treatment system for Set 1, Set 2 and Set 3, bioassay (Fish acute toxicity test) performed to only one sample in order to monitor detoxification of ozone.

5.6.1. Results of Set 1

After characterization of Set 1, in the first experiment, chemical treatment with both $Al_2(SO_4)_3$ and $FeCl_3$ was performed. Then ozonation applied to the supernatant collected after jar test.

In the second experiment, ozonation was the first step performed. The sample taken after ozonation was chemically treated with both $Al_2(SO_4)_3$ and $FeCl_3$. After each step COD was measured in order to determine individual removal efficiencies and overall efficiencies for Set 1.

For measuring optimum pH, samples were taken into five 500 ml flasks and the same quantity of coagulant was added into the flasks. To adjust pH, according to the type of coagulant, NaOH or lime was used. After 2 min of rapid mix and 15 min of slow mix, sample was settled for 30 min and for each pH range COD was measured in the supernatant of the flasks.

The results were shown in tables and figures as follows;

Table 5.3 Optimum pH determination for $FeCl_3$ – Set 1

Set 1 - %10 FeCl3 + NaOH (for opt. pH measurement)					
pH	**COD inlet** (mg/l)	**Coagulant** FeCl3 (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
4	9500	300	2375	75	Dark brown, %22
5	***9500***	***300***	***1666***	***82***	***Dark brown, %22***
6	9500	300	2000	79	Brown, %18
7	9500	300	2069	78	Brown, %20
8	9500	300	2714	71	Brown, %20

The results in Table 5.3 were figured in Figure 5.5. pH 5 is determined as the optimum pH for $FeCl_3$ after 2 min rapid mix and 15 min. slow mix.

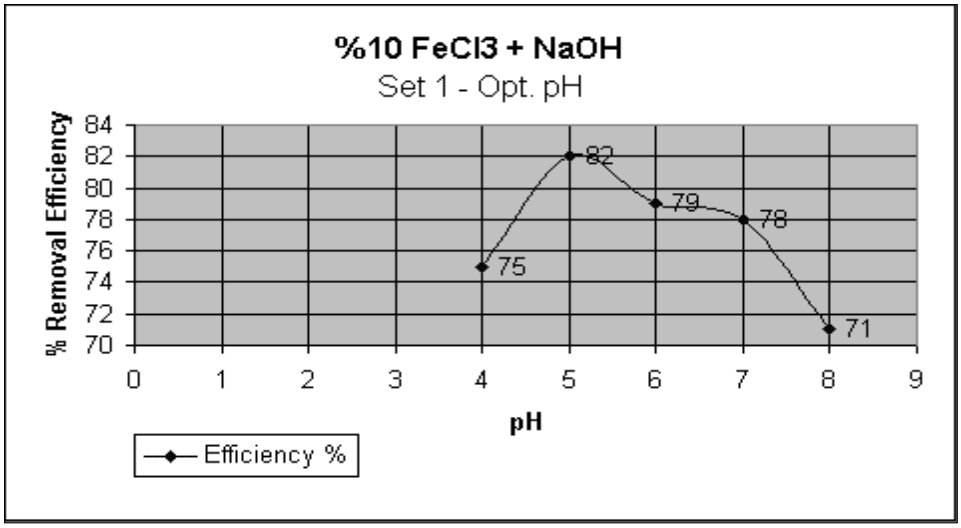


Figure 5.5. Optimum pH determination for $FeCl_3$ – Set 1

Table 5.4 Optimum pH determination for $Al_2(SO_4)_3$ – Set 1

Set 1 - %10 Alum + Lime (for opt. pH measurement)					
pH	**COD inlet** (mg/l)	**Coagulant** Alum (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
4	9500	300	3150	67	Yellow, %16
5	9500	300	2765	71	Yellow, %18
6	9500	300	2510	74	Yellow, %22
7	***9500***	***300***	***2310***	***76***	***Yellow, %18***
8	9500	300	2620	72	Yellow, %20

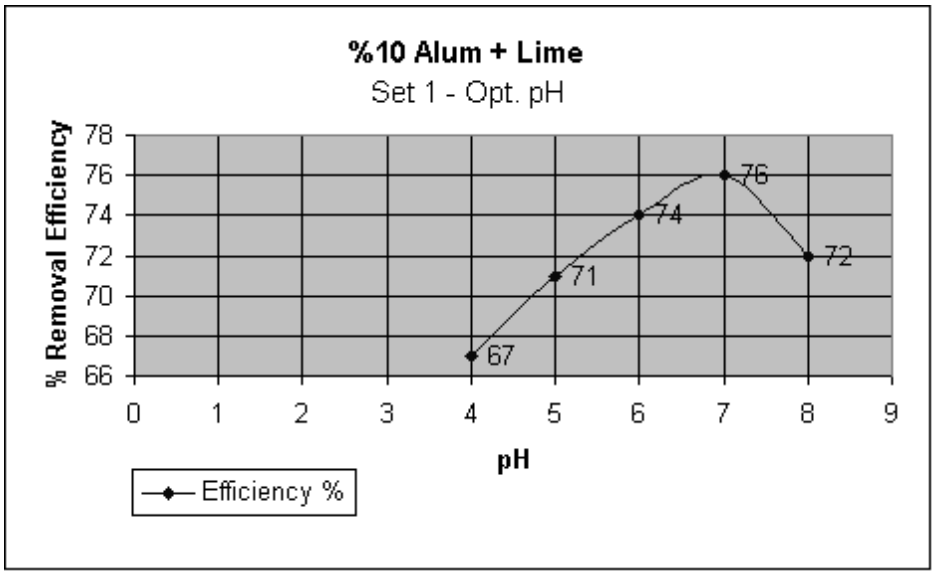


Figure 5.6. Optimum pH determination for $Al_2(SO_4)_3$ – Set 1

During each jar test, lime, H_2SO_4 and NaOH were used to adjust pH. OH^- ions, required for coagulation, were supplied by addition of NaOH and lime into the water.

For $FeCl_3$ optimum pH has been determined as 5 and for $Al_2(SO_4)_3$ optimum pH was 7 as seen in the Figure 5.6. After determination of optimum pH, optimum dosages for these coagulants were determined.

In order to determine optimum dosage, raw sample was taken into five 500 ml flasks. Coagulant was added into the mixing sample until flocks started to occur to determine minimum dosage. Starting from minimum dosage five different coagulant portions (200 mg, 400 mg, 600 mg, 800 mg, 1000 mg) were applied into each of five flasks. Because of their acidic property both $FeCl_3$ and $Al_2(SO_4)_3$ decreased pH to the range of 2-3. Adding these supplementary chemicals into the flasks OH^- concentration of sample increased and this helped flocculation process occur sufficiently.

After 2 min rapid mix and 15 min slow mix, flocs were settled for 30 min and the volumes of settled sludge were determined. COD, TSS, Oil &Grease tests were performed to the sample taken from the supernatant of chemically treated waste.

Results related to optimum dosage experiments were given in tables and figures as follows.

Table 5.5. Optimum dosage determination for $FeCl_3$ – Set 1

Set 1 - %10 FeCl3 + NaOH (for opt. dosage)					
pH	**COD inlet** (mg/l)	**Coagulant** FeCl3 (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
5	9500	150	4150	57	Dark brown, %10
5	9500	300	1660	82	Dark brown, %22
5	9500	450	1580	83	Dark brown, %22
5	***9500***	***500***	***1470***	***85***	***Dark brown, %26***
5	9500	600	1560	83	Dark brown, %22

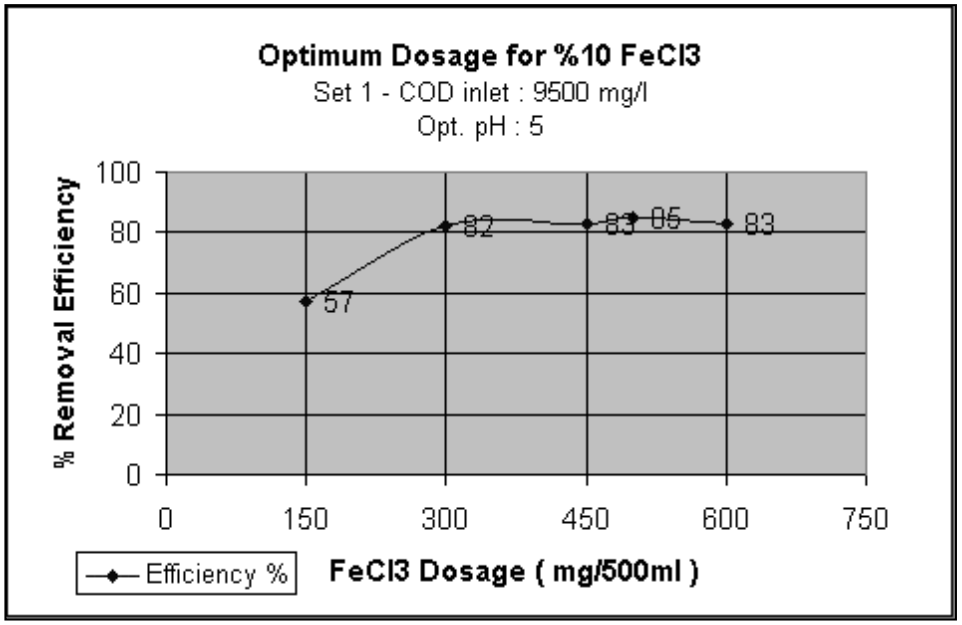


Figure 5.7. Optimum dosage determination for $FeCl_3$ – Set 1

After determination of optimum dosages for both $Al_2(SO_4)_3$ and $FeCl_3$ removal efficiencies of the coagulants were calculated. When alum is added to wastewater the insoluble aluminum hydroxide is a gelatinous floc that settles slowly through the wastewater, sweeping out the suspended material and producing other changes. Alkalinity is also an important parameter for chemical precipitation by alum. If less than required amount of alkalinity is available in water then it must be added. During the study lime is used to supply the required alkalinity in the waste. A sufficient quantity of lime must be added to combine with all the free carbonic acid and with the carbonic acid of the bicarbonates to produce calcium carbonate.

The result is shown in Figure 5.7 and Figure 5.9.

After chemical treatment supernatant of the samples were collected for ozonation.

Chemically treated wastewater, as shown in the figure had a sufficient result. In order to increase the removal efficiency of treatment system ozone gas was used as a helping agent. Due to oxidizing power of ozone gas, it was also applied for detoxification to Set 1. It is observed that after chemical treatment application of ozone gas increased the overall treatment efficiency of the system.

Results of the ozonation process applied to Set 1 are shown in the following figures.

During the ozonation process, in order to evaluate the results correctly, ozone dosage was calculated. According to both of these results and experimental studies, the ratio of utilized ozone and COD removal was determined. Applied ozone is defined as total quantity of off gas released and residual ozone dissolved in wastewater. During ozonation both off gas and residual ozone were determined according to Standard Methods and the results were neglected when compared to quantity of applied ozone.

As a conclusion, it was assumed that applied ozone was equal to utilized ozone.

During the study the calculations related to ozone dosage were made according to this assumption.

Table 5.6. Ozone Application Data Table

Data for ozone Application					
Contact Time	15 min	30 min	45 min	60 min	90 min
Applied Ozone	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min
Utilized Ozone A	7155 mg	14310 mg	21465 mg	28620 mg	42930 mg
* Residual Ozone	-	-	-	-	-
** Off Gas	0,3 mg/l				
COD (Removed) **B**	760 mg/l	870 mg/l	890 mg/l	895 mg/l	930 mg/l
A / B (mgO_3 / mg COD)	9,5	16,5	24	33	46

* Residual Ozone is determined in the range of 0,1-0,3 mg/l
** Off gas is neglected in terms of applied ozone

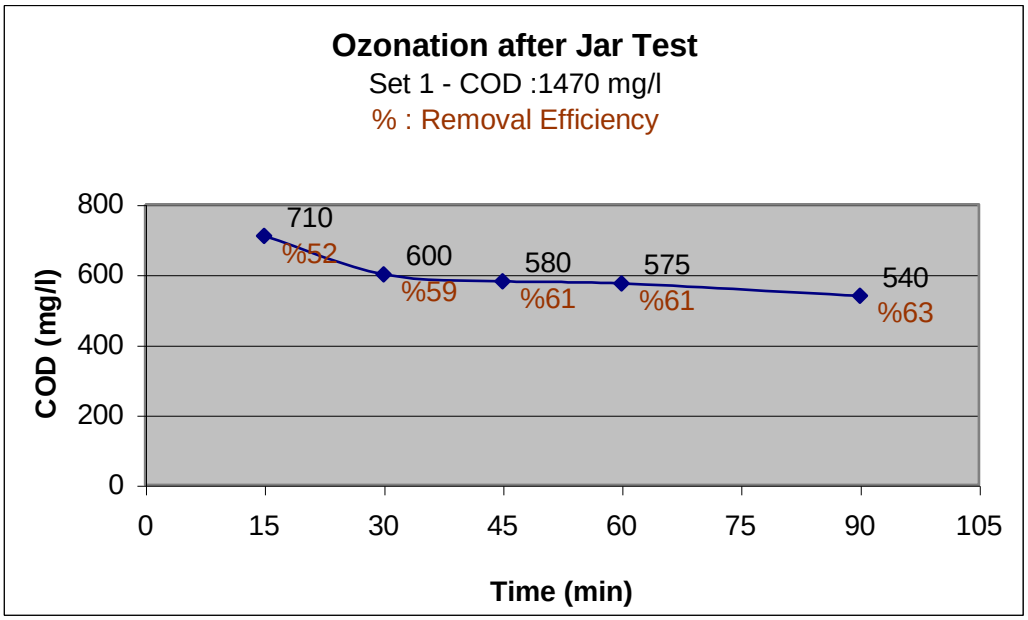


Figure 5.8. Ozonation after Chemical Treatment with $FeCl_3$ – Set 1

In Figure 5.8, results showed that 45 min of ozonation after chemical treatment had the optimum COD removal efficiency of %61. Because of not much difference between 90 min and 45 min ozonation removal efficiency results, 45 min of ozonation, which is both economic and has sufficient efficiency in comparison to 90 min of ozone application, is selected as optimum ozone dosage.

Table 5.7. Optimum dosage determination for $Al_2(SO_4)_3$ – Set 1

Set 1 - %10 Alum + Lime (for opt. dosage)					
pH	**COD inlet** (mg/l)	**Coagulant** Alum (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
7	9500	150	2426	74	Yellow, %18
7	***9500***	***300***	***2360***	***75***	***Yellow, %24***
7	9500	450	2558	73	Yellow, %22
7	9500	500	2598	72	Yellow, %22
7	9500	600	2780	70	Yellow, %20

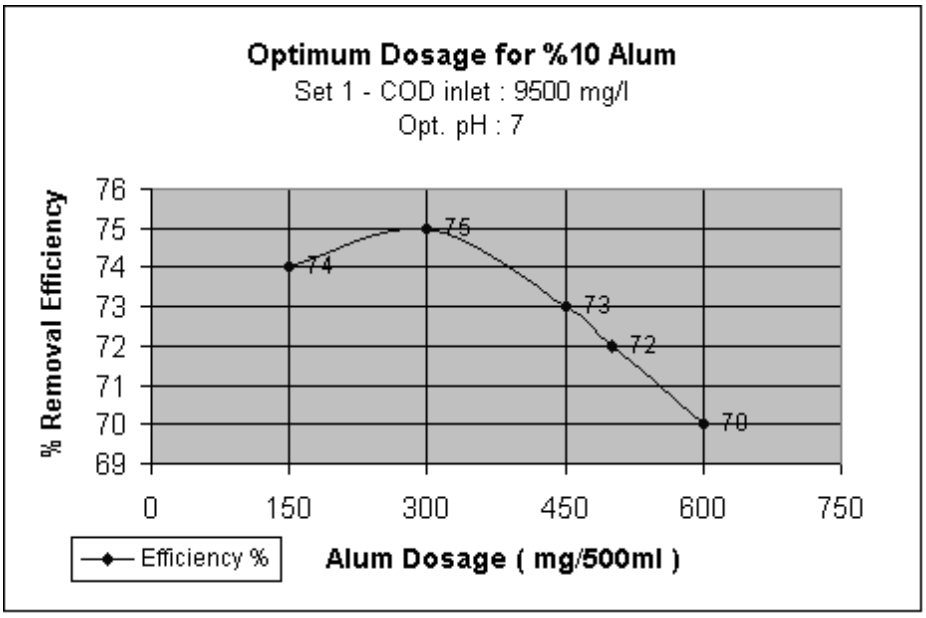


Figure 5.9. Optimum dosage determination for $Al_2(SO_4)_3$ – Set 1

Table 5. 8. Ozone Application Data Table

Data for ozone Application					
Contact Time	15 min	30 min	45 min	60 min	90 min
Applied Ozone	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min
Utilized Ozone (A)	7155 mg	14310 mg	21465 mg	28620 mg	42930 mg
*** Residual Ozone**	-	-	-	-	-
**** Off Gas**	0,3 mg/l				
COD (Removed) (B)	1240 mg/l	1560 mg/l	1600 mg/l	1710 mg/l	1720 mg/l
A / B (mgO_3 / mg COD)	5,5	9	13	17	25

* Residual Ozone is determined in the range of 0,1-0,3 mg/l
** Off gas is neglected in terms of applied ozone

Figure 5.10. Ozonation after Chemical Treatment with $Al_2(SO_4)_3$ - Set 1

In the second experiment ozonation was the first process applied to the samples. After ozonated samples were taken into the Jar test in order to determine the chemical treatment efficiency after ozonation.

In the characterization step of Set 1 COD was measured as 9500 mg/l. After 90 min of ozonation COD parameter was determined as 7500 mg/l with %21 removal efficiency. According to these results, chemical treatment experiments were performed and the results were shown in the following tables and figures.

Table 5.9. Jar Test of Ozonated Sample – $FeCl_3$ – Set 1

Set 1 (ozonated) - %10 FeCl 3 + NaOH (for opt. dosage)					
pH	**COD inlet** (mg/l)	**Coagulant** FeCl 3 (mg/ 500 ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
5	7500	200	2940	62	Dark brown, %18
5	7500	300	2380	68	Dark brown, 22
5	7500	400	2180	71	Dark brown, 20
5	***7500***	***500***	***2120***	***72***	***Dark brown, 24***
5	7500	600	2350	69	Dark brown, 20

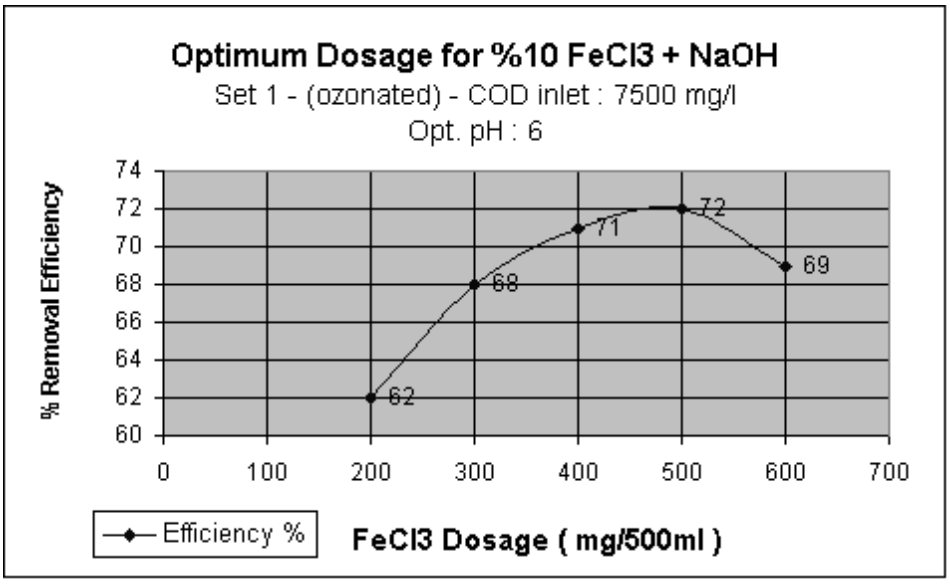


Figure 5.11. Jar Test of Ozonated Sample – $FeCl_3$ – Set 1

Table 5.10. Jar Test of Ozonated Sample – $Al_2(SO_4)_3$ – Set 1

Set 1 (ozonated) - %10 Alum + Lime (for opt. dosage)					
pH	**COD inlet** (mg/l)	**Coagulant** Alum (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
7	7500	200	4560	39	Yellow, %20
7	7500	300	2950	63	Yellow, %20
7	7500	400	2600	65	Yellow, %18
7	***7500***	***500***	***2490***	***67***	***Yellow, %24***
7	7500	600	2480	67	Yellow, %22

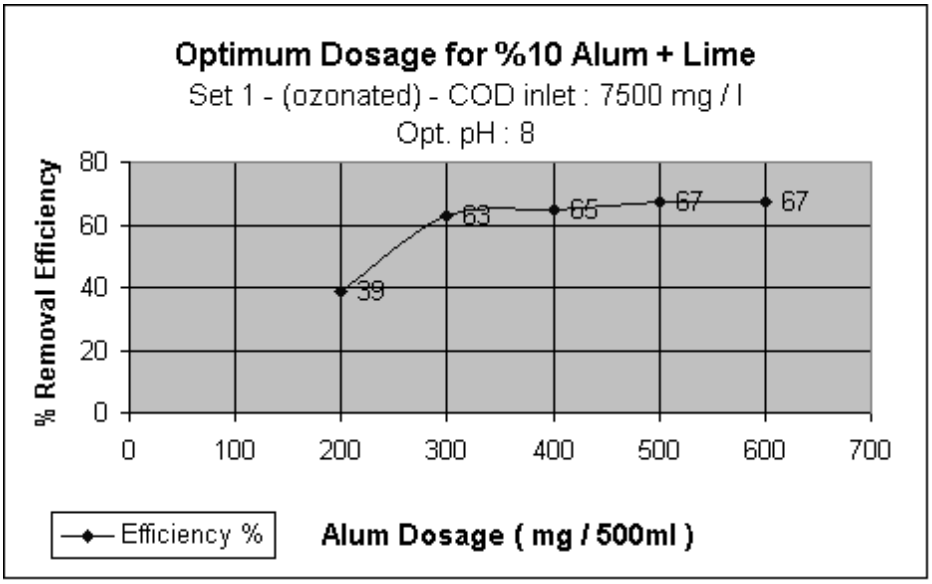


Figure 5.12. Jar Test of Ozonated Sample – $Al_2(SO_4)_3$ – Set 1

5.6.2. Results of Set 2

Set 2 was collected 2 weeks later after Set 1 was collected. The sample was characterized and the same experimental procedure applied to Set 1 was also applied to Set 2. Results were shown in following tables and figures.

Table 5.11. Optimum pH for $FeCl_3$ – Set 2

Set 2 - %10 FeCl3 + NaOH (for opt. pH measurement)					
pH	**COD inlet** (mg/l)	**Coagulant** FeCl3 (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
4	25000	500	11145	55	Dark brown, %10
5	25000	500	7620	68	Dark brown, %22
6	***25000***	***500***	***7090***	***71***	***Brown, %28***
7	25000	500	7225	70	Brown, %26
8	25000	500	7550	69	Brown, %24

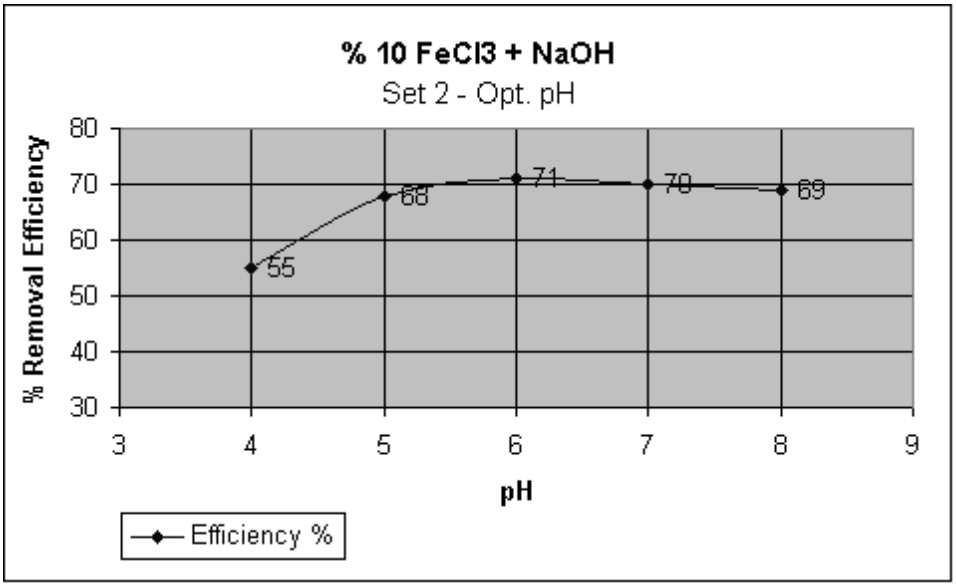


Figure 5.13. Optimum pH for $FeCl_3$ – Set 2

Table 5.12. Optimum pH for $Al_2(SO_4)_3$ - Set 2

Set 2 - %10 Alum + Lime (for opt. pH measurement)					
pH	**COD inlet** (mg/l)	**Coagulant** Alum (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
5	25000	1000	16200	35	Yellow, %10
6	25000	1000	12500	50	Yellow, %16
7	25000	1000	8950	65	Yellow, %24
8	***25000***	***1000***	***8400***	***68***	***Yellow, %26***
9	25000	1000	8450	68	Yellow, %26

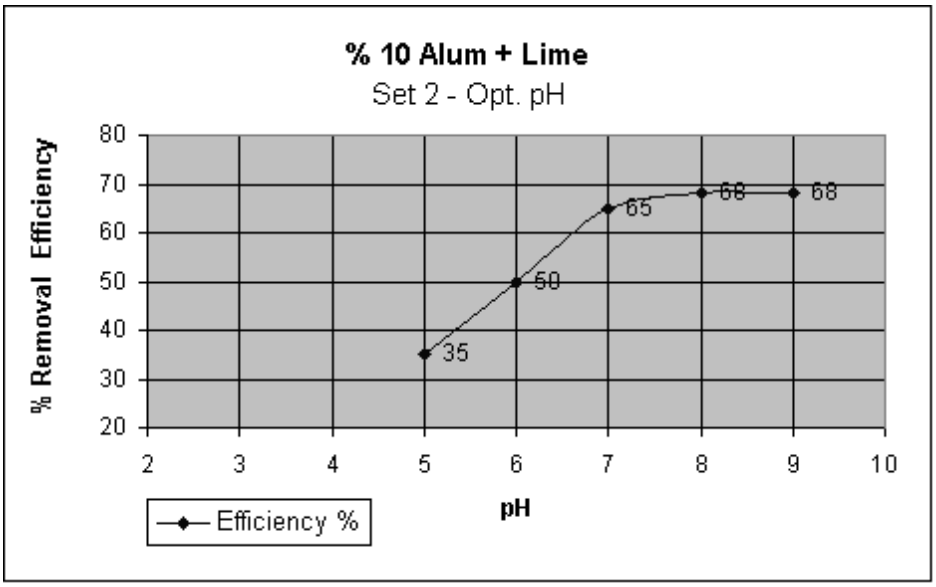


Figure 5.14. Optimum pH for $Al_2(SO_4)_3$ - Set 2

According to characterization of Set 2, it had the highest COD parameter of 25000 mg/l. As shown in tables increase in COD parameter made coagulant dosage also increase. Optimum dosage was determined as 1200 mg/500ml $FeCl_3$ for Set 2 at optimum pH of 6. Removal efficiency was %80. To supply alkalinity required for precipitation in water both lime and NaOH was used with $FeCl_3$ Experiments revealed that NaOH was a good supplementary agent in the case of using to adjust pH to desired range. After flocs settled sludge volume determined and sludge percentage was calculated as %26 of 500 ml.

Table 5.13. Optimum dosage determination for $FeCl_3$ – Set 2

Set 2 - %10 FeCl3 + NaOH (for opt. dosage)					
pH	**COD inlet** (mg/l)	**Coagulant** FeCl3 (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
6	25000	500	9650	61	Dark brown, %10
6	25000	800	6420	74	Dark brown, %22
6	25000	1000	5400	78	Dark brown, %24
6	***25000***	***1200***	***5300***	***80***	***Dark brown, %26***
6	25000	1400	5625	77	Dark brown, %22

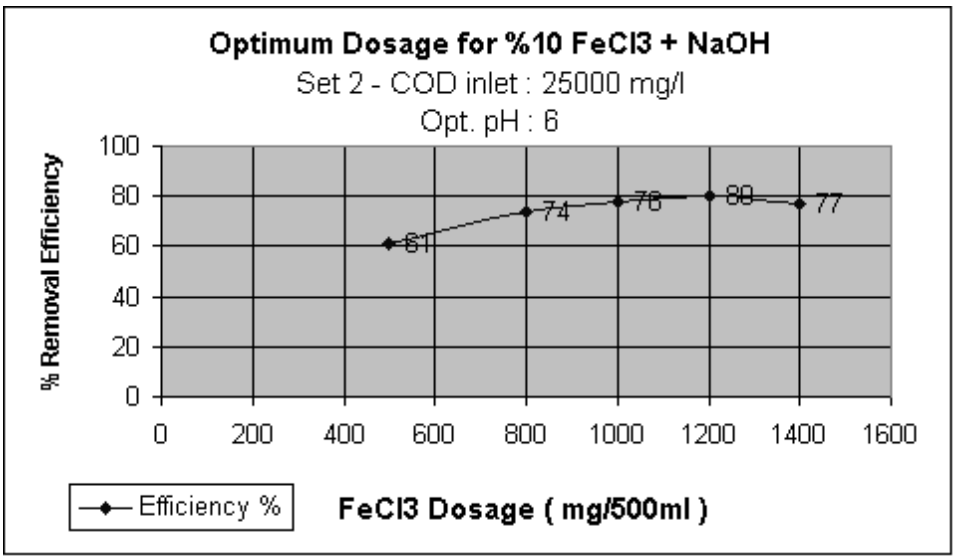


Figure 5.15. Optimum dosage determination for $FeCl_3$ – Set 2

Table 5.14. Ozone Application Data Table

Data for ozone Application					
Contact Time	15 min	30 min	45 min	60 min	90 min
Applied Ozone (mg/ min)	477	477	477	477	477
Utilized Ozone (A)	7155 mg	14310 mg	21465 mg	28620 mg	42930 mg
*** Residual Ozone**	-	-	-	-	-
**** Off Gas**	0,2 mg/l				
COD (Removed) (B)	700 mg/l	2200 mg/l	3450 mg/l	3450 mg/l	3470 mg/l
A / B(mgO_3 / mg/l)	10	6,5	6,2	8	12

* Residual Ozone is determined in the range of 0,1-0,3 mg/l
** Off gas is neglected in terms of applied ozone

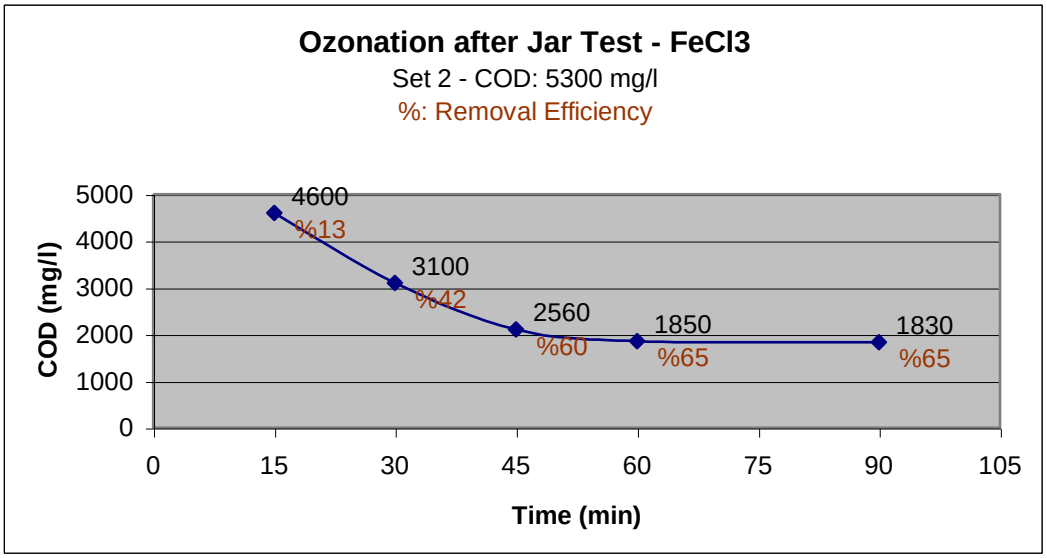


Figure 5.16 Ozonation after Chemical Treatment with $FeCl_3$ – Set 2

In Table 5.14 ozonation results after 15 min, 30 min, 45 min, 60 min, 90 min were shown. For each contact time COD tests were performed and treatment efficiencies were determined. In figure 5.16 both COD parameters and removal efficiencies were shown.

Table 5.15. Optimum dosage determination for $Al_2(SO_4)_3$ – Set 2

Set 2 - %10 Alum + Lime (for opt. dosage)					
pH	**COD inlet** (mg/l)	**Coagulant** Alum (mg/ 500 ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
8	25000	600	21000	16	Yellow, %4
8	25000	900	19400	22	Yellow, %6
8	25000	1000	13800	45	Yellow, %10
8	***25000***	***1200***	***6320***	***74***	***Yellow, %24***
8	25000	1400	12100	52	Yellow, %18

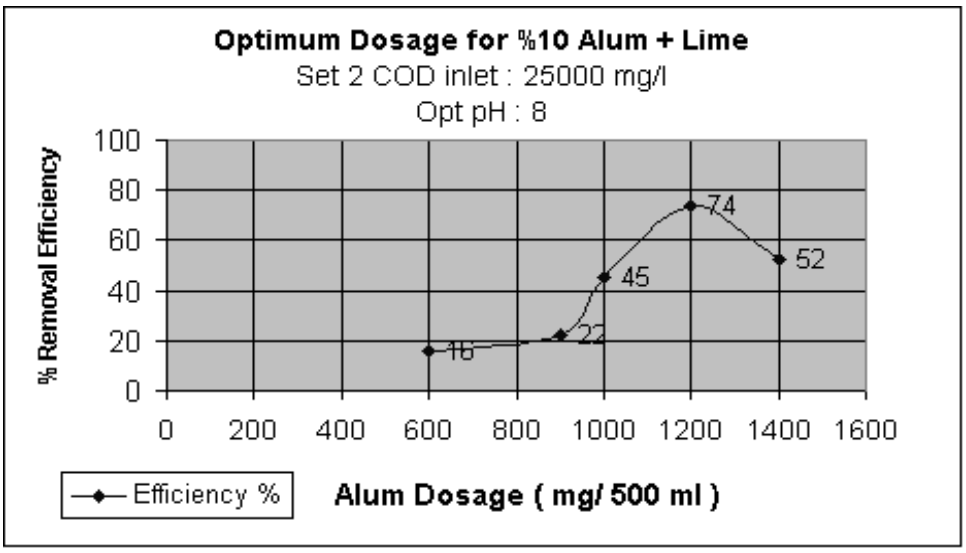


Figure 5.17. Optimum dosage determination for $Al_2(SO_4)_3$ – Set 2

Table 5.16. Ozone Application Data Table

Data for ozone Application					
Contact Time	15 min	30 min	45 min	60 min	90 min
Applied Ozone	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min
Utilized Ozone (A)	7155 mg	14310 mg	21465 mg	28620 mg	42930 mg
*** Residual Ozone**	-	-	-	-	-
**** Off Gas**	0,3 mg/l				
COD (Removed) (B)	585 mg/l	1630 mg/l	3460 mg/l	3980 mg/l	4150 mg/l
A / B (mgO_3 / mg/l)	12	8,7	6	7	10

* Residual Ozone is determined in the range of 0,1-0,3 mg/l
** Off gas is neglected in terms of applied ozone

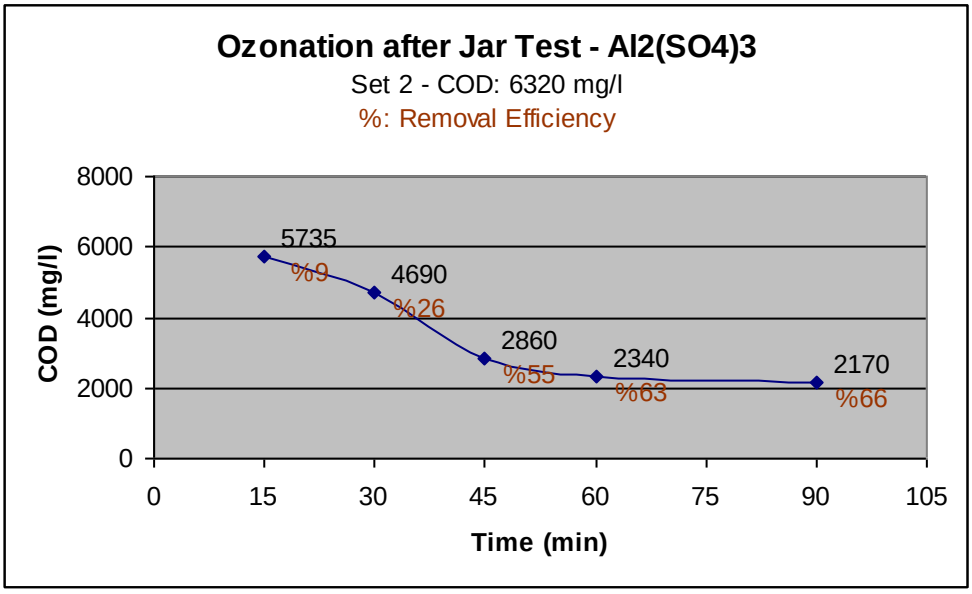


Figure 5.18 Ozonation after Chemical Treatment with $Al_2(SO_4)_3$ – Set 2

In the second step ozonation is the first process applied to the samples. After ozonated samples were taken to the Jar test to determine the chemical treatment efficiency after ozonation.

In the characterization step of Set 2, COD was measured 25000 mg/l. After 90 min ozonation COD parameter was determined as 19000 mg/l with removal efficiency of % 24 in the terms of COD. According to these results, chemical treatment experiments were performed and the results were shown in tables and figures as follow

Table 5.17. Jar Test of Ozonated Sample – $FeCl_3$ – Set 2

Set 2 (ozonated) - %10 FeCl3 + NaOH (for opt. dosage)					
pH	**COD inlet** (mg/l)	**Coagulant** FeCl3 (mg/500ml)	**COD outlet** (mg/l)	**Efficiency** %	**Sludge** Settled for 30 min.
6	19000	400	10600	44	Dark brown, %10
6	19000	600	8650	54	Dark brown, %10
6	19000	800	7500	60	Dark brown, %20
6	***19000***	***1000***	***6355***	***67***	***Dark brown, %24***
6	19000	1200	6600	65	Dark brown, %20

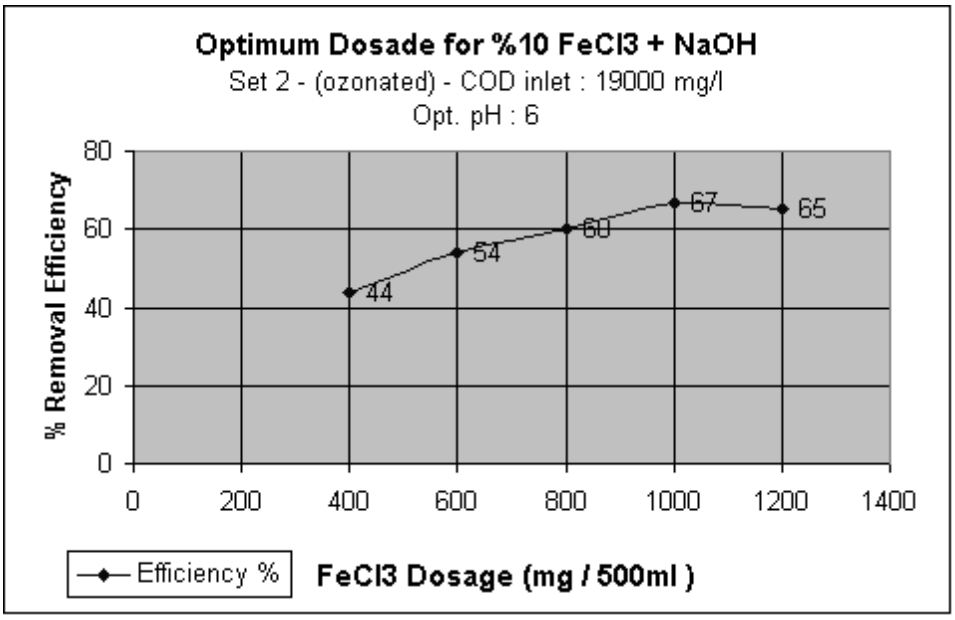


Figure 5.19. Jar Test of Ozonated Sample – $FeCl_3$ – Set 2

Table 5.18. Jar Test of Ozonated Sample – $Al_2(SO_4)_3$ – Set 2

Set 2 (ozonated) - %10 Alum + Lime (for opt. dosage)					
pH	COD inlet (mg/l)	Coagulant Alum (mg/500ml)	COD outlet (mg/l)	Efficiency %	Sludge Settled for 30 min.
8	19000	400	16680	12	Yellow, %20
8	19000	600	14500	24	Yellow, %20
8	19000	800	12650	33	Yellow, %18
8	19000	1000	7100	63	Yellow, %24
8	***19000***	***1200***	***7080***	***64***	***Yellow, %22***

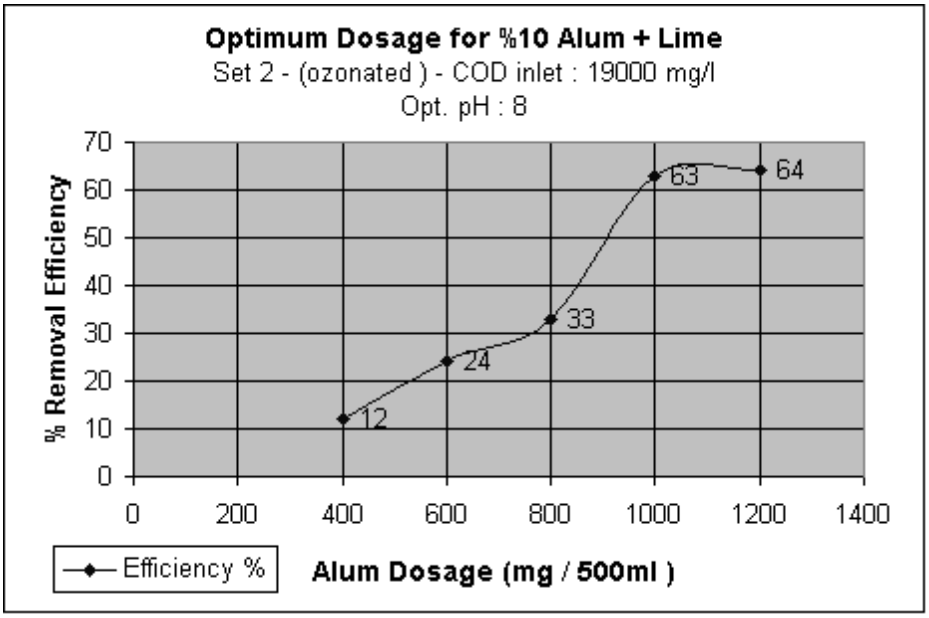


Figure 5.20. Jar Test of Ozonated Sample – $Al_2(SO_4)_3$ – Set 2

5.6.3. Results for Set 3

The experimental procedure that was performed to Set 1 and Set 2 was also applied to Set 3. Among these three sets Set 3 had the highest COD of approximately 30000 mg/l.

During chemical treatment experiments it was observed that $Al_2(SO_4)_3$ was not effective to reach desired removal efficiency for Set 3. Flocks did not settle but floated. The result was shown in Figure 5.21.

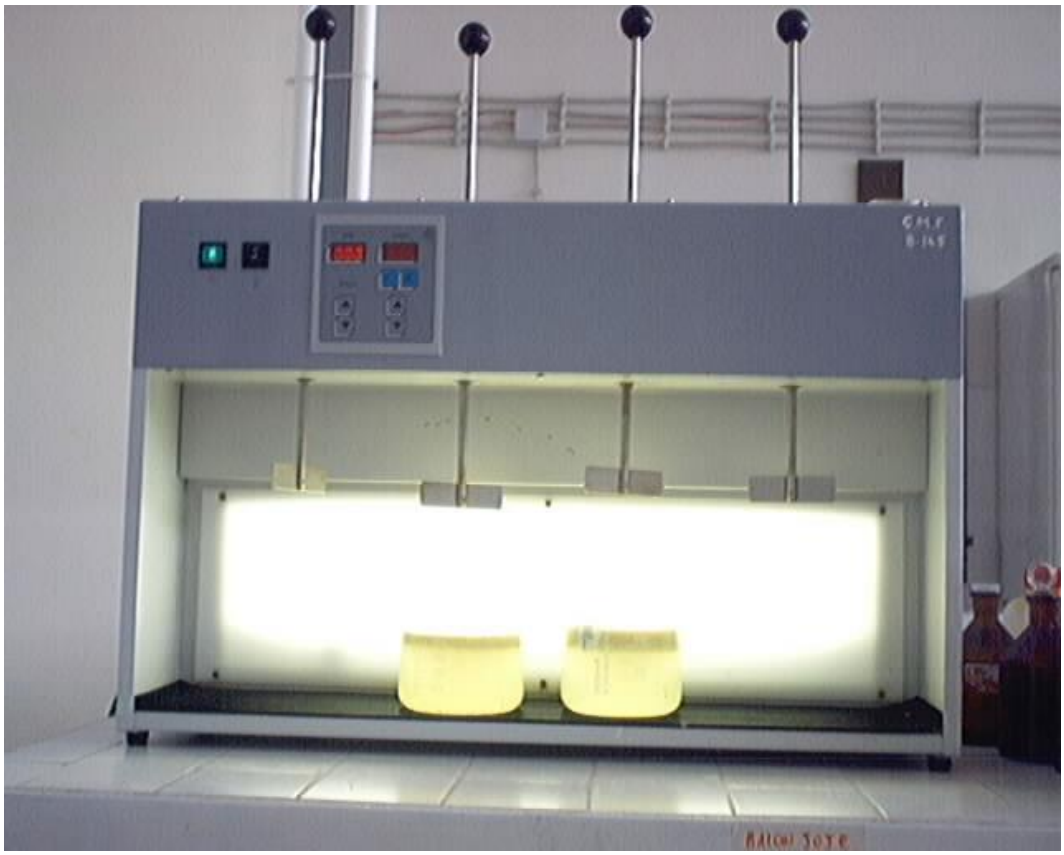


Figure 5.21. Jar Test Results of Set 3 – $Al_2(SO_4)_3$

High oil & grease content of Set 3 made it difficult to precipitate the sample. As seen in Figure 5.21 flocs occurred in the flasks after 2 min of rapid and 15 min of slow mixing. Instead of precipitation for Set 3 flotation of sludge was observed. When alum has been added into the waste for coagulation pH decreased below 3 and therefore, acid cracking was observed in the sample. Because of both oil content (gasoline-based) of the waste and pin point formed TSS parameter, also considering acid cracking, flotation of flocks was observed instead of precipitation. It is determined that COD removal efficiency for the subnatant was high enough. Therefore, it can be stated that main part of the COD parameter comes from oil content of the waste. After serial optimum coagulant trials, $FeCl_3$ was determined as the optimum coagulant, which had higher removal efficiency for Set 3. In the following tables and figures experimental results for Set 3 were given.

Table 5.19. Optimum dosage determination for $FeCl_3$ – Set 3

Set 3 - %10 FeCl3 + NaOH (for opt. dosage)					
pH	**COD inlet**	**Coagulant**	**COD outlet**	**Efficiency**	**Sludge**
	(mg/l)	FeCl3 (mg/500ml)	(mg/l)	%	Settled for 30 min.
6	29000	500	12520	57	Dark brown, %10
6	29000	800	8450	71	Dark brown, %22
6	***29000***	***1000***	***5860***	***80***	***Dark brown, %22***
6	29000	1200	6010	79	Dark brown, %26
6	29000	1400	5980	79	Dark brown, %22

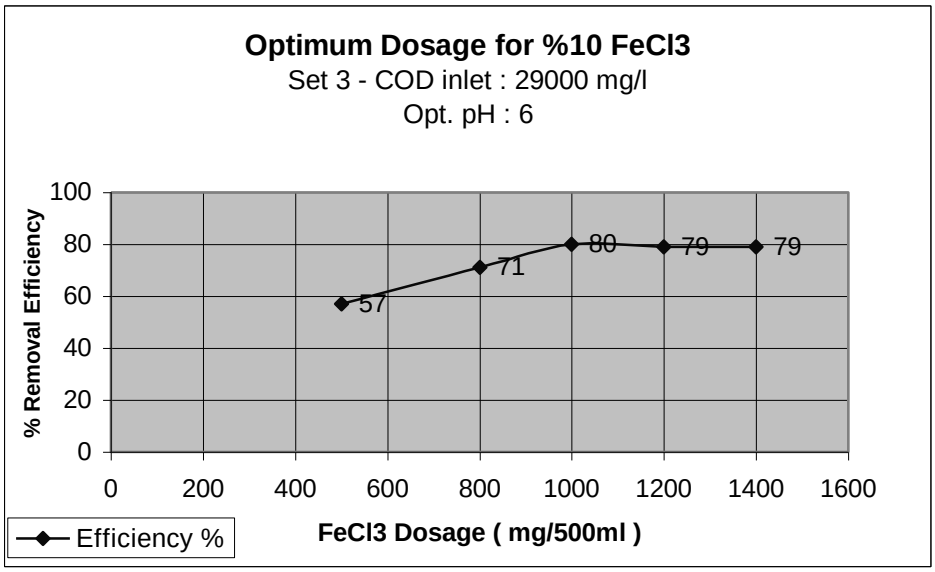


Figure 5.22. Optimum dosage determination for $FeCl_3$ – Set 3

After chemical treatment experiments ozone gas was applied to the sample and results were shown in Figure 5.23

Table 5.20. Ozone Application Table

Data for ozone Application					
Contact Time	15 min	30 min	45 min	60 min	90 min
Applied Ozone	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min	477 mg/ min
Utilized Ozone (A)	7155 mg	14310 mg	21465 mg	28620 mg	42930 mg
*** Residual Ozone**	-	-	-	-	-
**** Off Gas**	0,3 mg/l				
COD (Removed) (B)	810 mg/l	1640 mg/l	2810 mg/l	3620 mg/l	3660 mg/l
A / B (mgO_3 / mg/l)	8,7	8,7	7,5	8	12

* Residual Ozone is determined in the range of 0,1-0,3 mg/l
** Off gas is neglected in terms of applied ozone

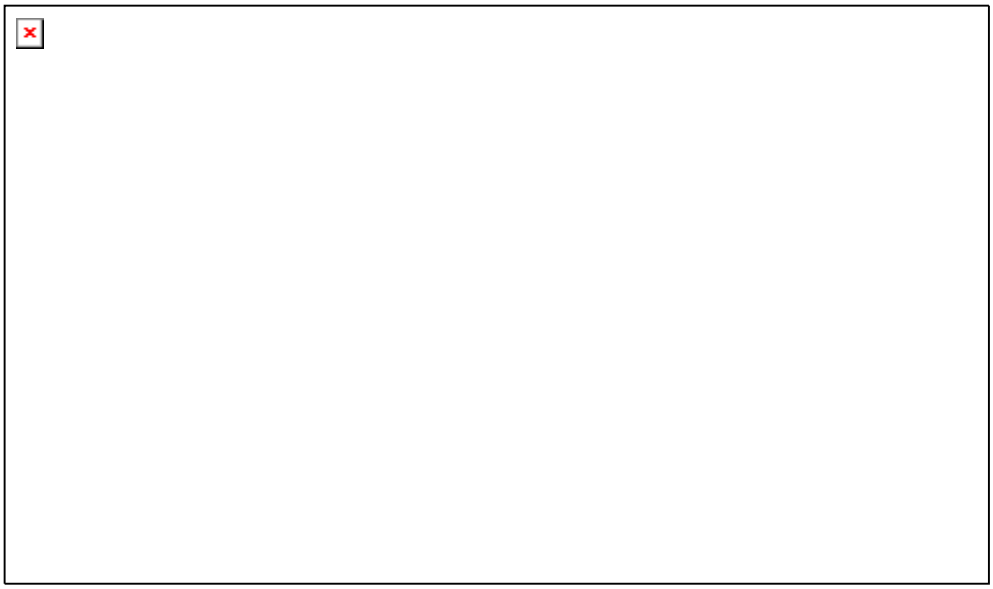


Figure 5.23. Ozonation after Jar-Test – Set 3

To determine the efficiency of ozone for raw sample, Set 3 was ozonated for 120 min. In the characterization step of Set 3, COD was measured as 29000 mg/l. After 90 min of ozonation COD parameter was determined as 19000 mg/l with %24 removal efficiency. According to these results, chemical treatment experiments were performed and the results were shown in tables and figures as follow

Table 5.21. Jar Test after Ozonation - $FeCl_3$ – Set 3

Set 3 (ozonated) - %10 FeCl3 + NaOH (for opt. dosage)					
pH	**COD inlet**	**Coagulant**	**COD outlet**	**Efficiency**	**Sludge**
	(mg/l)	FeCl3 (mg/500ml)	(mg/l)	%	Settled for 30 min.
6,5	22400	500	18800	16	Dark brown, 90 ml
6,5	22400	700	10920	51	Dark brown, 110 ml
6,5	22400	900	7940	65	Dark brown, 100 ml
6,5	***22400***	***1100***	***6080***	***73***	***Dark brown, 120 ml***
6,5	22400	1300	6110	72	Dark brown, 100 ml

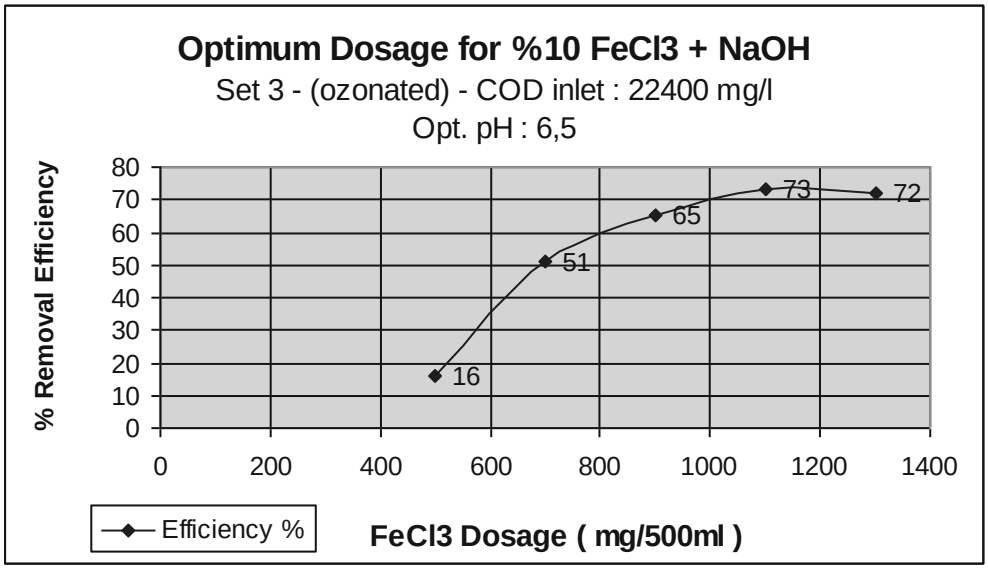


Figure 5.24. Optimum dosage determination for $FeCl_3$ – Set 3

To investigate detoxification property of ozone gas a bioassay test (Acute Fish Toxicity Test) was performed. To run this experiment, Set 1 with 9500 mg/l COD is chosen as wastewater.

Overall removal efficiency of chemical treatment and ozonation process for Set 1 was determined as %93. Ozone was used as a helping agent for chemical treatment with its strong oxidizing ability. Depending on its oxidizing power it is also used for detoxification of hazardous wastes.

A number of terms are utilized in expressing toxicity test results Acute toxicity is toxicity which is severe enough to produce a response rapidly (typically a response observed in 48 or 96 hours). Acute means short and does not necessarily imply mortality. LC_{50} is the concentration of effluent in dilution water that causes mortality to 50 percent of the test population.

Toxicity testing has been widely validated in recent years. Even though organisms vary in sensitivity to effluent toxicity, the EPA has documented that toxicity of effluents correlate well with toxicity measurements in the receiving waters when effluent dilution is measured.

The samples for bioassay tests were prepared as shown in Table 5.22

Table 5.22. Preparation of diluted samples

Acute Fish Toxicity Test for Set 1		
Concentrations (%)	Wastewater Volume (l)	Dilution Water Volome (l)
50	5	5
20	2	8
10	1	9

As it is seen in the figure, raw sample has determined highly toxic for a creature to live because of the poisonous effect of the chemicals that are used during production processes. In order to decrease toxicity parameter of the hazardous waste ozonation was performed for 90 min. after chemical treatment.
Results of ozonated sample were shown in Table 5.23 and in Figure 5.25

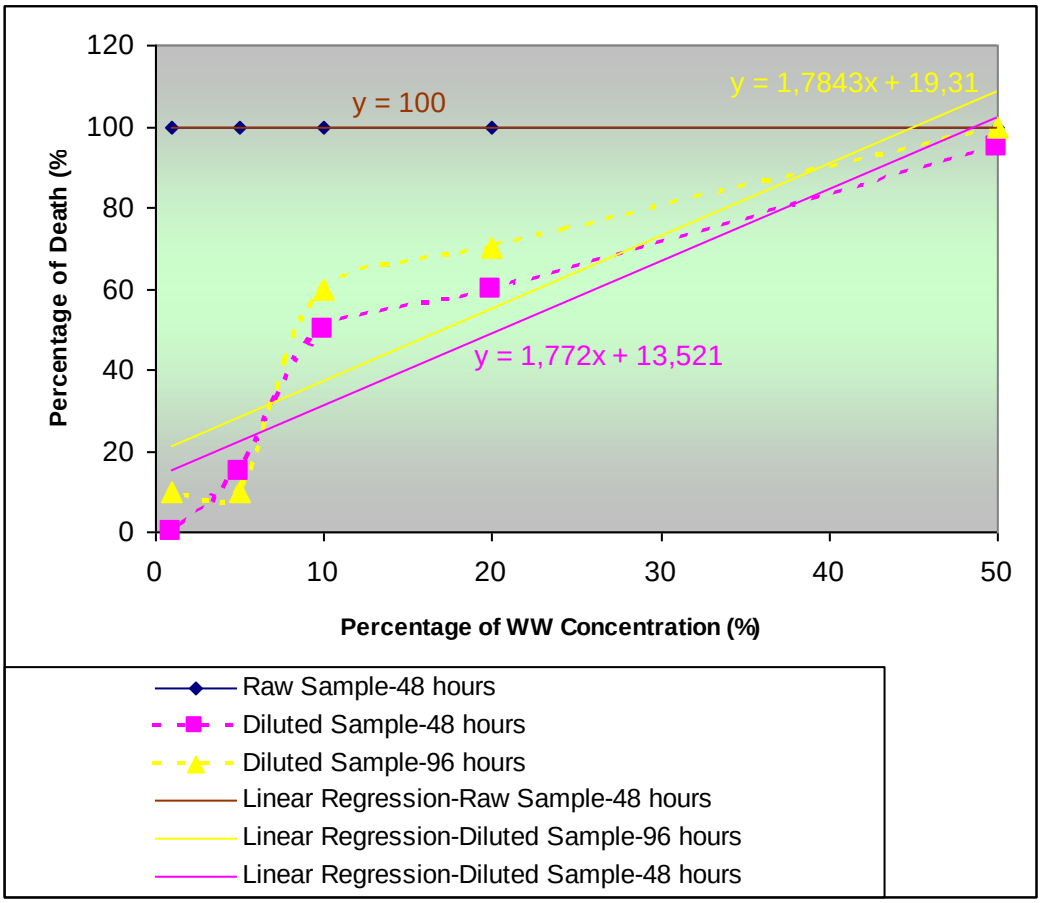


Figure 5.25. Bioassay after chemical treatment and ozonation for Set 1

Table 5.23. Acute Toxicity Test Results For Set 1 After Ozonation

Acute Toxicity Test Results For Set 1 After Ozonation					
Concentration percent of WW (%)	Number of fishes	Percentage of death (%) 48 hours	96 hours	*LC_{50}	$TU_{(a)}$
50	10	95	100		
20	10	60	70		
10	*10*	*50*	*60*	**17**	**6**
5	10	15	10		
1	10	0	10		

*LC_{50} is given as concentration percentage of the waste water (WW)

Experiments for 48 hours were not considered during LC_{50} calculation. Results were given in terms of 96-hour bioassay tests. To determine LC_{50}, 50 is replaced with **y** in regression equation (**y** = 1,7843x + 19,31).

$y = 1,7843x + 19,31 \quad \Rightarrow \quad 50 = 1,7843x + 19,31$

$x = \mathbf{LC_{50}} \cong 17$

$\mathbf{TU_{(a)}} = 100 / 17 \cong 6$

6. RESULTS AND CONCLUSION

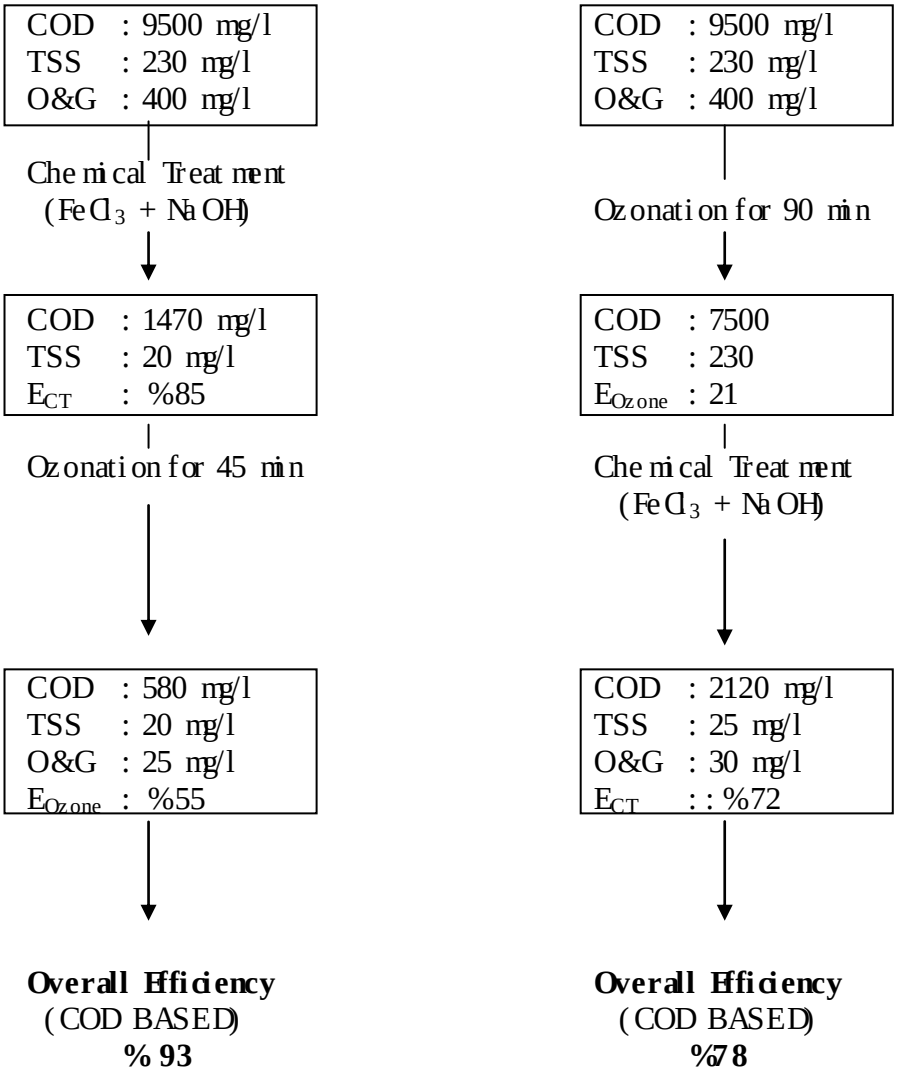
Within the concept of the study, the results of experimental studies that are related to the main scope of hazardous waste management are given in this section.

The hazardous waste investigated during the study, is a liquid-formed toxic waste, which also has the properties of both flammability and reactivity with water. The waste is generated from the combination of both cleaning of the reactors that are used for formulation of liquid and powder pesticide and laundry wastewater.

Hazardous waste that has been investigated during the study is listed in EPA hazardous waste lists and Turkish Hazardous Materials Regulation as F003, F004, F005, K043, K099 and Y4, Y9, Y10 respectively. It is determined that neither management nor control methods for this listed hazardous waste has been stated in the regulation. Considering both in-situ and on-site control systems, experimental studies were performed in the study in order to manage this hazardous waste. Thereupon, depending on the existing treatment system in the pesticide industry, chemical treatment and detoxification performance was determined.

Overall removal efficiencies show that chemical treatment and ozonation processes, if applied respectively, are sufficient enough to achieve high removal efficiency in COD base. According to test results, $FeCl_3$ has been determined as optimum coagulant relatively.

Performing experimental procedure to the sample called Set 1 with COD of 9500 mg/l, the results in the Figure 6.1 and 6.2 were summarized.



O & G: Oil & Grease
E_{CT} : Removal Efficiency of Chemical Treatment
E_{Ozone} : Removal Efficiency of Ozonation

Figure 6.1 Overall Efficiency Table for Set 1-$FeCl_3$

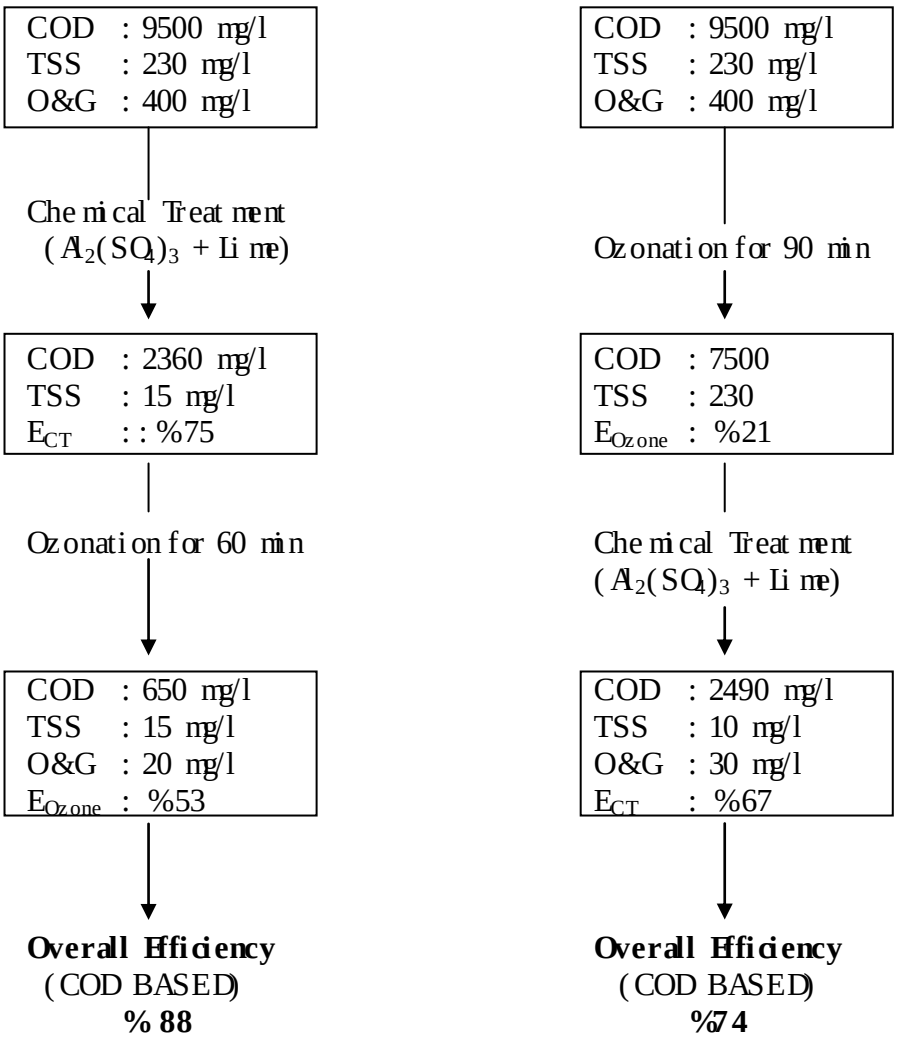


Figure 6.2. Overall Efficiency Table for Set 1- Alum

In the existing wastewater treatment system of the industry, an oil separator has separated oil concept of the waste. It is determined that the separation process has increased the overall removal efficiency of treatment system. However, variations of coagulation and ozonation processes can be suggested as a modification of the treatment system due to its higher overall removal efficiencies determined in the study.

Inspite of the fact that ozone application into the water helps coagulation, it may be considered that OH radicals were utilized by oil based compounds by cyclic reactions and decreased chemical treatment efficiency.

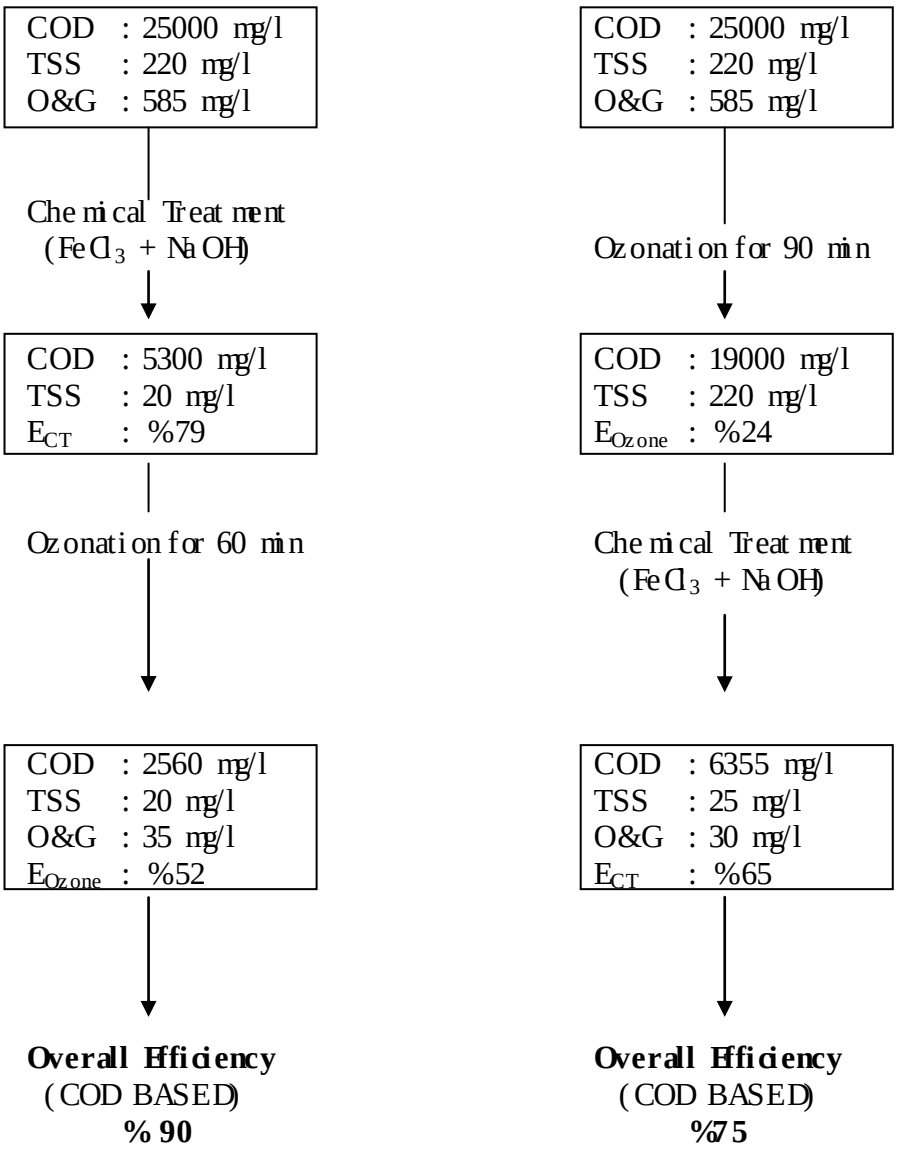


Figure 6.3. Overall Efficiency Table for Set 2-$FeCl_3$

With regard to hazardous waste composition, big differences in COD base among three samples, which were collected in different periods, were determined. However, approximately, same removal efficiencies as Set 1 were measured for Set 2 with COD of 25000 mg/l. These results were shown in Figure 6.3 and 6.4 above.

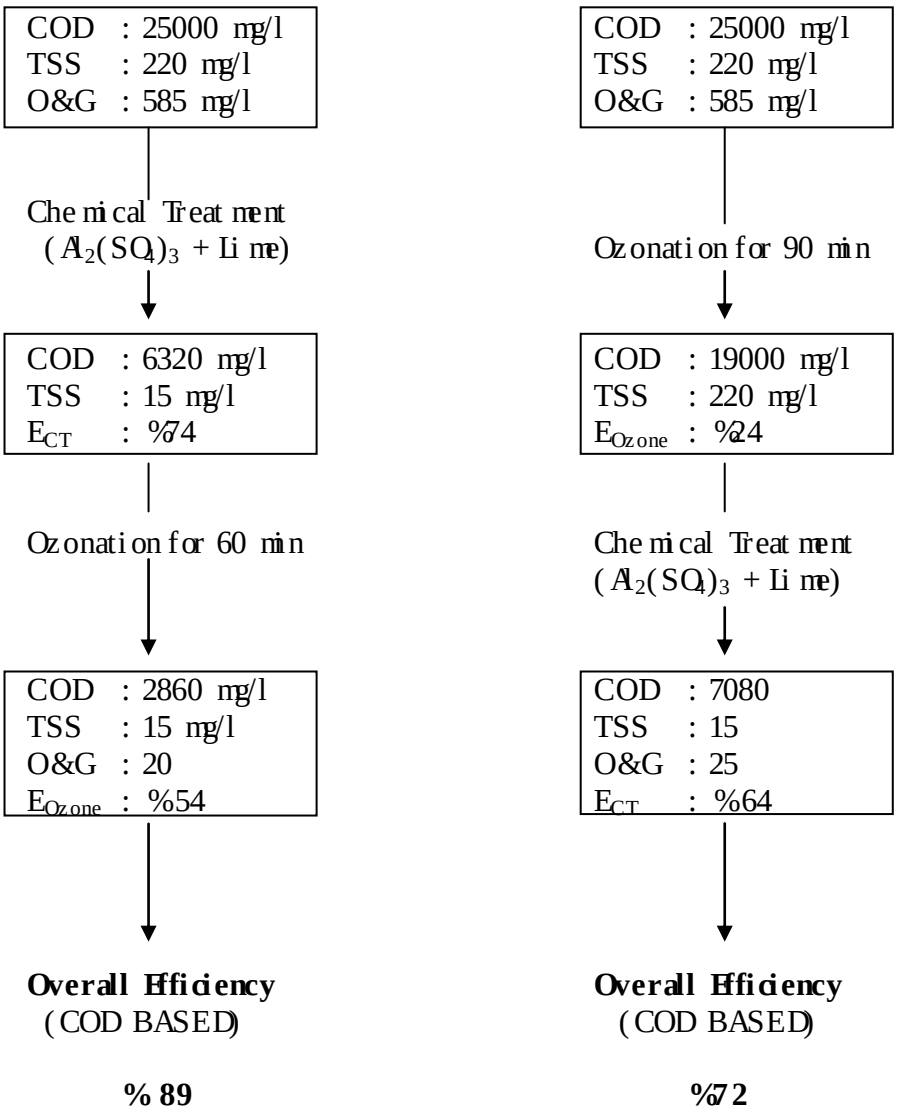


Figure 6.4. Overall Efficiency Table for Set 2- Alum

Although the difference in the COD parameter is thought to be related to the oil and grease content of the waste, it is observed that oil and measured grease parameter did not confirm this assumption. Therefore, the COD equivalents of cleaning reagents such as gasoline and solvents, were evaluated as a possible reasons for the difference in COD parameter but not oil and grease. Due to TOC parameter is more reliable than COD parameter to monitor removal efficiencies, it is determined that suggested to perform TOC parameter instead of COD measurement.

To discuss the results easily, overall efficiencies of the experiments performed during the study were figured as follows.

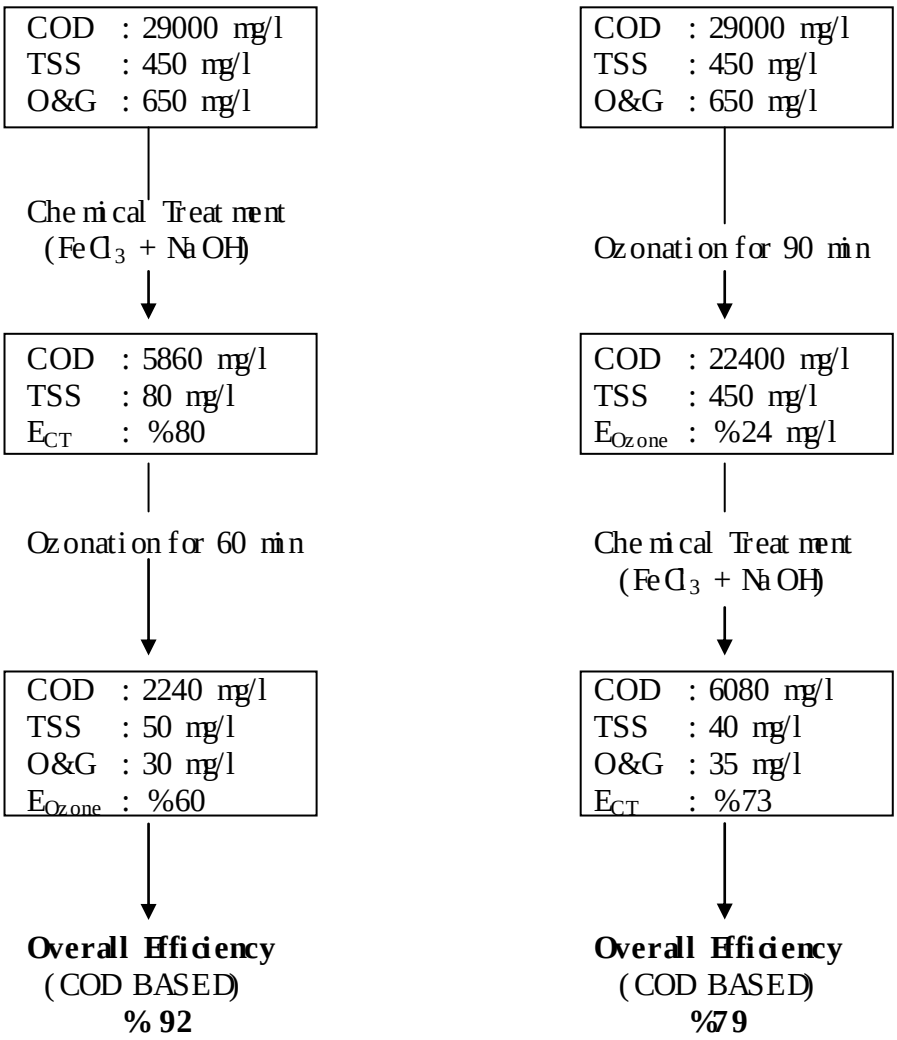


Figure 6.5. Overall Efficiency Table for Set 3-$FeCl_3$

After jar test repeated for Set 3 (29000 mg/l COD), it was observed that pin point formed flocks were floating instead of precipitation. Therefore alum has not been considered as an applicable coagulant for Set 3.

Jar test and ozonation results with $FeCl_3$ were determined approximately same as other two samples and are shown in Figure 6.5.

The priority hazardous waste characteristic of the sample investigated in the study has been determined as "toxicity" from both EPA hazardous waste lists and acute fish toxicity test. According to the standard acute fish toxicity test, the toxicity parameter of the raw sample was determined as infinite.

In the study, acute fish toxicity test was performed to treated sample Set 1. After bioassay test $TU_{(a)}$ was determined as 6 considering that it was infinite for raw sample. This reduction of toxicity parameter showed that ozone can be used for detoxification of hazardous wastes as an aid process in the existing treatment system of the pesticide industry.

Due to high calorific value of the raw sample, dioxin controlled incineration process can be considered as an appropriate management method for this hazardous waste. This pesticide industry is considered as small quantity generator with 2 m^3/day of waste generation. Therefore this incineration process should be applied at a hazardous waste site (on-site) instead of an in-situ application after this highly calorific waste is mixed with other wastes to be incinerated.

Although it is also possible to recover the spent chemicals by solvent-solvent extraction method, coagulation and ozonation variations experienced during the study were considered as a more appropriate and economic management alternatives due to existing treatment system in the industry.

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