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GRADUATE SCHOOL OF
APPLIED AND NATURAL SCIENCES**

MSc Thesis

**TREATMENT OF AN INDUSTRIAL WASTEWATER
BY BIOLOGICAL OXIDATION AND/OR CHEMICAL
OXIDATION**

Gülin AYTİMUR

Department of Chemical Engineering

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Supervisor: Prof Dr. Süheyda Atalay

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Jüri Başkanı : Prof. Dr. Süheyda ATALAY

Raportör Üye : Prof. Dr. Süheyda ATALAY

Üye : Prof.Dr. Bikem ÖVEZ

Üye : Prof.Dr. Ayşen TÜRKMAN

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ÖZET**ENDÜSTRİYEL BİR SIVI ATIĞIN KİMYASAL VE/VEYA
BİYOLOJİK OKSİDASYON YÖNTEMLERİ İLE ZARARSIZ
HALE GETİRİLMESİ**

AYTİMUR, Gülin

Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü

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Bu çalışmada, Afyon Alkaloit Fabrikası atıksuyunun, biyolojik ve kimyasal oksidasyonla ve bu proseslerin çeşitli kombinasyonları ile arıtımı incelenmiştir. Biyolojik arıtım için aktif çamur, kimyasal arıtım için ise Katalitik ıslak hava oksidasyonu yöntemleri kullanılmıştır. Atıksu biyolojik arıtıma tabi tutulduğunda; havalandırma süresi (4, 6, 8 gün)ve hava akış hızının (3, 4,5 L/dak) KOİ giderimi üzerinde etkisi incelenmiştir. 6 günlük havalandırma süresinin uygun olduğuna karar verilmiştir. Aynı zamanda hava akış hızının artması, KOİ giderimini de artırmıştır. Katalitik ıslak hava oksidasyonu deneylerinde sıcaklığın (140, 150, 160°C) ve katalizör yüklemesinin (0.5, 1 g/L) etkileri incelenmiştir. 1 g/L katalizör yüklemesi ve 150°C sıcaklığın uygun olduğu saptanmıştır. Kombine proseslerde, biyolojik olarak arıtılmış atıksular katalitik ıslak hava oksidasyonuna, kimyasal olarak arıtılan atık sular biyolojik arıtıma tabi tutulmuştur. Fakat her iki kombinasyonun da çok etkili olmadığı biyolojik arıtımın ise tek başına yeterli olabileceği saptanmıştır. Ek olarak, aktif çamur prosesinin kinetiği Monod modeline göre incelenmiştir.

Anahtar sözcükler: atıksu arıtımı, aktif çamur, katalitik ıslak hava oksidasyonu, Monod modeli

ABSTRACT

**TREATMENT OF AN INDUSTRIAL WASTEWATER BY
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The treatment of Afyon Alcaloide Factory Wastewater, a high strength industrial wastewater, was carried out by biological and chemical oxidations and plus by the appropriate combinations of them. As biological treatment, activated sludge and as chemical treatment catalytic wet air oxidation (CWAO), processes were used. In biological process, the effect of retention time (4, 6, 8 days) was tested and 6 days of retention time was decided to be appropriate. It was also seen that as air flowrate increased COD removal also increased. In CWAO, effects of temperature (140, 150, 160°C) and catalyst loading (0.5, 1 g/L) were tested. The optimum temperature and catalyst loading were found to be 150°C and 1g/L, respectively. In combined processes, biologically treated wastewater was subjected to CWAO and also chemically oxidized wastewater was subjected to biological treatment. Combinations of the both processes seemed not so effective. Biological treatment alone was preferable. Also the kinetics of activated sludge process was modelled according to Monod Equation.

Keywords: wastewater treatment, activated sludge, catalytic wet air oxidation, Monod model

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1. INTRODUCTION

In recent years, industrial aqueous wastes containing high amounts of organic substances have been one of the most important urban problems. The disposal of these wastes constitutes a serious problem for environment and human health. In order to reduce the harmful effects of these disposals, appropriate hazardous waste treatment methods should be considered. There are several treatment processes applicable biologically or chemically. In some cases applying just one treatment process is enough, but sometimes just one can't be efficient. This situation obliges to use a combination of them to improve the elimination of wastes (Benites et al., 1999). There are some combined processes that are already being applied in certain chemical companies (Oliviero et al., 2000).

Biological oxidation is a commonly applied method in wastewater treatment (Lei et al., 2000). Activated sludge treatment is the most widely used biological method to deal with various kinds of wastewater because of its simplicity and relatively low cost. Basically, the activated sludge process uses microorganisms in suspension to oxidize soluble and colloidal organics to CO_2 , water and cell mass in presence of molecular oxygen (Metcalf and Eddy, 1991). In this process the wastewater is aerated in the reactor, then the solids are settled out in a settling tank. Bacteria containing activated sludge are continually recirculated back to the aeration basin to increase the rate of organic decomposition.

The activated sludge process is nowadays used for

- Communal wastewater treatment
- Industrial wastewater treatment
 - Food
 - Leather and paper
 - Petrochemical and organic chemical industries
 - Oil refineries

According to Beltrame(1988), the microorganisms in an activated sludge system can only handle chemical wastewaters containing relatively low concentrations of organic compounds (Lin and Ho, 1996). According to Mishra (1995), as those occurring in many heavy chemical and petrochemical industries need to be treated by other methods. The wet air oxidation (WAO) treatment process represents such method (Lin and Ho, 1996).

WAO is a well established technique for the treatment of hazardous, toxic and nonbiodegradable wastestreams. The organic substances in wastestreams are oxidized in the aqueous phase with peroxide, ozone, air or oxygen.

WAO is a wastewater technology based on the oxidation of pollutants at high temperature and high pressure in liquid phase (Genç et al., 2002). The oxidizing power of WAO is based on the high solubility of oxygen at these severe conditions and high temperature that increases

the reaction rates and production of free radicals. The working conditions of the WAO are the temperatures of 125-300⁰C and pressures of 0.5-20 MPa (Genç et al., 2002).

Since maintaining the WAO treatment process at the indicated operating conditions is energy consuming, it is highly desirable to operate WAO treatment process at sufficiently lower temperature and pressure which enables retention of good oxidation efficiency of WAO process (Lin and Ho, 1996). The catalytic wet air oxidation (CWAO) operates at lower temperatures and pressures. So this version can be applied or also a combined system (biological/chemical) to the various types of wastes.

The present study intends to reduce the organic matter in Afyon Alcaloide Factory (which produces raw morphine and its derivatives) wastewater by adequate treatment strategies. Three different treatment strategies are applied to Afyon Alcaloide Factory wastewater. These are;

1. Only biological treatment of the factory effluent
2. Only applying catalytic wet air oxidation to the factory effluent
3. Various combinations of catalytic wet air oxidation and biological treatment

2. WASTEWATER AND WASTEWATER TREATMENT

2.1. What Are Some Different Types Of Water Pollution?

Water is essential for life. It covers 71% of the earth's surface and makes up 65 % of human bodies. If water becomes polluted, it loses its value to people economically and aesthetically, and can become a threat to people's health and to the survival of the fish living in it and the wildlife that depends on it.

Wastewater is used water. It includes substances such as human waste, food scraps, oils, soaps and chemicals. In homes, this includes water from sinks, showers, bathtubs, toilets, washing machines and dishwashers. Businesses and industries also contribute their share of used water that must be cleaned. Wastewater also includes storm runoff. Although some people assume that the rain that runs down the street during a storm is fairly clean, it isn't. Harmful substances that wash off roads, parking lots, and rooftops can harm rivers and lakes (www.geocities.com/RainForest/5161/water1.htm).

Microbiological

Disease-causing (pathogenic) microorganisms, like bacteria, viruses and protozoa can cause water pollution.. Some serious diseases like polio and cholera are waterborne.

(www.geocities.com/RainForest/5161/water1.htm)

Chemical

A whole variety of chemicals from industry, such as metals and solvents, and even chemicals which are formed from the breakdown of natural wastes (ammonia, for instance) are poisonous to fish and other aquatic life. Pesticides used in agriculture and around the home insecticides for controlling insects and herbicides for controlling weeds are another type of toxic chemical. Materials like detergents and oils float and spoil the appearance of a water body, as well as being toxic; and many chemical pollutants have unpleasant odors.

Oxygen-depleting Substances

Many wastes are biodegradable, that is, they can be broken down and used as food by microorganisms like bacteria. Biodegradable wastes are preferable to non-biodegradable ones, because they will be broken down and not remain in the environment for very long times. Too much biodegradable material, though, can cause the serious problem of oxygen depletion in receiving waters. Like fish, aerobic bacteria that live in water use oxygen gas which is dissolved in the water when they consume their "food". If there is too much "food" in the water, the bacteria that are consuming it can easily use up all of the dissolved oxygen, leaving none

for the fish, which will die of suffocation. Once the oxygen is gone (depleted), other bacteria that do not need dissolved oxygen take over. But while aerobic microorganisms use dissolved oxygen convert the nitrogen, sulfur, and carbon compounds that are present in the wastewater into odorless and relatively harmless oxygenated forms like nitrates, sulfates and carbonates, these anaerobic microorganisms produce toxic and smelly ammonia, amines, and sulfides, and flammable methane (swamp gas).

Nutrients

The elements phosphorus and nitrogen are necessary for plant growth, and are plentiful in untreated wastewater. Added to lakes and streams, they cause nuisance growth of aquatic weeds, as well as "blooms" of algae, which are microscopic plants. This can cause several problems.

Suspended matter

Some pollutants are dissolved in wastewater, meaning that the individual molecules or ions of the substance are mixed directly in between the molecules of water. Other pollutants, referred to as particulate matter, consist of much larger but still very small particles, which are just suspended in the water. Although they may be kept in suspension by turbulence, once in the receiving water, they will eventually settle out and form silt or mud at the bottom. These sediments can decrease the depth of the body of water. If there is a lot of biodegradable organic material in the sediment, it will become anaerobic and contribute to

problems mentioned above. Toxic materials can also accumulate in the sediment and affect the organisms, which live there and can build up in fish that feed on them, and so be passed up the food chain, causing problems all along the way

(www.geocities.com/RainForest/5161/water1.htm).

2.2 Why Treat Wastewater?

It's a matter of caring for environment and for our human health. There are a lot of good reasons to keep water and environment clean (<http://ga.water.usgs.gov/edu/wuww.html>).

Fisheries

Clean water is critical to plants and animals that live in water. This is important to the fishing industry, sport fishing enthusiasts, and future generations.

Wildlife Habitats

Rivers and ocean waters teem with life that depends on shoreline, beaches and marshes. They are critical habitats for hundreds of species of fish and other aquatic life. Migratory water birds use the areas for resting and feeding.

Recreation and Quality of Life

The scenic and recreational values of waters are reasons many people choose to live where they do. Visitors are drawn to water activities such as swimming, fishing, boating and picnicing.

Health Concerns

If it is not properly cleaned, water can carry disease.

2.3.Wastewater Treatment

As the human population increases, the implementation of innovative wastewater treatment processes becomes increasingly important. Planning and implementing innovative wastewater treatment improvements is both time-consuming and capital-intensive.

(http://www.hazenandsawyer.com/services/services_wwt.htm)

The major contaminants found in wastewater are biodegradable organics, volatile organic compounds, recalcitrant organics, toxic metals, suspended solids, nutrients (nitrogen phosphorus), microbial pathogens, and parasites (Bitton, 1994).

The objectives of waste treatment processes are the following (Bitton, 1994):

- Reduce the organic content of wastewater
- Removal / reduction of nutrients (N,P)
- Removal or inactivation of pathogenic microorganisms and parasites

2.3.1. Wastewater Treatment Plants

Wastewater treatment plants can be divided into two major types (<http://www.geocities.com/RainForest/5161/wwtps.htm>);

- Biological
- Physical/Chemical

Biological plants are more commonly used to treat domestic or combined domestic and industrial wastewater from a municipality.

Physical/chemical plants are more often used to treat industrial wastewaters directly, because they often contain pollutants which cannot be removed efficiently by microorganisms although industries that deal with biodegradable materials, such as food processing, dairies, breweries, and even paper, plastics and petrochemicals, may use biological treatment. And biological plants generally use some physical and chemical processes, too.

A **physical process** usually treats suspended, rather than dissolved pollutants. It may be a simply allowing suspended pollutants to settle out or float to the top naturally-- depending on whether they are more or less dense than water. Or the process may be aided mechanically, such as by gently stirring the water to cause more small particles to bump into each other and stick together, forming larger particles which will settle or rise faster a process known as flocculation.

Some examples of **chemical treatment processes**, in an industrial setting, would be converting a dissolved metal into a solid, settleable form by precipitation with an alkaline material like sodium or calcium hydroxide. Dissolved iron or aluminum salts or organic coagulant aids like polyelectrolytes can be added to help flocculate and settle (or float) the precipitated metal converting highly toxic cyanides used in mining and metal finishing industries into harmless carbon dioxide and nitrogen by oxidizing them with chlorine destroying organic chemicals by oxidizing them using ozone or hydrogen peroxide, either alone or in combination with catalysts (chemicals which speed up reactions) and/or ultraviolet light.

A typical wastewater treatment plant comprises the following four steps;

- Preliminary Treatment
- Primary Treatment
- Secondary Treatment
- Tertiary or Advanced Treatment

Preliminary Treatment

Objective is to remove or reduce the size of large objects so that the plant equipment is not damaged.

Primary Treatment

Objective is to remove settleable and floatable solids from the wastewater stream. Treatment is brought about by physical processes (unit operations) such as screening and sedimentation.

Secondary Treatment

Objective is to remove additional suspended solid, organic matter and nutrients. Biological (activated sludge, trickling filter, oxidation ponds) and chemical (disinfection) unit processes are used to treat wastewater.

Tertiary or Advanced Treatment

Objective is to remove further BOD, nutrients, pathogens and parasites, and sometimes toxic substances.

A typical wastewater treatment plant can be seen in Figure 2.1 (<http://ohioline.osu.edu/aex-fact/0768.html>).

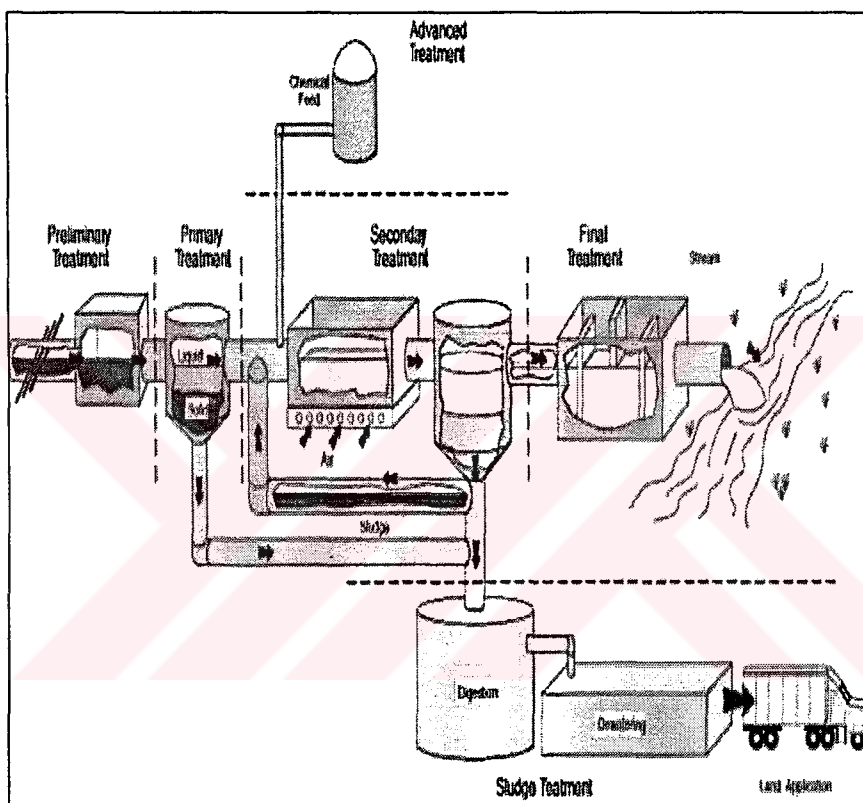


Figure 2.1 A typical wastewater treatment plant

3. ACTIVATED SLUDGE PROCESS

3.1.Overview of Biological Wastewater Treatment

Biological processes have important applications in treating wastes. The objectives of biological treatment of wastewater are;

- To coagulate and remove nonsettable colloidal solids
- To stabilize the organic matter

There are five major biological processes, which are used for wastewater treatment. These are aerobic processes, anoxic processes, anaerobic processes, combined aerobic, anoxic and anaerobic processes and pond processes. The detailed information about these groups are identified in Table 3.1 (Metcalf and Eddy, 1991).

Table3.1 Major biological treatment processes used for wastewater treatment

Type	Common name	Use
<p>Aerobic Processes: <i>Suspended-Growth</i></p>	<p>Activated-Sludge Process Conventional (plug-flow) Complete-mix Step aeration Pure oxygen Sequencing batch reactor Contact stabilization Extend aeration Oxidation ditch Deep tank Deep shaft Suspended-growth nitrification Aerated lagoons Aerobic digestion Conventional air Pure oxygen Trickling filters</p>	<p>Carbonaceous BOD removal, nitrification</p>
<p><i>Attached-Growth</i></p>		<p>Nitrification Carbonaceous BOD removal, nitrification Stabilization, carbonaceous BOD removal Carbonaceous BOD removal, nitrification</p>

<p><i>Combined suspended- and attached growth processes</i></p> <p>Anoxic Processes: <i>Suspended-growth Attached-growth</i></p> <p>Anaerobic Processes: <i>Suspended-growth</i></p>	<p>Low-rate High-rate Roughing filters Rotating biological contactors Packed-bed reactors Activated biofilter process, trickling-filter solids-contact process, biofilter activated-sludge process, series trickling-filter activated-sludge process</p> <p>Suspended-growthdenitrification Fixed-film denitrification</p> <p>Anaerobic digestion Standard rate, single-state High-rate, single-rate Two-stage Anaerobic contact process Anaerobic filter process</p>	<p>Carbonaceous BOD removal Carbonaceous BOD removal, nitrification Carbonaceous BOD removal, nitrification</p> <p>Denitrification Denitrification</p> <p>Stabilization, carbonaceous BOD removal Stabilization, carbonaceous BOD removal Stabilization, carbonaceous BOD removal Carbonaceous BOD removal Carbonaceous BOD removal, waste stabilization, denitrification</p>
<p><i>Attached-growth</i></p>		

<p>Combined aerobic, anoxic, and anaerobic Processes: <i>Suspended-growth</i> <i>Combined suspended and attached-growth</i> Pond Processes</p>	<p>Expanded bed</p> <p>Single- or multi-stage processes, various proprietary processes</p> <p>Single- or multi-stage processes</p> <p>Aerobic ponds</p> <p>Maturation (tertiary) ponds</p> <p>Facultative ponds</p> <p>Anaerobic-ponds</p>	<p>Carbonaceous BOD removal, waste stabilization</p> <p>Carbonaceous BOD removal, nitrification, denitrification, phosphorus removal</p> <p>Carbonaceous BOD removal, nitrification, denitrification, phosphorus removal</p> <p>Carbonaceous BOD removal</p> <p>Carbonaceous BOD removal, nitrification</p> <p>Carbonaceous BOD removal</p> <p>Carbonaceous BOD removal, wastestabilization</p>
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The principal applications of these processes are for:

- The removal of carbonaceous organic matter in wastewater (usually measured as Biochemical Oxygen Demand (BOD), total organic compound (TOC), or Chemical Oxygen Demand (COD)).
- Nitrification
- Denitrification
- Phosphorus removal
- Waste stabilization

(Metcalf and Eddy, 1991)

3.2 Activated Sludge Process

Activated sludge is a suspended growth process that was started in England in 1914 and was so named because it involved the production of an activated mass of microorganisms, activated sludge (Bailey and Ollis, 1977), capable of aerobically stabilizing the organic content of a waste. Activated sludge is probably the most versatile of the biological treatment processes capable of producing an effluent with any desired BOD. The process has thus found wide application among domestic wastewater and industrial wastewater treatment.

Suspended particles, colloidal and completely dissolved organic or inorganic substances are eliminated from the wastewater by mainly microbial metabolic processes, or they are turned into harmless compositions.

Activated sludge is a biological contact process where bacteria, fungi, protozoa and small organisms such as rotifers and nematode worms are commonly found. The bacteria are the most important group of microorganisms for they are the ones responsible for the structural and functional activity of the activated sludge floc. All types of bacteria make up activated sludge. The predominate type of bacteria present will be determined by the nature of the organic substances in the wastewater, the mode of operation of the plant, and the environmental conditions present for the organisms in the process (Pekin, 1983; www.me.cc.va.us).

Fungi are relatively rare in activated sludge. When present, most of the fungi tend to be of the filamentous forms, which prevent good floc formation and therefore decrease the efficiency of the plant. A high carbohydrate waste, unusual organic compounds, low pH, low dissolved oxygen concentrations, and nutrient deficiencies stimulate fungi growths.

The other forms of microorganisms present in activated sludge play a minor role in the actual stabilization of the organic in wastewater.

3.3. Types of Activated Sludge Process

Below some different types of activated sludge process are explained (http://www.cee.vt.edu/program_areas/environmental/teach/gwprimer/group12/types.htm).

Plug Flow

Wastewater is routed through a series of channels constructed in the aeration basin.

As the wastewater goes through the system, BOD and organics concentration are greatly reduced.

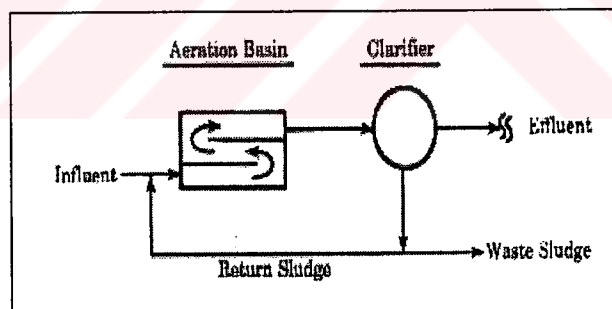


Figure 3.1 Flow diagram of plug flow for the activated sludge process

Complete Mix

Wastewater is immediately mixed throughout the entire contents of the aeration basin (mixed with oxygen and bacteria).

Since the wastewater is completely mixed with bacteria and oxygen, the volatile suspended solids concentration and oxygen demand are the same throughout the tank.

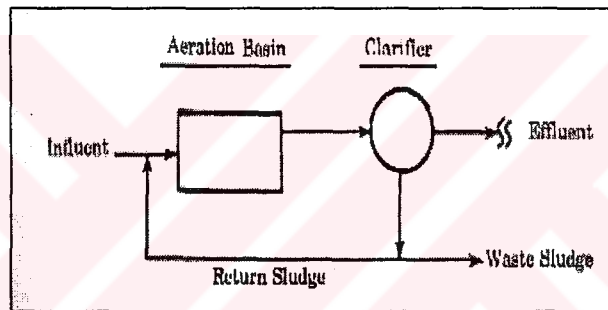


Figure 3.2 Flow diagram of complete mix for the activated sludge process

Contact Stabilization

Microorganisms consume organics in the contact tank. Raw wastewater flows into the contact tank where it is aerated and mixed with bacteria. Soluble materials pass through bacterial cell walls, while insoluble materials stick to the outside. Solids settle out later and are wasted from the system or returned to a stabilization tank. Microbes

digest organics in the stabilization tank, and are then recycled back to the contact tank, because they need more food.

Detention time is minimized, so the size of the contact tank can be smaller.

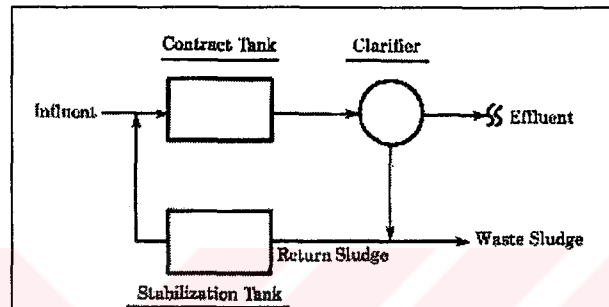


Figure 3.3 Flow diagram of contact stabilization for the activated sludge process

Extended Aeration

This type is used to treat industrial wastewater containing soluble organics that need longer detention times. This is the same as complete mix, with just a longer aeration.

Its advantage is the long detention time in the aeration tank; providing equalization to absorb sudden/temporary shock loads. Less sludge is generally produced because some of the bacteria are digested in the aeration tank.

Other Modifications

Oxidation ditch, step feed, tapered aeration and kraus processes are other types of activated sludge process, which are less common.

3.4 Process Description

In water there are many different microorganisms (bacteria, protozoa), which decompose dissolved and colloidal particles of a mostly organic nature. In wastewater treatment, the decomposing process is very intensive meaning that the organisms have to be stimulated to be more active. This is achieved by giving them a continuous supply of air.

Organic waste is introduced into a reactor where an aerobic bacterial culture is maintained in suspension. In the reactor, bacterial culture carries out the conversion in general accordance with the stoichiometry shown in Eqs.3. 1 and 3. 2.

Oxidation and synthesis:



Endogenous respiration:



(Metcalf and Eddy, 1991)

3.5 Process Design Consideration

The activated sludge process is usually employed following primary sedimentation. The wastewater contains some suspended and colloidal solids and when agitated in the presence of air, the suspended solids form nuclei on which biological life develop and gradually build up to larger solids, which are known as activated sludge.

Activated sludge is a brownish floc-like substance consisting of organic matter obtained from the wastewater and inhabited by myriads of bacteria and other forms of biological life. Activated sludge with its living organisms has the property of absorbing or adsorbing colloidal and dissolved organic matter. The biological organisms utilize the absorbed material as food and convert it to inert insoluble solids and new bacterial cells. Much of this conversion is a step-by-step process. Some bacteria attack the original complex substances to produce simpler compounds as their waste products. Other bacteria use the waste products to produce simpler compounds and the process continues until the final waste products can no longer be used as food for bacteria. The generation of activated sludge or floc in wastewater is a slow process and the amount so formed from any volume of wastewater during its period of treatment is small and inadequate for the rapid and effective treatment of the wastewater, which requires large concentrations of activated sludge. Such concentrations are built up by collecting the sludge produced from each volume of wastewater treated and re-using it in the treatment of subsequent wastewater flows. The sludge so re-used is known as returned

sludge. This is a cumulative process so that eventually more sludge has been produced and is available to maintain a viable biological population of organisms to treat the incoming wastes. The surplus, or excess activated sludge, is then permanently removed from the treatment process and conditioned for ultimate disposal.

The activated sludge must be kept in suspension during its period of contact with the wastewater being treated by some method of agitation. The activated sludge process, therefore, consists of the following steps:

- Mixing the activated sludge with the wastewater to be treated (mixed liquor).
- Aeration and agitation of this mixed liquor for the required length of time.
- Separation of the activated sludge from the mixed liquor, in the final clarification process.
- Return the proper amount of activated sludge for mixture with the wastewater.
- Disposal of the excess activated sludge.

3.5.1. Mixing the activated sludge with the wastewater to be treated

The first step in the activated sludge process is to bring the microorganisms in contact with the organics of the wastewater. This is generally accomplished by the rapid mixing of the return sludge with the wastewater at the inlet of the aeration tank.

3.5.2 Aeration and agitation of mixed liquor

Aeration serves at least three important functions: (1) mixing the returned sludge with effluent from primary treatment, (2) keeping the activated sludge in suspension, and (3) supplying the oxygen to the biochemical reactions necessary for the stabilization of the wastewater. The theoretical oxygen requirement can be computed by knowing the BOD of the waste, the amount of organisms wasted from the system per day and the degree of treatment (whether a nitrified effluent is required). For practical purposes, enough air should be added to the waste to maintain at least 2 mg/L of dissolved oxygen under all conditions of loading in all parts of the aeration tank. The air requirements for good treatment can be satisfied either by a diffused air system or by mechanical aerators.

3.5.3 Separation of activated sludge from the mixed liquor

The function of the secondary clarifier is to separate the activated sludge solids from the mixed liquor. These solids represent the colloidal and dissolved solids that were originally present in the wastewater. In the aeration unit they were incorporated into the activated sludge floc, which are settleable solids. The separation of these solids, a critical step in the activated sludge process, is accomplished in the secondary or final settling tanks.

The cycle of sludge removal from the secondary tanks is much more important than with primary tanks. Some sludge is being removed continuously to be used as returned sludge in the aeration tanks. The excess sludge must be removed before it loses its activity because of the death of the aerobic organisms resulting from lack of oxygen at the bottom of the tank. Anaerobic sludges in the final clarifier can cause "rising sludge". This should not be confused with a bulking sludge. Rising sludges are a result of denitrification and septicity. It is possible, where facilities are available, to reactivate return sludge in separate reaeration tanks before addition to the wastewater. However, it is much wiser to retain the activity of the sludge by prompt withdrawal from the tank.

3.5.4. Return sludge requirements

The purpose of return sludge is to maintain a concentration of activated sludge in the aeration tank sufficient for the desired degree of treatment. The return sludge volume may range from 10 to 50 percent of the volume of wastewater being treated and sometimes more. For a conventional plant, the percentage is usually between 20 and 30 percent. The best concentration must be determined for each plant by trial operation and should be carefully maintained by controlling the proportion of return sludge.

3.5.5 Sludge wasting from activated sludge

Excess activated sludge should be wasted as required to maintain the desired solids concentration in the aeration tank. This can be done by either withdrawing mixed liquor directly from the aeration tank or to waste from the sludge return line. The wasted mixed liquor can then be discharged to a thickening tank or to the primary tanks where the sludge settles and mixes with the raw primary sludge. The waste sludge, usually from the sludge return line, is further thickened by final sedimentation, centrifuging, or flotation thickening and then treated by biological or chemical means.

3.6 Process Microbiology

Activated sludge can be defined as "a mixture of microorganisms which contact and digest bio-degradable materials (food) from wastewater. The bacteria are the most important microorganisms because they are responsible for the decomposition of the organic material in the influent. Bacteria make up about 95% of the activated sludge biomass. These single celled organisms grow in the wastewater by consuming (eating) bio-degradable materials such as proteins, carbohydrates, fats and many other compounds.

(<http://www.dnr.state.wi.us/org/water/wm/ww/tech/biol.htm>)

Bacteria

When there is plenty of food available, bacteria use the food mostly for growth and some for energy.

A growing bacterium have flagella (hair-like structures on the outside of the cell) which makes it motile, able to move in search of food.

A bacterium reproduces into two bacteria. The cell splits into two smaller cells and this process occurs over and over again.

When there is very little food available, the bacteria use the limited food to produce energy and to maintain the cell. Very little is available for growth so less reproduction occurs.

With little food available, and in an attempt to conserve energy, the bacterium loses its flagella and thus, its motility.

The waste products start to form a thick slime layer outside the cell wall, making the cells stick together.

The growth characteristics of bacteria are better understood by studying the growth curve (Metcalf and Eddy. ,1991).

Lag-phase During this phase bacteria become acclimated to their new surroundings. They are digesting food, developing enzymes and other things required for growth.

Accelerated Growth-phase The bacteria are growing as fast as they can, since there is an excess of food. The cells are mostly dispersed, not sticking together.

Declining Growth-phase Reproduction slows down because there is not an excess of food. A lot of food has been eaten and there are now a large number of bacteria to compete for remaining food, so the bacteria do not have enough remaining food to keep the growth rate at a maximum.

Stationary-phase The number of bacteria is the highest possible, but not much food is left, so the bacteria cannot increase in number. There is some reproduction, but some cells are also dying, so the number of bacteria remains relatively constant. The bacteria have now lost their flagella and have a sticky substance covering the outside of the cell, allowing them to agglomerate into floc. In fact, the floc gets big enough

that if aeration and mixing were stopped, the floc could settle to the bottom.

Death-phase The death rate increases with very little if any growth occurring. Therefore, the total number of living bacteria keeps reducing. The bacteria are just trying to keep alive.

Protozoa and Rotifers

The presence of particular types of protozoans is related to effluent quality and plant performance. Protozoan play secondary but important role in purification of aerobic wastewater.

The protozoans in the activated sludge treatment process fall into three major classes: amoebae, flagellates, and ciliates (free-swimming, crawling, and stalked).

3.7 Process Design and Control Relationships

In Table 3.2 the detailed information about the design parameters for activated sludge process is given (Metcalf and Eddy, 1991).

F/M (Food to Microorganism ratio)

F/M ratio is named as loading criteria. This ratio can be defined as

$$\frac{F}{M} = \frac{S_0}{\theta X} = d^{-1}$$

Where

S_0 : Influent BOD or COD concentration, mg/L

θ = retention time, days

X = concentration of volatile suspended solids, mg/L

The amount of biodegradable matter the bacteria use for food by is determined by measuring the amount of or COD in the influent to the aeration basin. The weight of microorganisms in the mixed liquor is estimated by measuring the amount of volatile suspended solids (VSS) in the activated sludge. The F/M ratio gives information about growth and cell condition. If the F/M ratio is high, the microorganisms normally grow quite rapidly (a lot of "food" available in comparison to the amount of microorganism); if the F/M ratio is low, the microorganisms normally grow very slowly (because little food is available for growth) (Soyupak, 1987; Topacik, 1987; <http://www.dnr.state.wi.us/org/water/wm/ww/tech/biol.htm>).

Hydraulic Retention Time

The hydraulic retention time for the reactor is defined as volume of reactor, V_r , over influent flowrate. It is the period that the wastewater will be in the aeration tank during this time.

$$\theta = \frac{V_r}{Q} \quad (\text{days}) \quad (3.1)$$

Q = Influent flowrate (volume/time)

V_r = Volume of reactor
(Soyupak, 1987).

Sludge Age

Mass of organisms in the reactor divided by mass of organisms removed from the system each day

$$\theta_c = \frac{V_r X}{Q_w X + Q_e X_e} \quad (\text{days}) \quad (3.2)$$

Q_w = Wasted water flowrate (volume/time)

Q_e = Effluent Flowrate (volume/time)

X = Concentration of microorganism, mass/unit volume

(Soyupak, 1987)

Sludge Volume Index

Volume occupied by 1 g activated sludge mixed liquor solids after settling 30 minutes in Imhoff Cone (Dinçer, 1987).

Sludge Recycle Ratio

As explained in section 3.5.4, in order to provide constant microorganisms concentration in the system, some of the sludge must be recycled back to the aeration tank from the settling tank. The ratio of this recycle is defined as ;

$$R = \frac{Q_r}{Q} * 100 \quad (3.3)$$

Q_r = Flowrate of recycle sludge, mL/day

Q = Influent flowrate, mL/day

pH

The enzymes which regulate many of the biochemical reaction in bacteria are very pH dependent. The optimum pH should be between 7.2 and 7.4 for the proper activated sludge microorganisms to dominate (Erden,1999).

Nutrients

Microorganisms require certain nutrients for growth. The basic nutrients of abundance in normal raw sewage are, nitrogen (N), phosphorus (P), with the ratio of COD:N:P ratio approximately equal to 100:5:1.

Chemical Oxygen Demand(COD)

The chemical oxygen demand (COD) is the amount of oxygen required to degrade the organic compounds of wastewater to carbon

dioxide and water. Measurements of COD in water is a way of determining the degree of pollution by discharges of organic matter. The bigger the COD value of waste water, the more oxygen the discharges demand from water bodies. In some contexts, the relationship between COD and Biological Oxygen Demand (BOD) refers to the amount of oxygen that would be consumed if all the organics in one liter of water were oxidized by bacteria and protozoa) can be used to determine whether the water contains toxic substances.

The COD tests involve using strong chemical reagents to oxidize the organics. The dichromate reflux method is preferred because of superior oxidizing ability, applicability to wide variety of samples, and ease of manipulation. This test is used often by wastewater treatment plants to help characterize the plant's influent. The test involves using strong chemical reagents to oxidize the organics. Oxidation of most organic compounds is 95 to 100 % of the theoretical value (APHA, 1985).

Table 3.2 Characteristic values of the design parameters for activated sludge processes

Process	θ_c (d)	θ (h)	F/M	Qr/Q	X (mg/L)
Conventional	5-15	4-8	0.2-0.4	0.25-0.75	1,500-3,000
Complete-mix	5-15	3-5	0.2-0.6	0.25-1	3,000-6,000
Step-aeration	5-15	3-5	0.2-0.4	0.25-0.75	2,000-3,500
Modified-aeration	0.2-0.5	1.5-3	1.5-5.0	0.05-0.15	200 – 500
Contact-stabilization	5-15	0.5-1	0.2-0.6	0.25-1	1,000-3,000
		3-6			4,000-10,000
Extended-aeration	20-30	18-36	0.05-0.15	0.75-1.5	3,000-6,000
Kraus process	5-15	4-8	0.3-0.8	0.5-1	2,000-3,000
High-rate aeration	5-10	0.5-2	0.4-1.5	1-5	4,000-10,000
Pure-oxygen	8-20	1-3	0.25-1.0	0.25-0.5	6,000-8,000

d: day

h: hour

3.8 Kinetics of Biological Growth

Biological growth can be investigated in two parts. These are (Metcalf and Eddy, 1991; Muslu, 1988);

1. Cell Growth

- Substrate Limited Growth
- Endogenous Decay

2. Substrate Utilization

1. Cell Growth

In continuous systems, the rate of bacterial cells can be defined by the following relationships

$$r_g = \mu \cdot X \quad (3.4)$$

r_g = Rate of bacterial growth, mass/(unit volume)(time)

μ = Specific growth rate, time⁻¹

X = Concentration of microorganism, mass/unit volume

- **Substrate Limited Growth**

In continuous system, there is substrate limited growth. Experimentally, it has been found that the effect of a limiting substrate can be defined using the following expression proposed by Monod

Monod Expression;

$$\mu = \frac{\mu_m S}{K_s + S} \quad (3.5)$$

If Eq 3.5 is substituted in Eq 3.4, the resulting equation for the rate of growth is;

$$r_g = \frac{\mu_m \cdot X S}{K_s + S} \quad (3.6)$$

Where; μ_m = Maximum Specific Growth Rate, time⁻¹

K_s = Half velocity constant, mass/unit volume

S = Substrate concentration

- **Endogenous Decay**

All the cells are not in log growth phase, so the rate of the growth must be corrected. There is a decrease in cell mass. This decrease is called as endogenous decay. It can be expressed as;

$$r_d = k_d X \quad (3.7)$$

k_d = Endogenous Decay Coefficient, time⁻¹

When Eq 3.7 is combined with 3.6, the expression for the net rate of bacterial growth is obtained;

$$r_g' = \frac{\mu_m X S}{(K_s + S)} - k_d X \quad (3.8)$$

2. Substrate Utilization

In the system, a portion of the substrate is converted to new cells. The quantity of the new cells produced is reproducible for given substrate. The below relationship has been developed between the rate of substrate utilization and the rate of growth.

$$r_g = Y \cdot r_{su} \quad (3.9)$$

Y = Maximum Yield Coefficient

Y is defined as the ratio of the cells formed to the mass of substrate consumed.

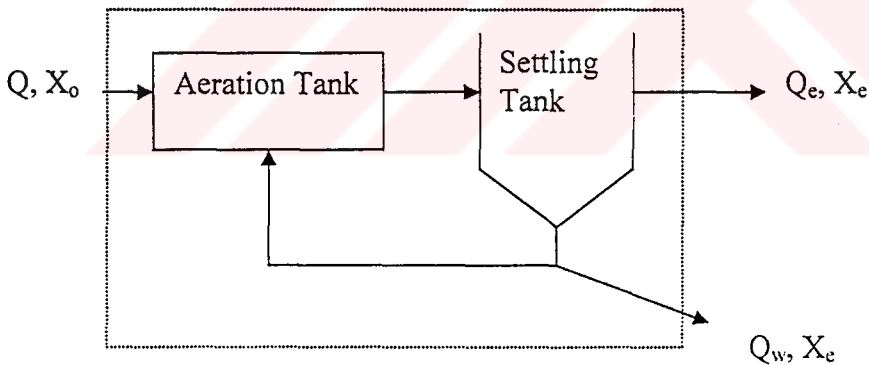
If Eq.3.6 is substituted in Eq.3.9, the rate of substrate utilization can be defined as;

$$r_{su} = \frac{\mu_m X S}{K_s + S} \quad k = \frac{\mu_m}{Y}$$

$$r_{su} = \frac{k X S}{K_s + S} = \frac{Q(S_0 - S)}{V} \quad (3.10)$$

k= Maximum rate of substrate utilization per unit mass of microorganisms

In order to apply growth and substrate removal kinetics to biological A mass balance around the system must be done



Accumulation = Inflow – Outflow + Net Growth

$$\frac{dX}{dt} V_r = QX_0 - (Q_w X + Q_e X_e) + V_r r_g' \quad (3.11)$$

Putting the derived expression (Eq3.8) for r_g'

$$\frac{dX}{dt} V_r = QX_o (Q_w X + Q_e X_e) + V_r \left(\frac{S_o - S}{\theta} Y - k_d X \right)$$

At steady state, $\frac{dx}{dt} = 0$, Assume $X_o \approx 0$

$$\frac{Q_w X + Q_e X_e}{X V_r} = \frac{Y(S_o - S)}{\theta X} - k_d \quad (3.12)$$

Remembering the sludge age expression;

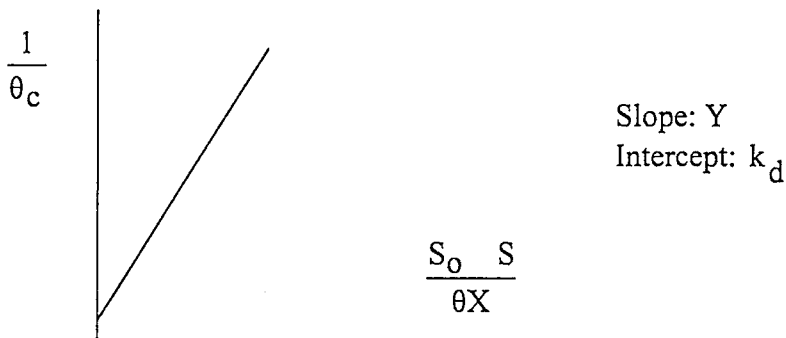
$$\theta_c = \frac{V_r X}{Q_w X + Q_e X_e} \quad (3.2)$$

As seen the left side of Eq 3.12 represents the inverse of sludge age.

$$\frac{1}{\theta_c} = \frac{Y(S_o - S)}{\theta X} - k_d \quad (3.13)$$

By, plotting $\frac{1}{\theta_c}$ vs $\frac{S_o - S}{\theta X}$, a line with slope, Y and with intercept k_d will

be obtained.

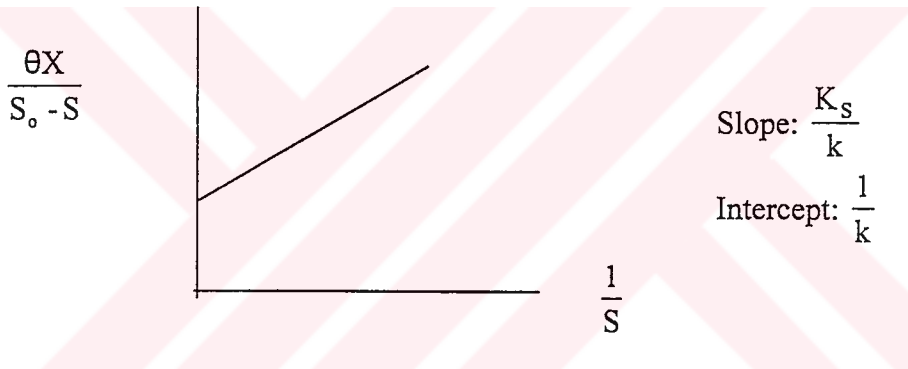


To find the kinetic coefficients, K_s and k , the expression 3.10 should be considered.

$$\frac{dS}{dt} = \frac{kXS}{K_s + S} = \frac{Q(S_0 - S)}{V} \quad (3.10)$$

$$\frac{\theta X}{(S_0 - S)} = \frac{K_s}{k} \frac{1}{S} + \frac{1}{k} \quad (3.14)$$

Plotting $\frac{\theta X}{S_0 - S}$ vs $\frac{1}{S}$ will give a line with slope K_s/k and intercept $1/k$.



4. WET AIR OXIDATION

4.1. Overview of Wet Air Oxidation

Oxidation is a process widely used for wastewater treatment, by which the pollutants are removed or converted into more biodegradable substances (Gomes et al., 2000).

Wet Air Oxidation (WAO) is a liquid phase reaction between organic material in water and oxygen. Wet air oxidation (WAO) is an attractive treatment for waste streams, which are too dilute to incinerate, and too concentrated for biological treatment. It can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures. It is also called flameless combustion (Holzer et al., 1992). Typical conditions for wet air oxidation range from 125 to 300 °C and at pressures from 0.5 to 20MPa. Residence times may change from 15 to 120 min, and the chemical oxygen demand (COD) removal may typically be about 75-90 % (Luck, 1999).

WAO is especially effective for wastes with a high organic matter, which cannot be removed by conventional treatment methods (Genç et al., 2002)

Insoluble organic matter is converted to simpler soluble organic compounds which are in turn oxidized and eventually converted to

carbon dioxide and water, without emissions of NO_x, SO₂, HCl, dioxins, furans, fly ash, etc (Luck, 1999).

Wet oxidation treatment can be used to treat high strength waste streams in order to make them more suitable to conventional treatments such as biological polishing, or as pretreatment for product recovery. Wet oxidation destroys the large molecules in waste (e.g., phenol), converting them predominantly to carbon dioxide with some formation of low weight carboxylic acids such as acetic acid, which is highly biodegradable. The effect of this treatment is to condition a waste that is:

- toxic
- reactive
- refractory to biotreatment
- or hazardous

into a waste readily suitable to biological treatment. Wet oxidation also achieves a big reduction of the waste Chemical Oxygen Demand (COD), and reduces loading to any downstream treatment process. In addition to waste destruction, wet oxidation can be used for chemical recovery by oxidation of organic contaminants

(<http://zimpro.usfilter.com/wetox/histrngthind2.htm>).

The basic idea of the process is to enhance contact between molecular oxygen and the organic matter to be oxidized. High temperature conditions convert the organic matter to carbon dioxide and water. The liquid phase is maintained by a high pressure which also

increases the concentration of dissolved oxygen and thus the oxidation rate (Debellefontaine and Foussard, 2000).

Properties of wet oxidation liquid effluent include:

- elimination of effluent toxicity
- significant Chemical Oxygen Demand (COD) reduction
- readily biodegradable residual organics

Properties of wet oxidation off-gas include:

- negligible NO_x and SO_2
- negligible particulates
- some VOCs, depending on the waste

4.2 Mechanism Of Wet Air Oxidation

At about 250°C , nearly all the compounds can be completely transformed except for acetic and propionic acids. Furthermore, under such conditions, the final product is not only carbon dioxide, but also various carboxylic acids, mainly acetic. The oxidation proceeds according to a chain reaction mechanism, presented in Figure 4.1, which highlights the particular role of acetic acid (Debellefontaine and Foussard, 2000).

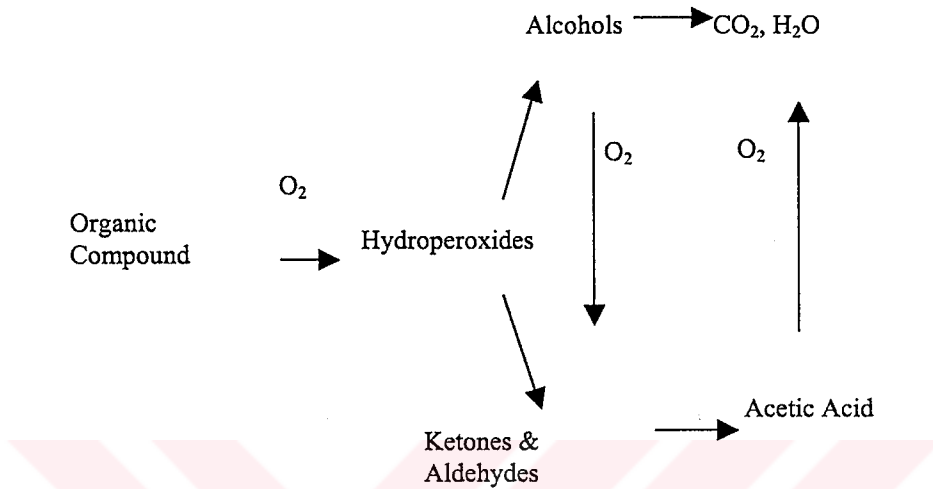


Figure 4.1. Simplified diagram for wet air oxidation

4.3 Wet Air Oxidation Technology

WAO process can be catalytic or noncatalytic. The severity of conditions required for the WAO can be reduced by use of catalysts without compromising the treatment efficiency, thus reducing corrosion problems.

4.3.1 Non-catalytic WAO technology

Zimpro process is the first commercial WAO process for the oxidation of sewage sludge, most of them for low pressure conditioning by partially oxidizing the organic fraction (Luck, 1999). Sludge

destruction is carried out with air oxidant, at 250-270 °C and under pressures of 8.5-12 MPa, in reactors presenting a ratio height diameter ranging between 5-20, while thermal conditioning is performed at 210-240°C .

The other type is Vertech process. The Vertech aqueous phase oxidation process (APO) treats sludge using pure oxygen in sealed below-ground oxidation vessel consisting of two concentric tube and heat exchange system (Luck, 1999).

4.3.2 Catalytic WAO technology (CWAO)

The challenging operating conditions of WAO provided a strong driving force to investigate catalysts which would allow substantial gains on temperature, pressure and residence time. Another major benefit of using catalysts in WAO is the oxidation of the refractory compounds, namely acetic acid and ammonia, at much lower temperatures than in the absence of catalyst (Luck, 1999).

It is believed that CWAO converts the organic and some inorganic matter to CO₂ with air by means of a suitable catalyst. In practice, it is better used when combined with other processes and especially suited for treating effluents, which are too dilute for biodegradation or too diluted for economic efficient incineration (Gomes et al., 2000).

The CWAO process is capable of converting all organic contaminants ultimately to carbon dioxide and water, and can also remove oxidizable inorganic components such as cyanides and ammonia. The process uses air as the oxidant, which is mixed with the effluent and passed over a catalyst at elevated temperatures and pressures. If complete COD removal is not required, the air rate, temperature and pressure can be reduced, therefore reducing the operating cost.

CWAO is particularly cost-effective for effluents that are highly concentrated (chemical oxygen demands of 10,000 to over 100,000 mg/l) or which contain components that are not readily biodegradable or are toxic to biological treatment systems. CWAO process plants also offer the advantage that they can be highly automated for unattended operation, have relatively small plant footprints, and are able to deal with variable effluent flow rates and compositions (<http://www.lenntech.com/cwao.htm>).

4.3.2.1 Heterogeneous cwao technology

Several crucial issues have to be solved related to chemical and physical stability of heterogeneous oxidation catalysts during WAO: leaching and sintering of the active phase and loss of surface area of the support. Leaching can be controlled to a large extent by a proper choice of the catalytic metal or metal oxide according to the available solubility data, and by pH control during CWAO. The same parameters are also of importance to control the hydrothermal stability of catalyst carrier. Oxides of Al, Hf, Zr and Ti have been shown to stable in Supercritical Water

oxygen (SCWO) conditions and should be selected as catalyst support. A catalyst composition based on Mn-Zn-Cr oxides to perform CWAO at temperatures in the range of 120-200⁰C, for the destructive catalytic oxidation of industrial wastes of an organic nature, to permit their economical disposal, to abate stream pollution, to inhibit stream contamination and to otherwise eliminate industrial and health problems associated therewith. Heterogeneous catalyst must show satisfactorily stability and durability in the severe operating conditions and acidic environments found in wet air oxidation systems (Luck, 1999).

In Table 4.1 summary of some reported heterogeneous CWAO researches are given.

The Osaka Gas Process:

The Osaka Gas Catalytic Wet Oxidation process is based on a mixture of precious and base metals on titania or titania-zirconia carriers (honey-comb or sphere) .

The Kurita Process:

Ammonia can also be selectively oxidized into N₂ and N₂O by the NO₂⁻ ion at lower temperatures than in presence of oxygen.

The NS-LC Process:

The NS-LC process involves a Pt-Pd / TiO₂-ZrO₂ honey-comb catalyst. Typical operating conditions of the NS-LC process at temperature 220 ⁰C, pressure 4MPa and space velocity 2 l/h. In these conditions the oxidation of compounds such as phenol, formaldehyde, acetic acid, glucose, etc. reaches 99% (Luck, 1999).

Table 4.1 Summary of reported heterogeneous CWAO research (Luck, 1999)

Catalyst		
Active Phase	Carrier	Application
Cu	Alumina	Phenol
	Alumina	Phenol
	Alumina	p - cresol
Cu	Alumina, Silica	Chlorophenols
Cu - Zn	Alumina, Silica	Phenol Compounds
Cu - Mg - La	Zn Aluminate	Acetic Acid
Mn	Alumina	Phenol
Mn	SR 115	Cholorophenols
Mn - Ce	None	Poly(ethylene glycol)
Mn - Zn - Cr	None	Industrial wastes
Cu - Co - Ti - Al	Cement	Phenol
Co	None	Alcohol, amines, etc.
Co - Bi	None	Acetic Acid
Co - Ce	None	Ammonia
Fe	Silica	Chlorophenols
Ru	Ceriumoxide	Alcohols, phenol, etc.
Ru	Ceriumoxide	Acetic Acid
Ru	Titania - Zirconia	Industrial Wastes
Ru - Rh	Alumina	Wet oxidized sludge
Pt	Titania	Phenol
Pt - Pd	Titania - Zirconia	Industrial wastes
Pt - Pd - Ce	Alumina	Black liquor

4.3.2.2 Homogeneous CWAO technology

An alternative to insoluble precious metals catalysts is the use of homogeneous transition metal catalysts. The catalyst not only greatly enhances the rate but also markedly the product distribution observed. Transition metal salts are frequently used to catalyze liquid phase oxidation reactions. The behaviour of these oxidations is similar to that of uncatalyzed homogeneous free radical mechanism. When a homogeneous catalyst is used, an additional processing step is required to recover the toxic catalyst from the effluent (Luck, 1999).

The Ciba-Geigy Process:

The Ciba process involves a copper salt, which is separated as copper sulfide and recycled into the reactor, which is lined with titanium to withstand corrosion (Luck, 1999).

The LOPROX Process:

The LOPROX process (low pressure wet oxidation) was developed by Bayer AG for the separate treatment of organic substances, which degrade too slowly in normal biological plants or adversely affect the degradation of other substances. Oxidation takes place with oxygen in the acidic range in multistage bubble column oxidation reactor, under relatively mild operating conditions (temperature below 200°C and pressures in the range of 0.5 – 2MPa) and is catalyzed by a combination of Fe²⁺ ions and quinone-generating substances. About 85-90% of the organic matter will be eliminated in the overall process, with 60-65%

oxidized to CO₂ directly in the oxidation reactor at approximately 190°C and 25% dissolved in the treated liquid phase as well biodegradable COD to be recycled in the wastewater treatment plant.

The Wet Peroxide Oxidation (WPO) Process:

The WPO process derived from the classical Fenton's reagent by IDE (France) and INSA-Toulouse allows high oxidation efficiencies (up to 98%) in mild conditions (90-130°C, 0.1-0.5MPa), using as oxidant hydrogen peroxide catalyzed by Fe²⁺ in solution at pH =3 (Luck,1999).

4.3.3.Recent developments

The ORCAN Process:

A modified WPO process has been recently developed in Switzerland. The oxidation reactor for carbon and nitrogen compounds (ORCAN) process pretreats refractory wastes at 120°C and 0.3MPa, with air as stoichiometric oxidants. The oxidation is catalyzed by Fe²⁺ ions as well as minor amounts of hydrogen peroxide (H₂O₂/COD = 0.2). The decomposition of H₂O₂ is likely to initiate the free radical chain mechanism at the relatively low pressure (Luck, 1999).

The ATHOS Process:

The sludge is by far the most important by-product of wastewater treatment, whose final destination must be managed from the stand point of a global and sustainable protection of the environment.

The ATHOS wet oxidation has three main steps: preparation of the sludge, oxidation and dewatering of the residual solid. In the units

sodium hydroxide is added to the sludge to maintain the pH of the oxidized sludge between 7.5 and 8.0, and the copper oxidation catalyst is added. A high pressure pump is then used to pump the thickened sludge into a regenerating heat exchanger to bring it to a temperature of 110°C. It enters a second series of exchangers, which bring it to the set temperature. Oxidation is carried out at a temperature of 235°C and a pressure of about 4MPa, in order to keep the sludge liquid (Luck, 1999).

4.4 Industrial Applications

WAO is used to treat hazardous industrial wastewaters and sludges. It can be used for pretreating concentrated waste prior to further treatment, for the virtually complete oxidation of organics in dilute wastewater or for the destruction of organic sludges.

WAO is applicable to industrial wastewaters containing organics and oxidizable inorganics such as cyanide. The process is typically used to oxidize sewage sludge, regenerate spent activated carbon and treat process wastewaters. Wastewaters treated using this technology include pesticide wastes, petrochemical process wastes, cyanide containing metal finishing wastes, spent caustic wastewaters containing phenolic compounds and some organic chemical production wastewaters. WAO can be used to treat wastewaters that have higher organic concentrations than are normally handled by biological treatment, carbon adsorption and chemical oxidation, but may be too dilute to be effectively treated by thermal processes such as incineration. WAO is most applicable for

waste streams containing dissolved or suspended organics in the 500 to 15000 mg/L range. Below 500 mg/L, the rates of WAO of most organic constituents are too slow to efficient application of this technology. WAO can be applied to wastes that have significant concentrations of metals (approximately 2%) whereas biological treatment, carbon adsorption and chemical oxidation may have difficulty treating such wastes (Luck, 1999).



5. EXPERIMENTAL STUDY

5.1 Experimental Set-Up

Two different experimental set-ups are used in this study

5.1.1 Experimental set up of activated sludge process

The activated sludge system mainly consists of an aeration and a settling tank as shown in Figure 5.1. The photograph of the setup is shown in Figure 5.2.

Below some specifications about the set-up is given.

Aeration Tank;

- Plexiglass (6mm thickness)
- 6.8L, cylindrical (H: 250mm D: 200mm)
- 2 Valves (inlet, exit)

Settling Tank;

- Plexiglass (6mm thickness)
- 3L, conic (H: 150mm)
- 2 Valves (exit, exit)

Pump

- Peristaltic pump for feed
- Aquarium pump for air
- Diaphragm pump for sludge recycle

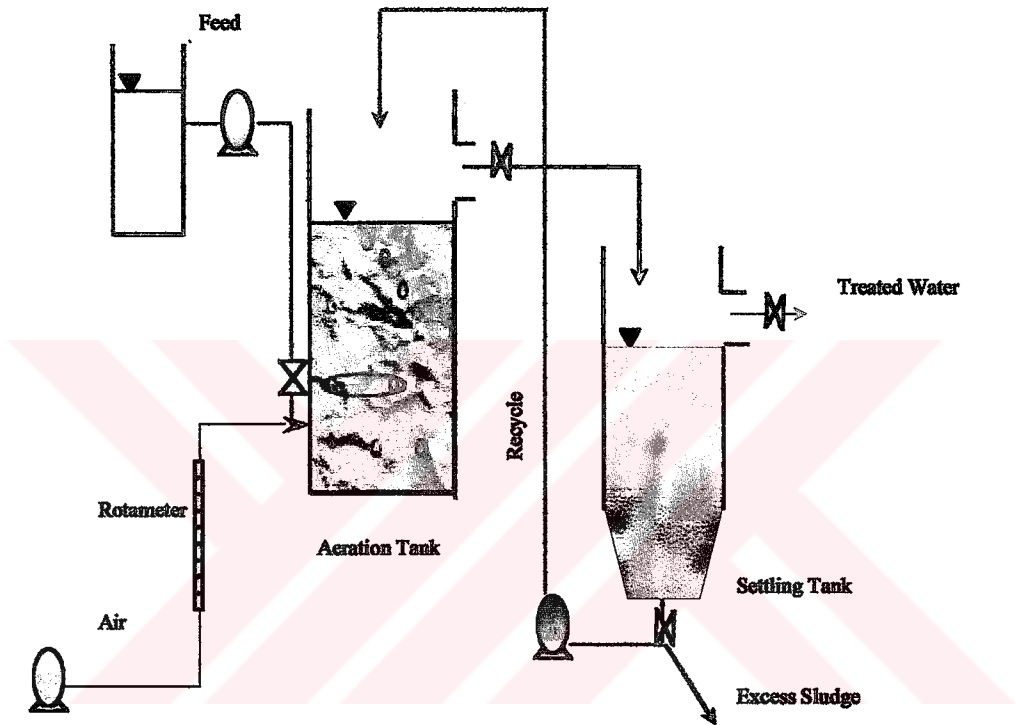


Figure 5.1 Schematic view of the experimental setup of activated sludge process

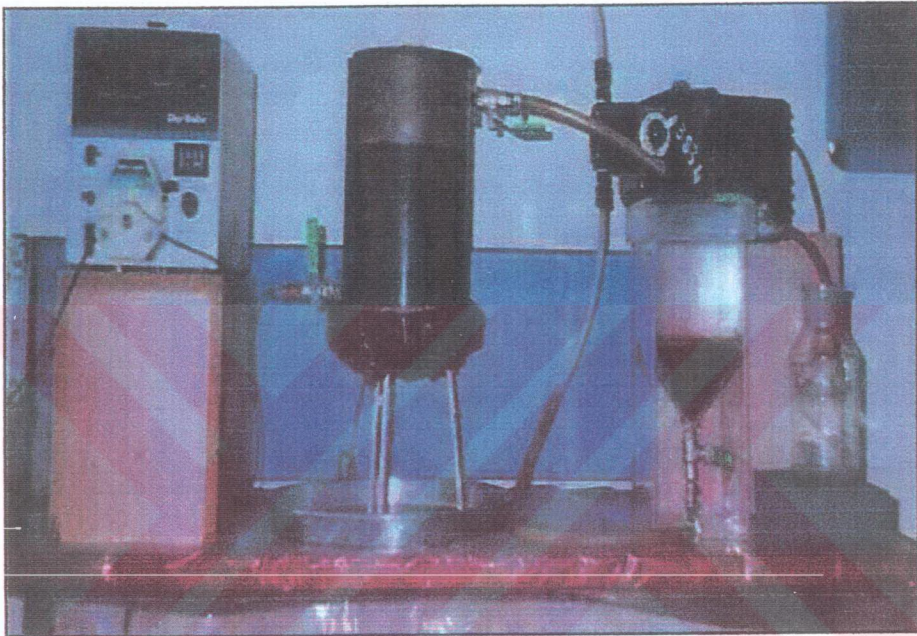


Figure 5.2 Photograph of the experimental setup of activated
sludge process

5.1.2 Experimental set up of wet air oxidation process

The experiments are carried out by using an experimental set up which mainly consists of a reactor, a condenser and suitable measuring devices for temperature, pressure and air flowrate. The schematic view and photograph of experimental set up are given in Figures 5.3 and 5.4, respectively.

- Temperature is controlled by thermocouple and PID control configuration
- Pressure is adjusted by a manual pressure indicator
- The off-gas stream flowrate is measured by a rotameter and adjusted with a needle valve placed on the exit pipe of the condenser
- Air is distributed throughout the reactor by the help of a sparger

Reactor

- semi-batch, bubble column type reactor
- stainless steel
- 500 mL

Condenser

The gas products of the reaction passes through a water cooled condenser and condensable portion of the gas returns back to the reactor again.

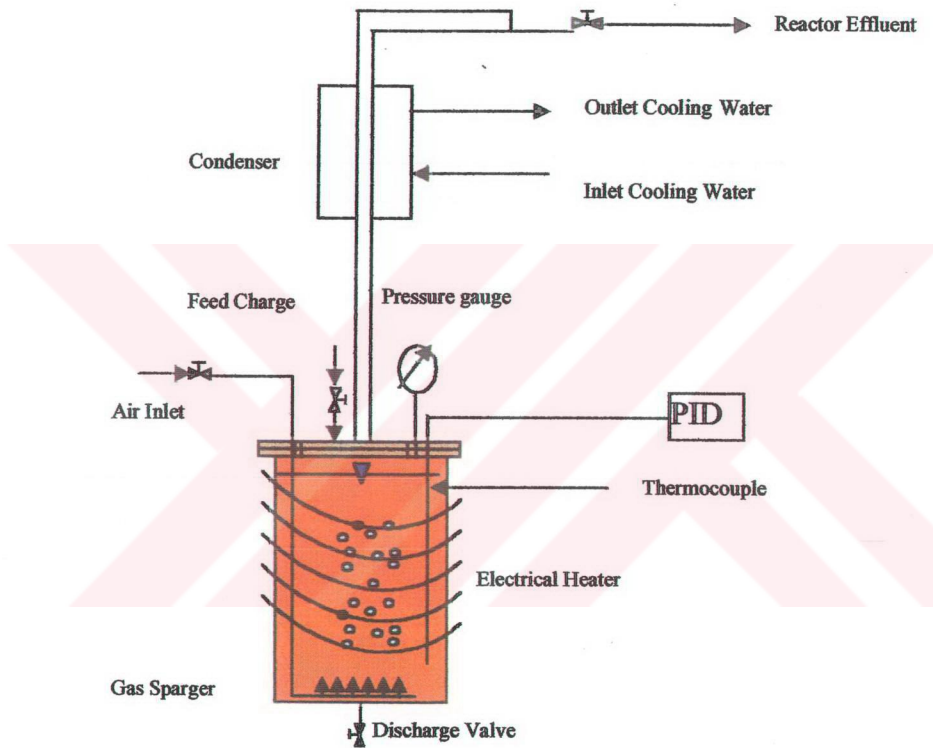


Figure 5.3 Schematic view of the experimental setup of CWAO process

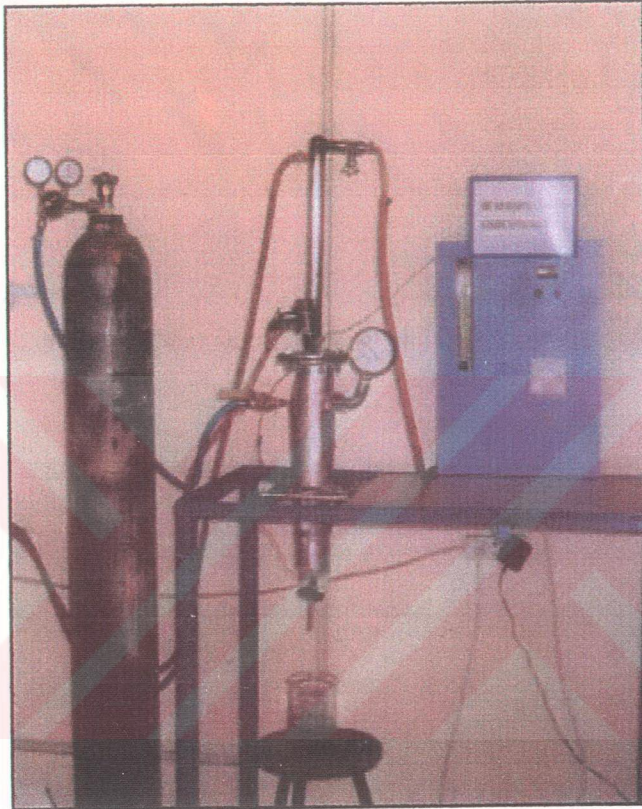


Figure 5.4 Photograph of the experimental setup of CWAO process

5.2 Experimental Procedure

5.2.1 Experimental procedure for activated sludge process

- Initially, adaptation of the wastewater to the activated sludge taken from an oil factory is provided. For the acclimation of biomass, an amount of wastewater and sludge are charged to the aeration tank in which aerated for several days. Once the experiment is ended, after a settling period, the biomass was separated and introduced again into the tank. This procedure is repeated with successive additions to the biomass of increasing volumes of wastewater. When a constant COD removal is obtained, the acclimation is considered to be achieved. (Benitez, et al., 1999; Tekin, 1991).

- The pH of filtered wastewater is adjusted to 7 by adding 3N NaOH solution.

- Sufficient amount of nutrient is added to wastewater to maintain COD:N:P mass ratio 100:5:1.

- According to the desired retention time, the flowrate of the wastewater is adjusted. After the aeration tank is full filled, the activated sludge and treated water mixture passes to the settling tank.

- Bacterial cells settle in the settling tank
- A portion of the sludge is recycled to activated sludge tank
- During the experiments, COD, sludge volume index, suspended solid analyses are done

- The treatment is lasted until the COD of the effluent is stabilized.

5.2.2 Experimental procedure for wet air oxidation process

- Before each experiment, the reactor is cleaned with distilled water.

- Desired amount of wastewater is taken and filtered with vacuum filtration.

- pH of wastewater is adjusted to 7 by addition of 3 N NaOH.

- Catalyst which is $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Ridel – de Haén) is added according to the desired loading value.

- Cooling water is supplied to the process.

- The reactor is heated to the desired temperature.

- When the reactor content reaches the desired temperature, air flow rate is initiated and the reactor is pressurized.

- During the experiment temperature, pressure and air flow rate are recorded every 5 minutes.

- The experiment lasted for 2 hours.

- At the end, the heater is turned off. Air flow is stopped. When the temperature is decreased to room temperature, the cooling water is turned off.

- At the end of each experiment COD analysis of the effluent is done.

5.3 Characteristics of the Wastewater Used

The wastewater used is supplied from alkaloid factory in Afyon in which morphine for pharmaceutical industry is produced.

The amount of wastewater produced at this factory is about 180000 m³/year.

The wastewater mainly contains organic compounds such as aniline, morphine and toluol.

Table 5.1 summarizes the features of the wastewater.

Table 5.1 Characteristics of the wastewater

COD(mg/L)	BOD5 (mg/L)	BOD5/COD	pH
25000-40000	3950-5700	0.15	4.5

5.4 Analysis

During the CWAO experiments the performance of the experiments is tested by analysing the COD of the effluent.

During the activated sludge experiments, the parameters measured continuously are; COD, sludge volume index and suspended solid.

5.4.1 COD Analysis

COD analysis is done according to the Closed Reflux Calorimetric Method in which organics are oxidized by boiling with chromic acid and sulfuric acids.

A calibration curve is obtained by different concentrations of Potassium Hydrogen Phthalate (KHP) solutions. The significant role of KHP is that, it can behave like an artificial pollutant.

The procedure of the analysis is as follows:

- At least 8 KHP standards are prepared whose COD values are between 50 to 900 mg/L to be able to obtain a calibration curve for mass spectrophotometer.
- 2.5 mL of sample, 1.5 mL of potassium dichromate standard solution and 3.5 mL of H₂SO₄ standard are put into the tubes. The same procedure is carried for blank reagent.
- The diluted samples are boiled at 148 °C for two hours.

- Absorbances are read from mass spectrophotometer, then with the help of calibration curve COD values are determined.

5.4.2 Suspended Solid Analysis

Suspended solid can lead to the development of sludge deposits and anaerobic conditions.

- After the wastewater sample has been filtered by $0,45\mu$ pore size, it is dried in oven for an hour then weighted and subtracted from previously tared filter. The filtration is done with vacuum pump and filtration set.

- The difference between filter with residue of wastewater and tare of filter gives the SS value of the wastewater.

5.4.3 Sludge Volume Index

- Imhoff Cone is used to determine settleable solids in wastewater.
- Volume occupied by 1 gr of activated sludge mixed liquor solids after settling 30 minutes in a Imhoff Cone. The important criterion here is to take as possible as homogeneous sample.

5.5. Experiments

Three different treatment strategies are applied to Afyon Alcaloide Factory wastewater. These are;

1. Only biological treatment of the factory effluent
2. Only applying catalytic wet air oxidation to the factory effluent
3. Combination of catalytic wet air oxidation and biological treatment
 - a. First biological treatment and as a succeeding step chemical treatment
 - b. First chemical treatment and as a succeeding step biological treatment

The experiments performed and the parameters tested are tabulated in Table 5.2.

Table 5.2 Experiments performed and the parameters that are tested

EXPERIMENTS	SAMPLE (INITIAL COD (mg/L))	OPERATING CONDITIONS	PARAMETERS THAT ARE TESTED
Activated Sludge Process (ASP)	Factory effluent (27700)	F _{air} : 3 L/min	Retention times: 4, 6, 8 days
	Factory effluent (27700)	Retention Time: 6 days	F _{air} : 3, 4.5 L/min
Catalytic Wet Air Oxidation (CWAO)	Factory effluent (27700)	Catalyst: FeCl ₂ .4H ₂ O P : 6.5 atm F _{air} : 0.94 L/min	Temperature: 140, 150, 160°C Catalyst Loading: 0.5, 1 g/L
Combination (ASP (first)+CWAO)	ASP effluent(7850)	Retention Time: 6 days F _{air} : 3 L/min Catalyst: FeCl ₂ .4H ₂ O P : 6.5 atm F _{air} : 0.94 L/min	Temperature: 140, 150, 160°C Catalyst Loading: 0.5, 1 g/L

Combination (ASP (first)+CWAO)	ASP effluent(3422)	Retention Time:6 days F _{air} : 4.5 L/min Catalyst: FeCl ₂ .4H ₂ O P : 6.5 atm F _{air} :0.94 L/min	Temperature:140, 150, 160°C Catalyst Loading: 0.5,1 g/L
	ASP effluent(10400)	Retention Time:8 days F _{air} : 3 L/min Catalyst: FeCl ₂ .4H ₂ O P : 6.5 atm F _{air} :0.94 L/min	Temperature:140, 150, 160°C Catalyst Loading: 0.5,1 g/L
Combination (CWAO(first)+ASP)	CWAO effluent(18000)	Catalyst: FeCl ₂ .4H ₂ O P : 6.5 atm F _{air} :0.94 L/min Retention Time:6 days F _{air} : 4.5 L/min	-
ASP experiments for evaluation of kinetic parameters	Factory effluent (27700)	Retention Time:6 days F _{air} : 4.5 L/min	Kinetic parameters are calculated

6. RESULTS AND DISCUSSION

6.1 Direct Biological Treatment

In the set of these experiments, effects of retention time and air flowrate are examined.

First keeping air flowrate constant (3L/min) retention time of 4, 6, 8 days are tested. In the second case, at retention time of 6 days, two different air flowrates (3 L/min, 4.5 L/min) are studied.

6.1.1 Retention time effect

Sample: Factory wastewater with initial COD of 27700 mg/L

Air Flow Rate: 3 L/min

Table 6.1 and Figure 6.1 show the results obtained at each studied retention time. The COD removals are defined in the form;

$$\text{COD Removal\%} = \frac{\text{COD}_o - \text{COD}_f}{\text{COD}_o}$$

COD_o = Initial COD value (mg/L)

COD_f = Final COD value (mg/L)

The final COD values are measured until the COD of the effluents reach steady state condition. The experiments usually reached steady state between 15-30 days. Consequently, the COD removals (%) are calculated with the final COD referring stabilized COD values.

Table 6.1. Effect of Retention time on COD Removal (%)

Retention Time (days)	COD(mg/L)	COD Removal %
4	14400	48.01
6	7850	71.66
8	10400	62.45

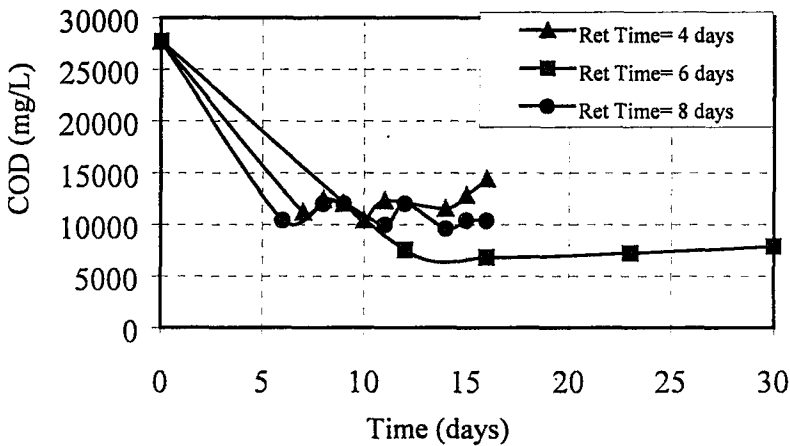


Figure 6.1 COD values vs time at 3 different retention tTimes

Figure 6.2 represents the COD removal performance as a function of retention time. As seen in this figure, retention time of 4 days attains COD removal of only 48.01%. Retention time of 8 days gives better result (62.45%) than 4 days retention time. However, in the case of 6 days retention time, the COD removal achieved (71.60%) is the most evident. Probably, in retention time of 8 days, because of high toxicity of the wastewater, the microorganisms died.

For the following studies, retention time of 6 days is concluded to be the most suitable.

The detailed results are given in Appendix section.

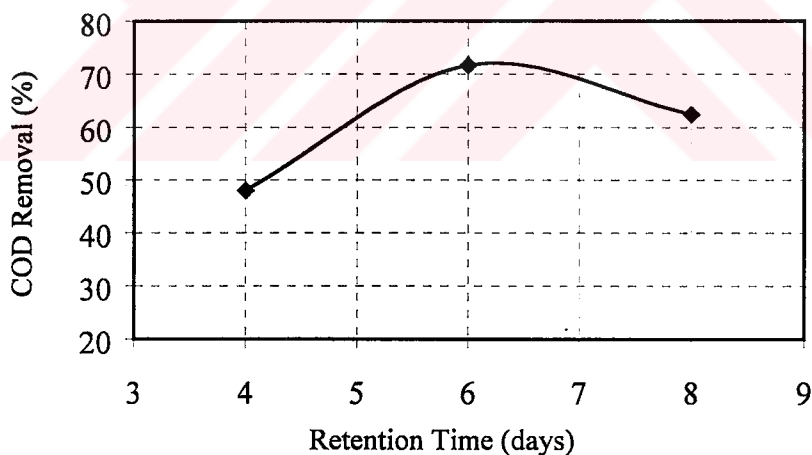


Figure 6.2 COD removal values vs retention time

6.1.2 Air flow rate effect:

Sample: Direct factory effluent with initial COD 27700 mg/L

Retention Time: 6 days

Since from the preceding studies, the appropriate retention time was decided to be 6 days, the air flowrate effect is tested at 6 days of retention time.

In Table 6.2 COD values and COD removals at different air flow rates are tabulated and in Figure 6.3, these values are plotted.

Table 6.2 Effect of air flowrate on COD removal

Air Flow Rate (L/min)	COD(mg/L)	COD Removal %
3	7850	71.66
4.5	3422	88

As seen from the Figure 6.3, COD falls with time as a consequence of the treatment and COD removals are stabilized at 71.66% and 88% at air flowrates of 3 L/min and 4.5 L/min, respectively.

Although effect of air flow rate is not directly proportional to COD removal, (increasing air flow rate 1.5 times, did not decrease COD value

at the same ratio), increasing the air flow rate, increases the COD removal. The reason of this could be evaluated more clearly by measuring dissolved oxygen concentration in the tank.

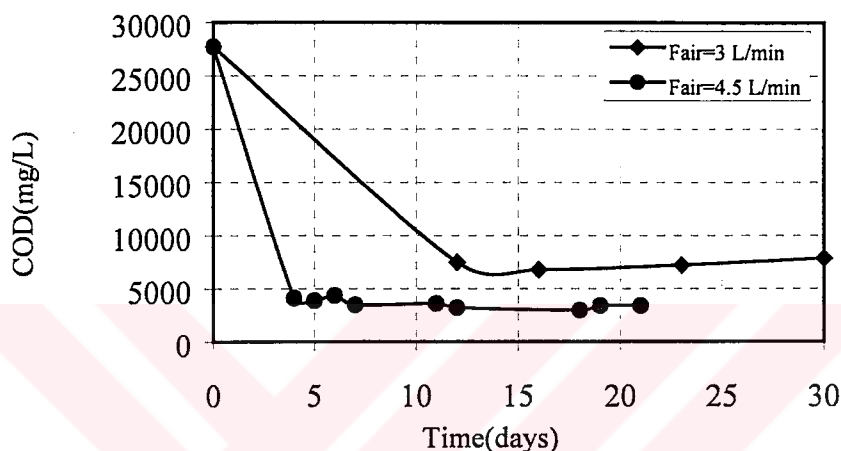


Figure 6.3 COD values vs time at two different air flowrates

6.2 Direct Catalytic Wet Air Oxidation

In this series of experiments, effect of temperature and catalyst loading on COD removal % are examined.

Sample: Factory Wastewater with initial COD 27700 mg/L

Catalyst: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

P : 6.5 atm

F_{air}: 0.94 L/min

Table 6.3 depicts the results of analyses of effluents from direct CWAO experiments.

Table 6.3 Experimental results of direct CWAO experiments

Temperature (°C)	Catalyst Loading (0.5 g/L)		Catalyst Loading (1 g/L)	
	COD(mg/L)	COD Removal%	COD(mg/L)	COD Removal%
140	23830	13.97	23640	14.66
150	21395	22.76	18234	34.17
160	20895	24.57	18155	34.46

The CWAO treatment of the wastewater was examined at 3 different temperatures and at two different catalyst loadings. The operating conditions tested, are selected by the help of the literature studies (Holzer et al., 1992). The COD removal increased with the reaction temperature as shown in Figure 6.5. But as shown in Figure 6.4, there is a sharp, significant increase in percentage COD removal as the temperature is increasing from 140 to 150°C. As temperature is increased from 150 to 160°C, the increase becomes insignificant. The same behaviour is investigated by both catalyst loading values.

Two different catalyst loading (0.5 g/L, 1 g/L) values are examined. It can be concluded from Figure 6.5 that, increasing the amount of catalyst loading, increases the percentage COD removal. For example, at 160°C when catalyst loading is 0.5 g/L, percentage COD removal is 25%. At the same temperature when the catalyst loading is 1 g/L, the percentage COD removal increases to 35%. Although

increasing the catalyst loading increased the COD removal, its effect is not directly proportional on COD removal since doubling the catalyst loading did not double COD removal.

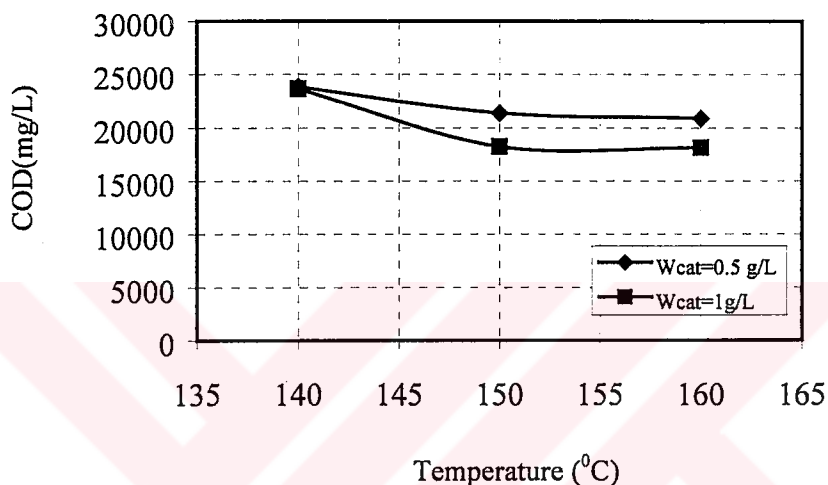


Figure 6.4 COD vs temperature at two different catalyst loading values (Direct CWAO experiment)

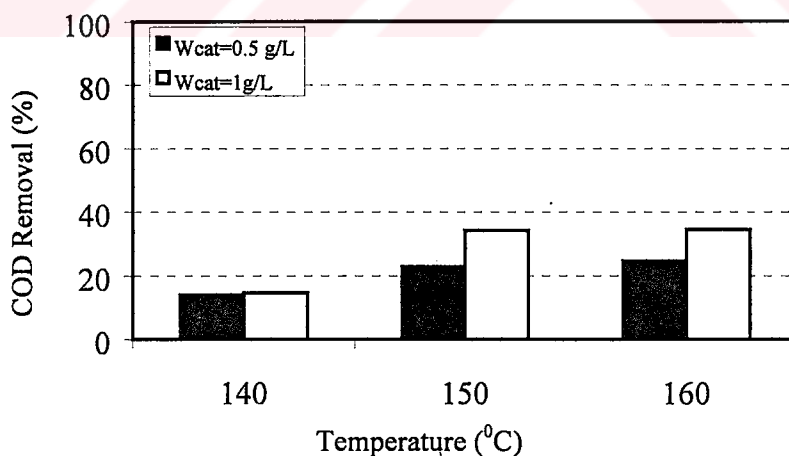


Figure 6.5 COD removals vs Temperature at two Different Catalyst Loading Values (Direct CWAO experiment)

6.3 Combination of Biological and Chemical Treatment

The treatment of Afyon Alcaloide Factory wastewater is performed by combined process constituted by different combinations of biological and chemical treatment

6.3.1 First biological treatment and as a succeeding step chemical treatment

Biologically treated wastewater at different retention times (6 and 8 days) are subjected to Wet Air Oxidation. Temperature and catalyst loading effect on % COD removal are tested.

6.3.1.1 CWAO application following activated sludge with retention time of 6 days and air flow rate of 3 L/min

(Initial COD=7850 mg/L)

Catalyst : $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

P : 6.5 atm

F_{air} :0.94 L/min

The experimental results are tabulated in Table 6.4 and plotted in Figure 6.6 and 6.7.

Table 6.4 Experimental results (CWAO of biological treatment (6 days, 3 L/min) effluent

Temperature (°C)	Catalyst Loading (0.5 g/L)		Catalyst Loading (1 g/L)	
	COD(mg/L)	COD Removal%	COD(mg/L)	COD Removal%
140	4976	36.61	4220	46.24
150	3936	49.86	3586	54.32
160	4100	47.77	3398	56.71

As seen in Table 6.4, Figures 6.6 and 6.7, as the operating temperature is increased from 140 °C to 150°C, COD value of wastewater decreased sharply at both catalyst loading values. Above 150°C a significant increase in % COD removal is not observed. Hence for practical purpose, a temperature of 150°C is considered sufficient for the present CWAO process because of higher energy consumption with a higher operating temperature 1 g/L of catalyst loading gives better result than that of 0.5 g/L. The max % COD removal is 56.7 for 1g/L of catalyst loading while it is 49.8 for 0.5 g/L of catalyst loading. Although better COD removal is obtained at catalyst loading 1 g/L, it is not as effective as in single CWAO experiments to direct factory effluent.

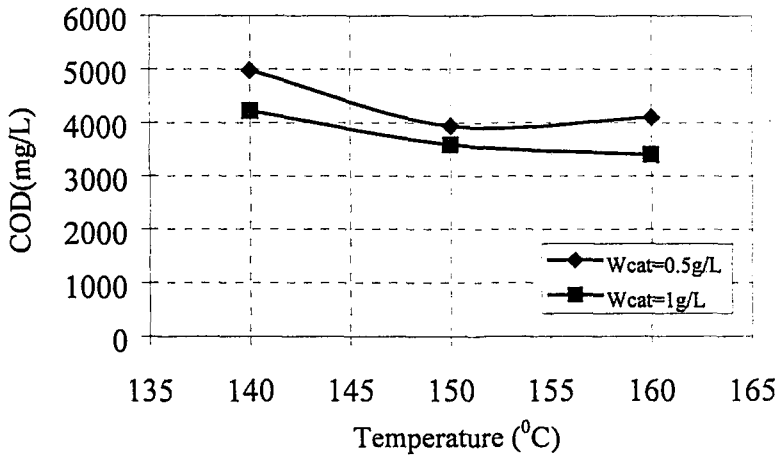


Figure 6.6 COD Values vs temperature at two different catalyst loading values (CWAO of biological treatment (6 days, 3 L/min)effluent)

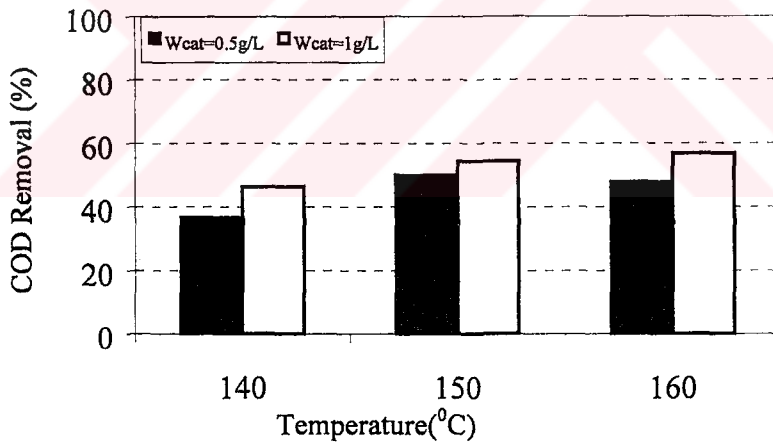


Figure 6.7 COD Removals vs Temperature at two Different Catalyst Loading Values of CWAO experiments of ASP effluent

6.3.1.2 CWAO application following activated sludge with retention time of 6 days and air flow rate of 4.5 L/min

(Initial COD=3422 mg/L)

Catalyst: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

P : 6.5 atm

F_{air} : 0.94 L/min

The results of CWAO experiments are given. In Table 6.5

Table 6.5 Experimental results, CWAO application following biological treatment (6 days, 4.5 L/min) effluent

Temperature ($^{\circ}\text{C}$)	Catalyst Loading (0.5 g/L)		Catalyst Loading (1 g/L)	
	COD(mg/L)	%COD Removal	COD(mg/L)	%COD Removal
140	3200	6.49	3400	0.64
150	3100	9.41	3000	12.33
160	3000	12.33	2612	23.67

As illustrated in Figure 6.9, at both catalyst loading values and different temperatures COD value of wastewater does not change significantly. From these results, it can be concluded that, probably COD is decreased as much as can be in biological treatment. COD value can't

be decreased below 3400 mg/L, at least with this type of chemical treatment.

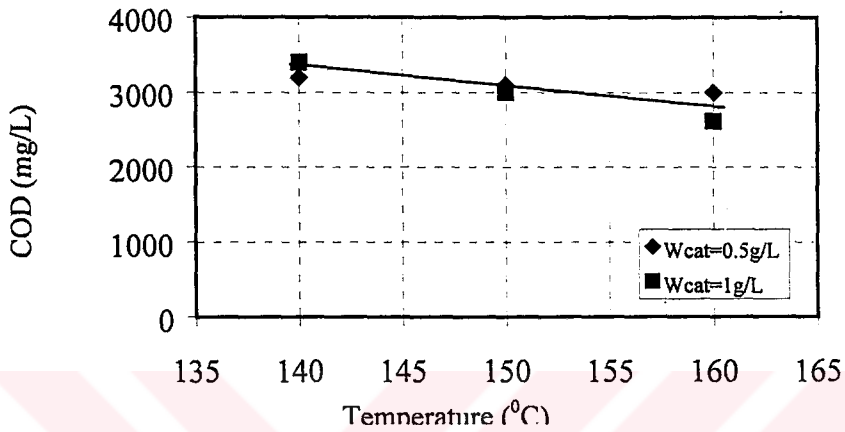


Figure 6.8 COD values vs temperature at two different catalyst loading values (CWAO of biological treatment (6 days, 4.5L/min)effluent)

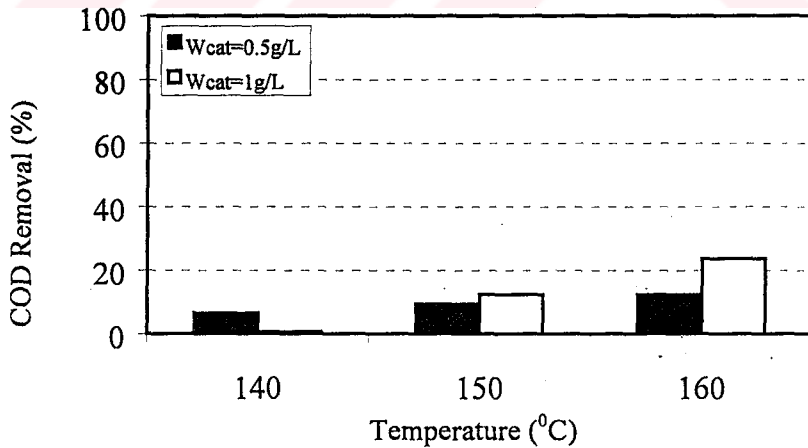


Figure 6.9 COD Removals vs temperature at two different catalyst loading values(CWAO of biological treatment (6 days, 4.5L/min)effluent)

6.3.1.3 CWAO application following activated sludge with retention time of 8 days and air flow rate of 3 L/min

($F_{air}=3L/min$, initial COD=10400 mg/L)

Catalyst: $FeCl_2 \cdot 4H_2O$

P : 6.5 atm

F_{air} : 0.94 L/min

The experimental results are presented in Table 6.6.

Table 6.6 Experimental results of CWAO experiments (CWAO of biological treatment (8 days, 3 L/min) effluent)

Temperature ($^{\circ}C$)	Catalyst Loading (0.5 g/L)		Catalyst Loading (1 g/L)	
	COD(mg/L)	COD Removal%	COD(mg/L)	COD Removal%
140	5650	45.67	5402	48.06
150	5140	50.58	4770	54.13
160	5300	49.04	4800	53.85

There is a slight change in percentage COD removal when temperature is increased from 140 $^{\circ}C$ to 150 $^{\circ}C$ as seen in Figure 6.10 and 6.11. At the temperature above 150 $^{\circ}C$, the percentage COD removal approximately remains constant. For example at catalyst loading of 1 g/L

at 140°C, percentage COD removal is 48%, but at 150°C and 160°C percentage COD removals are about 54%.

In this case, in contrast to the factory direct effluent WAO experiments, the effect of catalyst loading on COD removal is not very effective as seen Figure 6.10 and 6.11. For example, at 150°C the percentage COD removals for catalyst loading 0.5 g/L and 1 g/L are 51% and 54%, respectively.

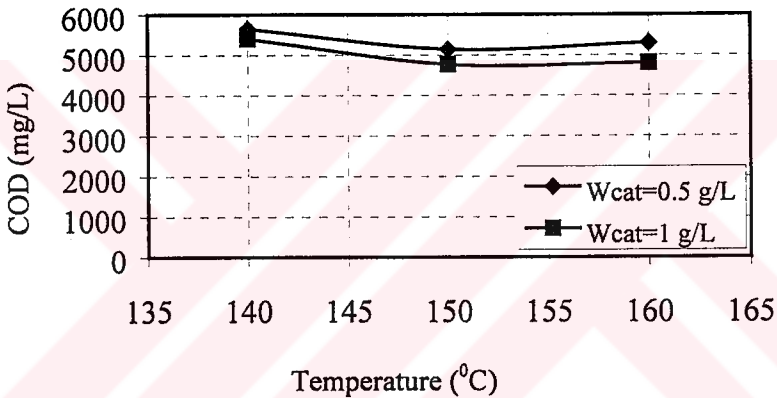


Figure 6.10 COD Values vs temperature at two different catalyst loading values(CWAO of biological treatment (8 days, 3L/min)effluent)

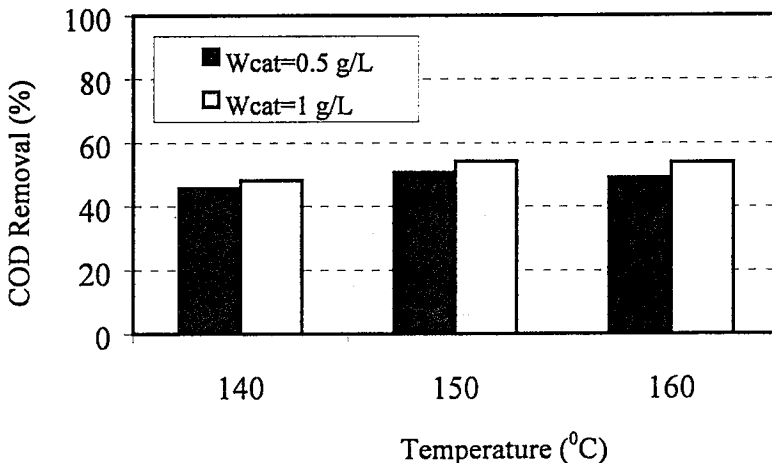


Figure 6.11 COD removals vs temperature at two different catalyst loading values(CWAO of biological

6.3.2 First Chemical Treatment and as a Succeeding Step

Biological Treatment

Sample= Wet Air Oxidation Effluent

(@ T=150⁰C, 6.5 atm, 1g/L FeCl₂.4H₂O catalyst loading)

(COD (after CWAO) \cong 18000 mg/L)

Retention Time =6 Days

F_{air}=4.5 L/min

In this set of experiments, CWAO has been applied to alkaloid industry wastewater as a pretreatment and as a succeeding step biological treatment. The operating conditions of activated sludge process and CWAO process are selected according to the previous studies.

Table 6.7 Experimental results (biological treatment of CWAO effluent)

TIME(Days)	COD(mg/L)	% COD Removal
5	4644	74.20
6	4270	76.28
7	3480	80.67
8	3268	81.84
9	3200	82.22
12	2800	84.44
16	2820	84.33
19	2900	83.89

The application of biological treatment alone leads a COD value of 3422 mg/L (see section 6.1.2). Applying CWAO as pretreatment (Figure 6.12 and 6.13) is resulted in COD value of 2900 mg/L). In this case, it seems that additional CWAO application might not be necessary.

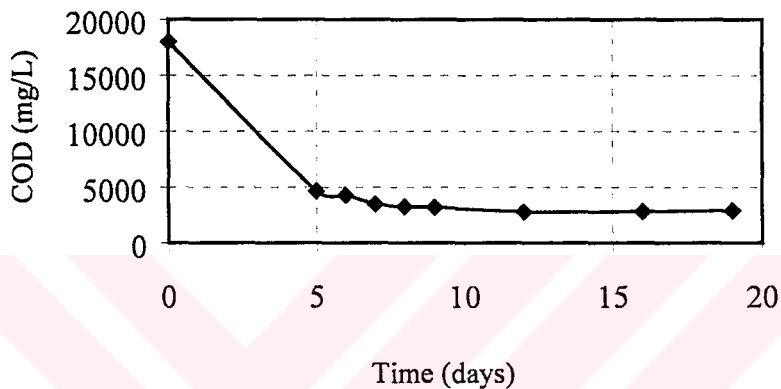


Figure 6.12 COD values vs time (biological treatment of CWAO effluent)

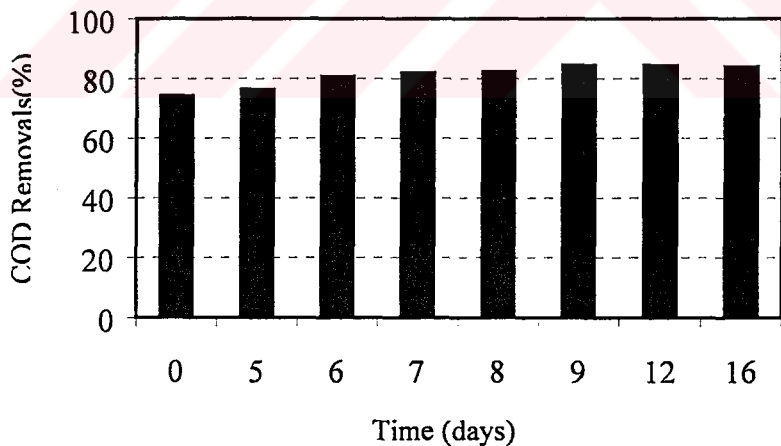


Figure 6.13 COD removals vs time (biological treatment of CWAO effluent)

6.4 Evaluation of the Kinetic Parameters for the Monod Model

The related equations and the procedure for calculating the specific kinetic parameters for this model are given in Section 3.7.

The set of experiments done for the evaluation of kinetic parameters are explained in section 5.5.

The experimental data taken for evaluation of kinetic constants are tabulated in Table 6.8.

In Figure 6.14, a schematic sketch of activated sludge unit is given.

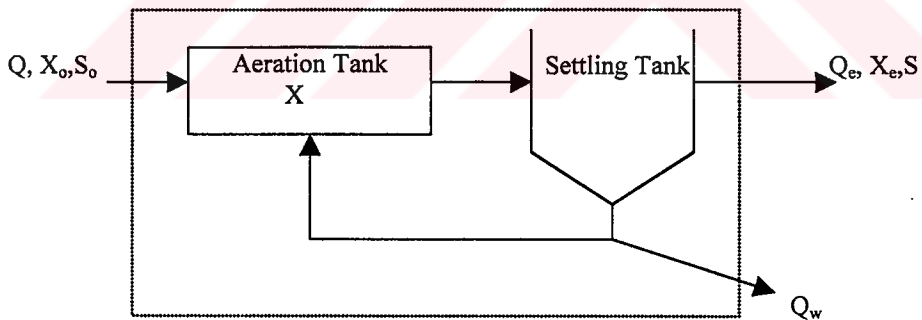


Figure 6.14. Schematic sketch of activated sludge unit

Table 6.8. Experimental results

Q(L/day)	X(mg/L)	Xe(mg/L)	So(mg/L)	Qw(L/day)	S(mg/L)
1.12	4200	800	25600	0.1872	3000
1.12	3400	670	25600	0.288	4000
1.12	3100	600	25600	0.36	4800

Below an example solution procedure is given and the other results are tabulated in Table 6.9.

To find the kinetic parameter; the expression below must be considered.

$$\frac{1}{\theta_c} = \frac{Y(S_0 - S)}{\theta X} - k_d \quad (3.13)$$

As explained before $\frac{1}{\theta_c}$ vs $\frac{S_0 - S}{\theta X}$ must be plotted.

$$\theta_c = \frac{V_r X}{Q_w X + Q_e X_e} \quad (3.2)$$

$$\theta_c = \frac{6.8 * 4200}{0.1872 * 4200 + (1.12 - 0.1872) * 800} = 18.64$$

$$\frac{1}{\theta_c} = 18.64 \text{ 1/day}$$

$$\frac{S_o - S}{\theta X} = \frac{25600 - 3000}{6 * 4200} = 0.8863 \text{ (1/days)}$$

$$\frac{\theta X}{S_o - S} = 1.1283 \text{ days}$$

$$\frac{1}{S} = \frac{1}{3000} = 0.000333 \text{ L/mg}$$

The other calculated values are given in Table 6.9

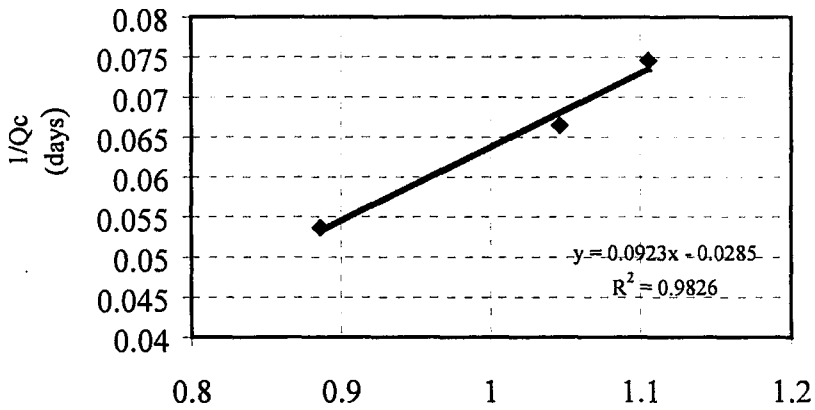
Table 6.9. Calculated values for evaluation of kinetic parameters

θ_c (day)	$\frac{S_o - S}{\theta X}$ ($\frac{1}{\text{day}}$)	$\frac{\theta X}{S_o - S}$ (day)	$\frac{1}{S}$ ($\frac{\text{L}}{\text{mg}}$)	$\frac{1}{\theta_c}$ ($\frac{1}{\text{day}}$)
18.64	0.886275	1.128319	0.000333	0.053658
15.046	1.046367	0.955688	0.00025	0.066464
13.409	1.105123	0.904876	0.000208	0.074573

Remembering the expression

$$\frac{1}{\theta_c} = \frac{Y(S_o - S)}{\theta X} - k_d \quad (3.13)$$

$\frac{1}{\theta_c}$ vs $\frac{S_o - S}{\theta X}$ must be plotted



$$\frac{S_0 - S}{tX} \text{ (1/day)}$$

Figure 6.15. Evaluation of the kinetic parameters of the Monod Model

Slope: $Y=0.0923 \text{ mg MLSS/ mg COD}$

intercept: $k_d=0.0285 \text{ 1/day}$

To find the kinetic coefficients, K_s and k

$$\frac{tX}{(S_0 - S)} = \frac{K_s}{k} \frac{1}{S} + \frac{1}{k} \quad (3.15)$$

Plotting $\frac{tX}{S_0 - S}$ vs $\frac{1}{S}$

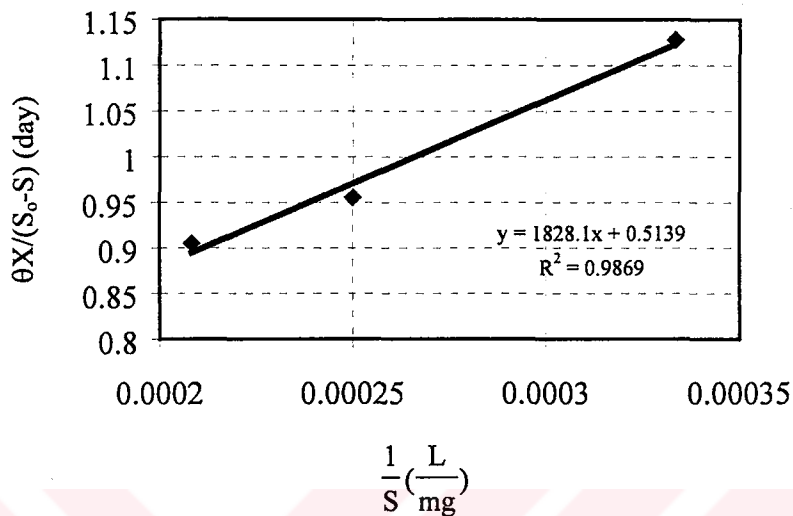


Figure 6.16. Evaluation of the kinetic parameters of the Monod Model

Slope: $\frac{K_s}{k}$

Intercept: $\frac{1}{k}$

$k=1.95 \text{ 1/day}$

$K_s=3558 \text{ mg/L COD}$

7. CONCLUSION

The aims of this study are to determine and to present efficient and economical operating conditions for the treatment of Afyon Alcaloide Factory Wastewater by chemical, biological oxidations and plus by combinations of them.

Biological treatment of the wastewater

- Retention time effect: The most appropriate COD removal is achieved at 6 days retention time by which COD value is decreased from 27700 mg/L to 7850 mg/L (71.66 % removal).
- Air flowrate effect: At the same retention time increasing the air flowrate from 3 L/min to 4.5 L/min raised the COD removal to 88% leading a COD value of 3422 mg/L.

For biological treatment of wastewater, 6 days of retention time; 4.5 L/min of air flowrate are decided to be appropriate operating conditions.

CWAO of the wastewater

- Temperature effect:, Increasing the temperature from 140 °C to 150 °C helps to enhance the efficiency of the treatment. But an

evident effect is not seen at 160⁰C. So it can be concluded that the temperature of 150⁰C is appropriate.

- Catalyst Loading Effect: Doubling the catalyst loading did not double the % COD removal, but increased it from 23% to 34% at temperature of 150⁰C.

In CWAO experiments, the highest percentage COD removal (35%) is achieved at 160 ⁰C and 1 g/L of catalyst loading, leading a COD value of 18155 mg/L. In the biological treatment experiments, COD value is decreased down to around 3500 mg/L giving a total percentage COD removal of 88%. From the comparison of the two treatment methods it seems that a single CWAO process is not very efficient.

In combined process of biological pretreatment plus CWAO, CWAO of biological treatment effluents (obtained at 6 days retention time and 8 days retention time at 3 L/min of air flow rate) seems suitable. In contrast to this, application of CWAO to biologically treated wastewater at 6 days of retention time at 4.5 L/min air flow rate is not so necessary. In all sets, again 150⁰C is found to be adequate, but the effect of catalyst loading on the treatment efficiency is not very significant.

In the other combination, CWAO pretreatment plus biological treatment, COD is decreased to 2900 mg/L from COD value of CWAO effluent of 18000 mg/L. As mentioned before, by biological treatment alone the approximately the same result can be obtained. Consequently, also this combination seems unnecessary.

The kinetic study performed according to the Monod Model leads to the following values; 0.0923 mg MLSS/ mg COD, 1.95 1/day, 0.0285 1/day, 3558 mg/L COD, Maximum Yield Coefficient; Y , Maximum rate of substrate utilization; k , Endogenous Decay Coefficient; k_d Half velocity constant; K_s , respectively.

The objective of this study was to reduce the organic matter in Afyon Alcaloide Factory wastewater by adequate treatment strategies in order to meet the discharge standards (COD < 200 mg/L). Unfortunately, in all the experiments performed, the discharge standards could not be reached. Hence the studies should be continued. As recommendation for the future studies the following ideas can be considered:

- Changing some operating conditions of CWAO process, more efficient results can be obtained (such as higher pressures and temperatures, different catalyst types and etc.).
- Combinations of the biological treatment process by other chemical treatment processes

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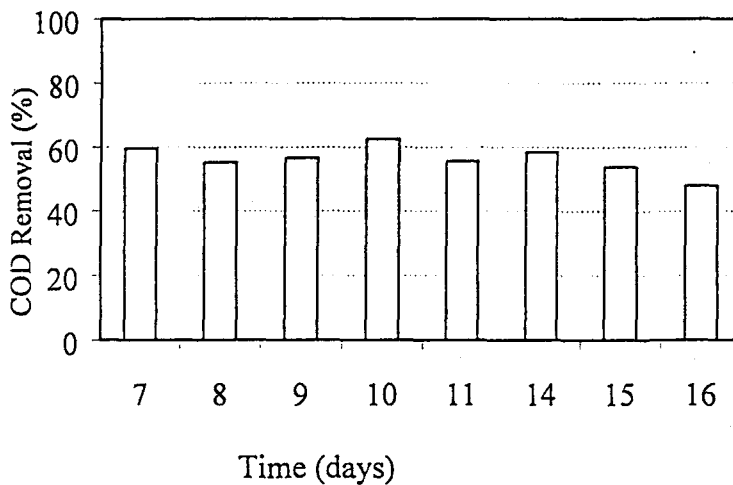
<http://www.zimpro.usfilter.com/wetox>

APPENDIX

➤ **Activated Sludge Experiments at Retention Time of 4 days,
Fair=3 L/min**

TableA1: Experimental Results

Time (days)	COD (mg/L)	% COD Removal
7	11200	59.57
8	12400	55.23
9	12000	56.68
10	10400	62.45
11	12300	55.60
14	11500	58.48
15	12800	53.79
16	14400	48.01



FigureA1 COD Removal vs day

Average COD=12125 mg/L

% COD Removal based on average COD=56.23%

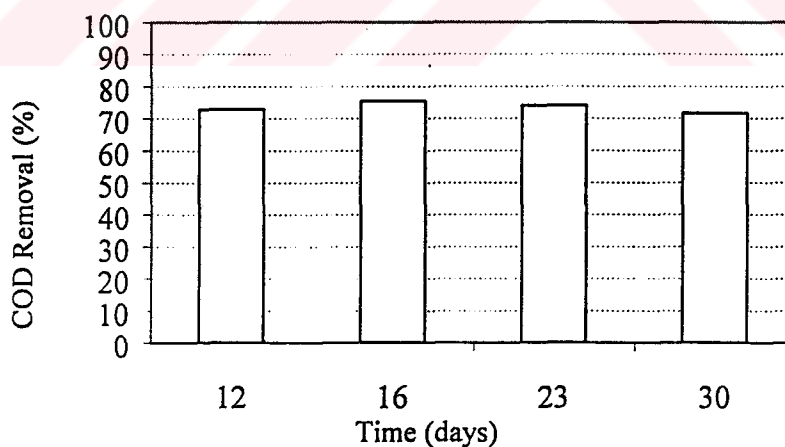
➤ **Activated Sludge Experiments at Retention Time of 6 days,
Fair=3 L/min**

Table A2: Experimental Results

Time (days)	COD (mg/L)	% COD Removal
12	7500	72.92
16	6800	75.45
23	7200	74.01
30	7850	71.66

Average COD=7338 mg/L

% COD Removal based on average COD=73.51%



FigureA2 COD Removal vs day

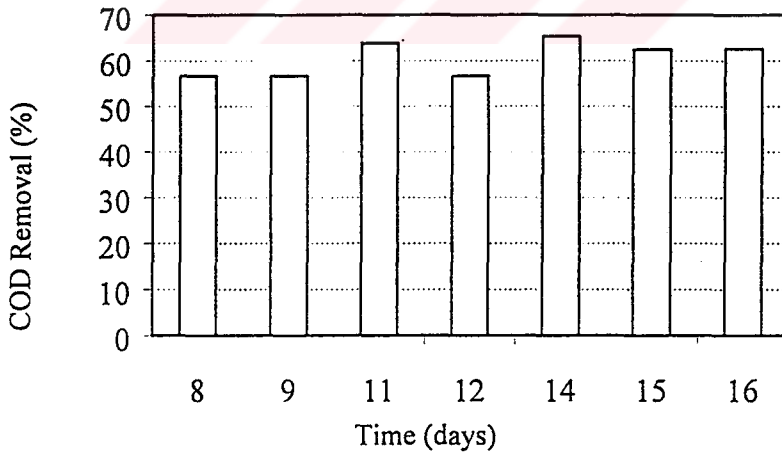
➤ **Activated Sludge Experiments at Retention Time of 8 days**

Table A3: Experimental Results

TIME (Days)	COD (mg/L)	% COD Removal
6	10400	62.45
8	12000	56.68
9	12000	56.68
11	10000	63.90
12	12000	56.68
14	9600	65.34
15	10400	62.45
16	10350	62.64

Average COD=10844 mg/L

% COD Removal based on average COD=60.85%



FigureA3 COD Removal vs day

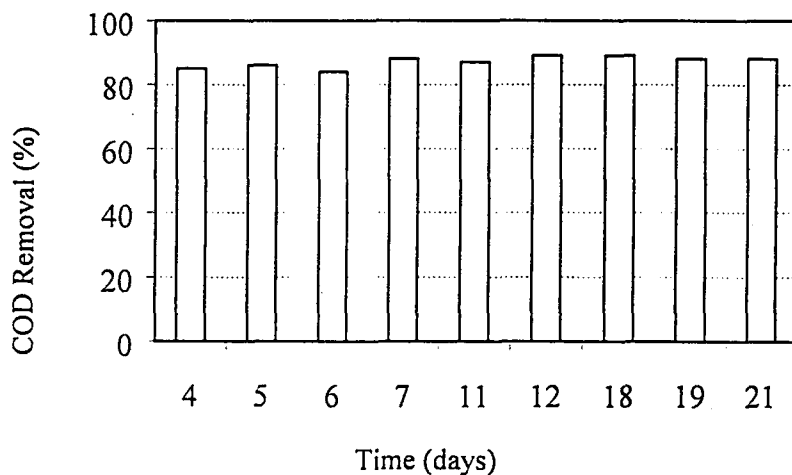
➤ **Activated Sludge Experiments at Retention Time of 6 days
and Air Flow Rate of 4.5 L/min**

Table A4: Experimental Results

TIME(Days)	COD(mg/L)	% COD Removal
4	4140	85
5	3880	86
6	4380	84
7	3500	88
11	3634	87
12	3218	89
18	3000	89
19	3425	88
21	3422	88

Average COD=3622 mg/L

% COD Removal based on average COD=86.92%



FigureA4 COD Removal vs day

RESUME

Gülin AYTİMUR was born in İZMİR in 1976. She was graduated from high school in 1994. She received B.S. in Chemical Engineering department from the Engineering Faculty of Ege University in 1999.

She participated a seminar called "Pollution Prevention and Hazardous Waste Management" organized by Aegean Initiative framework in Greece-Rhodes in 2002, July.

She presented a poster entitled " Treatment of Nonbiodegradable Industrial Wastewaters by Chemical Oxidation and Biological Oxidation" ISWA 2002 World Environment Congress and Exhibition congress in July 2002.

She also presented an oral presentation in Chemical Engineering congress (UKMK5), in Ankara in September 2002.

She has been working as a research assistant in Process and Reactor Design department of Ege University since 1999.