ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

CHARACTERIZATION AND TREATABILITY STUDIES OF METAL FINISHING INDUSTRY WASTEWATER

M.Sc. THESIS

Gülten YÜKSEK

Department of Environmental Engineering

Environmental Biotechnology Programme

SEPTEMBER 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

METAL SON İŞLEME TESİSİ ATIKSULARININ KARAKTERİZASYONU VE ARITILABİLİRLİĞİNİN İNCELENMESİ

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Gülten Yüksek, a **M.Sc.** student of ITU **Institute of Science Engineering and Technology** student ID **501101804**, successfully defended the **dissertation** entitled "**CHARACTERIZATION AND TREATABILITY STUDIES OF METAL FINISHING INDUSTRY WASTEWATER**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Assoc. Prof. Didem OKUTMAN TAŞ** Istanbul Technical University	.....
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Date of Submission : 10 September 2012
Date of Defense : 19 September 2012

Dedicated to my beloved mother and father,

FOREWORD

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ABBREVIATIONS

$\mathbf{b_H}$	**:** Endogenous decay rate (per day)
$\mathbf{k_{hs}}$	**:** Maximum spesific hydrolysis rate for soluble COD component (per day)
$\mathbf{k_{hx}}$	**:** Maximum spesific hydrolysis rate for particulate COD component (per day)
$\mathbf{K_S}$	**:**Half saturation constant for growth (mg COD/L)
$\mathbf{K_{XS}}$	**:** Hydrolysis half saturation constant for soluble COD component (mg COD/mg cell COD)
$\mathbf{K_{XX}}$	**:** Hydrolysis half saturation constant for particulate COD component (mg COD/mg cell COD)
OUR	**:** Oxygen uptake rate (mg/L.h)
$\mathbf{S_H}$	**:** Rapidly hydrolyzable COD (mg COD/L)
$\mathbf{S_I}$	**:** Soluble inert COD (mg COD/L)
$\mathbf{S_P}$	**:** Soluble residual microbial product (mg COD/L)
$\mathbf{X_H}$	**:** Heterotrophic biomass (mg COD/L)
$\mathbf{Y_H}$	**:** Heterotrophic yield coefficient (mg cell COD/mg COD)
$\mathbf{\mu_H}$	**:** Heterotrophic growth rate (per day)

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CHARACTERIZATION AND TREATABILITY STUDIES OF METAL FINISHING INDUSTRY WASTEWATER

SUMMARY

Role of treatment facilities in the prevention of pollution in the aquatic environment is substantially important. Operating the wastewater treatment plant efficiently is more sensitive issue than the entity of treatment plants. In order to evaluate the efficiency of a wastewater treatment plant, raw wastewater characterization have to be known. In this study, the wastewater sources of the metal finishing industry have been investigated, characterized and the efficiency of the operating wastewater treatment plant have been evaluated. Especially three processes in the facility intensively consumes water and produce wastewater. These processes are metal surface pre-treatment, painting and enamel coating processes. Between these processes, pollution load of enamel coating process is the most intensive one. The process that produce the highest amount of wastewater is surface metal pretreatment process. After determination of wastewater sources of the facility, samples are taken and characterized during the year.

In the wastewater treatment plant, while domestic wastewater have been treated by conventional activated sludge process, industrial wastewater have been treated both by chemical treatment and activated sludge processes. The chemical treatment for industrial wastewater contains coagulation and flocculation processes followed by the activated sludge process.

The parameters in characterization studies have been determined according to "Water Pollution and Control Regulation". In addition to these regulation parameters, irrigation parameters which takes place in the "Wastewater Treatment Plant Technical Procedures Communication" have been also identified. In addition to the characterization studies, respirometric analyses were conducted to evaluate biological treatability of the wastewater. In continuation of the studies, chemical treatability studies were performed, the optimum pH and chemical dosages were determined according to the wastewater character. Regarding to these performed studies, it is observed that discharged wastewater is complied with the values of the legal requirements.

In addition, inert Chemical Oxygen Demand (COD) concentrations were determined in order to evaluate the biological treatability of the wastewater. In this experiment, the COD removal of three types of raw wastewater and the filtered samples of the same wastewater were monitored in the aerated reactors. 30-40 mg VSS/L biomass was added in the reactors and the COD removal in reactors were analyzed until the complete mineralization was observed in the system.

Biological treatability studies were continued using four different type wastewaters as domestic, painting, enamel and rinsing wastewater, and they were respirometrically analyzed using industrial and domestic activated sludge. Besides

these four raw wastewater types, that are wastewater samples chemically treated in the laboratory were also respirometrically analyzed using industrial and domestic activated sludge samples. In all respirometric analyses, oxygen consumption rate and COD removal were monitored.

Jar test experiments were performed in order to determine optimum coagulant dosages. The wastewater samples were prepeared in the laboratory by mixing painting and enamel wastewaters with a ratio of 3:1. Rinsing wastewater was not added in the prepared wastewater for jar test, to prevent the dilution of pollution load. In this study, $FeCl_3$ solution, $FeCl_3$ containing commercial solutions and $Al_2(SO_4)_3$ solution were used as coagulant, while HCl, NaOH solution in pH adjustment, and polyelectrolyte as flocculant. 1-10-25-50-75-100 and 150 mg/L were chosen as coagulant concentrations during jar test. Total Suspended Solids (TSS) of mixed solution, pH, COD and Total Dissolved Solids (TDS) of supernatant were monitored. According to sludge separation quality and the other parameter's concentration, 50 mg/L dosage was choosen as the optimum dosage. Also some of the heavy metals concentrations (e.g., ferrous, total chrome, aluminium, and zinc) in the effluent for these dosages were analyzed.

In the consequence of inert COD evaluation experiments, soluble inert COD value of enamel, painting and rinsing wastewater were determined as 7%, 6.4% and 12% while particular inert COD values were determined as 14.4%, 10.2% and 0%, respectively.

Painting, enamel and rinsing wastewater showed inhibitory effect on domestic activated sludge, while the organic matter removal was observed for painting, enamel and rinsing wastewater with the acclimated industrial activated sludge. Hence chemical treated wastewater had very low pollution load, oxygen uptake rate did not increased when wastewater was added in the system.

In summary, as a result of the observed low pollution load in the raw wastewaters and respirometric analyses, biological treatment step of industrial wastewater which constitue a significant percentage of the the overall energy requirement of wastewater treatment plant may not be a necessary step in the operating wastewater treatment plant.

METAL SON İŞLEME TESİSİ ATIKSULARININ KARAKTERİZASYONU VE ARITILABİLİRLİĞİNİN İNCELENMESİ

ÖZET

Sucul ortamdaki kirliliğin önlenmesinde arıtma tesislerinin oynadığı rolün büyüklüğü tartışılmaz ölçüde büyüktür. Ancak arıtma tesisinin verimli olarak işletilmesi hem çevre kirliliğinin önlenmesinde hem de tesisi işleten tarafın yüklendiği mali sorumluluk dikkate alındığında tesisin kurulmasından çok da önemli olduğu görülmektedir. Bu amaçla; bir metal son işleme tesisinde mevcut arıtma tesisinin arıtma verimliliği incelenmiştir.

Seçilen işletmenin özellikle üç prosesinde yoğunlukla su tüketimi yapılmakta ve atıksu oluşumu gözlenmektedir. Bu prosesler; işlenmek üzere gelen metal plakaların üzerindeki koruyucu yağ tabakasının arındırılması işlemi olan metal yüzeyi yıkama, işlenen parçaları renklendirme işlemi olan boyama ve ısıya dayanıklı olması gereken parçalar için uygulanan emaye kaplama işlemleridir. Bu proseslerden miktarca en fazla debide su tüketen proses yıkama prosesi iken, yıl bazında değişmekle birlikte kirlilik yükü en fazla olan proses emaye kaplamadır. Tesisin atıksu kaynaklarının incelenmesiyle birlikte atıksu arıtma tesisinin belirlenen noktalarından bir yıl boyunca dört kez numune alınarak, karakterizasyon çalışması yapılmıştır. Alınan numunelerden ilk alınan numuneler grab numune olup, diğer üç numune alımında kompozit numune türü seçilmiştir. Arıtma tesisinde endüstriyel atıksuların ve evsel nitelikli atıksuların arıtıldığı iki farklı aktif çamur ünitesi bulunmaktadır. Evsel nitelikli atıksular sadece aktif çamur sistemi ile arıtılırken, proses kaynaklı endüstri suları ise, koagülasyon ve flokülasyonu kapsayan kimyasal bir arıtımdan geçirildikten sonra farklı bir aktif çamur ünitesinde biyolojik arıtımdan geçirilmektedir. Endüstriyel atıksu arıtma ünitesi, kesikli ve sürekli arıtım ünitelerinden oluşmaktadır. Kesikli arıtımda, boyama ve emaye kaplama proseslerinden kaynaklanan kirlilik yükü yüksek atıksular arıtılırken, sürekli arıtım ünitesinde daha düşük kirlilik yüküne sahip durulama atıksuları ve kimyasal arıtımdan çıkan atıksular arıtılmaktadır. Evsel ve endüstriyel atıksular ayrı ayrı arıtıldıktan sonra bir noktada birleşerek alıcı ortama deşarj edilmektedir. İşletmenin endüstriyel atıksuyunun karakterizasyonunda daha önceki yıllarda yüksek miktarda KOİ ve yağ gres kirliliği görülürken, işletmenin üretim prosesinde daha çevreci teknolojilerin kullanımına geçmesiyle, atıksu karakterizasyonundaki kirlilik yükü azalmıştır. Bu durum da atıksu karakterizasyonuna uygulanan arıtım proseslerinin değerlendirilmesini gündeme getirmiştir.

Arıtma tesislerinin verimliliğinin incelenebilmesi için, öncelikle gelen atıksu karakterizasyonunun belirlenmesi gerekmektedir. Bu çalışmada metal işleme tesisinin atıksu kaynakları tespit edilmiş ve karakterizayonu yapılarak, mevcut arıtma tesisinin verimliliği araştırılmıştır. Atıksu karakterizasyonu için; işletmenin arıtımdan geçen atıksuyunun alıcı ortama deşarj edilmesi sebebiyle sorumlu olduğu Su Kirliliği Kontrolü Yönetmeliği Deşarj Limitleri'nde yer alan kirlilik parametrelerinin tespitine

öncelik verilmiştir. Geleneksel parametreler dışında atıksuyun sulama suyu olarak kullanımının uygunluğunun araştırılması için Atıksu Arıtma Tesisi Teknik Usuller Tebliği'nde yer alan sulama suyu parametreleri olan iletkenlik, klorür, toplam çözünmüş madde, ve bulanıklık parametreleri de incelenmiştir. Karakterizasyon çalışmaları dahilinde, endüstriyel ve evsel biyolojik arıtma havuzlarından çamur numuneleri alınmıştır. Özellikle endüstriyel biyolojik havalandırma havuzunda var olan köpük problemi incelemek için alınan çamur numunesi mikroskop altında incelenmiştir. Bunlara ek olarak, atıksuyun biyolojik arıtılabilirliğinin belirlenmesi kapsamında emaye, boyahane ve yıkama atıksularının inert KOİ değerleri belirlenmiştir. İnert KOİ değerlerinin belirlenmesi için, üç ham atıksu kaynağının ve aynı atıksuların süzülmüş örneklerinin konduğu reaktörlerin içine 30-40 mg UAKM/L biyokütle ilavesinden sonra oksijen sınırlaması olmadan uzun süre reaktörlerin KOİ giderimi takip edilmiştir. Deneyler sistem tamamen mineralize olana kadar devam ettirilmiştir.

Karakterizasyon çalışmalarının sonuçlandırılmasıyla birlikte arıtma tesisinden alınan evsel, boyahane, emaye ve yıkama atık sularından oluşan dört farklı ham atıksu numunesinde biyolojik arıtıma uygunluğunun tespit edilmesi için respirometrik çalışmalar yapılmıştır. Biyolojik arıtılabilirlik deneyleri esnasında kullanılan çamurlar mevcut atıksu arıtma tesisinin evsel ve endüstriyel atıksuyun arıtıldığı aktif çamur ünitelerinden alınan çamur numuneleri ile gerçekleştirilmiştir. Yapılan respirometrik çalışmalarda, iki farklı çamurda bu dört ham atıksu ve laboratuar şartlarında kimyasal yöntemle arıtılmış atıksu örnekleri karşılaştırılmış ve oksijen tüketim hızlarındaki değişim takip edilmiştir. Respirometrik çalışmalar sırasında yapılan her sette KOİ giderimi de izlenmiştir.

Tesiste uygulanan kimyasal arıtım için optimum pH, kimyasal dozajı ve türünün uygunluğunun değerlendirilebilmesi için laboratuar koşullarında "Jar Testi" ile kimyasal arıtılabilirlik çalışmaları yapılmıştır. Yapılan kimyasal arıtılabilirlik çalışmalarında atıksu karışımı laboratuar ortamında tesisin mevcut durumunu karakterize edecek şekilde, debisel oranlar dikkate alınarak hazırlanmıştır. Kimyasal arıtılabilirlik için hazırlanan atıksu karışımına, düşük kirlilik yüküne sahip ancak debisel yükü yoğun olan yıkama suları katılmamıştır. Böylelikle arıtılabilirlik çalışmasında kullanılacak atıksuyun sistemdeki en kötü durumu temsil edecek kirlilik yüküne sahip olması hedeflenmiştir. Çalışmalarda koagülant olarak; laboratuardaki saflık oranı yüksek olan $FeCl_3$ kimyasalından hazırlanan çözelti, işletmeden alınan saflık oranı düşük olan ticari $FeCl_3$ çözeltisi ve alum olarak bilinen Al_2SO_4 çözeltisi kullanılmıştır. Bunlara ek olarak; pH ayarlaması için HCl, NaOH çözeltileri ve flokülasyon için anyonik polielektrolit çözeltisi kullanılmıştır. Toz kimyasallardan hazırlanan koagülantlar için jar testinde 1-10-25-50-75-100 ve 150 mg/L dozajları, sıvı ticari $FeCl_3$ çözeltisi için ise 1-10-25-50-75-100 ve 150 µL/L dozajları denenmiştir. Bütün koagülant dozajlarının denemelerinin tam karışımında AKM parametresinin, çamur hacminin ve çöktürme sonrası üst fazda ise pH, KOİ, bulanıklık parametrelerinin takibi yapılmıştır. Hem belirtilen parametrelerin değerlendirilmesi hem de çamur faz ayrımının en iyi 50 mg/L ve 50 µL/L dozajlarında görülmesi sebebiyle, bu dozajların uygulandığı numunelerde demir, toplam krom, alüminyum ve çinko gibi ağır metallerin takibi yapılmıştır.

Yapılan karakterizasyon çalışmaları sonucunda, yıl içinde arıtma tesisine gelen KOİ değerlerinde değişimlerin olmasının yanında, genel olarak ham atıksu kaynaklarında kirlilik yükünün çok yüksek olmadığı görülmektedir. Bununla beraber deşarj edilen

atıksuda ise yasal gereklilikler kapsamında istenilen değerlerin altında olduğu tespit edilmiştir.

Inert KOİ değerlendirmeleri sonucunda ise; emaye, boyahane ve sürekli arıtıma gelen ham atıksu numunelerinde sırasıyla çözünmüş inert KOİ değerinin %7, %6.4 ve %12 oranlarında iken partikül inert KOİ değerinin ise %14.4, %10.2 ve %0 oranlarında olduğu görülmüştür.

Respirometrik çalışmalar sonucunda; boyahane, emaye ve sürekli arıtıma gelen atıksuyun evsel biyolojik arıtma çamuru üzerinde inhibe edici etki gösterdiği görülürken, endüstriyel çamurun bu atıksu türüne aklime olması sebebiyle az da olsa bu atıksuda faaliyet gösterebildiği görülmüştür. Kimyasal arıtım ile arıtılan atıksudaki KOİ miktarının çok düşük olması sebebiyle aktif çamur sisteminin tüketilebilecek besin bulamaması nedeniyle sisteme atıksu ilavesi yapıldığında OTH değerinde bir artışa neden olmamıştır. Bu durumdan dolayı atıksu ilave edildikten sonra oksijen tüketiminde bir değişiklik görülmemiştir. Atıksu arıtma tesisine gelen atıksu karakterizasyonu, kimyasal arıtım çıkışındaki arıtım verimliliği ve respirometrik çalışmaların sonuçları dikkate alındığında ciddi enerji tüketimine neden olan endüstriyel biyolojik arıtımın çok gerekli olmadığı ön görülmüştür.

1. INTRODUCTION

1.1 Importance of the Research

From the Industrial Revolution until now, due to increase in purchasing power, welfare level has been increased and because of this, purchasing rate gradually increased every year. Depending on the purchasing rate, increasing of production rate affects the over use of natural resources and deterioration in the balance of the ecosystem.

In order to minimize these negative effects without decreasing welfare level, governments have regularized many legislations for industries. Water Quality and Control Legislation is one of the legislations example in Turkey. Additionally, voluntary environment standards have also been published (i.e., Water footprint of product, LCA in water management) to supply enough knowledge about environmental attitude of producers.

The other example can be given as "water exploit index" which is prepared by EU Commission. This index has been prepared in order to show that whether water consumption of EU Countries is sustainable and conscious. At the same time this index points some water consumption limitation that can be met in the future for countries, industries and consumers. In production process in order to perform appropriate water management, the following points have to be considered.

- Optimizing water consumption
- Researching environmental effects of chemicals that are used in processes and using more environmentally friendly chemicals
- Reusing wastewater in the process after advance treatment methods.

Especially reusing wastewater in the process have crucial role to decrease the water requirement of industry. In this way, resource efficiency can be managed in sustainability limits. The other important subject is relationship between water and energy resources. Water resources have been used to get energy, in wastewater treatment and water supply issues, energy also has been used.

All of these developments help to the producers to control and monitor their production system, in an environmental frame. This concept makes consumers sure to get environmentaly-friendly product and also helps to decrease negative environmental effects of industry.

2. BACKROUND

2.1 Metal Finishing Industry

In order to meet customer's request; with the increased metal ware usage and the necessity of more long-lasting product, active and rapidly production was appeared. For this reason, during surface treatment and coating processes different types of methodologys can be applied. Surfaces of metal ware are passed from several processes to protect it against corrosion, to make more attractive for decorative purpose, to enhance conductivity, and to make easy their usage.

The US Department of Commerce classification codes divide this industry by product and services. SIC code 34 is further divided as follows:

- SIC 341- Metal Cans and Shipping Containers,
- SIC 342- Cutlert, Handtools, and General Hardware,
- SIC 343-Heating Equipment, Except Electric and Warm Air, and Plumbing Fixtures,
- SIC 344- Fabricated Structural Metal Products,
- SIC 345- Screw Machine Products, and Bolts, Nuts, Screws, Rivets, and Washers,
- SIC 346- Metal Forging and Stampings,
- SIC 347- Coating, Engraving, and Allied Services,
- SIC 348- Ordnance and Accessories, Except Vehicles and Guided Missiles,
- SIC 349- Miscellaneous Fabricated Metal Products (Aydın, 2005).

NACE stands for "General Name for Economic Activities in the European Union" and is based on the European standard for industry classifications. In Turkey, knowledge about metal finishing sector also are searched under title of "NACE, Code 28.51 and 27.51". This code's name is "Metal Coating and Processing" that contains the following processes (Engin et al., 2011);

- Metal Coating- Anodizing,
- Metal Heat Processes,
- Metal Treating, Sand Spraying and Polishing,

- Metal Colorization,
- Plastic Coating, Enamel Coating and Varnishing,
- Hardening of metals.

2.2 Metal Coating Process

Basic operations of industrial metal coating processes are surface preperation, coating and rinsing stages. All metal coating, surface preperation, cleaning and rinsig processes are called as "surface treatment". As seen in Figure 2.1, after the surface treatment process, metal pieces are send to montaging unit. In metal coating operations; physical, chemical and electrochemical methods can be used (Hassanali, 2005).

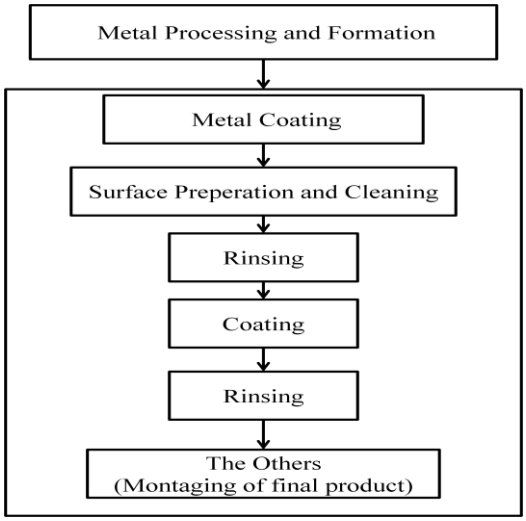

Figure 2.1: Basic processess in the metal finishing sector (Engin et al., 2011).

Mass balance of the industry was given in the Figure 2.2. While energy, raw materials and chemicals are used as input, emission, solid waste and wastewater are produced along with production as output.

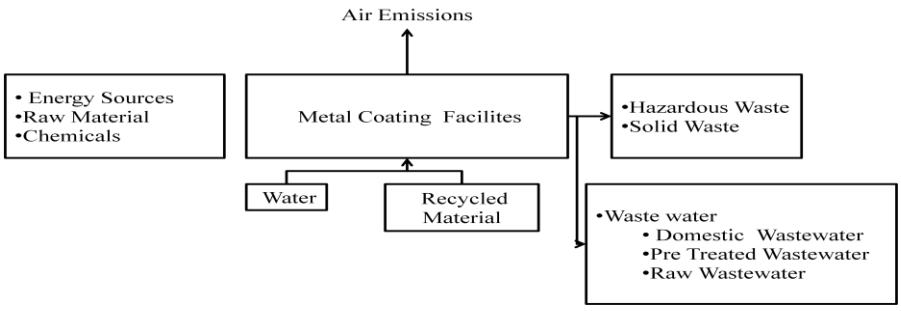

Figure 2.2: Basic mass balance in the metal coating facilities.

In surface preperation process; contaminants that create bonding problems on metal surfaces include grease, dust, dirt, oil and oxide caused by air corrosion. Grease and oil not only interfere with bonding, but also block efficiency of preparation operations. A metal adherent requires solvent cleaning, abrasive blasting, priming, or a combination of preparation methods depends upon the next step of process.

The wastewater that is used in the research is produced by large appliance coating industry. Specifically, metal surface treatment and coating applications includes all of the activities that involve coatings, thinners, and cleaning materials used in large appliance coating operations. These activities include:

- Surface preparation of the large appliance parts or products;
- Preparation of coatings for application;
- Applying the coatings;
- Flash-off, drying, or curing the coatings;
- Cleaning of coating equipment;
- Storage of coatings, thinners, and cleaning materials;
- Conveying of these materials; and
- Handling and conveying of waste materials generated by the coating operation (USEPA, 2007).

In addition to paint coating, enamel coating application is also an applied coating process in this industry. The main purpose of enamel coating is surface protection. Metal surfaces are protected from corosion and are gained esthetic features by enamel coating. Technically, enamel coated metals are steel, pig iron, aluminum and alloyed aluminum. Application of coating processes are wet and powder implementations. Spray, dipping and brush methods are prefered in wet implamentations (Evcin, 2006).

Recently, as a results of the developments in the related technologies, more technologic and more environmental friendly coating methods are emerged. The newest coating method is “Nano-Ceramic Coating Application”. In this metod, the strategy employed to develop nanostructured coatings concentrated on the composition similar to currently available conventional coatings and to use existing deposition equipment to fabricate them. As only the microstructure of the coatings was changed, it greatly simplified the process of implementing the new technology in

both military and commercial applications. One of the coatings under development, a plasma sprayed nanoceramic composite with a composition of Al_2O_3-13 TiO_2, has exhibited wear resistance, bond strength, and toughness unprecedented in a ceramic, and is now in use aboard Navy surface ships and submarines, reducing maintenance costs due to wear and corrosion (Kabacoff, 2002).

The applications for nanostructure Al_2O_3-13 TiO_2 coatings can be grouped according to the properties to be exploited. In the first case, the simplest applications are those in which the nanostructure coatings replace existing conventional ceramic coatings. In such cases, the advantage is greater longevity and reliability. The second case is as a replacement for hard chrome coatings. Here, the advantages are lower cost, elimination of toxic hazardous materials and in some cases improved performance as a result of the non-metallic nature of ceramics. Metallic surfaces which are in contact with seawater for long periods experience buildup of calcareous deposits. Actuator rods with such buildups can severely damage seal areas when the rods are retracted. Also ceramics do not promote galvanic corrosion, which occurs when two dissimilar metals are in contact with an electrical conductor such as seawater. In spite of these advantages, conventional ceramic coatings frequently cannot be used over metallic coatings because they lack sufficient bond strength and toughness where nanostructured ceramics overcome this limitation. In fact, nanostructure coatings (Al_2O_3 - $13TiO_2$) are now being used to coat titanium components on seawater-exposed portions of submarines specifically to eliminate galvanic corrosion on nearby steel structures.

Other nanostructured coating materials are under development and are expected to become available in the near future. These include cemented carbides, such as Tungsten Carbide-Cobalt (WC-Co) and other ceramics, such as chrome oxide and stabilized zirconia. All of these coatings are expected to find a wide range of application and should greatly benefit both military and commercial operating and maintenance costs (Kabacoff, 2002). The application of nano- tecnologic coating methods was showed in Figure 2.3. As seen in the figure, the method is more efficient than the others in terms of adhesion of the coating to the surface. In addition, powder coating methods is more eco-friendly due to the less wastewater generation.

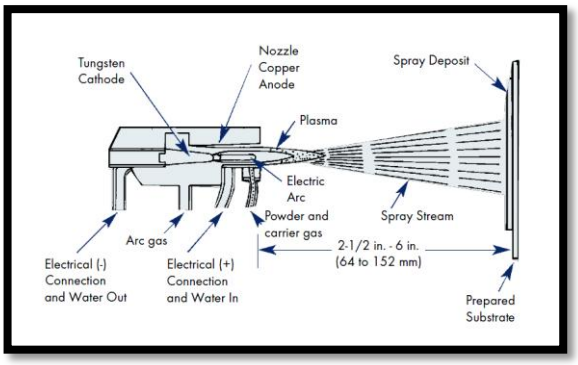

Figure 2.3: Application of nano-technology coating.

2.3 Environmental Evaluations of The Coating Application

Environmental problems should be integrated with privileged subjects of the enterprise, to incorporate in production structure. For example, if environmental problems combine with waste minimization, recycle, compliance with legislation, improving customer satisfaction, cost reduction, and economic gain, precedence of environmental issues can be changed in the industry (Engin et al., 2011).

In Table 2.1, wastes produced in the facility were compared with the literature. In the facility, there are only two types of liquid wastes that are the result of the industrial activity and solvent consumption.

Table 2.1: Evaluations of liquid wastes in metal finishing industry (Engin et al., 2011).

Liquid Wastes	General	In this facility
Industrial waste	Rinse water, cooling water, steam condensate, boiler blow down and wash water	Rinse water, cooling water, steam condensate, boiler blow down and wash water
Spent plating waste	Contaminated or spent electroplating or electroless plating bath solutios	-
Spent process baths	Contaminated or spent etchants and cleaners (alkaline, acid, and cyanide cleaning solutions)	-
Strip and pickle baths	Nitric, sulfuric, hydrochloric /hydrofluoric acids used to strip metals from work piece racks	-
Exhaust/scrubber solutions	Solutions collected in exhaust and air emission control devices	-
Spent solvents	Halogenated solvents, alcohols, acetone, methylene chloride and others used for degreasing	Only Halogenated solvents, alcohols, acetone
Samples of plating solution	Samples provided by vendors that are not intended for use	-

In metal coating industry, the most important environmental problems are energy, water and raw material consumption, as well as liquid and/or solid emissions. In Table 2.2, Environmental operational costs of metal coating industry were collected under three different titles and the main costs have been originated from wastewater management.

Table 2.2: Environmental operational costs (Haveman, 1995).

Receiving Media	Costs (%)
Air	8
Water	62
Waste	32

2.3.1 Consumed water

Rinsing and cooling processes are the most water-consuming processes. The considerable amount of water are dissappeared by evaporation, the other water consumption comes from solution preparation (EU, 2006).

Generally, water-consumption takes place in the following places (Berk, 2004);

- Cooling water
- In the boiler room
- Rinsing process
- Preparation of solutions
- In the paint bath

2.3.2 Air emissions

Air emissions can be composed of the vapours which are produced by degreasing, rinsing and coating processes. Besides these, air emissions also consists of gases, dusts, and smoke (Engin et al., 2011).

2.3.3 Hazardous waste

This type wastes cannot be decomposed biologically and are required special treatment methods before storage period. Hazardous materials, which are produced in the metal coating industry, are cyanides, acids, alkalis, heavy metals and residuals. Different chemicals originated from electro-coating industries have to be collected

and treated separately. If the type of wastes were combined, explosive reactions can be occurred (Engin et al., 2011).

2.3.4 Noise and odor problems

Metal coating process does not contain a significant noise source. However, some activities consist of a little noise. These activities are loading of components, mechanical cleaning and polishing, fans and motors. In addition to noise problems, odor problems also are not significant environmental problems in this sector. But some amount of odor may be formed by acid vapors (EU, 2006).

2.3.5 Wastewater

Amount of produced wastewater from this sector is not significant when it is compared with the others. But toxicity of produced wastewater is relatively high. The main wastewater sources can be summarized as follows;

- Industrial wastewater: Rinsing water, cooling water, degreasing water, steam condensate, boiler blow down water,
- Water generated from dirty and waste electro coating or other type coating baths,
- Nitric, sulfuric, hydrochloric and hydrofluoric acid containing wastewater,
- Exhaust washing solutions (Engin et al., 2011).

Due to many reasons, the heavy metals in the industrial wastewater reduce efficiency of wastewater treatment plant. Wastewaters mostly contains cadmium, chrome, cobalt, copper, ferrous, lead, nickel and zinc as heavy metals.

2.3.6 Solid waste

The sources of solid waste generated from this industries are listed below:

- Industrial wastewater treatment sludge: This types sludges generally contains cadmium, copper, nickel and zinc as heavy metals,
- Contaminated waste,
- The others: Residuals of absorbers, filters, empty containers, plant metal grids and abrasive blasting (Engin et al., 2011).

2.4 Key Environmental Issues About Sector

The main environmental issues are arised from energy, water and raw materials consumption. As a result of these consumptions, many type of wastes are produced.

In terms of raw material consumption, the chemicals used have the potential to cause environmental harm particularly to surface waters, ground waters and soil. Metals removed from wastewaters by chemical treatment end up in solid wastes and, together with some used process solutions, may need special management for recovery or disposal. The sector is a significant user of electricity, water and non-renewable resources (metals). Therefore the following issues are crucial:

- minimization of the consumption of raw materials, energy and water,
- minimization of emissions by process management and pollution control,
- minimization of waste production and its management.

The measure to achieve better environmental performance is complex and has to be assessed in respect to their potential impacts on the products and other processes (both pre- and post-treatment), as well as the benefits from environmental point of view. Best available techniques will be balanced against these criteria and therefore include changes within process units as well as end-of-pipe abatement techniques. Coating applications is the part of metal finishing industry. The wastewater that is used in this study, is produced from coating applications. Environmental effects of coating applications were listed in Table 2.3.

Table 2.3: Environmental effects of coating applications (EPA, 2007).

Principal substances of concern	Medium affected		
	Water	**Soil**	**Air**
Metals:			
Zinc	√	√	
Copper	√	√	
Nickel	√	√	
Chromium	√	√	√
Lead	√	√	
Cadmium	√	√	√
Non-metals			
Cyanides	√	√	√
Hypochlorite	√		√
AOX (absorbable organic halogens)	√	√	
Peroxides			
Surfactants:			
Dispersing agent, emulsifiers, detergent, wetting agent	√		
Complexing Agents:			
EDTA	√		

Table 2.3 (Cont.): Environmental effects of coating applications (EPA, 2007).

Principal substances of concern	Medium affected		
	Water	**Soil**	**Air**
Tartrate, EDDS, NTA, guconate, quadrole	√		
Sodium dittrionite	√		
Acids and Alkalis:			
Hydrochloric, nitric, phosphoric, sulphuric, hydrofluoric, acetic	√	√	√
Sodium, potassium, hydroxides, lime	√	√	√
Other Ions:	√	√	
Solvents:			
Trichloroethylene (TRI)	√	√	√
Tetrachloroethylene (PER)	√	√	√
Trichlorotrifluoroethane (CFC-113)	√	√	√
Methylene chloride	√	√	√
Gases			
Chlorine			√
Dusts		√	√
Wastes	√	√	√

2.5 Environmental Evaluation of New Trend Technologic Coating Processes

Nano technologic coating methods are environmentally friendly processes that are recently started to be applied in metal finishing industries. In this section, environmental effects of nano technologic coating methods were shared.

In addition to its low energy needs, this method contains neither phosphates nor toxic heavy metals and far less sludge is generated in production than with iron phosphating process. The method again lowers cost by reducing wastewater treatment, waste disposal, plant cleaning and maintenance.

The coating thickness can range from less than a micrometer to few tens of micrometers depending on the solution and application. Normally, with a much thinner coating, it can perform comparable to or better than anodizing/conversion oxide or organic primer/paint.

These nano-ceramic hybrid coatings form strong chemical bonds with both metal surfaces and organic adhesives or paints. Typically, there is a much stronger mechanical interlock than it is realized between traditional anodized surfaces and topcoats which results in a thinner nano-ceramics coating compared to anodizing/conversion or organic primer/paint.

The chemical composition of the coatings can be tailored to enhance many different properties such as adhesion, corrosion-resistance, wear-resistance, hydrophobicity or anti-finger-print.

By modifying the compositions, this process has been applied to many different metals and alloys (e.g., Al, Cu, Ti, Zn, Mg, and stainless steel) and showed superior performance (Chu et al., 2011).

3. WASTEWATER CHARACTERIZATION

3.1 Wastewater Composition

Wastewater in general, contains a number of different organic and inorganic components.

In wastewater, organic components can be classified in three ways;

- Characterization of components depending on chemical structure (e.g. oils, proteins, carbohydrates),
- Characterization of components depending on size distribution,
- Characterization of organic components depending on the biodegradability rate.

The first approach has very limited use because the application is extremely difficult and not practical (Okutman, 2001). Especially third approach is more appropriate than the others for biological treatment assessment. Because organic materials are main parameter in biological degradation.

3.2 Description of Organic Materials in Wastewater

Identification of the organic content of wastewaters has always been the major drawback for appropriate evaluation of biological treatment systems. While inorganic substrates such as nitrogen and phosphorus can be measured directly and incorporated into stoichiometric expressions, the same is not possible for organic carbon.

COD is the best-known parameter as an indicator of organic components. Since their discovery at the beginning of the twentieth century, activated sludge system, have been mostly used for organic carbon removal, especially for industrial wastewaters. In these systems, the large spectrum of different organic compounds in the influent could only be characterized by means of collective parameters. BOD and COD should be recognized as the most widely used parameters for organic carbon in wastewater characterization and activated sludge modeling. Total organic carbon (TOC) is also used for the same purpose, mainly in experimental biodegradation studies (Orhon et al., 2009).

3.3 Biodegredability of Organic Substances in The Wastewater

The COD is now considered not only as a single overall substrate parameter, but also as a spectrum of organic carbon fractions that require further differentiation in terms of their biodegradation rates.

In Figure 3.1, total COD fractions were showed. Total COD is composed of total biodegradable COD and inert COD fractions. Total inert COD is formed by inert soluble and inert particulate COD fractions. As distinct from inert COD, there are three type of biodegradable COD. These are readily biodegradable, rapidly hydrolysable, slowly hydrolyzable COD. Total COD concentration is calculated as showed in **(3.1)**.

$$C_T = S_S + X_S + X_I + S_I + S_H \qquad \textbf{(3.1)}$$

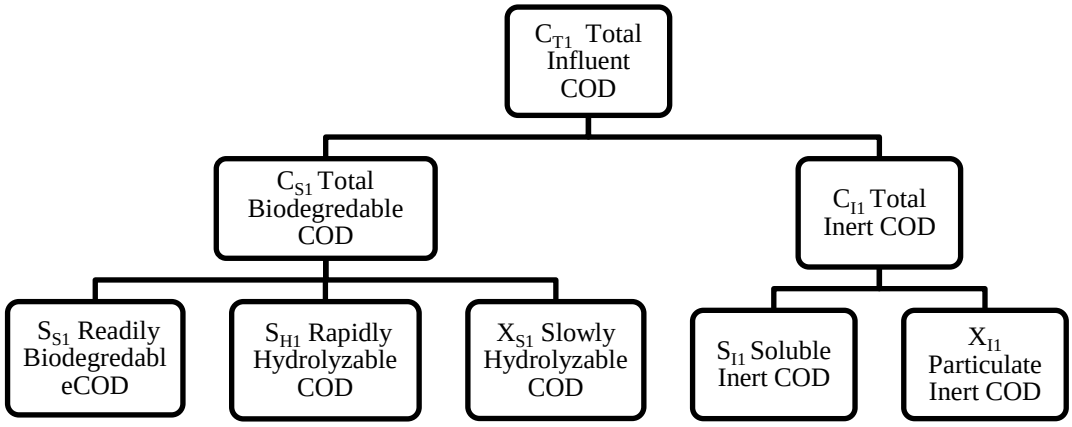

Figure 3.1: COD fractions in wastewater.

3.3.1 Readily biodegradable COD

The correct assessment of the readily biodegradable COD concentration (Ss) is important because this fraction is conceived as the rate limiting substrate component for heterotrophic growth. Methods used for its determination rely on respirometric measurements conducted under aerobic or anoxic conditions, in continuous or batch reactors. In the aerobic batch test adopted in this investigation, the selection of an appropriate initial F:M ratio provides a clear differentiation between oxygen

utilization rates (OUR) induced by Ss and Xs. The initial OUR stays constant over a period where the maximum growth rate is sustained; after the depletion of Ss, it drops to a lower level only correlated with the hydrolysis of Xs and the area above the second OUR plateau presumably reached after the depletion of all readily biodegradable substrate of influent origin (Orhon et al., 1997).

3.3.2 Hydrolysable COD

As a result of experimental observations, slowly biodegredable COD accounts for the major part of organic content in industrial wastewaters. Organic matter have been undergone from a sequence of complex reactions. As examples of the reactions, physical entrapment, adsorption to enzymatic breakdown and storage prior to biochemical oxidation and synthesis can be given.

In activated sludge, these reactions practically cannot be identified and described in detail. A single hydrolysis step is triggered to reflect the cumulative effect of all these complex interactions where this COD fraction as a whole, is assumed to be enmeshed in sludge and solubilised to readily biodegredable substrate.

In addition, especially for some industrial wastewaters, the hydrolysis rate for particulate hydrolysable COD is very close to what generally identifies endogenous respiration. Endogenous metabolism can be explained as the sum of all biochemical activities of microorganisms in the absence of utilizable extra cellular compounds likely to serve as source of energy and biosynthesis.

The observation challenges the validity of the values generally adopted for endogenous decay rate and underlines the possibility of significant interference of the slowly hydrolysable COD in the aerobic stabilization tests used for the experimental assessment of the endogenous decay (Orhon et al., 2009).

In Figure 3.2 and 3.3 fractions of soluble and particulate COD have been shared. In both of the COD type, there are parts of biodegrable COD, inert COD and inert microbial product.

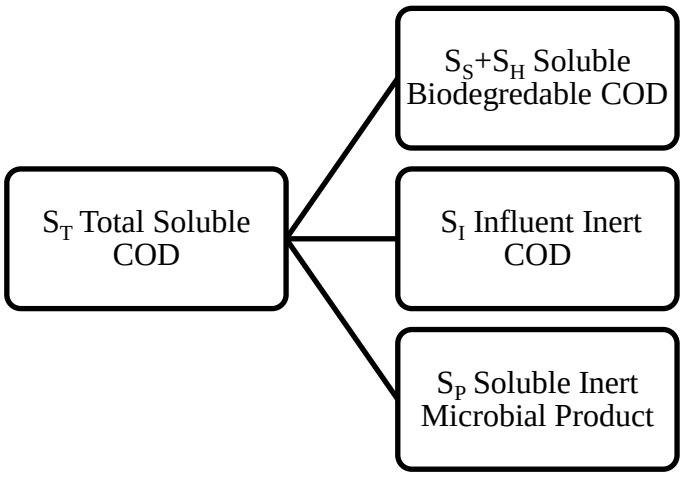

Figure 3.2: Soluble COD fraction.

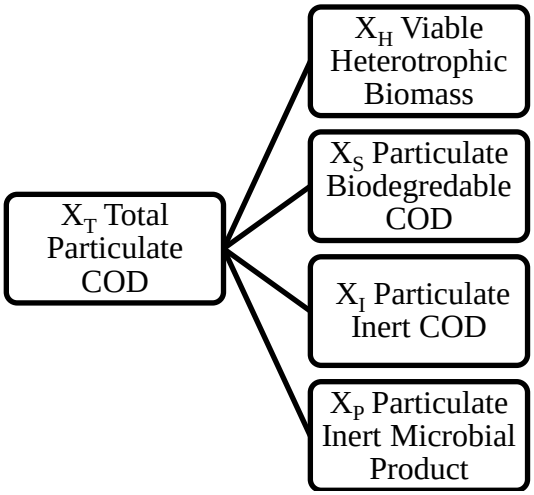

Figure 3.3: Particulate COD fraction.

3.4 Generation of Residual Microbial Product

Models structured upon viability and the active biomass inherently include generation of residual microbial products. These products are both particulate and soluble in nature and they are differentiated by virtue of their resistance biodegradation under the operating conditions of activated sludge (Orhon et al., 2009).

3.4.1 Particulate residual microbial product

Cellular decay is generally associated with generation of inert endogenous mass so particulate residual organic products. Active biomass fraction does not undergo any further reaction and accumulates in the activated sludge as particulate residual microbial products Xp (Orhon et al., 2009).

3.4.2 Soluble residual microbial product

Soluble residual (inert) microbial products, Sp is one of the most important parameters in the performance evaluation of the activated sludge systems, as it controls together with the inert COD of influent origin the magnitude of effluent soluble COD.

At the high sludge age levels normally adopted for the treatment of industrial wastewaters, a significant part the soluble COD in the effluent is not remaining fraction of the influent substrate which is depleted, but it is presumably organic matter released through microbial activities (Orhon et al., 1991).

4. BIOLOGICAL TREATABILITY STUDIES

4.1 Process Stoichiometry and Process Kinetics in Aerobic Systems

4.1.1 Process stoichiometry in aerobic systems

Removal of substrate in aerobic systems is related with mechanism of biomass production and amount of consumed oxygen. The excess sludge that was generated in these systems have to be throw from the system. Yield coefficient is major model component to explain oxygen consumption and excess sludge generation. Yield coefficient point out amount of biomass production per amount of organic substrate removal. Growth process and endogenous decay process are basic major concept which are directly related with yield coefficient.

Yield coefficient concept are used as two different type coefficients. These are real yield coefficient and net yield coefficient. In growth process, the numerical relationship between biomass and substrate are determined by real yield coefficient. The link between net yield coefficient and real yield coefficient are shown in Figure 4.1.

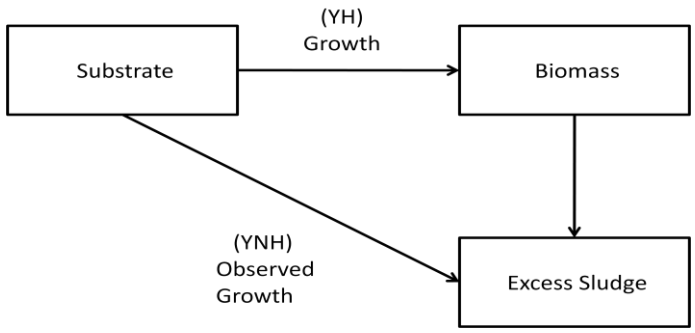

Figure 4.1: Relationship with net yield coefficient and real yield coefficient (Orhon et al, 2009).

Yield coefficient are calculated in formulation **(4.1)**.

$$Y_H = \frac{\text{Oxygen equivalent of synthesized biomass}}{\text{Oxygen equivalent of decomposed substrate}} \qquad \textbf{(4.1)}$$

In heterotrophic growth, because of oxygen equivalent are determined with COD parameter, Y_H could also be defined as **(4.2)**;

$$Y_H = \frac{\text{COD of synthesized biomass}}{\text{COD of decomposed substrate}} \quad \textbf{(4.2)}$$

4.1.2 Process kinetics in aerobic systems

4.1.2.1 Microbial growth

Microbial growth rate is shown as the following differential **(4.3)** equation.

$$\frac{dX}{dt} = \mu X \quad \textbf{(4.3)}$$

In this equation X and μ are defined as;

X= Biomass concentration [M (biomass)/L^3]

μ=Specific growth rate [T^{-1}]

In activated sludge systems growth process, Monod model is most common model which is used. Specific growth rate (μ) is defined with the equation **(4.4)**.

$$\mu = \mu_{\max} \frac{S}{K_S + S} X \quad \textbf{(4.4)}$$

In this equation;

$\hat{\mu}_H$ = maximum specific growth rate [T^{-1}]

K_S= Half saturation constant [M (substrate)/L^3]

S= Substrate concentration [M (substrate)/L^3]

If microbial growth and substrate removal equations are written together **(4.5)**,

$$\frac{dX}{dt} = \mu_{\max} \frac{S}{K_S + S} X \quad \textbf{(4.5)}$$

equation is obtained.

If definition of growth is composed with substrate removal and microbial growth **(4.6)** equation is obtained.

$$\frac{dX}{dt} = -Y\frac{\mathrm{dS}}{\mathrm{dt}} \qquad \textbf{(4.6)}$$

In equation **(4.6)**, yield coefficient is shown as unit of growth per unit substrate removal rate.

4.1.2.2 Kinetics of particular substrate removal

Mechanism of particular substrate removal is occurred at three steps.

- Adsorptions and storage,
- Disruption of complex organic molecules by enzymes,
- Absorption and synthesize.

Owing to extracellular enzymes on the microorganisms surface, storage substrate is hydrolyzed and turned into soluble form. Finally soluble substrates are adsorbed by biomass (Okutman, 2001).

4.2 The Aim and Object of the Research

The aim of the research is to characterize the metal surface coating application industry wastewater and to evaluate the efficiency of the potential wastewater treatment system.

The object of this research;

1. To determine the processes that cause wastewater production,
2. To characterize wastewater of the metal fihishing industry,
3. To analyze treatability of wastewater by chemical and biological methods,
4. To evaluate the efficiency of wastewater treatment plant units, in the light of experimental result.

5. MATERIALS AND METHODS

5.1 General Information About the Industry

The metal finishing industry that this study is conducted is located in Bolu, Turkey. Approximately 1961 staff are working in the factory. Although the number of shifts in the factory is flexible it is generally two. The annual production capacity of the facility in 2011 was 2,108,664 pieces.

Domestic wastewater and industrial wastewater are two types of wastewater streams that come from the production process. Industrial wastewater is first subjected to chemical treatment and then followed by the biological treatment. Domestic wastewater is only treated by biological activated sludge system. After the treatment processes two types of wastewater flows are discharged to receiving media together. The parameters concentrations in the treated wastewater has to be below the Water Pollution Control Regulation's limits.

The water requirement of the factory is supplied from well water. Green area in the factory is approximately 0.02 square kilometer and this area is watered with well water. In the production processes, painting and enamel processes are the most intense pollution sources for the wastewater treatment plant.

In Table 5.1, amount of consumed water and produced wastewater were given for the last four years. In 2010 and 2011 even if an increase in consumed water was observed; actually production capacity in the facility was increased by 7.5%. As shown in Table 5.1, a significant increase in water consumption per product was not observed for the last four years.

Table 5.1: Amount of consumed water and produced wastewater.

Year	2008		2009		2010		2011	
	[m^3]	[m^3/pr]	[m^3]	[m^3/pr]	[m^3]	[m^3/pr]	[m^3]	[m^3/pr]
Consumed Water	239,445	0.12	206,010	0.11	240,492	0.12	266,087	0.12
Produced Wastewater	205,920	0.10	135,002	0.07	171,770	0.09	190,940	0.08

Water obtained from wells are used in the processes after treating with reverse osmoses process. The deionized part of water are called softened water, while the raw part of water are called hard water. The deionized water is used in painting, enamel processes and cafeteria. The details about the sources of consumed water in the facility are shown in Figure 5.1.

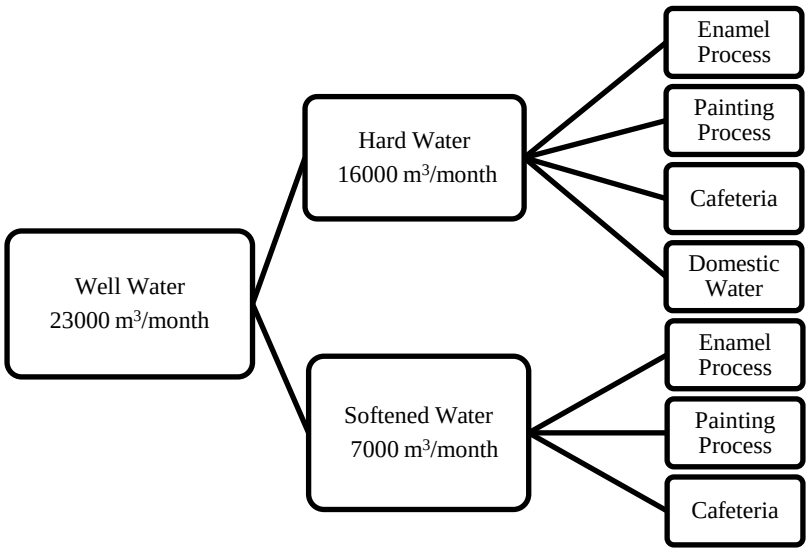

Figure 5.1: Well water usage in the facility.

In Table 5.2, the amount of domestic and industrial wastewater in the last four years were shared. Both of industrial and domestic wastewater amount seemed to increased but in the reality it is related with amplification of the production rate and workers number. In contrast to increase in total amount of wastewater, amount of wastewater per product was decreased (Table 5.1).

Table 5.2: Total amount of produced industrial and domestic wastewater.

Year	Domestic Wastewater	Industrial Wastewater	Total
	[m^3]	[m^3]	[m^3]
2009	67,002	68,000	135,002
2010	73,320	98,450	171,770
2011	76,440	114,500	190,940

Industrial wastewater and total discharged wastewater are measured automatically by flow meter. Additionally, domestic wastewater flow rate was calculated by subtracting the total amount of industrial wastewater discharged from overall wastewater generated.

Classification of domestic and industrial wastewater sources were described in Figure 5.2. Approximately 20 m^3 and 15 m^3 wastewater reaches to the treatment plant from cooling tower and chiller, respectively (Figure 5.2). This wastewater flows can be expressed as out of process wastewater.

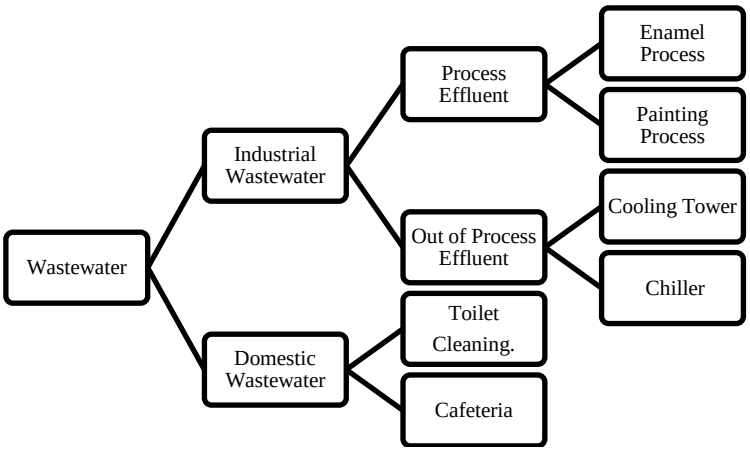

Figure 5.2: Classification of domestic and industrial wastewater sources.

5.2 Evaluation of Water Consumption-Process in the Facility.

Each piece produced in the industry is subjected to degreasing process, rinsing, nanoceramics coating and deionization rinsing process, consecutively. Finally, the pieces become ready to the painting process. In this process, there are water consumption and wastewater production. The details about processes were shared below.

Surface Pre-Treatment Process: In this process, all sheet metal pieces, coming from mechanical production or sub- industry are cleaned and coated with nanoceramics material. Without considering painting type, firstly sheet metal pieces have to be exposed to this treatment.

Enamel Process: In the facility, there are two different enamel coating unit. They are called as Enamel Process 1 and Enamel Process 2. This application, which is used to bring more thermal resistance, is inert surface coating technology. Stages of enamel process were schematized in Figure 5.3. There are two degrasing and two rinsing stages in the process. But in addition to this, there are also enamel coating stage. Wastewater is not produced at this stage. Thus, enamel coating stage have not been shared in this figure. The wastewater that comes from degreasing stages have been treated at batch treatment unit, while wastewater of rinsing stages have been treated

at continuous treatment unit. Pollution load of degreasing wastewater was higher than rinsing wastewater in terms of oil and COD parameters.

Painting Process: In the painting process, product parts which are exposed to heat (200°C) are painted. The parts subjected to surface treatment, drying, painting and cooking operations, consecutively. The painting process is varied by paint color or speciality. Silver process, white-black process and antifinger process are in the painting process. Silver and white-black process are varied by paint color, while antifinger process have been related paint speciality. The products which were passsed from antifinger stages, become stainproof of fingerprint.

As shown in Figure 5.3, degreasing wastewater and first hot rinsing wastewater of silver process are treated at batch treatment, while the first and second rinsing wastewater are treated at continuous treatment.

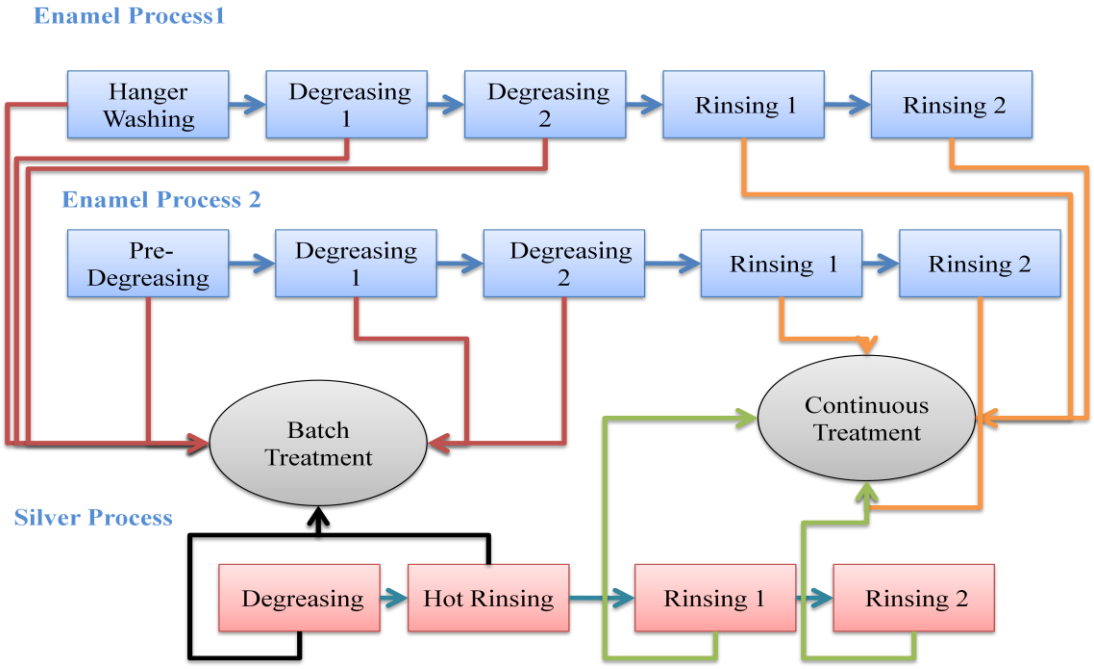

Figure 5.3: Wastewater flows arriving to the wastewater treatment plant from enamel and silver process.

Details of white-black and antifinger process are schematized in Figure 5.4. As shown this figure, wastewater that comes from two degreasing, second and third rinsing and de-ionized stages of white-black process are treated at batch treatment, while wastewater that comes from first rinsing, pre-deionized and bonderite stages are treated at continuous treatement.

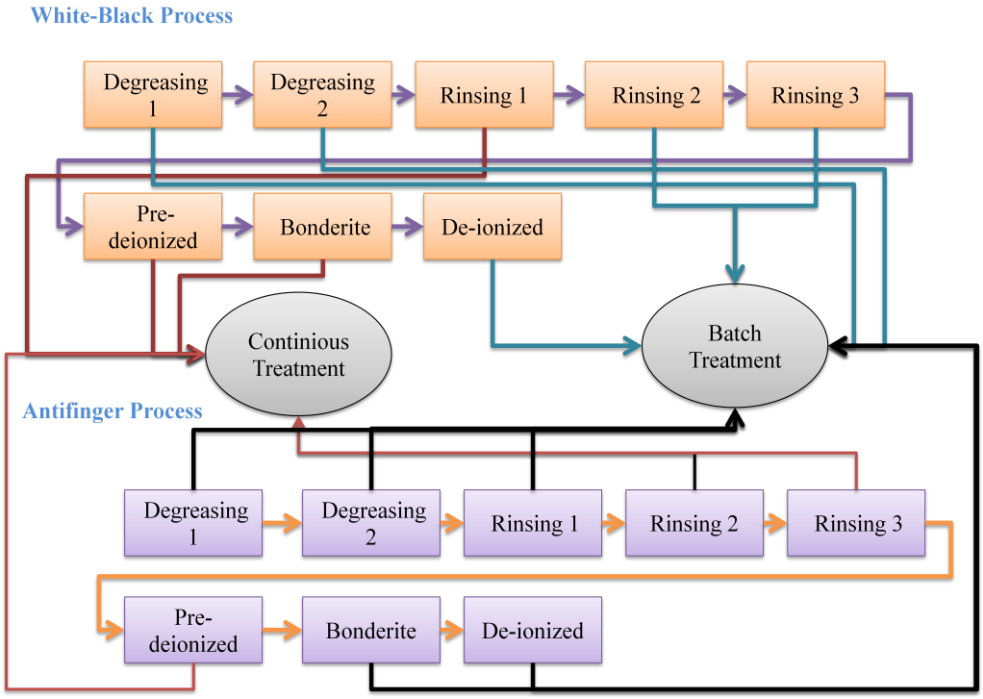

Figure 5.4: Wastewater flows arriving to wastewater treatment plant from painting process.

Finally, wastewater that comes from two degreasing, first rinsing, bonderite and deionized stages of antifinger process are treated at batch treatment and the other wastewater sources of antifinger process are treated at continuous treatment.

Powder Painting: In powder coating process, the pieces that come from pre surface treatment process, are painted under dried condition. Powder painting is done by paint guns automatically. In the facility, this type of painting process have also been implemented. There is no water consumption or wastewater production in this process.

As drying oven and powder painting oven, there are two types of drying oven in the process. Drying Oven; the pieces that are treated in surface treatments line, are dried in this oven. There is no water consumption or wastewater production in this process. Powder Painting Oven; after coating process, the pieces that are coated with powder paint are exposed to drying oven.

Details about domestic wastewater sources in the facility were described in Figure 5.5. As shown in the figure, there are generally three different types of wastewater sources.

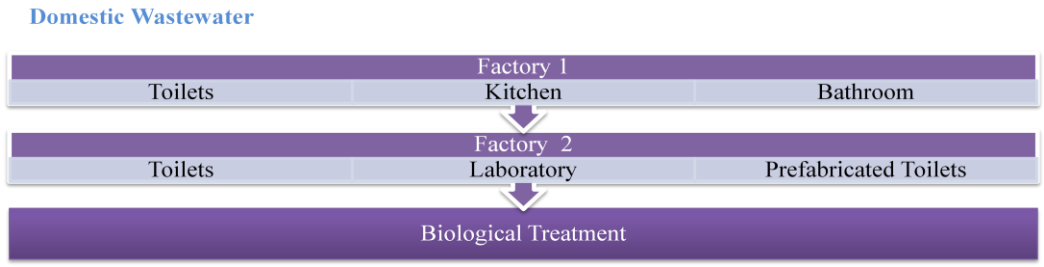

Figure 5.5: Domestic wastewater sources in the factory.

5.3 Basic Knowledge About the Wastewater Treatment Plant

5.3.1 Industrial wastewater treatment process

Industrial wastewater treatment process was schematized in Figure 5.6. Firstly, in order to homogenize the wastewaters, the painting and enamel wastewaters are collected in the equalization tank in batch treatment process. The sink mixers is used to mix wastewaters in the tanks. In the reaction tank, HCl and $FeCl_3$ solutions was added into the mixed wastewater for pre-oxidation. Because oil concentration of that type wastewaters is very high, the wastewater was send to the flotation unit after the reaction tank. After that, the wastewater was exposed to neutralization, coagulation and flocculation processes. The wastewater that is treated at batch treatment process, is directed to continuous treatment process and then to the industrial biological treatment porcess. The industrial biological treatment prosess is composed of activated sludge system.

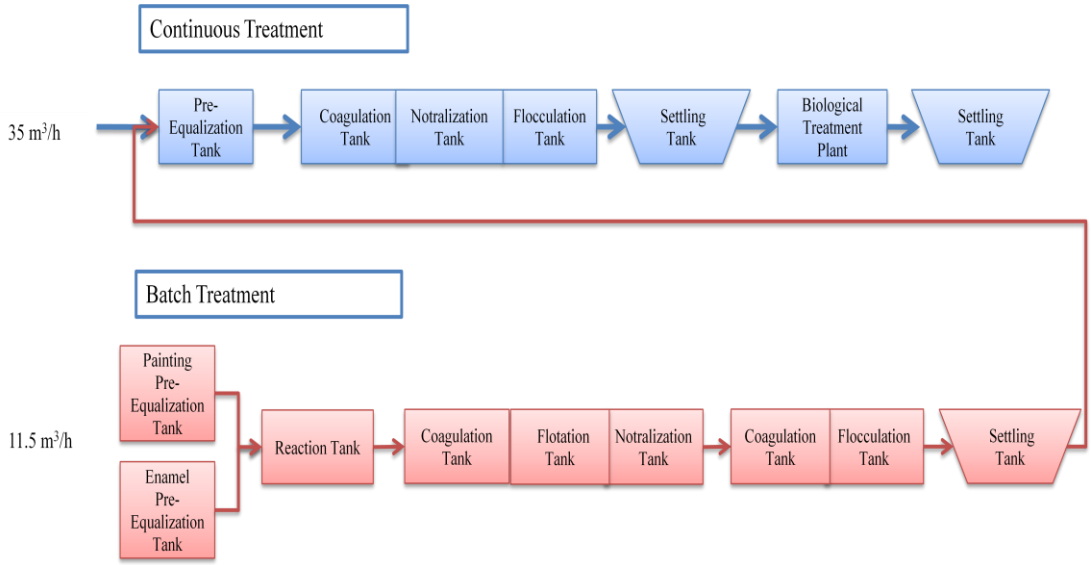

Figure 5.6: Units of industrial treatment plant.

5.3.2 Domestic wastewater treatment process

Domestic wastewaters are treated by biological activated sludge process. The simplified schema of the process is shown in Figure 5.7. The air required for biological treatment process, meets also the mixing requirement in the aeration tank. Domestic wastewater is directed to the settling tank to separate wastewater from the sludge.

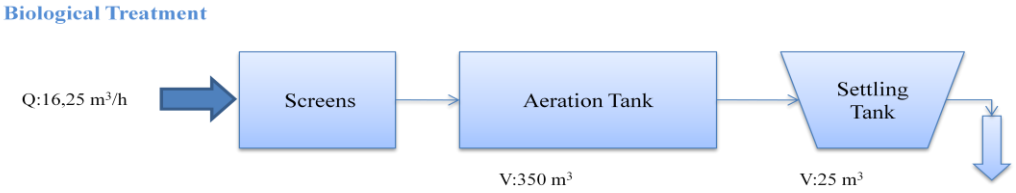

Figure 5.7: Biological treatment units for domestic wastewater.

If processes of the wastewater treatment plant are summarized, as shown in Figure 5.8, the industrial wastewater and domestic wastewater are treated separately.

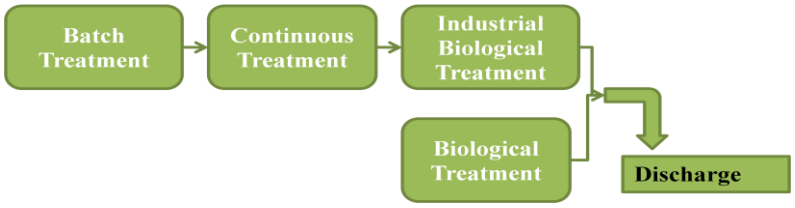

Figure 5.8: Simplified representation of wastewater treatment process.

In Table 5.3 and Figure 5.9, amount of chemical consumption in the wastewater treatment plant were shared. As shown in the table, five types of chemical are used in the plant. But predominatly HCl, NaOH and $FeCl_3$ have been used. When the amount of the consumptions in the last three years were compared, it was observed that the amount of consumed chemicals have not been increased significantly.

Table 5.3: Chemical consumption in the wastewater treatment plant.

Year	2009		2010		2011	
Chemical Name	Amount	Unit	Amount	Unit	Amount	Unit
HCl	94,800	[Kg]	111,880	[Kg]	143,380	[Kg]
NaOH	59,860	[Kg]	73,120	[Kg]	71,140	[Kg]
$FeCl_3$	56,590	[Kg]	43,800	[Kg]	39,060	[Kg]
Lime	18,750	[Kg]	2,500	[Kg]	5,000	[Kg]
Polyelectrolyte	100	[Kg]	100	[Kg]	100	[Kg]
Industrial Wastewater treated	68,000	[m^3]	98,450	[m^3]	114,500	[m^3]

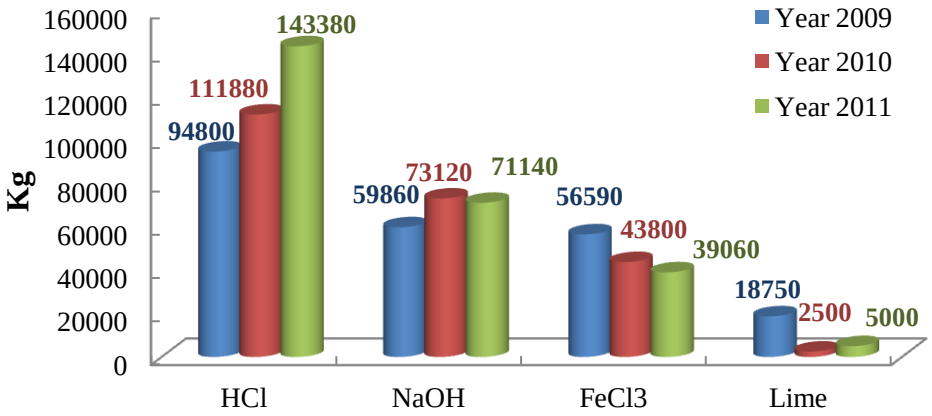

Figure 5.9: Chemical consumption in the wastewater treatment plant.

In the treatment plant, the treated domestic and industrial wastewater are combined and discharge to the Kuruçay River as a receiving medium. Because of discharge point, the facility have to be comply with discharge limits of Water Pollution and Control Regulation as given in Table 5.4.

Table 5.4: Water pollution and control regulation discharge limits.

Parameters	Unit	Water Pollution and Control Regulation Discharge Limits
Ammonium nitrogen (NH_3-N)	[mg/L]	20
Suspended Solid (SS)	[mg/L]	125
Fluoride	[mg/L]	50
Chemical Oxygen Demand (COD)	[mg/L]	100
Nitrite Nitrogen (NO_2-N)	[mg/L]	5
pH	-	6-9
Oil-Grease	[mg/L]	20
Aluminum (Al)	[mg/L]	2
Copper (Cu)	[mg/L]	2
Zinc (Zn)	[mg/L]	2
Iron (Fe)	[mg/L]	3
Cadmium (Cd)	[mg/L]	0.2
Chrome (Cr^{+6})	[mg/L]	0.5
Total Chrome	[mg/L]	2
Lead (Pb)	[mg/L]	1
Nickel (Ni)	[mg/L]	2
Toxicity	[mg/L]	4

5.4 Sampling

The sampling points were schematized in Figure 5.10. In the wastewater treatment plant, seven sampling points were chosen to take wastewater samples. These points are;

- Rinsing pre-equalization tank,
- Painting pre-equalization tank,
- Enamel pre-equalization tank,
- Effluent water of batch treatment plant,
- Influent water of domestic wastewater treatment plant,
- Effluent water of domestic wastewater treatment plant,
- Effluent water from discharge point.

In addition to these sampling points, during four days, activated sludge samples were taken from industrial and domestic biological treatment system.

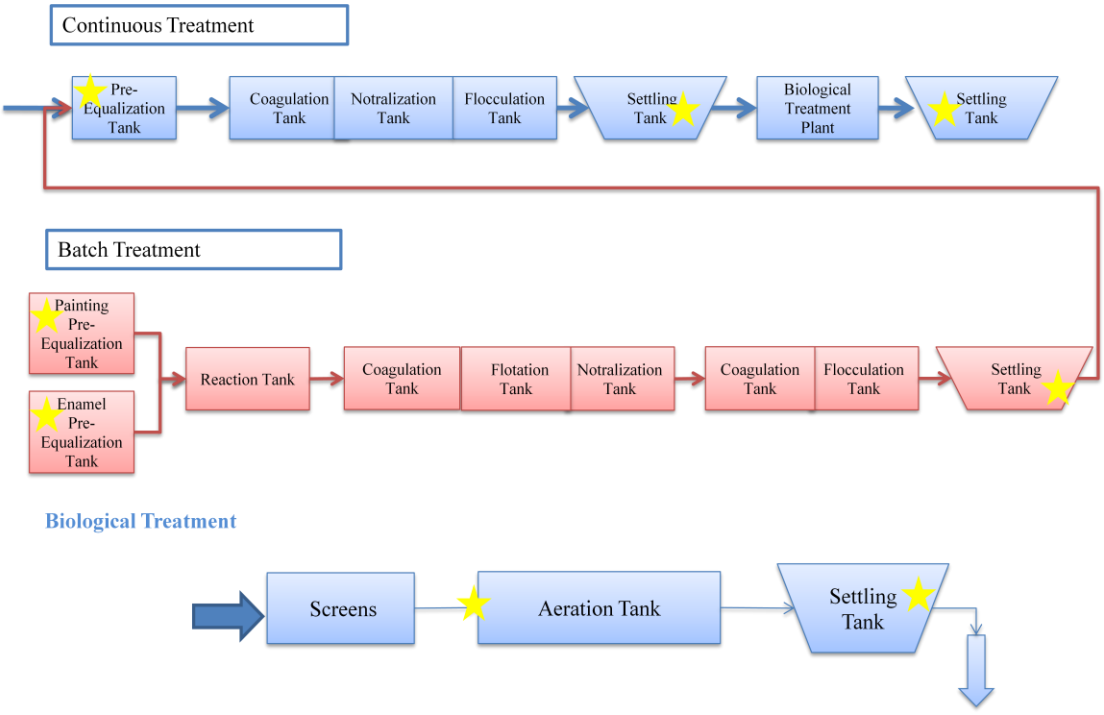

Figure 5.10: Sampling points in the wastewater treatment plant.

Details about sampling type and period were described in Table 5.5. The first sample was taken from the same sampling points, at the same time, in four day long. The other three samples were taken as composite sample. Generally, the volumes of samples taken were varied between 12 L and 15 L.

Table 5.5: Details about sampling period and type.

Sample No	Season	Date	Time	Sampling Type
1	Spring	09.12.2012 09.13.2012 09.14.2012 09.15.2012	14:00-14:25*	Grab Sampling
2	Winter	01.18.2012	08:00-18:00	Composite Sample
3	Winter	03.07.2012	11:00-17:00	Composite Sample
4	Spring	04.25.2012	09:00-17:00	Composite Sample

*Samples were taken everyday in the same time

5.5 Analytical Methods

5.5.1 Conventional parameters

In the experiments, pH, Suspended Solid (SS) and volatile suspended solids (VSS) analysis were performed as defined in the Standart Methods (AWWA,2005).

The COD samples were filtered through 0.45 μm membrane filters and performed as described in the ISO 6060 method (ISO 6060, 1989). pH measurements were performed by a Orion 520 Aplus pH meter (USA).

5.5.2 Ion chromotography

Nitrate, nitrite and phosphate concentrations were determined using a Dionex ICS-1500 ion chromatography unit (Dionex Corporation, Sunnyvale, CA) equipped with a conductivity detector, a Dionex IonPac AG14A (4×50 mm) guard column, and a Dionex IonPac AS14A (4×250 mm) analytical column. The unit was operated in autosuppression mode with 1 mM $NaHCO_3$:8 mM Na_2CO_3 eluent with a flow rate of 1 mL/min. All standards and samples were filtered through 0.2 μm membrane filters prior to injection. The minimum detection limits for nitrate, nitrite and phosphate were 0.8, 0.8 and 1.6 mg/L, respectively.

5.5.3 Oil and Grease

The soxhlet extraction method was used in the analysis (AWWA, 2005). The sample is placed in a porous extraction thimble and immersed in the solvent. The extraction comprises a series of batch processes involving distillation and condensation of the solvent along with periodic fill-in and siphoning of the solvent in and out of the extraction chamber. This causes an intimate mixing of the sample with the solvent.

The extraction also requires a relatively large quantity of solvent and usually a pre-concentration step is necessary. During each cycle, a portion of the nonvolatile compound dissolves in the solvent. After many cycles, the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.

After extraction the solvent is removed, typically by means of rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded. The oil and grease is expressed as milligrams per liter as given in the following equation **(5.1)**.

$$Q\&G(mg/L) = \frac{(\mathrm{A} - \mathrm{B}) \times 1000}{\mathrm{V}_{\mathrm{sample}}} \qquad \textbf{(5.1)}$$

Where,

A: weight of the container after distillation [g]

B: weight of the clean container

5.5.4 Fish bioassay

Fish bioassay analysis were performed as defined in the Standart Methods (AWWA, 2005). Effluent wastewater taken from the wastewater treatment plants was diluted in certain volume percentages (25%, 50% and 100%) and the mortality of lepistes (*Poecilia reticulate*) was monitored after 48 h of incubation period at ambient temperature. In the monitoring period, the air and food which are required for the fish have been supplied.

5.5.5 Atomic absorption spectrophotometry

The aqua regia method involving concentrated HNO_3 and HCl (1:3 proportion) (EPA-ROC, 1994) and using a conical beaker heated on a hot plate was used as the standard method to digest the samples for the total analysis of Cd, Cr, Cu, Ni, Pb, and Zn. Samples were analyzed on a flame atomic absorption spectrophotometer (AAS) (CONTRA 700 Model) (Analytik Jena, Germany) after calibration with suitable standards.

Cr^{+6} quantification: Samples were prepared for analysis firstly by adjusting the pH of the samples to 9.0 and thereafter the samples were allowed to precipitate in the form

of Cr^{+3} hydroxide. After settling, the mixture was immediately filtered to eliminate the sludge formed (Ölmez, 2009). Chromium was analyzed in the filtrates by atomic absorption spectroscopy using a CONTRA 700 Model atomic adsorption spectrophotometer after prepearing the samples according to the Standard Methods (EPA-ROC, 1994) . The filtration of the samples was carried out using 0.45 μm PVDF syringe Millipore (USA) filters.

5.5.6 Microscobic analysis with gram staining

Some bacteria species are very important to show the treatment efficiency for activated sludge systems. If there are some problems (bulking, foaming etc...) about activated sludge systems, microbial analysis methods are very important to determine the main solution. In this research, gram staining method has been used. The Gram stain differentiates Bacteria as Gram positive and Gram negative based on their cell wall structure. The first stain, crystal violet, forms complex with Gram's iodine solution. Subsequent rinsing with alcohol dehydrates the Gram positive cells causing the pores to close, thus the complex is retained and a darkly stained specimen results. In Gram negative cells, alcohol penetrates the lipid-rich outer layer and the complex is easily removed leaving these cells colourless. Gram negative cells are then counterstained with Safranin, providing a colour contrast.

5.6 Chemical Treatability Studies

Chemical treatiability of the wastewater with optimum chemical (coagulant) dossage was identified using alum, iron (III) chloride and lime where optimum pH and coagulant dosage were determined.

The test was performed using F105A0112 Velp Jar Test Type FC6S (U.K). The jar test set is means to estimate the coagulant dosage and the effective pH regions, and to explore the use of polymers with respect to the type and dosage. The jar test system consist of six jars, about 1000 ml in size. The system permits all six jar to be controlled simultaneously (e.g. start and stop and rational speed of paddles).

Different dosages of coagulant are added to the respective jars to determine the optimum dosage range. The coagulant was added simultaneously after the rapid mixing is started. First the samples were mixed rapidly for 3 min at 100 rpm and then about 15-20 min slow mixing to simulate flocculation followed by 30 min settling.

The turbidities, COD and heavy metal (Al, Zn, Fe, T.Cr) concentrations of the supernatants were measured. The settled sludge amount were measured using graduated cylinders.

5.7 Determination of Initial Inert COD

Initial inert COD components of the three type of influent wastewaters generated form painting process, enamel process and rinsing process were assessed. The first three reactors were fed with raw wastewater and the other three reactors were fed with filtered wastewater (Table 5.6). The same seed taken from industrial activated sludge aeration tank, was used in all the reactors.

As explained above, six batch reactors were prepared. The reactor volumes were chosen as two liters. The filtered wastewater used in the reactor was the filtrate from 0.45 μm membrane filter.

After the addition of solution A and B pH was adjusted to 7 with 1 N H_2SO_4 or 1 N NaOH if necessary. All the reactors were seeded with the activated sludge which is taken from activated sludge of industrial treatment, by using the minimum amount of biomass, about 30-40 mg/L VSS, in order to prevent the effect of external particulate inert interference. As shown in Figure 5.11, the reactors were aerated so that oxygen is not a rate limiting parameter.

The total and soluble COD profiles of the six wastewater reactors were monitored for a period long enough to ensure the depletion of all the biodegradable substrate and the mineralization of all biomass (i.e., until the final COD values were constant).

Table 5.6: Wastewater sources in inert COD experiments.

Reactor No	Wastewater Type
1	Raw Enamel Process
2	Raw Painting Process
3	Raw Rinsing Process
4	Filtered Painting Process
5	Filtered Enamel Process
6	Filtered Rinsing Process

Figure 5.11: Reactors of inert COD analysis.

5.8 Biological Treatability Studies

The respirometric analyses were conducted with relevant biomass seeding alone to assess biological treatability of the wastewaters as well as to reflect the activity of the activated sludge in the treatment plant. Samples with desired So/Xo ratios are added to the reactor and the OUR data was monitored and measured as mg/L.h. Experimental studies are conducted by using activated sludge from the aeration tank of industrial and domestic biological treatment units.

AppliTek Ra-Combo respirometer was used for the respirometric analyses. Nitrification inhibitor (Formula 2533TM, HACH Company) was used to prevent any possible interference induced by nitrification. Also Sol A and Sol B (Table 5.7) were added in the reactors to satisfy the requirement of trace elements for biological activity.

Table 5.7: Ingredients of solution A and B.

Solution A		Solution B	
Chemicals	**[g/L]**	**Chemicals**	**[g/L]**
NH_4Cl	120	$MgSO_4.7H_2O$	15
KH_2PO_4	160	$FeSO_4.7H_2O$	0.5
K_2HPO_4	320	$CaCl_2$	2
-	-	$MnSO_4.\ 7H_20$	0.41
-	-	$ZnSO_4.\ 7H_2O$	0.5

In respirometric analyses 1.5 L of sludge sample was put into the reactor and the b_H level was monitored for at least 15 minutes and then 1 L of wastewater was added. In order to eliminate any confusion the b_H data in the respirometric analysis results section were given as diluted by the factor of 1.5:2.5. Respirometric results were modeled using Activated Sludge Model (ASM 1) with Aquasim.

6. RESULT & DISCUSSIONS

6.1 Wastewater Characterization

The results in table 6.1 and 6.2 represent the results of the first taken grab samples, while the results in table 6.3 represent the results of fourth sample. During September month, total COD concentration of painting wastewater was approximately 190 mg/L, soluble COD concentration was 65 mg/L, and TSS was 37 mg/L. In the same sample, total COD concentration of enamel wastewater was approximately 615 mg/L, soluble COD concentration was 300 mg/L, and TSS was 146 mg/L. Total COD concentration of rinsing wastewater was approximately 155 mg/L, soluble COD concentration was 50 mg/L, and TSS was 19 mg/L. In addition to industrial wastewater characterization, total COD, soluble COD, and TSS concentrations of domestic wastewater were 675 mg/L, 360 mg/L, and 182 mg/L, respectively.

As a result of four set sampling characterization, the variability of COD concentration in the raw wastewater have drew attention. The reasons of this variability can be a result of the cleaning and maintenance activities and the variations in the production rate**.**

According to the Table 6.1 the process generating most poluted wastewater is the the enamel process. Hovewer, when the flow rate of these processes were compared, it was observed that the flowrate of enamel process wastewater is less than the others.

Table 6.1: The raw wastewater characterization- conventional parameters-1.

Wastewater Sample	pH	TSS [mg/L]	VSS [mg/L]	Total COD [mg/L]	Soluble COD [mg/L]
Painting	8.1 ± 0.2	37 ± 18	28 ± 12	190 ± 70	65 ±10
Enamel	8.5 ± 0.6	146 ±13	101 ± 11	615 ± 155	300 ± 70
Rinsing	7.7 ± 0.7	19 ± 11	10 ± 8	155 ± 85	50 ± 5
Domestic	7.3 ± 0.2	182 ± 35	166 ±28	675 ±215	360 ± 70

Phosphating process are used on steel parts for corrosion resistance, lubricity or as a foundation for subsequent coating or painting. It serves as a conversion coating in

which a dilute solution of phosphoric acid and phosphate salts is applied via spraying or immersion. As the phosphating process is eliminated, considerable amount of phosphorus pollutants in industrial raw wastewater was not expected. But the pollutants, phosphorus and nitrogen types, are analyzed in rinsing and domestic wastewater. In the results, TKN concentration of rinsing wastewater are less than 1.5 mg/L, while TKN concentration of domestic wastewater are approximately 100 mg/L. Also TP concentration of rinsing wastewater is 4 mg/L, while TP concentration of domestic wastewater is approximately 14.2 mg/L. The other pollutant concentrations of rinsing and domestic wastewater are shown in Table 6.2.

Table 6.2: The raw wastewater characterization-conventional parameter-2.

Wastewater Sample	TP [mg/L]	PO_4^{-3}-P [mg/L]	TKN [mg/L]	Ammonia [mg/L]	NO_2^--N [mg/L]	NO_3^--N [mg/L]
Rinsing	4.0 ± 1.3	<2	<1.5	<5	1.8 ± 0.6	<1
Domestic	14.2 ± 1.6	5.5 ± 1	100±5	50±14	<1	<1

The heavy metal concentrations in raw industrial wastewaters, which are shown in Table 6.3, were not very significant and they complied with the discharged regulation of "Water Quality and Control Legislation".

Table 6.3: The raw wastewater characterization-heavy metals.

Wastewater Sample	Cu	Zn	Cd	Pb	Mn	Al	T. Cr	Cr^{+6}	Fe	Ni
	[mg/L]									
Painting	<0.2	1.2	<0.05	<1	<0.1	<1	<0.2	<0.2	1,06	<0.3
Enamel	<0.2	0.2	<0.05	<1	0.3	<1	<0.2	<0.2	<1	<0.3
Rinsing	<0.2	1.1	<0.05	<1	0.2	<1	<0.2	<0.2	<1	<0.3

In small quantities, certain heavy metals are nutritionally essential for a healthy life but they become toxic when they are not metabolized by the body and accumulate in the soft tissues (Saidi, 2010). Heavy metals only does not accumulate in the soft tissues, they accumulate in different forms in nature. Toxic effect of heavy metals are originated by two factors. These are; metal concenrations and metal types. Even small concentrations, the presence of multiple species of heavy metals shows synergetic effects. The order of toxicity of the five metals to the microbial

community was generally Cd>Cu > Pb > Zn > Cr (Saidi, 2010). For this reason, in order to decrease toxic effects, coagulation and floculation processes are required.

Recently, because of extinction in natural resources, sustainable consumption consept was generated. In this concept, methods of reuse and recycle gained importance for environmental management in industry. In the facility, reuse of the treated wastewater to irrigate garden is also an alternative that should be evaluated. According to irrigation regulation, the raw and effluent wastewater concentrations are shown in Table 6.4 & 6.5.

In Table 6.4 and 6.5 both of the raw and effluent wastewater have very high concentration of chloride, high level turbidity and conductivity. So that this wastewater can not be used to irrigate gardens without using advanced treatment method such as reverse osmosis, membrane filtration.

Table 6.4: The raw wastewater characterization to compliance with irrigation regulation.

Sample Point	Chloride	Sulphate	Floride
		[mg/L]	
Rinsing Wastewater	886+611	27.0±6	2.1±0.2
Domestic Wastewater	208±23	29±2	2.1± 0.1
Regulation Limits	<350 (Hazardous)	-	-

*Wastewater Treatment Plants Technical Methods Communiqué – Apendix 7

Table 6.5: The effluent wastewater characterization to compliance with irrigation regulation.

Sample Points	Conductivity [µs/cm]	Color [ptCo]	Turbidity [NTU]	TDS [mg/L]	Chloride [mg/L]	Sulphate [mg/L]	Floride [mg/L]
Effluent of Domestic Biological Treatment	995 ± 16	29.5 ± 4.1	15.0 ± 2.8	491 ± 17	157±3	34±1	1.2±0.023
Discharged Water	2565± 318	16.5 ± 0.6	23.0 ± 6.1	1253± 154	873±141	28 ± 1	2.1 ± 0.1
Regulation Limits	700-3000 (Middle Level Hazardous)	-	<2	500-2000 Middle Level Hazardous	<350 Hazardous	-	-

*Wastewater Treatment Plants Technical Methods Communiqué – Apendix 7

Characteristic of metal finishing wastewater differ from proces to process in literature. Three different research results are shared in Table 6.6. Except pH, chrome and copper parameters, the other parameter concentrations in the Sthionnopka and

collegues (2009) report have matched with laboratory results (Sthionnopka et al., 2009). On the other hand, except nitrate nitrogen concentration, the other parameters concentration in Gabaldon (2007) study, are nearly close to our results.

Table 6.6: Characterization of raw wastewater in different researches.

Parameters	(Wahaab et al., 2001)		(Sthionnopka et al., 2009).	(Gabaldon et al., 2007).
	Painting Wastewater	Phosphating Wastewater	Mixed Wastewater	Mixed Wastewater
pH	3-7.4	5.5-9	1.35	7.8-8.4
COD [mgO_2/L]	5905	2970	154	75-115
BOD [mgO_2/L]	2114	1610	<2	10-30
TSS [mg/L]	687	640	3	-
Total Phosphorus [mg P/L]	24	220	-	-
Oil &Grease [mg/L]	1470	430	-	-
SVI [mL/L] 30 min	2.5	1	-	-
NO_3-N [g/m^3]	-	-	-	700-1000
SO_4^{-2} [g/m^3]	-	-	-	6500-7500
Heavy Metals [mg/L]				
Zinc (Zn)	0.6	22	28.02	3.50-9.56
Chromium (Cr)	0.05	0.3	39.14	-
Copper (Cu)	0.05	1.05	66.72	2.53-6.97
Cadmium (Cd)	0.03	0.06	ND*	ND*
Nickel (Ni)	0.34	8.20	0.046	0.21-0.92
Lead (Pb)	0.06	0.025	1.266	ND*
Ferrous (Fe)	-	-	1.822	-
Mercury (Hg)	-	-	0.004	-
Manganese (Mn)	-	-	0.040	-

*ND: Not detected

If COD concentration in the raw wastewater characterization are compared with Wahaab and collegues (2001) study in Table 6.6, it shows that the pollutant load is less than the literature (Wahaab et al., 2001). The reason for this can be explained by the replacement of phosphating process with the nanotechnology coating application in the production process. The heavy metal concentrations in Wahaab and collegues (2001) research comply with the laboratory results.

In Table 6.7 and 6.8, the value of conventional pollutant parameters (i.e., pH, TSS, VSS, COD) in the effluent wastewater was shared. The results reflect that discharged wastewater characterization is too low according to discharge limits.

Table 6.7: The effluent wastewater characterization-conventional parameters-1.

Sample Point	pH [mg/L]	TSS [mg/L]	VSS [mg/L]	Total COD [mg/L]	Soluble COD [mg/L]
Effluent of Batch Treatment	7.1 ± 0.6	<7	<7	95 ±40	50 ± 20
Effluent of Domestic Biological Treatment	6.5± 0.2	12 ± 7	10 ± 8	40 ± 10	<30
Discharged Water	7.5 ± 0.2	19 ± 3	16± 3	60 ± 35	<30
Discharge Limits*	6-9	125	-	100	-

*Discharge limits of "Water Quality and Control Regulations" for metal finishing industry.

Table 6.8: The effluent wastewater characterization-conventional parameters-2.

Sample Point	TP [mg/L]	PO_4-P [mg/L]	TKN [mg/L]	Ammonia [mg/L]	NO_2-N [mg/L]	NO_3-N [mg/L]
Effluent of Batch Treatment	x	x	<1.5	<5	x	x
Effluent of Domestic Biological Treatment	x	11.7±0.5	x	x	1.5±0.1	53.5±2.8
Discharged Water	2.5 ±0	<2	<1.5	<5	1.4±0.1	12.2± 6.1
Discharge Limits*	-	-	-	-	5	-

*Discharge limits of "Water Quality and Control Regulations" for metal finishing industry.

After the the treatment of wastewater in the batch treatment unit, the wastewater is combined with rinsing wastewater and treated chemically at continuous treatment unit and then in biological treatment unit. For this reason effluent of batch treament unit does not have to comply with discharge regulation. But even so, effluent characterization of batch treament is close to the discharge parameters.

Besides conventional parameters, aspect of heavy metals concentration, iron concentration is also below the limits of the regulation (Table 6.9).

Table 6.9: The effluent wastewater characterization-heavy metals.

Sample Points	Cu	Zn	Cd	Pb	Mn	Fe	Ni	Al	T.Cr	Cr^{+6}	Oil& Gress
	[mg/L]										
Effluent of Batch Treatment	<0.2	1.4	<0.05	<1	<0.1	<1	<0.3	<5	<0.2	<0.2	x
Discharged Water	<0.2	0.9	<0.05	<1	<0.1	<1	<0.3	<5	<0.2	<0.2	8.4± 2.5
Discharge Limits*	2	2	0.2	1	-	3	2	2	2	0.5	20

*Discharge limits of "Water Quality and Control Regulations" for metal finishing industry.

According to the characterization results, pollution loads of the raw wastewater were not very high. For this reason, application of the chemical treatment process to the wastewater can be sufficient to decrease the toxicity effects and as well as to achive the standards limitations.

6.2 Changes in Raw Wastewater Characterization

The variation in the pH values were followed by the grab and composite samples during a year. According to the results it was observed that pH values were not changed substantially. In metal finishing industry wastewater, pH values varies from process to process. In the literature, for example accroding to Gabaldon and collegues (2007) researches (Table 6.6) pH values varies between 7.8-8.4 and this values are very close to the experimental results in Figure 6.1.

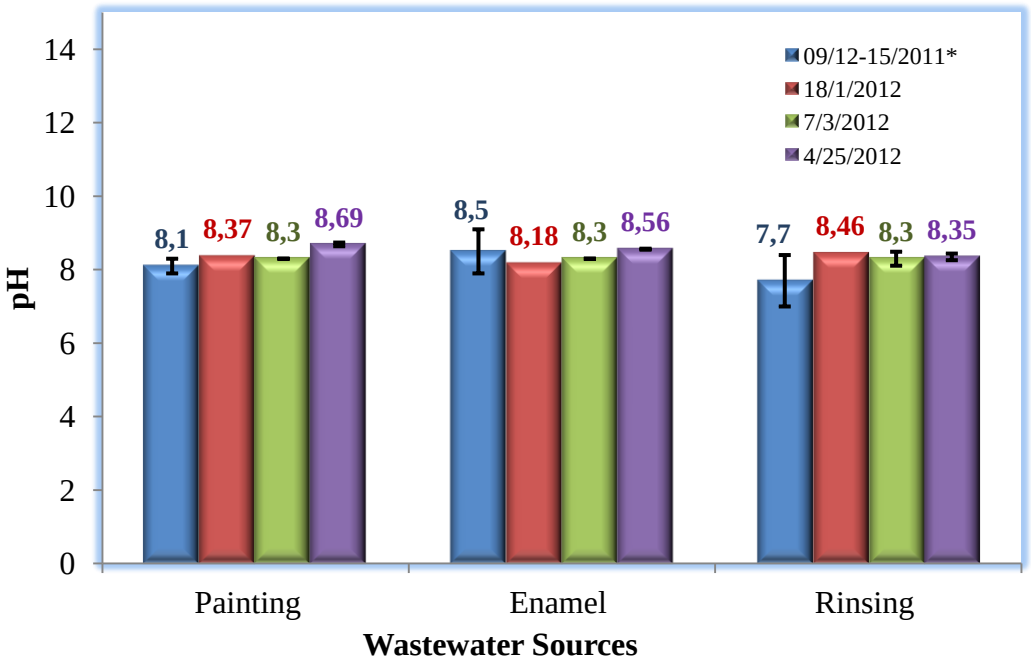

Figure 6.1: Annual pH changes in raw wastewater.

In Figure 6.2, COD concentration of three different wastewater was shared. COD concentration of painting, enamel and rinsing wastewater were 60-265 mg COD/L, 220-615 mg COD/L and 55-155 mg COD/L, repectively. Especially, COD concentration of enamel wastewater varied, but last three COD concentration was between 220-280 mg COD/L. The results showed that grab samples may also reflect particular situation in the production process. When first grab samples were taken, although production proceses were the same, COD concentration have shown variety. This situation may be because a result of the day off in the production or discharging of painting and coating baths.

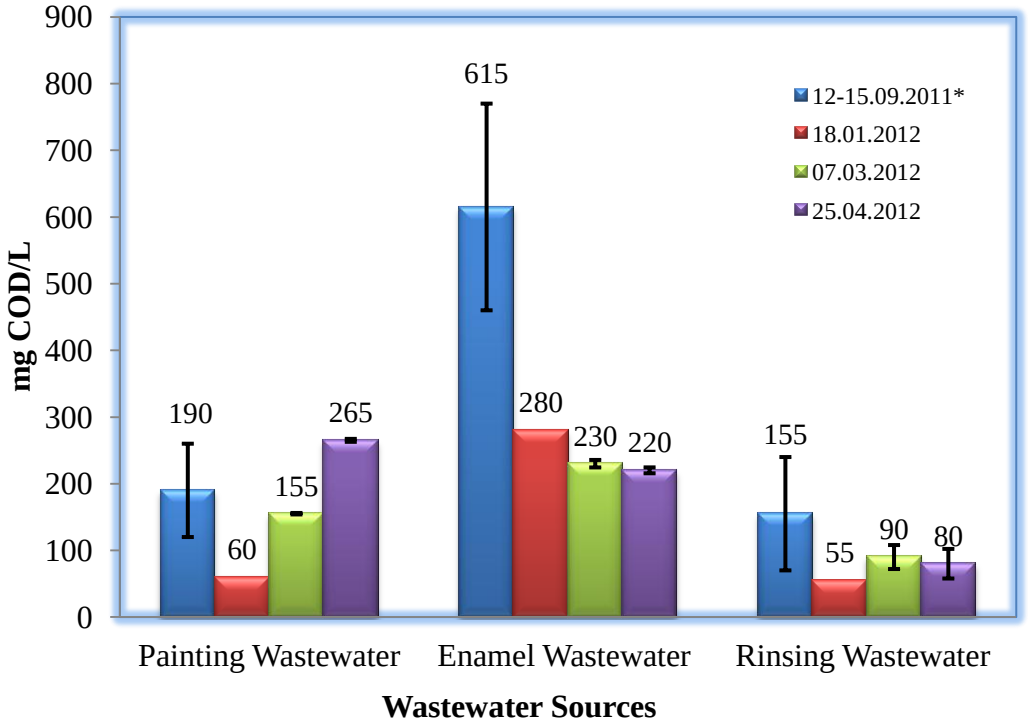

Figure 6.2: Annual COD changes in the raw wastewater (*grab samples results).

In Table 6.6, the wastewater characterization of metal finishing industry is given and facility of wastewater resources were divided into two part as painting and phosphating wastewater. The facility in this research, stopped the application of the phosphating technology a few years ago. When using phosphating process, COD concentration of mixed raw painting and enamel wastewater was between 1780-2000 mg/L. Elimination of the phosphating process have contributed to sustainable environment and decreased COD concentration.

According to the recent characterization results, the COD concentrations reported in the literature range between 75-154 mg/L, respectively (Sthionnopka et al., 2009; Gabaldon et al., 2007). If the values in Figure 6.2 compared with the values in Table 6. 6, it was observed that the values are close to each other.

6.3 COD Removal Efficiency in The Wastewater Treatment Plant

In Figure 6.3, COD removal efficiency of WWTP have been shared. Painting wastewater flowrate was three times more than enamel wastewater flowrate. In this case, COD removal efficiency of batch wastewater treatment was approximately 68%. COD removal efficiency of continous wastewater treatment was approximately

48%. When the flow rates originating from different processes were compared, it was observed that the flow rate of painting process is three times higher than the enamel process.

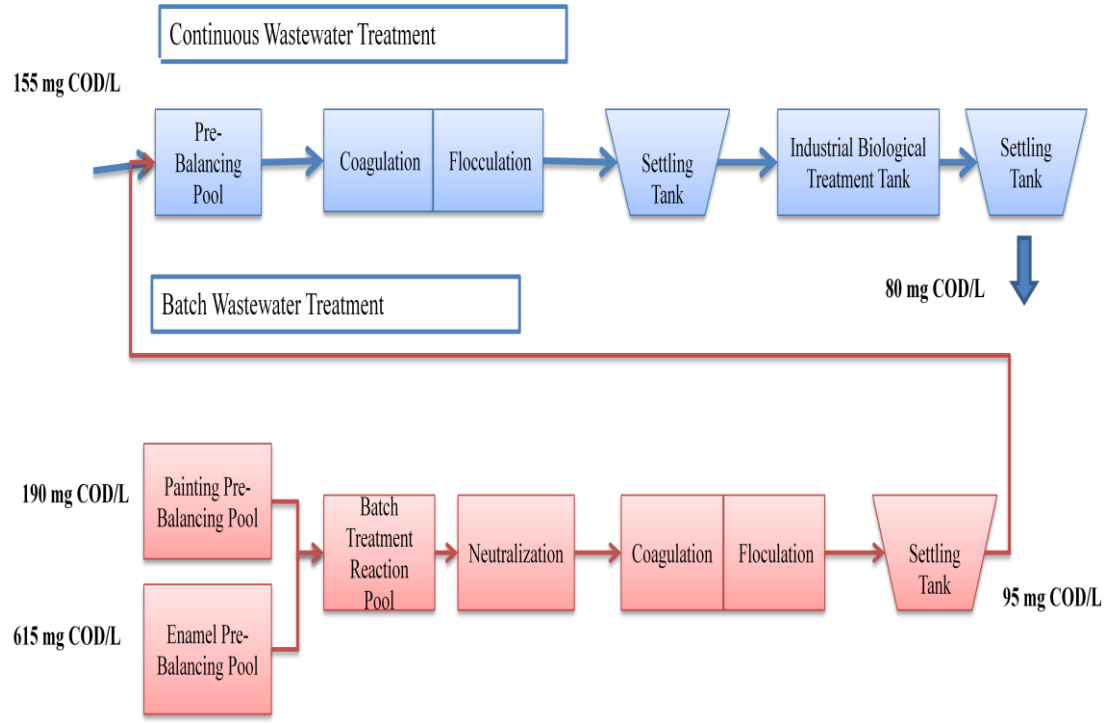

Figure 6.3: COD removal efficiency in WWTP.

COD removal efficiency in batch treatment process can be calculated as follows **(6.1)** and **(6.2)**;

$$\frac{(1\times 615)+(3\times 190)}{4} = 296.25 \cong 295 \text{mgCOD/L} \quad \textbf{(6.1)}$$

$$\frac{200}{295}\times 100 = 67.8\% \quad \textbf{(6.2)}$$

In continuous wastewater treatment process, rinsing wastewater is two times more than wastewater that comes from batch treatment process. COD removal efficiency in continuous treatment process is calculated as follows **(6.3)** and **(6.4)**;

$$\frac{(1\times 95)+(2\times 155)}{3} = 135 \text{mgCOD/L} \quad \textbf{(6.3)}$$

$$\frac{55}{135}\times 100 = 40.7 \cong 41\% \quad \textbf{(6.4)}$$

6.4 Compliance with Discharge Limitations

The results of the characterization studies were shared in previous parts. In this section of the study especially grab samples were obtained to conduct the chemical and biological treatability performances assessment experiments.

As shown in Figure 6.4, COD values of the samples which were taken during four days have been under the Regulation's limit. But in the fouth day, COD values were very close to the discharge limits. This results reflected that in the treatment plant COD values arriving to the plant may varies and this may result in the variation in the effluent concentrations. However, it should be underlined that the removal efficiencies of treatment plant secure the regulation limits.

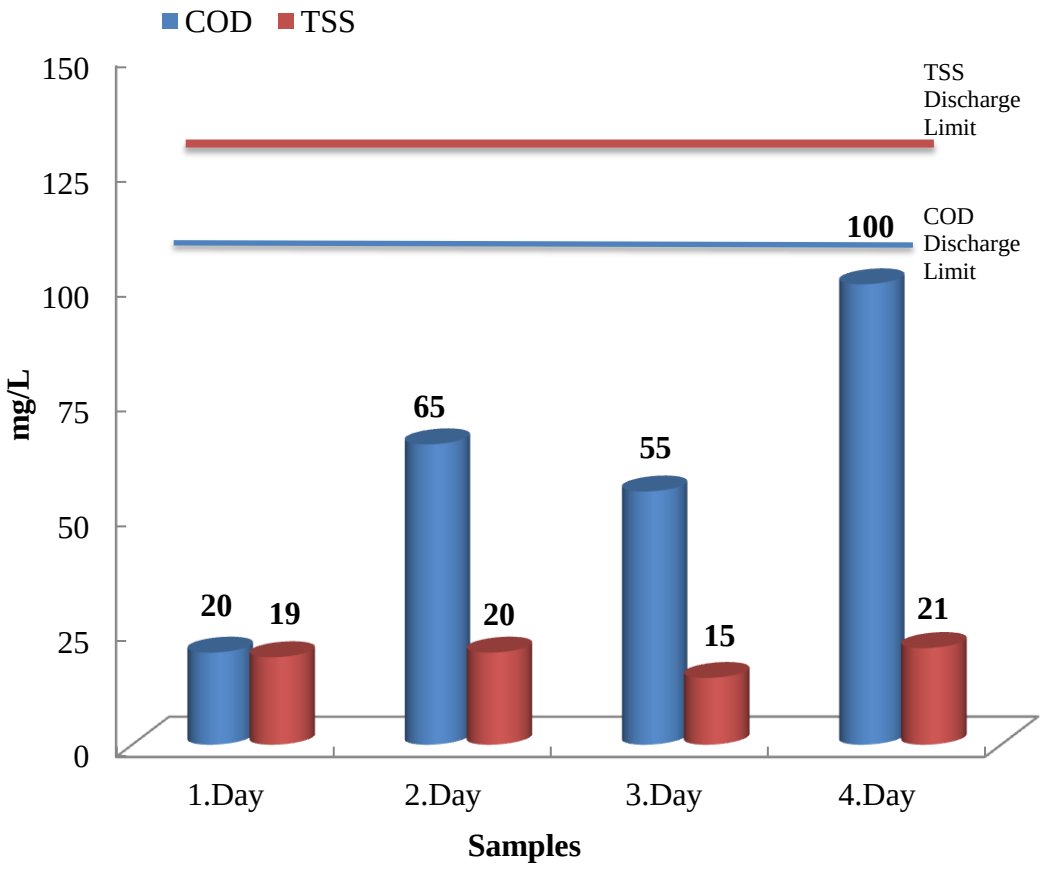

Figure 6.4: Compliance with "Water Quality and Control Regulation"-1.

In the regulations, discharged wastewater's pH value have to be in range of 7-9. As seen in Figure 6.5 the effluent wastewater pH values were in this range.

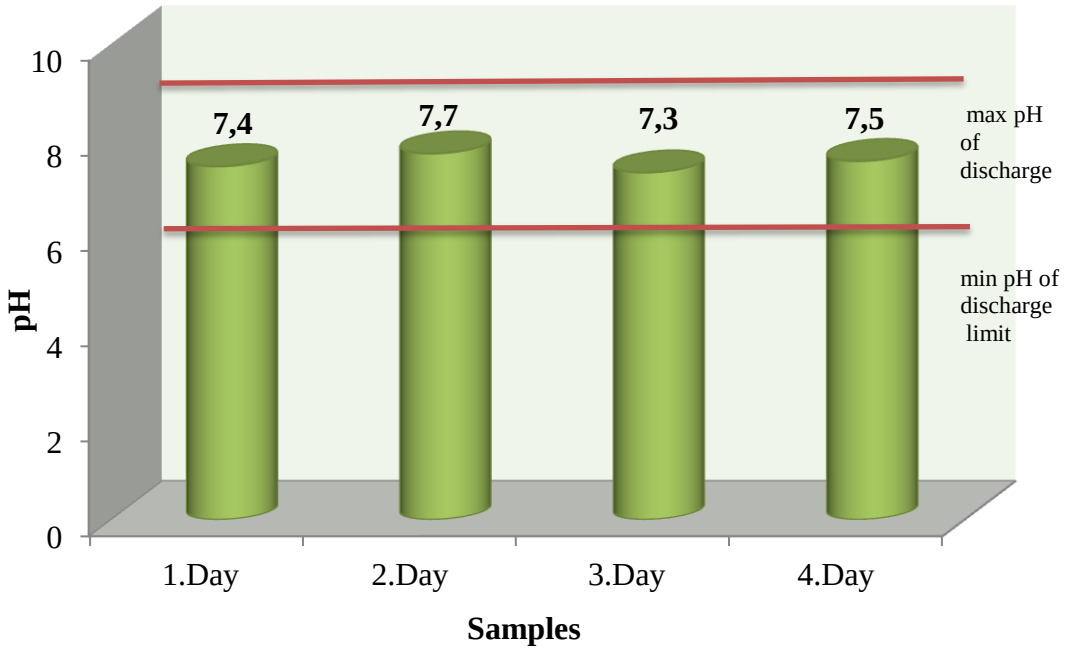

Figure 6.5: Compliance with "Water Quality and Control Regulation"-2.

Nitrite-nitrogen concentration were under the discharge limits during four days in Figure 6.6.

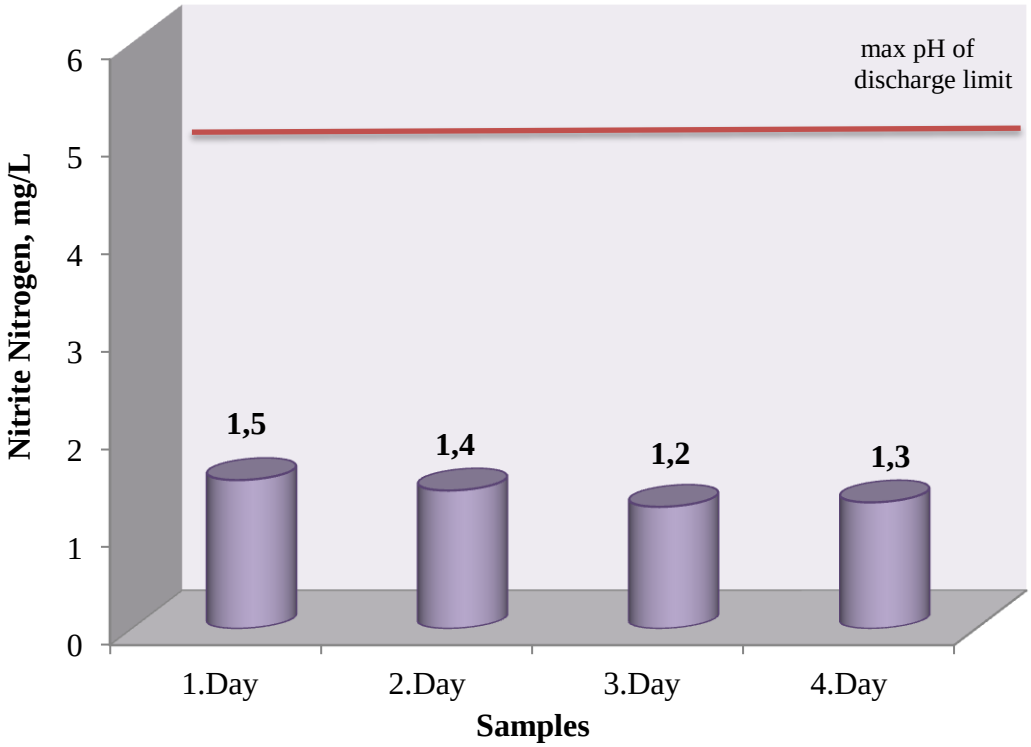

Figure 6.6: Compliance with "Water Quality and Control Regulation"-3.

Evaluation of effluent wastewater characterization have been shared in Table 6.10 where all the parameters are below the discharge limits.

Table 6.10: Evaluation of effluent wastewater characterization.

Parameter	Unit	Discharge Limit in Composite Samples	Composite Sampling Results
Chemical Oxygen Demand (COD)	[mg/L]	100	60±35
Total Suspended Solid (TSS)	[mg/L]	125	19±3
Oil and Grease	[mg/L]	20	8.4±2.5
Ammonium Nitrogen (NH_4-N)	[mg/L]	20	<5
Nitrite Nitrogen (NO_2-N)	[mg/L]	5	1.4±0.1
Total Chromium	[mg/L]	2	<0.2
Chromium (Cr^{+6})	[mg/L]	0.5	<0.2
Lead (Pb)	[mg/L]	1	<1
Cadmium (Cd)	[mg/L]	0.2	<0.05
Alumium(Al)	[mg/L]	2	<1
Iron (Fe)	[mg/L]	3	<1
Floride (F^-)	[mg/L]	50	2.1
Copper(Cu)	[mg/L]	2	<0.2
Nickel (Ni)	[mg/L]	2	<0.3
Zinc (Zn)	[mg/L]	2	0.9
Fish Toxicity (ZSF)	-	4	1
pH	-	6-9	7.5±0.2

6.5 Activated Sludge Properties in the Treatment Plants

Activated sludge MLSS and MLVSS concentrations of the industrial and domestic biological treatment processes have been followed seasonally and the results was given in Figure 6.7 and 6.8.

In winter season, organic fraction of the activated sludge of domestic wastewater treatment was calculated as 77%, in spring season this rate was increased to 87%.

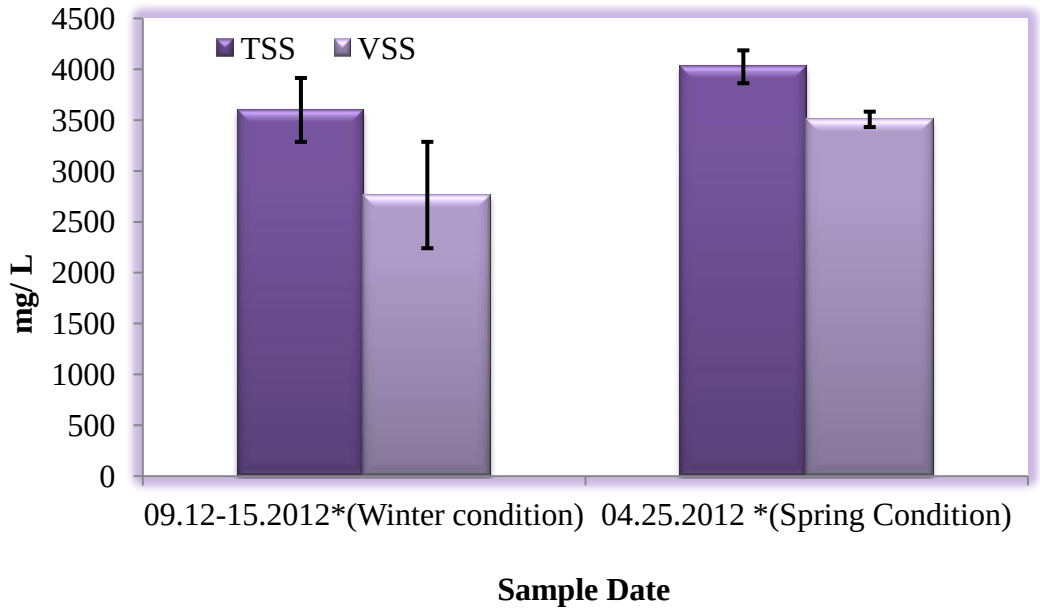

Figure 6.7: Total solid concentration of activated sludge for domestic wastewater treatment process (* grab samples results).

On the other hand, in winter season, organic fraction in activated sludge of industrial wastewater treatment was calculated as 66%, in spring season this rate was 64%. However, in March, this rate was increased to 83% because of the excess sludge feeding from biological aeration tank into the industrial treatment unit.

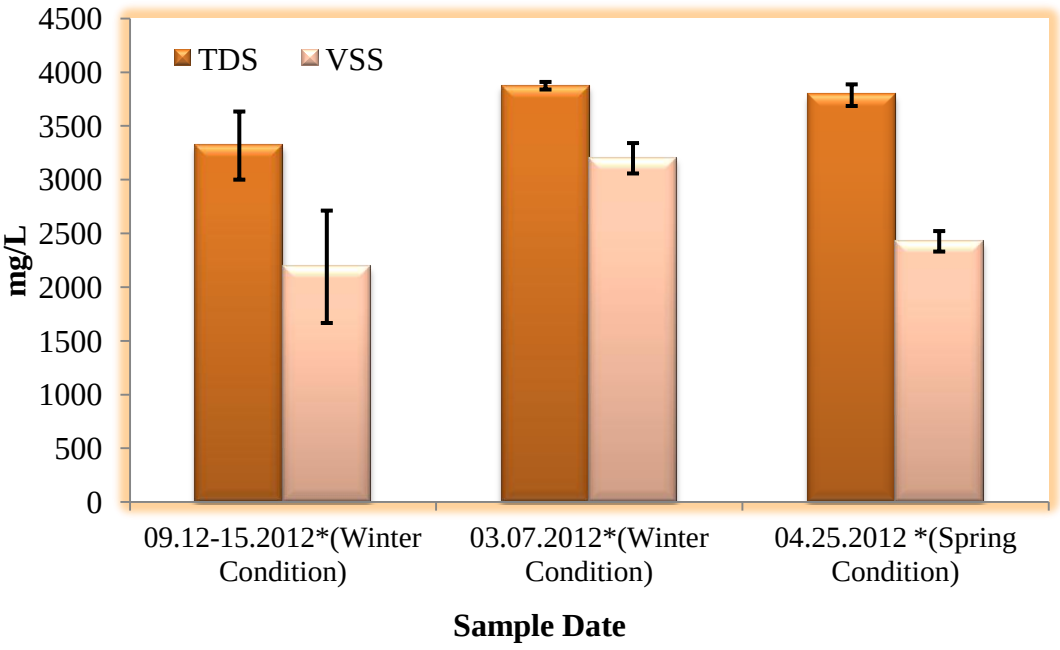

Figure 6.8: Total solid concentration of activated sludge for industrial wastewater treatment process.

6.6 Microscopic Observation of the Activated Sludge

According to the characterization studies, the industrial wastewaters which are treated chemically, have very low pollution load. In order to observe the microbial population as well as the floc structures and settling properties in the industrial wastewater biological treatment tank, activated sludge of industrial biological treatment process are examined. The results were shown in Figure 6.9, 6.10, 6.11. and 6.12. Climate of the city, where the facility is located, changes between continental climate and maritime climate. In this city, temperature difference between summer and winter season is very stricking. Temperature varies between +39,4°C to -31,5°C in the year. The activated sludge sample that was used in microscobic examination, were taken during strong winter condition.

Sludge from industrial treatment plants often display large variations in terms of the morphology of the floc. These situation can be explained with many reasons. Firstly, the floc in various industry sectors (particularly in those treating 'chemical' wastewater) is not really robust. The sludge often appears 'messy'. Also, growth of the filamentous bacteria, often results in large but markedly irregularly shaped flocs. Lastly, in fact, the normal floc quality must be establised individually for every industrial treatment plant. This must occur on the basis of the criteria below: shape, structure, strength, size and any other characteristics (Eikelboom, 2000).

According to the observations of activated sludge samples under the light microscop (Olympus BX50, Japan), the amout of the the flocs were not significant that resulted in a decrease in settling efficiency. An example of the floc structure for industrial activated sludge is shown in the Figure 4.15.

Three size classes are;

- Small flocs (diameter < 25 μm)
- Medium-sized flocs (diameter 25-250 μm)
- Large flocs (diameter > 250 μm).

Compact flocs settle more rapidly if they are larger. The floc size in a given activated sludge is considerably variable. Small flocs are nearly always present. A high percentage of small flocs (> 25%) can actually result in sludge being discharged with the effluent (Eikelboom, 2000).

The biggest floc diameter was only 219 micron (Figure 6.9) which is a medium sized flocs. But considerable amount of medium sized flocs were not observed while small flocs were very abundant in industrial activated sludge.

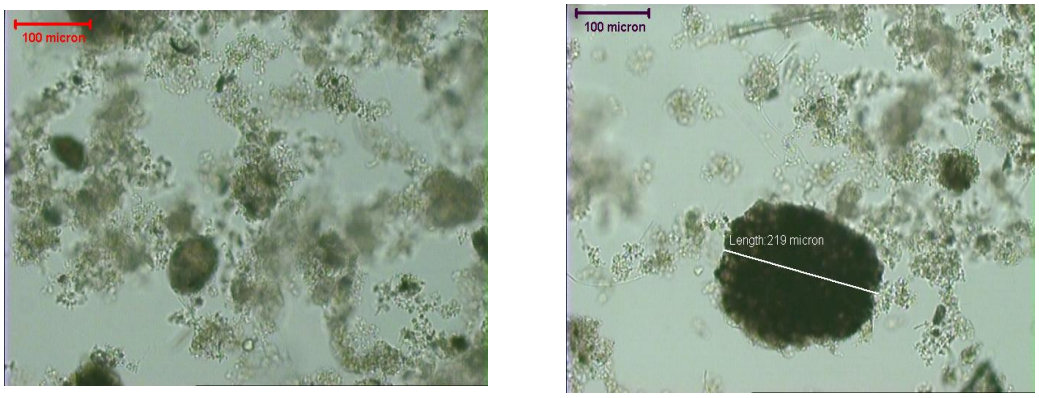

Figure 6.9: Activated Sludge from Industrial Biological Treatment Unit (sampling date 03.07.2012) (10X).

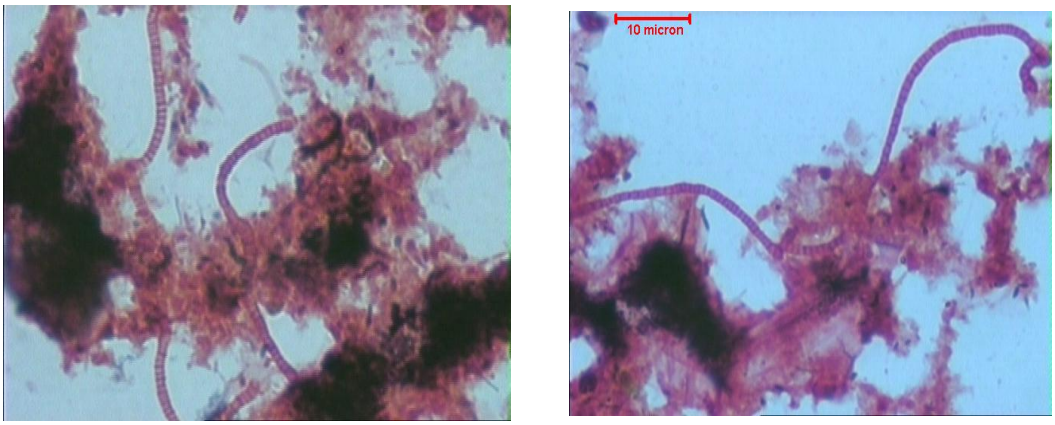

Figure 6.10: Activated Sludge from Industrial Biological Treatment Unit -Gram Staining (Sampling date: 03.07.2012) (100X).

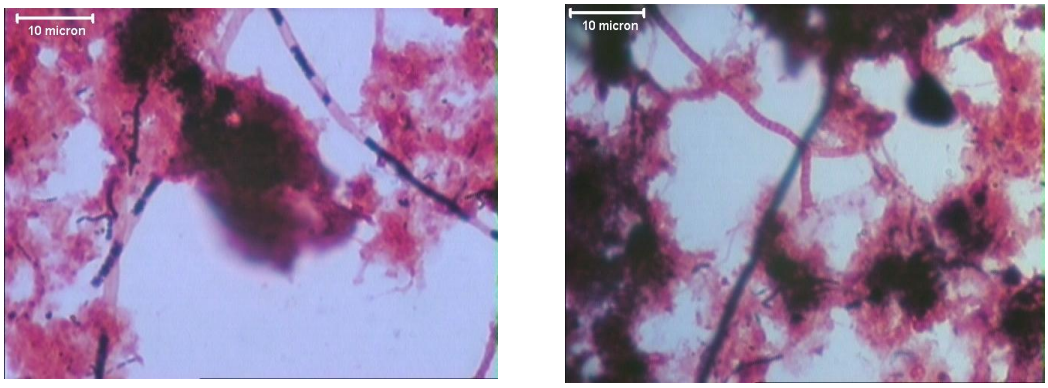

Figure 6.11: Activated Sludge from Industrial Biological Treatment Unit -Gram Staining (Sampling date: 03.07.2012) (100X).

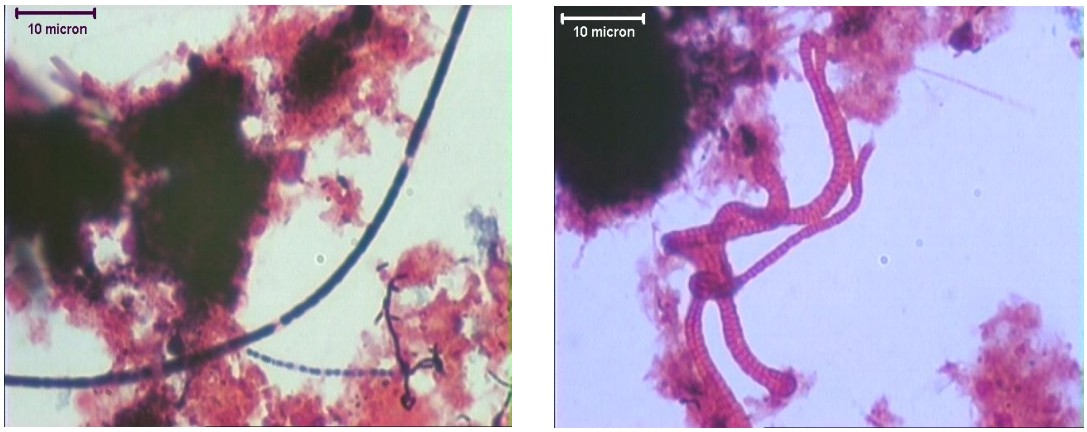

Figure 6.12: Activated Sludge from Industrial Biological Treatment Unit -Gram Staining (Sampling date: 03.07.2012) (100X).

In addition, while considerable amount of filamentous bacteria are noticed in the sludge, considirable amount of protozoa aren't observed reflecting less activity in activated sludge system. Protozoa in large numbers that are commonly associated with a polysaprobic condition where operational condition that mimics severely over loaded organic condition. The reason of the protozoa poverty can be explained also by the toxicity. Protozoa in the presence of toxic or inhibitory wastes become sluggish or inactive. The decrease in activity or termination of activity is caused by the attack of the toxic or inhibitory wastes on the enzyme systems or critical structural components of the protozoa (Gerardi, 2008). In addition, it is indicated in literature that filamentous organisms perform significant positive and negative roles in the activated sludge process. Positive roles include the degredation of BOD and the stabilization of floc formation. Filamentous organisms provide a "chain" of strength that enables floc particles to beter tolerate turbulance or shearing action and growth in size. But at the same time, when filamentous organisms are present in undesired numbers, they contribute to settleability problems in the secondary clarifier and loss of solid from secondary clarifier. In addition to these operational problems caused by filamentous organisms, some filamentous organisms produce foam (Seviour et al., 2010). Comparing these knowledge, the foamming problems observed in the plants (Figure 6.13) is a result of the excess filamentous bacteria. Excess filamentous bacteria growth is caused by low F/M ratio, nutrient concentration, pH, oxygen concentration and high sulphur concentration (Url-1). As a result of characterization studies, high pH values and low sulphur concentrations

observed in the wastewater. But foamming problems can be caused by low F/M ratio and low nutrient concentration.

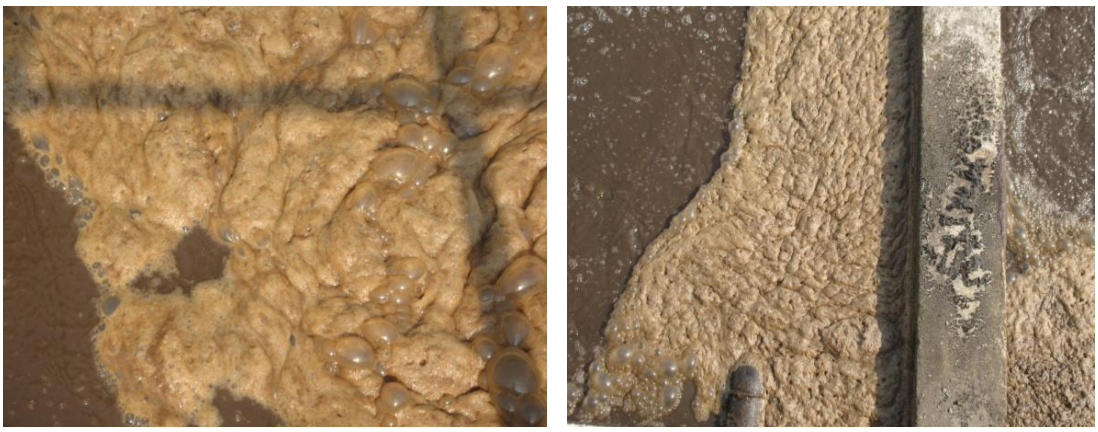

Figure 6.13: Foaming problem in the activated sluge (03.07.2012-Industrial activated sludge).

Sludge Volume Index (SVI) is an indication of the sludge settleability in the final clarifier. It is a useful test that indicates changes in the sludge settling characteristics and quality. If Sludge Volume Index (SVI) is;

<100mg/L, the settleability of sludge is good,

>100 mg/L, there is foaming sludge problem because of filamentous bacteria,

>150 mg/L, there is excessive foaming sludge problem because of filamentous bacteria.

Comparing the results in the Table 6.11 indicate that, although it is not very severe, there is foaming sludge in industrial activated sludge, while domestic activates sludge shows good performance of settleability.

The reason of these settling problems can be explained by the abudance of filamentous microorganisms as described above.

Table 6.11: Results of sludge volume index in winter conditions.

Time	Industrial Biological Treatment	SVI [mL/g]	Domestic Biological Treatment	SVI [mL/g]
30 min	350 ml/L	105	210 ml/L	58
60 min	210 ml/L	-	150 ml/L	-

6.7 Chemical Treatment Analysis

In this part of the study, coagulation and floculation experiments were performed for industrial wastewater. FeCl3, Al2(SO4)3 and FeCl3 solutions were used as coagulant and H2SO4, NaOH were used to adjust the pH to the desired range.

The wastewater used in the jar test experiments were prepared by mixing painting and enamel wastewater according to the flow rates coming to the treatment plant. The mixing ratio of wastewaters was 3:1 for Painting wastewater:Enamel wastewater. COD and TSS concentrations of mixed wastewater were 253 mg COD/L and 65 mg/L, respectively. pH of the mixed wastewater was 8. Examples for application of jar test have been shown in Figure 6.14. The yellow samples was the FeCl3 added samples, while the white ones was the alum added samples.

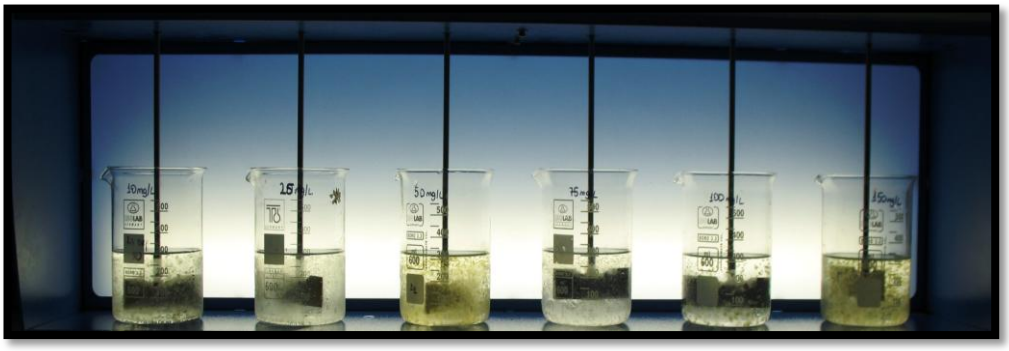

Figure 6.14: Jar test-1.

After mixing period in the jar test, as shown in Figure 6.14, the samples were settled. Supernetant of the samples were collected and analyzed. An example for settled samples was shown in Figure 6.15.

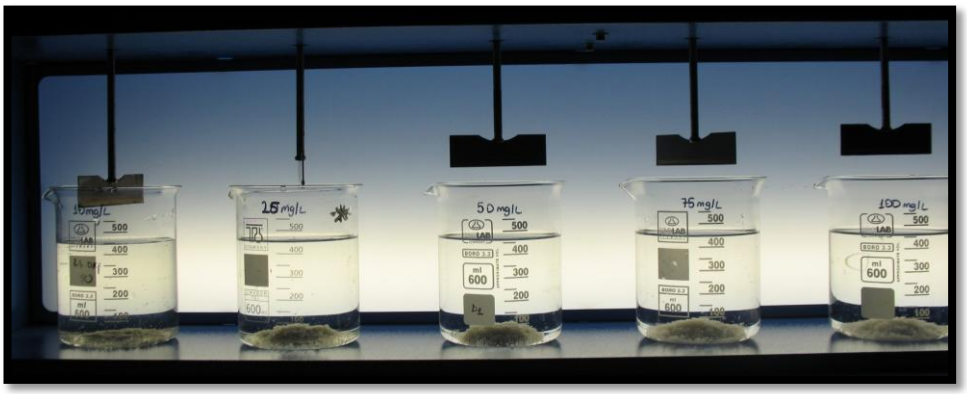

Figure 6.15: Jar test-2.

6.7.1 Commercial solution assay

Commercial solution which contained $FeCl_3$, was used in the Jar Test for "Commercial Solution Assay". In addition to this, pH of this solution was adjusted to 5.5 by HCl, according to the type of coagulant. Finally, 400 µL/L anyonic polyelectrolyte as a flocculant was used.

In the jar test, raw sample was taken into 500 ml flaks. Coagulant was added into the mixing sample until flocks started to occur to determine optimum dosage. Starting from minimum dosages 7 different coagulant dosages were applied.

After 5 min rapid mixing and 15 min slow mixing, flocs were settled for 30 min and the volumes of settled sludge were determined using graduated cylinders. COD, TSS and some heavy metals tests were performed to the sample taken from the supernatant of chemically treated wastewater.

COD, pH, turbidity results of chemical treatment was seen in Table 6.12 for different coagulant dosages. In terms of COD concentration, except 1 µL/L dosage, the COD concentrations have been complied with regulation limits at all coagulant dosages. Also pH control were required at 100 and 150 µL/L dosages.

Table 6.12: Commercial solution assay results.

Coagulant Dosage	Mixed Sample	Supernatant		
	TSS [mg/L]	pH	COD [mgCOD/L]	Turbidity [NTU]
1 µL/L	66	6.1	115	23
10 µL/L	95	6.2	50	5.5
25 µL/L	95	6.2	45	5
50 µL/L	96	6.3	45	4
75 µL/L	100	6.2	40	3
100 µL/L	123	5.6	40	3.5<x<4
150 µL/L	129	5.8	40	3.5
Regulation Limits	-	6-9	100	-

*Water Quality and Control Regulation

In Table 6.13, heavy metal concentration results have been shown for commercial solution assay. As a result of chemical treatment, aluminium, ferrous, zinc and total chrome concentration was complied with regulation limits.

Table 6.13: Heavy metal concentrations in the effluent of chemical treatment with 50 µL/L commercial coagulant added wastwater.

Heavy Metals	Concentrations [mg/L]	Regulation Limits [mg/L]
Al (Aluminium)	<1	2
Fe (Ferrous)	0.5	3
Zn (Zinc)	1.3	2
T. Cr (Total Chrome)	<0.2	2

Amount and volume of sludge was shown in Figure 6.16. As shown in figure, when amount of consumed coagulant was increased, amount and volume of produced sludge was also increased.

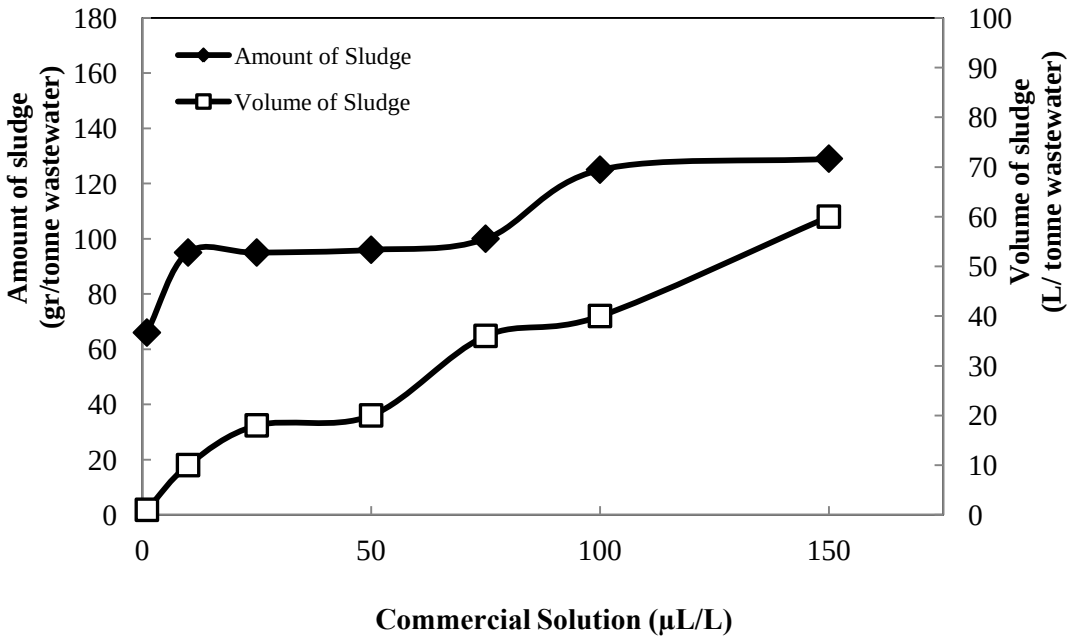

Figure 6. 16: Sludge production in commercial solution assay.

6.7.2 Alum solution assay

$Al_2(SO_4)_3$ solution was used in the Jar Test for alum solution assay. In addition to this, pH of this solution was adjusted to 6.5-7 by HCl and NaOH, according to the type of coagulant. In this assay, 400 µL/L polyelectrolyte as a flocculant was used. Same applications in commercial solution assay, were also performed for the alum solution assay.

COD, pH, turbidity results of chemical treatment were seen in Table 6.14 for different coagulant dosages. In terms of COD concentration, all COD concentrations

have been complied with regulation limits at all coagulant dosages. Also pH control were not required in alum solution assay.

Table 6.14: Alum solution assay results.

Coagulant Dosage	Mixed Sample	Supernatant Liquid		
	TSS [mg/L]	pH	COD [mgCOD/L]	Turbidity [NTU]
1 mg/L	72	7.40	100	15
10 mg/L	86	7.20	50	5
25 mg/L	87	7.15	50	2.5
50 mg/L	117	7.17	50	2
75 mg/L	113	7.05	45	2.5<x<2
100 mg/L	120	7.22	45	1.5
150 mg/L	185	7.24	40	1.5
Legislation Limits	-	6-9	100	-

In Table 6.15, heavy metal concentration results were shown for alum solution assay. As a result of chemical treatment, aluminium, ferrous, zinc and total chrome concentration was complied with regulation limits.

Table 6.15: Heavy metal concentrations in the effluent of chemical treatment with 50 mg/L alum dosage.

Heavy Metals	Concentrations [mg/L]	Regulation Limits [mg/L]
Al (Aluminium)	<1	2
Fe (Ferrous)	0.2	3
Zn (Zinc)	1	2
T. Cr (Total Chrome)	<0.2	2

Amount and volume of sludge was shown in Figure 6.17. As shown in figure, when amount of consumed coagulant was increased, amount and volume of produced sludge have been increased.

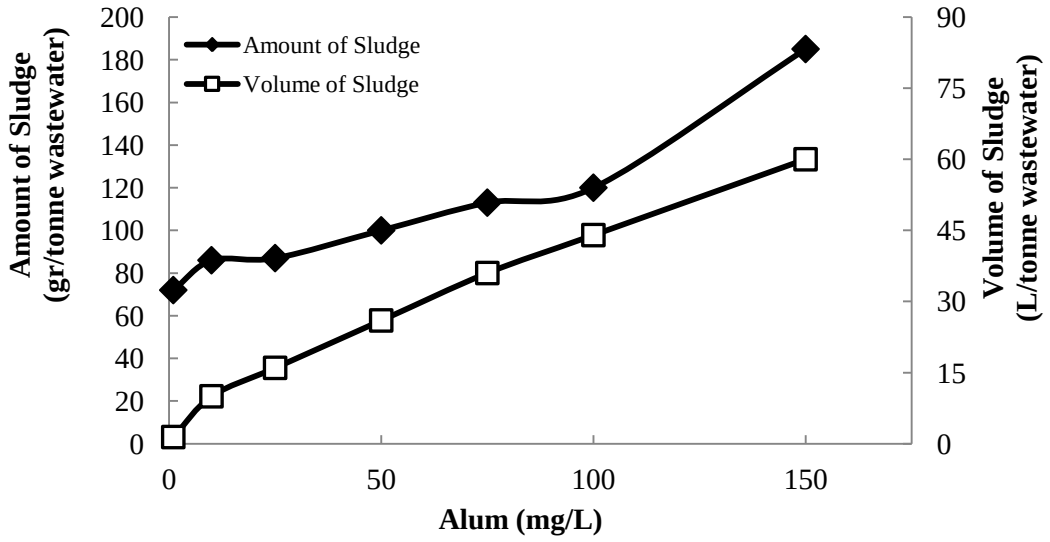

Figure 6.17: Sludge production in alum solution assay.

6.7.3 $FeCl_3$ solution assay

$FeCl_3$ solution was used in the Jar Test for $FeCl_3$ solution assay. In addition to this, pH of this solution was adjusted to 5.5 by HCl and NaOH, according to the type of coagulant. Finally, 666 µL/L polyelectrolyte as a flocculant was used. Same applications in commercial solution assay, were also performed in $FeCl_3$ solution assay.

COD, pH, turbidity results of chemical treatment were seen in Table 6.16 for different coagulant dosages. In terms of COD concentration, all COD concentrations have been complied with regulation limits at all coagulant dosages. Also pH control were not required in $FeCl_3$ solution assay.

Table 6.16: $FeCl_3$ solution assay results.

Coagulant Dosage	Mixed Sample	Supernatant Liquid		
	TSS [mg/L]	pH	COD [mgCOD/L]	Turbidity [NTU]
1 mg/L	50	6.04	100	15
10 mg/L	55	6.08	50	5.5
25 mg/L	80	5.97	50	4
50 mg/L	86	6.01	50	3
75 mg/L	118	6.34	45	2.5
100 mg/L	163	6.00	45	3.5
150 mg/L	180	6.02	45	3.5
Legislation Limits	-	6-9	100	-

In Table 6.17, heavy metal concentration results have been shown for $FeCl_3$ solution assay. As a result of chemical treatment, aluminium, ferrous, zinc and total chrome concentration was complied with regulation limits.

Table 6.17: Heavy metal concentrations in the effluent of chemical treatment with 50 mg/L $FeCl_3$ solution dosage.

Heavy Metals	Concentrations [mg/L]	Regulation Limits [mg/L]
Al (Aluminium)	<1	2
Fe (Ferrous)	0.5	3
Zn (Zinc)	0.6	2
T. Cr (Total Chromium)	<0.2	2

Amount and volume of sludge was shown in Figure 6.18. As shown in figure, when amount of consumed coagulant was increased, amount and volume of produced sludge was also increased.

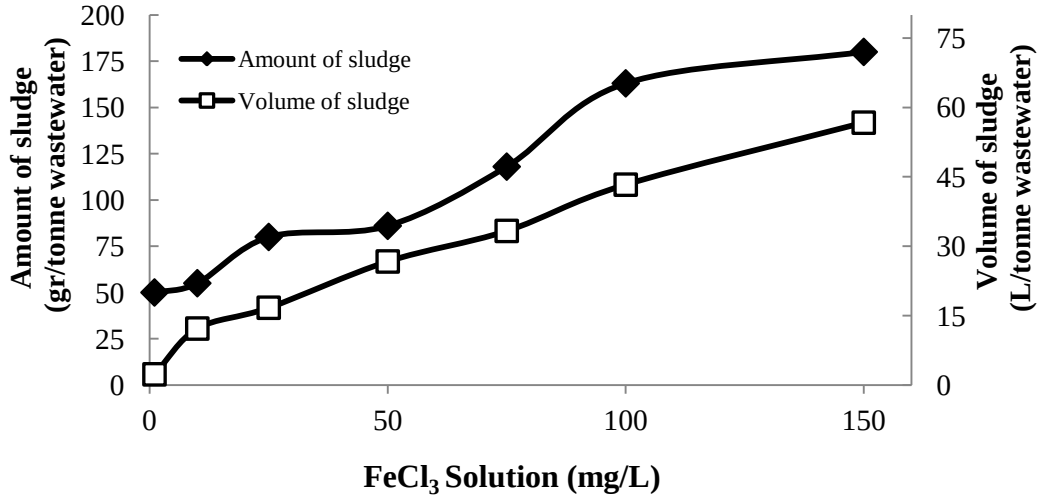

Figure 6.18: Sludge production in $FeCl_3$ solution assay.

6.7.4 pH evaluation assay

Lab scale $FeCl_3$ solution was used in the Jar Test for pH evaluation assay. pH of the solution was adjusted to 6.5, 7 and 8 by HCl and NaOH, according to the type of coagulant. In this assay, 666 µL/L polyelectrolyte was used as a flocculant. Same applications in commercial solution assay were also performed in pH evaluation assay.

COD, pH, turbidity results of chemical treatment were given in Table 6.18 for different coagulant dosages. In terms of COD concentration, all COD concentrations have been complied with regulation limits at all coagulant dosages. Also pH control were not required in pH evaluation assay.

Table 6.18: pH evaluation assay results.

pH Condition	Coagulant Dosage	Mixed Sample	Supernatant Liquid		
		TSS [mg/L]	pH	COD [mgCOD/L]	Turbidity [NTU]
	1 mg/L	50	6.04	100	15
pH=5.5	10 mg/L	55	6.08	50	5.5
	50 mg/l	86	6.01	50	3
	1 mg/L	94	7.39	70	11
pH= 6.5-7	10 mg/L	64	7.10	50	5
	50 mg/L	128	7.12	40	4
	1 mg/L	74	7.12	60	9
pH=8	10 mg/L	60	7.47	55	5.5
Orjina1 pH	50 mg/l	138	7.15	45	6
	1 mg/L	50	6.04	100	15
Legislation Limits		-	6-9	100	-

In Table 6.19, heavy metal concentration results were seen for pH evaluation assay. As a result of chemical treatment, aluminium, ferrous, zinc and total chrome concentration was complied with regulation limits.

Table 6.19: Effluent heavy metal concentrations at different pH values for 50 mg/L $FeCl_3$ solution dosage.

Heavy Metals	pH= 5.5	pH=6.5-7.0	pH=8.0	Legislation Limits
	[mg/L]	[mg/L]	[mg/L]	[mg/L]
Al (Aluminium)	<1	<1	<1	2
Fe (Ferrous)	0.5	0.6	0.8	3
Zn (Zinc)	0.6	0.6	0.7	2
T. Cr (Total Chrome)	<0.2	<0.2	<0.2	2

Amount and volume of sludge was shown in Figure 6.19. As shown in figure, when the amount of consumed coagulant was increased, amount and volume of produced sludge also was increased. Comparing with all pH conditions, produced sludge flocs were more dense and the sludge could be easily separated from water at pH 5.5.

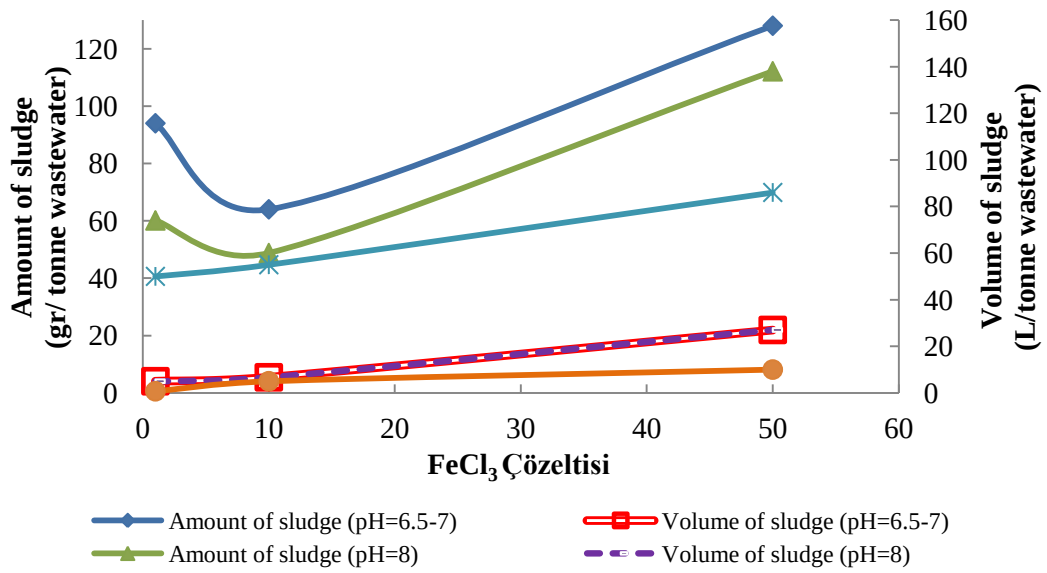

Figure 6.19: Sludge production in pH evaluation assay.

According to the results, chemical treatment experiments with $Al_2(SO_4)_3$ was not successful to obtain a high quality sludge. High quality sludges has compact, non-dispersible floc structure and has high settleability feature. In this way, the treated water can be separated from the sludge easily.

In Figure 6.20, according to filter pres efficiency, amounts of produced sludge were showed. The amounts of sludge that were shown above, were reflected dried solid contents of solids. But in the full scale application, the produced sludge have been passed from filter pres where the solid material content was accepted as at least 30% and at most 40%.

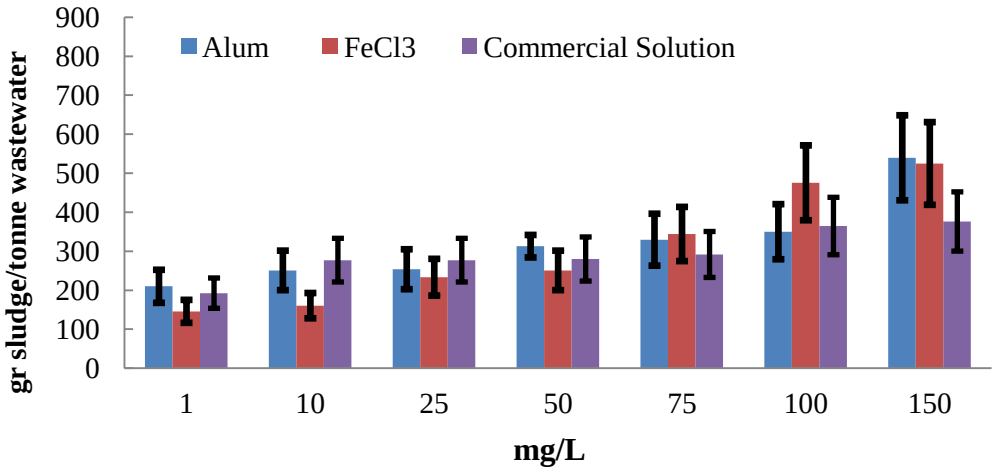

Figure 6.20: According to 30-40% filter press efficiency, amount of the produced sludge.

6.8 Determination of Inert COD Fractions.

The multicomponent modelling approach should be used in the design of activated sludge systems. In order to make accurate design calculations, assessment of inert particulate and soluble fraction of wastewater is essential. This study presents the data obtained for the inert particulate COD according to method in the literature (Okutman, 2001).

At the beginning of the study, total COD concentration of enamel and painting wastewater were 230 mg/L and 235 mg/L, respectively while total COD concentration of rinsing wastewater was 100 mg/L. The results of this study were listed in Table 6.20, 6.21 and 6.22. As shown in the Table 6.20, the initial soluble inert COD (S_I), is 16 mg/L and S_I makes up 7% of the total COD of enamel wastewater. In addition, the initial particulate inert COD (X_I) was calculated as 33 mg/L and X_I makes up 14.4% of the total COD of enamel wastewater. In total, total inert COD in enamel wastewater was determined as 49 m/L which constitutes 21.4% of the total COD content.

Table 6.20: COD fractions of enamel wastewater.

Unit	Soluble Inert COD (S_I)	Particulate Inert COD (X_I)
mg/L	16	33
% (In total wastewater)	7	14.4

In Table 6.21, COD fractions of painting wastewater was given. The initial soluble inert COD (S_I), is 15 mg/L and S_I makes 6.4% of the total COD of painting wastewater. The initial particulate inert COD (X_I), is 24 mg/L and X_I makes 10.2% of the total COD of painting wastewater. In total, total inert COD in painting wastewater was determined as 39 m/L which constitutes 16.6% of the total COD content.

Table 6.21: COD fractions of painting wastewater.

Unit	Soluble Inert COD (SI)	Particulate Inert COD (XI)
mg/L	15	24
% (In total wastewater)	6.4	10.2

In table 6.22, COD fractions of rinsing wastewater were given. The initial soluble inert COD (SI), is 12 mg/L and SI makes up 12% of the total COD of rinsing wastewater. The initial particulate inert COD (XI), makes up 0% of the total COD of rinsing wastewater. In total, total inert COD in rinsing wastewater was determined as 12 m/L which constitutes 12% of the total COD content.

Table 6.22: COD fractions of rinsing wastewater.

Unit	Soluble Inert COD (S_I)	Particulate Inert COD (X_I)
mg/L	12	0
% (In total wastewater)	12	0

6.9 Respirometric Analysis

Acute toxicity effects as well as biodegradability potentials of industrial wastewaters generated from the factory were assessed using two types af activated sludges obtained from the treatment plant of the same factory. The respirometric analyses were performed using the sludge samples taken from industrial activated sludge aeration tank and domestic activated sludge aeration tank. The details of the sets were given in Table 6.23.

Organic matter concentration of industrial wastewater was not very high. And industrial wastewater respirometrically was analyzed using industrial activated sludge in order to understand the treatment efficiency. In the wastewater treatment plant, the sludge requirement of industrial biological treatment have been supplied by domestic activated sludge. Because of this, industrial wastewater respirometrically analyzed using domestic activated sludge in order to determine the acute effect of industrial wastewater on the domestic sludge. Domestic wastewater is respirometrically analyzed with industrial and domestic activated sludge in order to evaluate treatment efficiency. Finally, the industrial wastewater, that is treated chemically is respirometricaly analyzed using both domestic and industrial activated sludge.

Table 6.23: The details of respirometric analyses.

SET	Sludge Type (1.5 L)	Wastewater Type (1 L)
SET 1	Industrial	Domestic
SET 2	Domestic	Domestic
SET 3	Industrial	Enamel
SET 4	Domestic	Enamel
SET 5	Domestic	Rinsing
SET 6	Industrial	Rinsing
SET 7	Domestic	Painting
SET 8	Industrial	Painting
SET 9	Industrial	Chemical treatment*
SET 10	Domestic	Chemical treatment*

*Chemical treatment effluent

6.9.1 Set 1

In Set 1, domestic wastewater is respirometrically analyzed using industrial activated sludge. Volume of sludge and wastewater is selected as 1.5 L and 1L, respectively. The experiment was continued about 7 hours. The degradation of organic matter nearly was completed on fifth hour. Soluble COD removal was monitored during the respirometric analyses. The results of Set 1 were shown in Figure 6.21. For Set 1; the soluble COD removal was calculated as 87%. Initial SS and VSS were 3790 mg/L and 2430 mg/L, respectively.

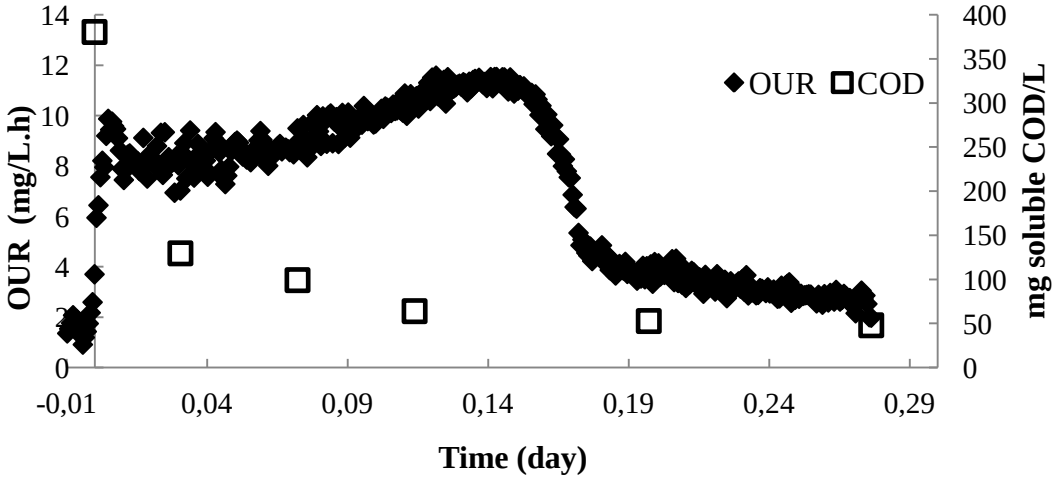

Figure 6.21: Respiromeric analysis results of Set 1.

As seen in Figure 6.21, maximum oxygen uptake rate after the feeding reached to 10 mg/L.h, while oxygen uptake rate was approximately 2 mg/L.h at b_H level.

6.9.2 Set 2

In Set 2, domestic wastewater is respirometrically analyzed using domestic activated sludge. Volume of sludge and wastewater is selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 2.5 hours. The degradation of organic matter nearly was completed on first hour. COD removal was monitored during the respirometric analyses. The results of Set 2 were shown in Figure 6.22. For Set 2; the COD removal was measured 87%, initial SS was 4027 mg/L and initial VSS was 3507 mg/L.

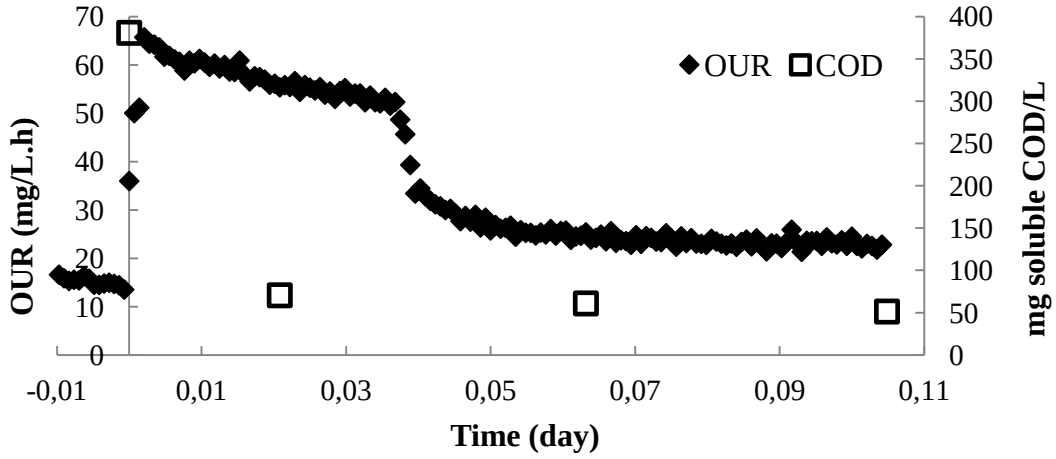

Figure 6.22: Respirometric analysis results of Set 2.

As seen in Figure 6.22, the oxygen uptake rate was approximately 12 mg/L.h at b_H level and maximum oxygen uptake rate reached to 70 mg/L.h after feeding.

Beside this, comparing Set 1 and Set 2, maximum oxygen uptake rate of domestic activated sludge was higher than industrial activated sludge. This showed that domestic activated sludge was more active than industrial activated sludge.

6.9.3 Set 3

In Set 3, enamel wastewater was respirometrically analyzed using industrial activated sludge. Volume of sludge and wastewater was selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 2 hours. As conventional parameters; COD removal were monitorized during the respirometric analyses**.** The results of Set 3 were shown in Figure 6.23. For Set 3; the COD removal was measured 63%, initial SS was 3790 mg/L and initial VSS was 2430

mg/L. Soluble COD concentration at time "0" was 120 mg/L. As seen in Figure 6.23, oxygen uptake rate was approximately 2 mg/L.h at b_H level and maximum oxygen uptake rate incresed only to 4.2 mg/L.h after feeding.

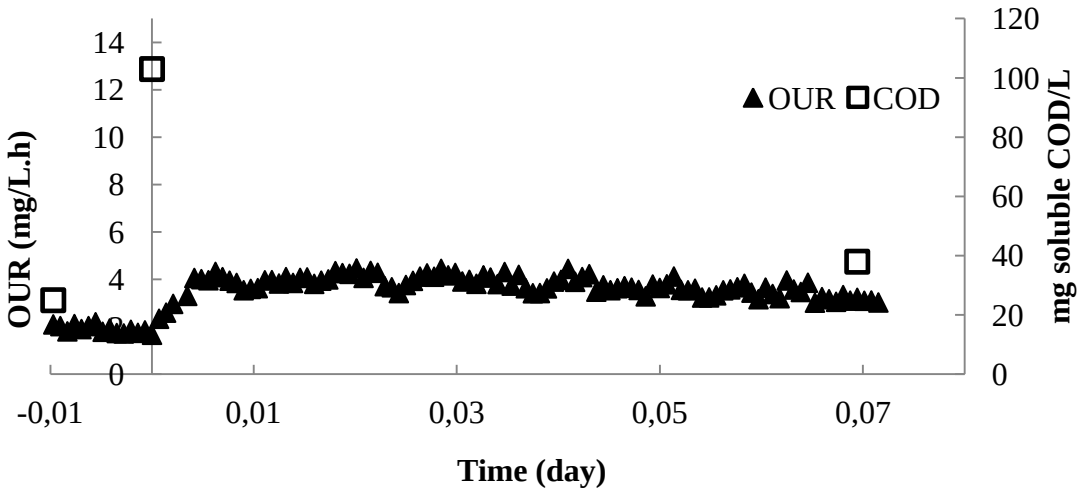

Figure 6.23: Respiromeric analysis results of Set 3.

When the wastewater was added in the reactor, oxygen uptake rate was increased barely due to the very low readily biodegradable organic matter content and lower hydrolysis rate of the wastewater.

6.9.4 Set 4

In Set 4, enamel wastewater is respirometrically analyzed using domestic activated sludge. Volume of sludge and wastewater was 1.5 L and 1 L, respectively. The experiment was approximately continued for 1.5 hours. As conventional parameter; COD removal was monitored. The results of Set 4 were shown in Figure 6.24. For set 4; the COD removal was nearly 49%, initial SS was 4027 mg/L and initial VSS was 3507 mg/L. For organic matter degredation, there are two improtant points. First, COD concentration at time "0" was 120 mg/L which is very low. Second, as shown in Figure 6.24, when the wastewater added in the system a significant change in the oxygen uptake rate was not observed. As seen in Figure 6.24, oxygen uptake rate was approximately 15 mg/L.h at b_H level an increase in the oxygen uptake rate was not observed after the feeding due to the very low biodegradable organic matter content of the wastewater and probable inhibitory effect on the domestic sludge which was not acclimated to this wastewater.

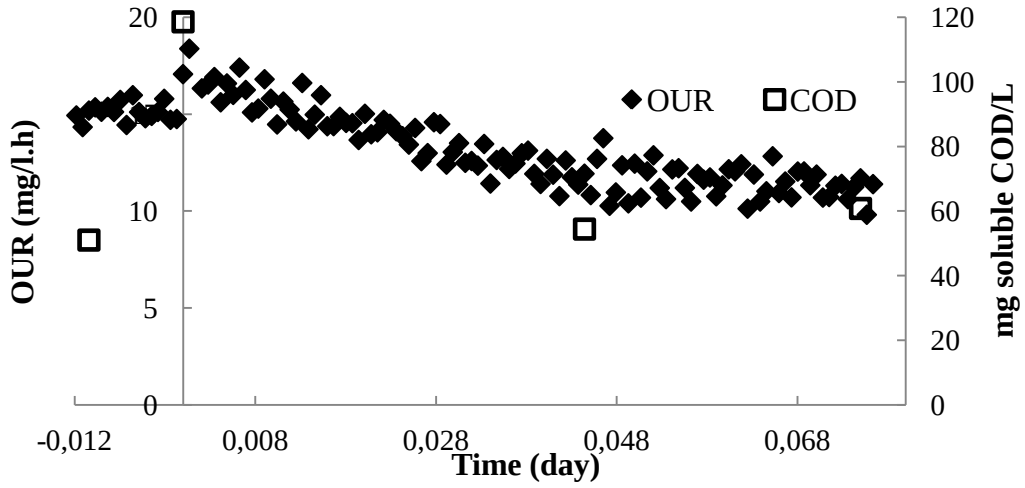

Figure 6.24: Respirometric analysis results of Set 4.

6.9.5 Set 5

In Set 5, rinsing wastewater is respirometrically analyzed using domestic activated sludge. Volume of sludge and wastewater was selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 10 hours. As conventional parameter, COD removal was monitored. The results of Set 5 were shown in Figure 6.25. For Set 5; the soluble COD removal was nearly 47%. Initial SS was 4027 mg/L and initial VSS was 3507 mg/L. For organic matter degredation, there are two improtant point. Firstly, COD concentration at time "0" was 55 mg/L which is very low. Secondly, as shown in Figure 6.25, when the wastewater added in the system, oxygen uptake rate kept decreasing conspicuously.

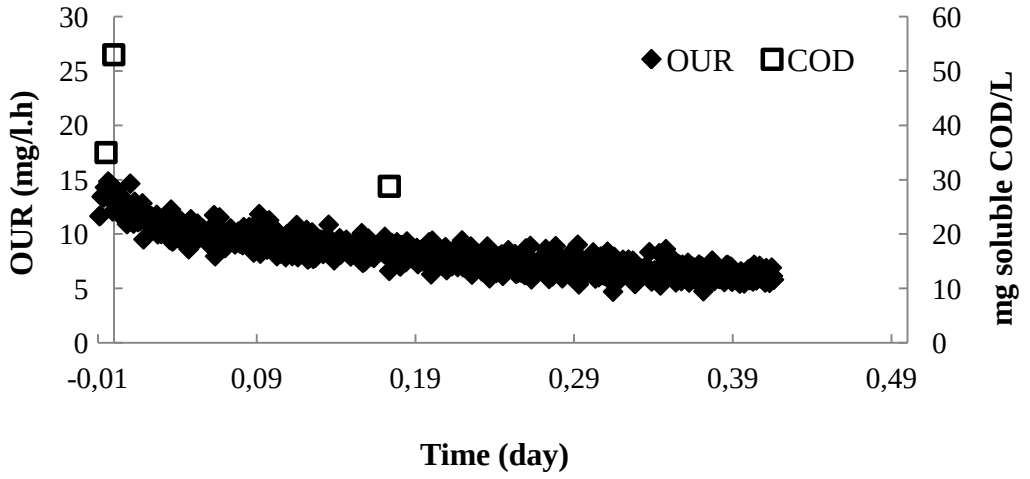

Figure 6.25: Respirometric analysis results of Set 5.

As seen in Figure 6.25, oxygen uptake rate was approximately 12 mg/L.h at b_H level. When the wastewater was added in the reactor, oxygen uptake rate was not increased due to the very low biodegradable organic matter content of the wastewater and probable inhibitory effect on the domestic sludge which was not acclimated to this wastewater.

6.9.6 Set 6

In Set 6, rinsing wastewater is respirometrically analyzed using industrial activated sludge. Volume of sludge and wastewater was selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 2 hours. As conventional parameters; COD removal were monitorized during the respirometric analyses. For Set 6; the soluble COD removal was measured 71%, initial SS was 3790 mg/L and initial VSS was 2430 mg/L. Firstly, COD concentration at time "0" was 45 mg/L which is again very low. Secondly, as shown in Figure 6.26, when the wastewater added in the system, oxygen uptake rate was increased barely.

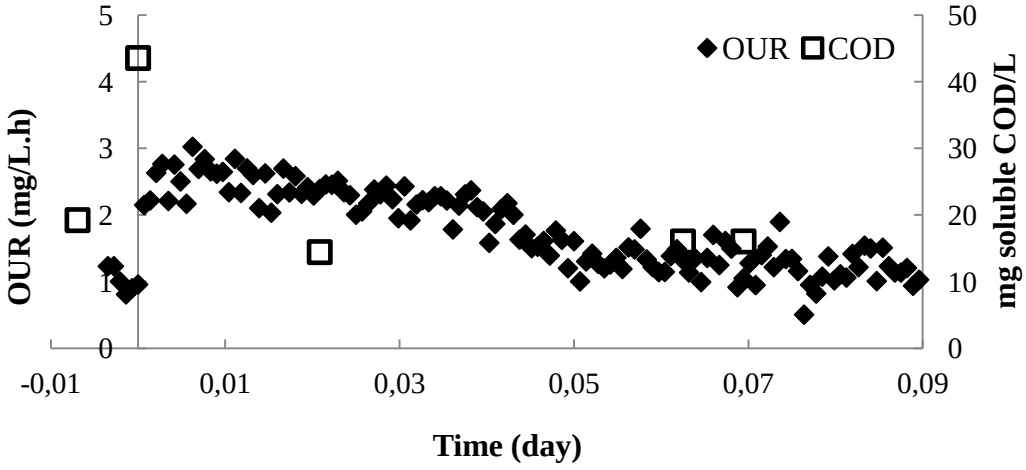

Figure 6.26: Repirometric analysis results of Set 6.

As seen in Figure 6.26, the oxygen uptake rate was 1mg/L.h at b_H level and increased to approximately 3 mg/l after feeding. When the wastewater was added in the reactor, oxygen uptake rate was increased barely due to the very low biodegradable organic matter content of the wastewater and lower hydrolysis rate. However, the inhibitory effect as in the previous case was not observed for this aclimated industrial sludge. Due to the very low biodegradable COD content of the rinsing wastewater, biological treatment for this wastewater may not be an efficient treatment system.

6.9.7 Set 7

In Set 7, painting wastewater is respirometrically analyzed using domestic activated sludge. Volume of sludge and wastewater was selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 1.5 hours. As conventional parameter, COD removal was moniterized. The results of Set 7 were shown in Figure 6.27. For Set 7; the COD removal was 65%, initial SS was 4027 mg/L and initial VSS 3507 mg/L. For organic matter degredation, there are two improtant point. First, soluble COD concentration at time "0" was 120 mg/L which is very low. Secondly, as shown in Figure 6.27, when the wastewater added in the system no change was observed in the oxygen uptake rate. This showed that, despite the low COD concentration of rinsing wastewater, activated sludge can be also inhibited .

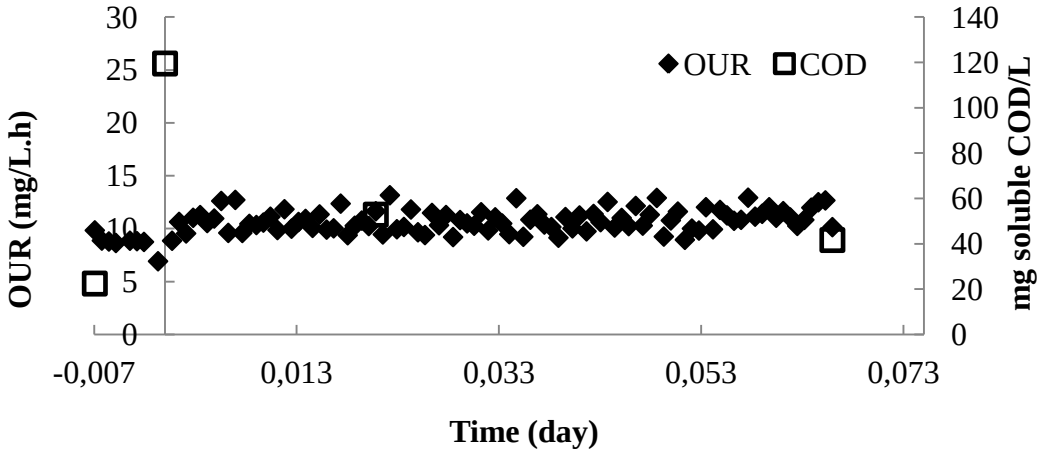

Figure 6.27: Respirometric analysis results of Set 7.

No change in the oxygen uptake rate showed that the COD content of the painting wastewater can not be degradaded with domestic activated sludge which was not acclimated to this wastewater.

6.9.8 Set 8

In Set 8, painting wastewater was respirometrically analyzed using industrial activated sludge. Volume of sludge and wastewater was selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 2 hours. As conventional parameter, COD removal was moniterized. The results of Set 8 were

shown in Figure 6.28. For Set 8; the COD removal was 74%, initial SS was 3790 mg/L and initial VSS 2430 mg/L. For organic matter degredation, there are two important point. First, soluble COD concentration at time "0" was 120 mg/L which is very low. Second, as shown in Figure 6.28, when the wastewater added in the system, oxygen uptake rate increased very little.

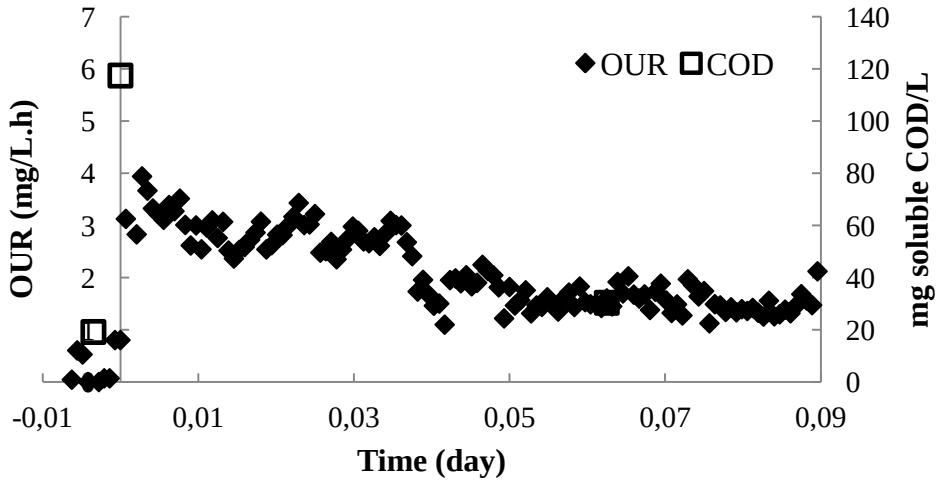

Figure 6.28: Respirometric analysis result of Set 8.

As seen in Figure 6.28, oxygen uptake rate was approximately 1 mg/L.h at b_H level and maximum oxygen uptake rate was incresed to 3 mg/L.h after feeding,. When the wastewater was added in the reactor, oxygen uptake rate was increased barely due to the very low biodegradable organic matter content of the wastewater.

6.9.9 Set 9

In this set, in order to see simulation of real treatment plant, a sample of composite wastewater was prepared and treated by coagulation and flocculation method. Wastewater mixing ratio was choosen same as in the Jar test method as explained before. In Set 9, effluent wastewater of chemical treatment was respirometrically analyzed using industrial activated sludge. Volume of sludge and wastewater was selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 2 hours. For Set 9; the soluble COD removal was measured 56%, initial SS was 3790 mg/L and initial VSS was 2430 mg/L. Firstly, soluble COD concentration at time "0" was 45 mg/L which is very low. Second, as shown in Figure 6.29, when the wastewater added in the system, oxygen uptake rate was increased barely.

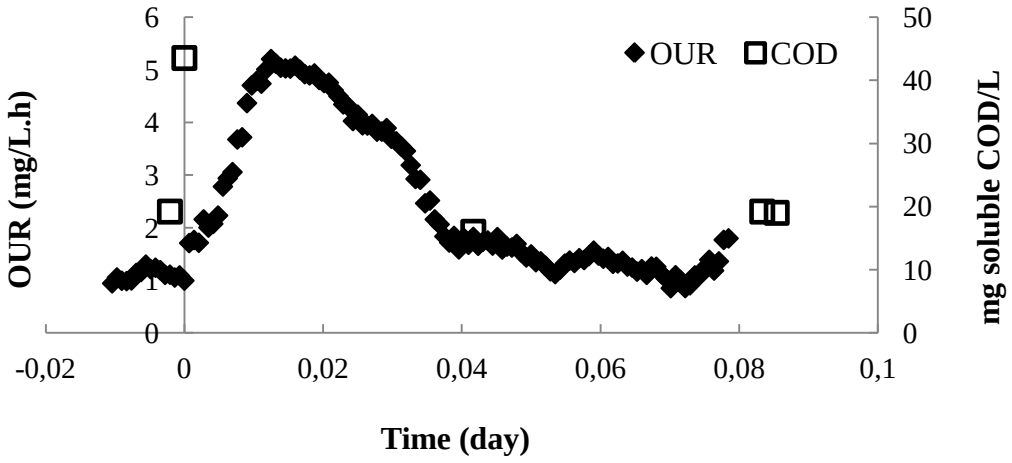

Figure 6.29: Repirometric analysis result of Set 9.

As seen in Figure 6.29, oxygen uptake rate before feeding was 1 mg/L.h and oxygen uptake rate increased slowly up to 5 mg/L.h after feeding. When the wastewater was added in the reactor, oxygen uptake rate increased barely due to the very low biodegradable organic matter content of the wastewater.

6.9.10 Set 10

In Set 10, effluent wastewater of chemical treatment was respirometrically analyzed using domestic activated sludge. Volume of sludge and wastewater was selected as 1.5 L and 1 L, respectively. The experiment was approximately continued for 5 hours. The results of Set 10 were shown in Figure 6.30. Initial SS was 4027 mg/L and initial VSS 3507 mg/L.

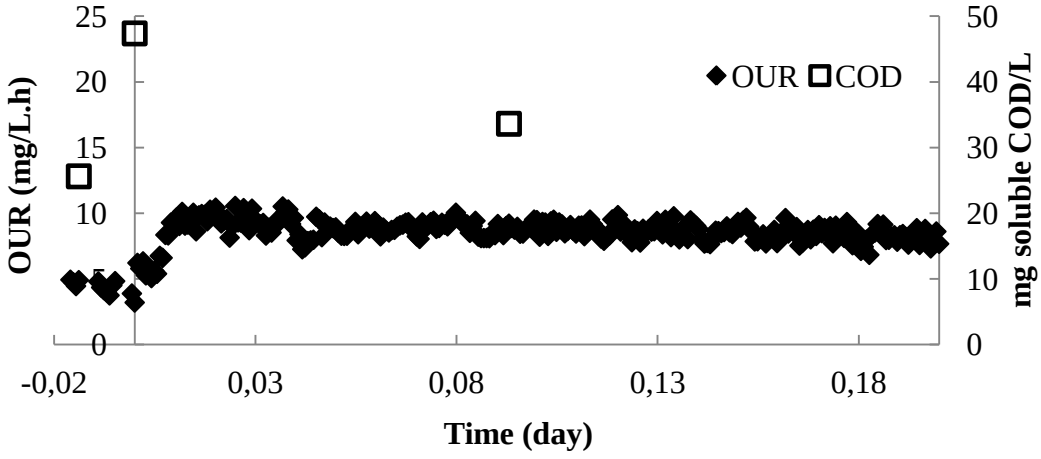

Figure 6.30: Respirometric analysis results of Set 10.

As seen in Figure 6.30, oxygen uptake rate before feeding was 5 mg/L.h and oxygen uptake rate was increased up to 10 mg/L.h after feeding.When the wastewater was added in the reactor, oxygen uptake rate was increased barely due to the very low biodegradable organic matter content of the wastewater. This figure also showed that chemical treatment decreased the inhibitory effect of wastewater on domestic sludge.

6.10 Model Results

The modelling evaluations, were performed using Activated Sludge Model 1 (ASM1) for domestic wastewater and chemically treated wastewater (Set 1, Set 2, Set 9, and Set 10). Industrial wastewater was showed inhibitory effect on domestic activated sludge. Due to the low COD concentration, COD removal could not be observed in the other respirometric analysis. Thus, only Set 1, 2, 9 and 10 were modelled.

6.10.1 Set 1& Set 2

In order to determine kinetic and stoichiometric coefficients model study was carried out with OUR profiles. As mentioned before, domestic wastewater respirometrically analyzed using industrial activated sludge and was modelled with Aquasim software. Model simulation and OUR results have been presented together in Figure 6.31. According to this model, 9% of activated sludge in industrial biological treatment was only active biomass.

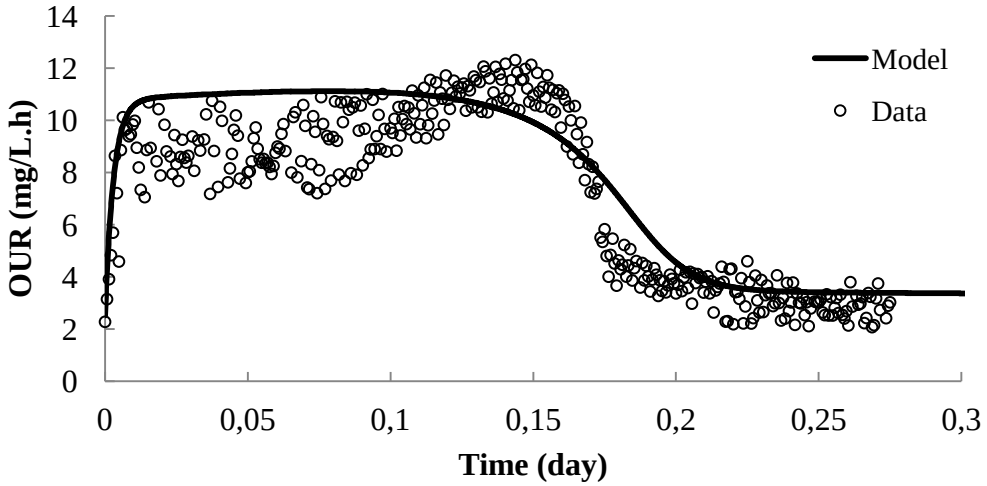

Figure 6.31: Modelling simulation for Set 1.

Model simulation and OUR results were presented together in Figure 6.31 and Figure 6.32 for Set 1 and Set 2, respectively. Domestic wastewater respirometrically analyzed using industrial activated sludge and domestic activated sludge in Set 1 and Set 2, respectively. According to the model results, only 35% of the activated sludge in domestic biological treatment was active biomass**.**

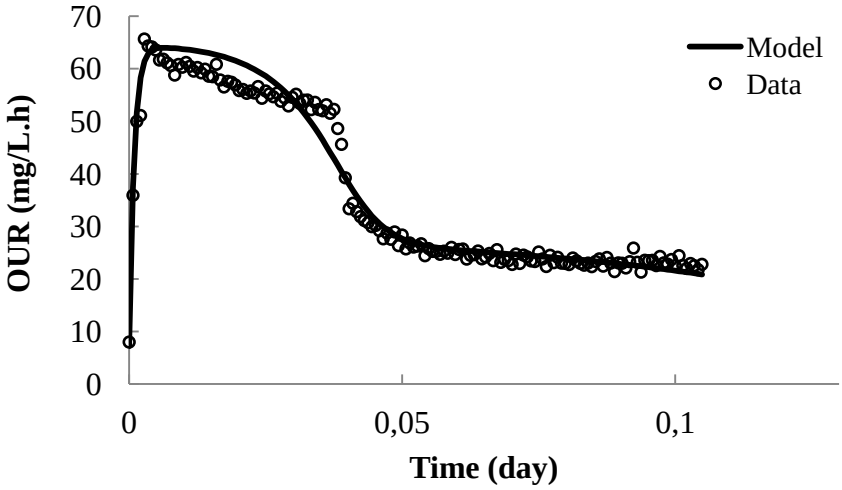

Figure 6.32: Modelling simulation for Set 2.

In table 6.24, kinetic and stochiometric coefficients for Set 1 and Set 2 was given. The heterortophic yield coefficient (Y_H), was varied from 0.62 to 0.67 g cellCOD/g COD for domestic wastewaters. This range also have been comply with the range in the literature (Ubay, 1997). In addition to this, Y_H coefficient of this Set, was determined as 0.64 g cellCOD/g COD.

Table 6.24: Kinetic and stoichimetric coefficient for Set 1&2.

Coefficients	Unit	Set 1	Set 2
b_H	1/day	0.24	0.24
$\hat{\mu}_H$	1/day	1.2	3
Y_H	g cell COD/g COD	0.64	0.64
X_H	mg COD/L	315	900
k_{hx}	1/day	0.30	1.6
K_{XX}	gCOD/g cell COD	0.70	0.03
K_S	mg/L	6	10

Growth rate is the one of most important coefficient in oder to observe biological activity. Results of the model calibration, outlined in Table 6.25, indicate a relatively low value of 1.20 day^{-1} for the specific maximum heterotrophic growth rate, $\hat{\mu}_H$. Commonly reported range for the same parameter is 4.0–6.0 day^{-1} for domestic sewage (Çokgör et al., 1998).

Endogenous decay rate have been varied from 0.1 to 0.65 1/day in the literature (Ubay, 1997). As shown in Table 6.24, decay rate of this set was determined as 0.24 1/day and this value have been complied with literature. Finally, half saturation coefficient have been varied from 2.5 to 30 mg/L in the literature (Ubay, 1997). The determined Ks value was in accordance with literature values.

Maximum hydrolysis rate for hydrolysable COD component (k_{hx}) of Set 1 and Set 2, were 0.30 and 1.6 1/day, while hydrolysis half saturation constant (K_{XX}) of Set 1 and Set 2 were 0.7 and 0.03 mgCOD/mgcellCOD, respectively. According to the modelling result, the maximum hydrolysis rate of Set 2 was found higher than Set 1, and the half saturation constant for hydrolysis was found lower than Set 1 because of unacclimated industrial sludge to domestic wastewater. When the results were compared with the literature values it was observed that, k_{hx} value of Set 1 and 2 was lower than the literature where maximum spesific hydrolysis rate was determined as 1.9 1/day, while hydrolysis half saturation constant was determined as 0.18 mg COD/mg cell COD for domestic sewage (Orhon et al., 2003). This can be explained by the lower enzymatic activity that is present in the used activated sludges.

6.10.2 Set 9 & Set 10

Effluent wastewater of the chemically treated wastewater respirometrically analyzed using industrial activated sludge in Set 9 and domestic activated sludge in Set 10. The respirometric OUR measurements of Set 9 and 10 were modelled using Aquasim software. Model simulation and OUR results have been presented together in Figure 6.33 and Figure 6.34.

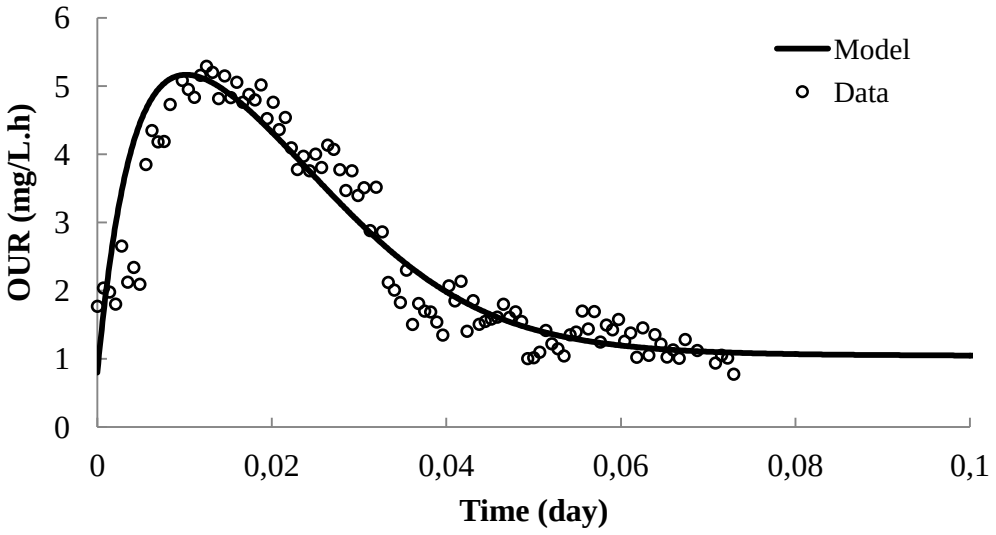

Figure 6.33: Modelling simulation for Set 9.

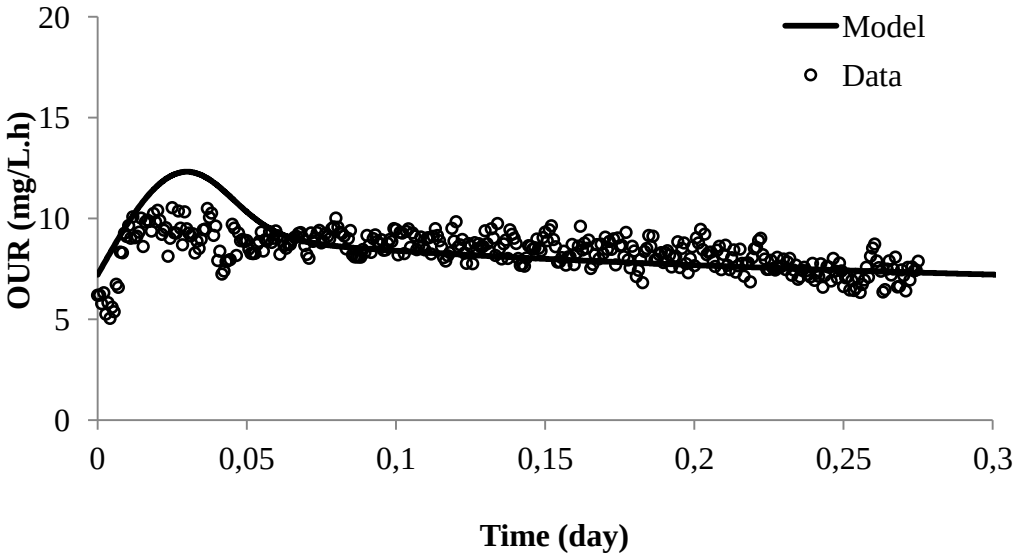

Figure 6.34: Modelling simulation for Set 10.

The obtained results from the modelling studies were compared with the previous model results for set 1 and 2. The coefficients b_H, μ_H and K_S of Set 9 and 10 were almost the same values. According to the previous result when the industrial wastewater was introduced to the domestic sludge, the wastewater inhibited domestic activated sludge. But as shown in Table 6.25, toxic effect of industrial wastewater have been decreased as a result of the applied chemical treatment.

Table 6.25: Important coefficient for Set 9 & 10.

Coefficients	Unit	SET 9	SET 10
b_H	1/day	0.24	0.24
$\hat{\mu}_H$	1/day	4.0	2.5
Y_H	(g cellCOD/g COD)	0.64	0.64
X_H	mg COD/L	100	900
k_{hx}	1/day	0.6	1
K_{XX}	(g COD/g cell COD)	0.7	0.15
K_S	mg/L	6	10

According to the models performed for chemically treated wastewater, 4% and 25% of activated sludge in industrial activated and domestic activated sludge was active biomass, respectively.

7. CONCLUSIONS

As a results of characterization studies, when compared to the other raw wastewaters in the metal finishing sector, low pollution load was observed for the investigated industry. In a year period, the COD parameter of the raw wastewater was changed between 300-600 mg COD/L. A significant fluctation was not observed for heavy metal concentration.

In chemical treatment assays, because of the low COD content of wastewater all coagulant dosages used in this study reflected nearly same removal efficiency. Heavy metal concentrations have been complied with discharge regulation for all tested coagulant dosages. Considering economic conditions and sludge production, optimum $FeCl_3$ coagulant dosage is determined as 50 mg/L and 50 μL/L.

Inert COD results showed that, inert COD fraction of enamel wastewaters constituted 21.4% of total COD, this value decreased to 16.6% in painting wastewater and 12% in rinsing wastewater. While considering the inert COD fractions, it should be considered that influent industrial wastewater has low biodegradable COD content.

The respirometric studies showed that, the industrial wastewater probably has inhibitory effect on domestic activated sludge. Industrial wastewater was treated using activated sludge of industrial wastewater slightly. The biomass was acclimated to the industrial wastewater. Additionaly, chemically treated wastewater was not inhibited the activated sludge, this showed that chemical treatment was decreased inhibitory effect of the industrial wastewater. In the light of respirometric results, the application of the biological treatment methods after chemical treatment are not proper for the studied industrial wastewaters because of the low COD concentrations and inhibitory effect.

In summary, all pollutant parameters of wastewater were compiled with discharge regulation limits. In the treatment plant only chemical treatment application for the

industrial wastewater can be sufficient in oder to remove conventional pollutants of industrial wastewater by taking “discharge regulation limits” into consideration.

8. FURTHER INVESTIGATION

In sustainable source management one of the most important issue is the consideration of the reuse of the genarated wastewater. In the face of industrialization, appropriateness of discharge limits for the ecosystem is the one of the topic that must be discussed. Facilities, shouldn't be only contented to comply with discharge regulation, but also they should reuse of wastewater to use in production process. In order to reuse wastewater, advanced treatment methods will be required. These methods are very expensive technologies and application of this methods is profitable when the reused water is provided big part water requirement of facility. In the light of these developments, appropriate advanced treatment method should be choosen and investigated to evaluate reuse wastewater genarated in the production process and for further considaration for irrigation.

REFERENCES

AWWA, (2005). Standard methods for the examination of water and wastewater, 21st ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.

Aydın, E., (2005). *Toxicity and inhibition evaluation of hazardous wastes from metal finishing process to vibrio fisc* (Master dissertation). Retrieved from: Istanbul Technical University.

Chu, J., Klos, K. P., Jan, F. and Henry, V. (2011). A reality for nano-technology-high performance metal surface finishing by nano- ceramic coating. *Nanmat Technology Co., Ltd, Nanmat Europe GmbH and NanoMate Technology Inc. Technical Report*.

Cokgör, EU., Sözen S., Orhon D. and Henze M.. (1998). Respirometric analysisi of activated sludge behavior- I. Assessment at the readily biodegradable substrate. *Wat. Sci. Tech.*, Vol. ***32*** (2),(pp. 461-475).

Eikelboom, D.H., (2000). Processs control of activated sludge plants by microscobic investigation. IWA Publishing, London.

Engin, S. and Altınışık, T. (2011). Sanayide daha etkili bir çevre yönetimi için temiz üretim: Metal kaplama sektörü. Milli produktivite merkezi yayınları.

EPA-ROC, (1994). The standard methods for determination of heavy metals in soils and plants. National Institute of Environmental Analysis of EPA-ROC, Taipei, Taiwan (in Chinese).

Europpean Commission (2006). Integrated pollution prevention and control (IPPC) reference document on best available techniques surface treatment of metals and plastic.

Evcimen, N., (2007). *Emaye üretiminde kaplama ve özelliklerinin araştırılması* (Master dissertation).

Evcin, A., (2006). Kaplama teknikleri ders notları. Afyon Karahisar Kocatepe University.

Gabaldón, C. Izquierdo, M. Martínez-Soria, V. Marzal, P. Penya-roja and J.M. Alvarez-Hornos F.J., (2007). Biological nitrate removal from wastewater of a metal finishing industry. *J.Hazard.* Materials Vol. ***148***, (pp. 485-490).

Gerardi, M., (2008). Microscobic examination of the activated sludge process. Wiley Publication.

Hassanali, M., (2005). Pollution prevention practices in small and medium sized metal finishers**.** *FES Outstanding Graduate Student Paper Series*: Vol: ***10***. N 3. ISSN: 1702-3548.

Haveman, M. (1995). Profile of the metal finishing industry. *Minneapolis Waste Reduction Instute For Training And Applications Research*. **MN 55414-4502**, Minneapolis.

Hendrick, D., (2006). Water treatment unit processess: Physical and chemical. *CRC Pressing.*

ISO 6060, (1989). Water quality determination of chemical oxygen demand. international standart.

Kabacoff, T.L., (2002). Nanoceramic coatings exhibit much higher toughess and wear resistance conventional coatings. In Christian E. Grethlein (Ed.), *Amptiac Quaterly:* Vol: ***6***. (pp. 37-67).

Okutman, D. (2001)**.** *Evsel atıksularda çökebilir KOİ ayrışmasının deneysel incelenmesi ve modellenmesi* (Master dissertation). Retrived from: Istanbul Technical University.

Orhon, D. and Okutman D. (2003)., Respirometric assessment of residual organic matter for domestic sewage. *Enzyme and Microbial Technology.* Vol. ***32*** (pp 560-566).

Orhon, D., Ateş, E., Sözen, S. and Cokgor, E.U. (1991). COD fractionation of domestic wastewaters. *Environmental Pollution.* Vol. ***95***. (pp. 191-204).

Orhon, D., Babuna, G.F. and Karahan, Ö. (2009). Industrial wastewater treatment by activated sludge: Enegetics and stoichiometry of substrate removal. IWA Publishing, London.

Ölmez, T. (2009). The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology. *Journals of Hazardous Material* Vol. ***162***. (pp. 1371-1378)

Saidi, M. (2010). Experimental studies on effect of heavy metals presence in industrial wastewater on biological treatment. ISSN: 0976-4402

Seviour, R. and Nielsen, P.H., (2010). Microbial ecology of activated sludge. IWA Publishing, London.

SKKY, (2004). Su Kirliliği Kontrolü Yönetmeliği, 31.12.2004 Tarih ve 25687 Sayılı Resmi Gazete, Ankara.

Sthiannopkao S and Sreesai S. (2009). Utilization of pulp and paper industrial wastes to remove heavy metals from metal finishing wastewater. *Journal of Environmental Management* Vol. ***90*** (11), (pp.3283-3289)

Ubay Çokgör, E., (1997). *Aerobic sistemlerde proses stokiometrisi ve kinetiğin respirometrik olarak değerlendirilmesi* (Doktoral dissertation). Retrived from: Istanbul Technical University

USEPA Environmental Protection Agency. (2007). Control techniques guidelines for large appliance coating.

Wahaab, R.A. (2001). Assessment of automobile industry wastewater treatment units. Environmental Contamination and Toxicology Vol.***66***, (pp.770-776).

Url-1 <http://eng.harran.edu.tr/moodle/moodledata/26/Cevre_mikrobiyolojisi_2_erkan_sahinkaya.pdf>, date retrieved 23.09.2012.

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