

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**TREATMENT OF TEXTILE WASTEWATER USING COMPLETELY  
MIXED ANAEROBIC REACTOR: START-UP**



**M.Sc. THESIS**

**Cenk Ali Bilgiç**

**Department of Environmental Engineering**

**Environmental Biotechnology Program**

**AUGUST 2020**



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**Cenk Ali Bilgiç  
(501171804)**

**Department of Environmental Engineering**

**Environmental Biotechnology Program**

**Thesis Advisor: Prof. Dr. Osman Atilla Arıkan**

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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**TEKSTİL ATIKSULARININ TAM KARIŞIMLI ANAEROBİK REAKTÖRLE  
ARITIMI: İŞLETMEYE ALMA**

**YÜKSEK LİSANS TEZİ**

**Cenk Ali Bilgiç  
(501171804)**

**Çevre Mühendisliği Ana Bilim Dalı**

**Çevre Biyoteknolojisi Programı**

**Tez Danışmanı: Prof. Dr. Osman Atilla ARIKAN**

**AĞUSTOS 2020**



Cenk Ali BİLGİÇ, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 501171804 successfully defended the thesis entitled “**TREATMENT OF TEXTILE WASTEWATER USING COMPLETELY MIXED ANAEROBIC REACTOR: START-UP**”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

**Thesis Advisor:**      **Prof. Dr. Osman Atilla ARIKAN** .....  
İstanbul Technical University

**Jury Members:**      **Doç. Dr. Mahmut Altınbaş** .....  
İstanbul Technical University

**Prof. Dr. Özer Çınar** .....  
Yıldız Technical University

**Date of Submission : 15 June 2020**  
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**To my beloved wife for being biggest supporter of my business and education  
life.**





## **FOREWORD**

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Cenk Ali BILGIC  
(Environmental Engineer)





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## **ABBREVIATIONS**

<b>ABR</b>	: Anaerobic Baffled Reactor
<b>ADMI</b>	: American Dye Manufacturer's Institute
<b>AFFB</b>	: Anaerobic Fixed Film Bioreactor
<b>ASBR</b>	: Anaerobic Sequencing Batch Reactor
<b>BOD</b>	: Biological Oxygen Demand
<b>COD</b>	: Chemical Oxygen Demand
<b>CSTR</b>	: Continuous Stirred Tank Reactor
<b>CWAO</b>	: Catalytic Wet Air Oxidation
<b>HRT</b>	: Hydraulic Retention Time
<b>MBR</b>	: Membrane Bioreactor
<b>MF</b>	: Microfiltration
<b>MLSS</b>	: Mixed Liquor Suspended Solid
<b>MLVSS</b>	: Mixed Liquor Volatile Suspended Solid
<b>NF</b>	: Nanofiltration
<b>ORP</b>	: Oxidation Reduction Potential
<b>PE</b>	: Polyethylene
<b>PLC</b>	: Programmable Logic Controller
<b>RO</b>	: Reverse Osmosis
<b>SAB</b>	: Submerged Aerated Biofilter
<b>SS</b>	: Suspended Solids
<b>TDS</b>	: Total Dissolved Solids
<b>TKN</b>	: Total Kjeldahl Nitrogen
<b>TSS</b>	: Total Suspended Solid
<b>UABS</b>	: Upflow Anaerobic Sludge Blanket
<b>UF</b>	: Ultrafiltration





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## **TREATMENT OF TEXTILE WASTEWATER USING COMPLETELY MIXED ANAEROBIC REACTOR: START-UP**

### **SUMMARY**

The textile industry is one of the major industries for many countries and it is developing day by day. In the textile industry, mainly fiber is turned into yarn, and yarn turns into a fabric that is used to manufacture end products such as clothes, curtains, towels and etc. and most of these end products are colored by dyes. The textile industry demands high water consumption because of processes applied. Dyes are the most important consumables for the textile industry. Consuming a high amount of water, dyes and other auxiliaries such as detergents, acids, inorganic salts and etc. make textile wastewater highly pollutant for the environment. Textile wastewaters contain a high amount of chemical oxygen demand (COD), total suspended solids (TSS), color, etc. and it is possible to say that COD and color removals are the main criteria researchers focus on. Because of its environmental impacts, regulations, and discharge criteria, demand for searching more feasible, cheaper, or more effective solutions has been increasing lately. There are many approaches for the treatment of textile wastewaters, such as physicochemical, biological or combined processes. Physicochemical systems effluents do not meet discharge limits alone although their investment costs are low. Due to the suitability of anaerobic processes for high COD containing wastewaters, these systems can easily be applied for the textile industry. Moreover, anaerobic systems have some additional advantages such as energy recovery. In addition to this, it is possible to reuse textile wastewater in case of applying well designed combined biological and physicochemical systems.

The purpose of this study was to investigate the treatability of synthetic textile wastewater by using pilot-scale anaerobic completely stirred tank reactor (CSTR) which was operated at mesophilic conditions (35°C) and infinite sludge age. However, technical and operational problems were occurred at the beginning of the study. For this reason, only the results of the start-up part was presented. Total duration of study was 264 days. The inoculum was supplied from Atakoy advanced biological wastewater treatment plant of Istanbul Water and Sewerage Administration (ISKI). The study was conducted in two phases. The first phase was operated for 81 days to investigate COD removal of synthetic textile wastewater which has an average of 2.400 mg COD/l initial concentration with 24 h HRT. The average COD removal was ~54% of the first phase. The second phase was investigated under two periods by using similar synthetic wastewater which has an average 875 mg COD/l and 975 mg COD/l for phase two/period one and phase two/period two, respectively. The first period of this phase was operated for 93 days with 24 h HRT and ~45% average COD removal was reached at this period. Moreover, the second period of this phase was run 90 days with 48 h for HRT and ~86% average COD removal was reached.

The average pH was around 6,9 and average MLSS concentration was in between 2.500-3.000 mg/l during the study. At the last period (phase two/period two) of the study, average MLVSS/MLSS ratio was calculated as 0,62 and 86% COD removal was achieved. This COD removal efficiency is comparable with literature.



## TEKSTİL ATIKSULARININ TAM KARIŞIMLI ANAEROBİK REAKTÖRLE ARITIMI

### ÖZET

Tekstil endüstrisi birçok ülke için lokomotif endüstrilerin başında gelmektedir. Gerek insanlara sağladığı iş imkânı, gerekse toplumun ihtiyaçlarına cevap vermesi açısından her geçen gün daha önemli hale gelmektedir. Tekstil endüstrisi ülkemiz için de önemli bir sanayi dalıdır. Ülkemiz tekstil ürünü ihraç eden ülkeler sıralamasında 7. sırada yer almaktadır. Tekstil endüstrisinde temel olarak elyaf ipliği, iplik kumaşa ve kumaş da elbise, havlu, bez perde vb. gibi nihai kullanıcı ürünlerine dönüşür. Bu amaçla yıkama, kurulama, boyama, ağartma gibi birçok proses kullanılmaktadır. Tekstil ürünlerinin üretimi sırasında yardımcı malzemeler de kullanılmaktadır. Bu malzemeler pH düzenleyici, beyazlatıcı, temizleyici olarak kullanılmakta olup içeriğindeki kimyasallar tekstil atıksularının kirlilik yükünü arttırmaktadır. Bu üniteler üretim çeşitliliğine göre değişiklik gösterir. Boyama bu üniteler arasında çevresel açıdan en çok kirliliğe sebep olan prosestir. Günümüzde ticari olarak çoğunlukla azo boyalar kullanılmaktadır. Tekstil atıksuyunun karakterizasyonunu etkileyen bazı parametreler şunlardır; kumaş türü, boya cinsi, proses tipi. Bununla birlikte diğer ünitelerde de su tüketimi yüksektir. Tekstil atıksuları yüksek kimyasal oksijen ihtiyacı (KOİ), askıda katı madde (AKM) ve renk içermektedir.

Tekstil atıksularının arıtımı uzun yıllardır araştırılan bir konu olup, bu amaçla fiziksel, kimyasal ve/veya biyolojik arıtım yöntemleri olmak üzere birçok yöntem denenmiş ve araştırılmıştır. Kimyasal arıtma sistemleri yüksek kimyasal tüketimi, işletme maliyeti ve çamur yönetimi gibi sorunlar sebebiyle pratikte çok tercih edilmemektedir. Biyolojik sistemler reaktör tipi, mikroorganizma çeşitliliği gibi konu başlıklarında detaylıca araştırılmıştır. Tekstil atıksularında arıtımı incelenen temel parametreler KOİ ve renk parametreleridir. Farklı ülkelerdeki tekstil atıksularının alıcı ortam deşarj standartları değerlendirildiğinde bu iki parametre ön plana çıkmaktadır. Bununla beraber ülkemizde toksisite değeri de dikkate alınmaktadır. Genel olarak tek başına kimyasal veya biyolojik sistemler ile tekstil atıksularının arıtıldığını gösteren birçok çalışma bulunmaktadır. Tekstil atıksuları içerisindeki KOİ biyolojik olarak kolay ayrışabilir olmadığı için biyolojik sistemler açısından zorlayıcı olmaktadır. Yine aynı şekilde üretimde kullanılan pH düzenleyiciler, tuzlar vb. ürünler sebebiyle, atıksudaki değişken ortam değerleri özellikle pH toleransı düşük olan biyolojik arıtma sistemlerinin verimini olumsuz etkilemektedir. Yapılan araştırmalar tekstil atıksularının arıtımı için ülkemizde en çok kullanılan yöntemin aktif çamur sistemi olduğunu göstermektedir. Aktif çamur sistemlerinin düşük ilk yatırım maliyeti gibi avantajları olsa da yüksek işletme-bakım maliyeti ve yüksek çamur miktarı gibi dezavantajları vardır. Anaerobik sistemlerin ilk yatırım maliyetleri yüksek olmasına rağmen, biyogaz eldesi, düşük çamur miktarı ve düşük işletme maliyetleri gibi avantajları vardır.

Anaerobik sistemler devreye alınma süresi uzun olmasına rağmen özellikle yüksek KOİ ve/veya biyolojik oksijen ihtiyacı (BOİ) içeren farklı endüstrilerin atıksularının arıtılmasında uygulanmıştır. Tekstil atıksularının anaerobik sistemlerle

arıtılabilirliğinin incelendiği çalışmalar, KOİ ve renk giderim veriminin birçok faktöre bağlı olduğunu göstermiştir. Ayrıca son yıllarda hibrit anaerobik-aerobik arıtma sistemlerinin gelişme gösterdiği görülmektedir. Tekstil atıksularının anaerobik yöntemler ile arıtılmasında dikkate alınması gereken parametreler; boya yapısı ve konsantrasyonu, hidrolik bekletme süresi (HBS), biyokütle konsantrasyonu, alternatif elektron alıcısı, giriş birincil besin konsantrasyonu ve çeşidi olarak sıralanabilir.

Tekstil atıksularının anaerobik ve aerobik şartlarda kullanılabilme avantajına sahip membran biyoreaktör sistemleri de araştırmacılarca incelenmiştir. Membran biyoreaktörlerin arıtma verimlerinin yüksek olmasına rağmen tıkanma ve bakım problemleri dolayısıyla efektif olmadıkları araştırmacılarca belirtilmiştir. Bununla birlikte ters ozmoz, ultrafiltrasyon ve nanofiltrasyon da tekstil atıksularının arıtılması amacıyla araştırılmış olup yüksek debilerde artan maliyetler dolayısıyla halihazırda tercih edilmedikleri görülmüştür.

Bu çalışmada sentetik tekstil atıksuyunun mezofilik şartlarda anaerobik arıtılabilirliğinin araştırılması hedeflenmiştir. Sistem olarak 40 cm çapında ve 80 cm yüksekliğinde 55 litre aktif hacme sahip pilot ölçekli anaerobik reaktör kullanılmıştır. Bununla birlikte çalışmanın başında teknik ve işletme problemleriyle karşılaşmıştır. Bu nedenle çalışmada işletmeye alma kısmı esnasında elde edilen sonuçlar sunulmuştur. Reaktörde aşı için İSKİ Ataköy İleri Arıtma Tesisinden alınan çamur kullanılmıştır. Çalışma sırasında mikroorganizma konsantrasyonu 2.500-3.000 mg/l aralığında tutulmuştur. Çalışma toplam 264 gün sürmüş olup, temel olarak iki aşamada yürütülmüştür. Anaerobik reaktör 154. güne kadar saha şartlarında gözlenme amacıyla aktif olarak çalışan kumaş boyama fabrikası olan bir boya firmasına yerleştirilmiştir. Bu süreçte elektrik kesintileri, ekipman arızaları, vb. teknik ve işletme problemleri yaşanmıştır. Birinci aşamada reaktör 24 saat hidrolik bekleme süresinde (HBS) ortalama KOİ değeri 2.400 mg/l olan sentetik atıksu ile 81 gün işletilmiş olup, ortalama ~54% KOİ giderim verimi elde edilmiştir. İkinci aşamada ise reaktör iki farklı HBS’de işletilmiştir. Bu aşamada giriş KOİ suyu konsantrasyonu düşürülmüş olup HBS önce 24 saat sonra 48 saat olarak belirlenmiştir. Ayrıca sentetik atıksuyun karakterizasyonu değiştirilmiş olup KOİ konsantrasyonu azaltılmış, makro nütrientlerin konsantrasyonu ise artırılmıştır. İkinci aşama/birinci periyot 93 gün sürmüş olup, ortalama 875 mg/l KOİ konsantrasyonuna sahip sentetik atıksu için 24 saatlik HBS’de ortalama ~45% KOİ giderim verimi gözlenmiştir. İkinci aşama/ikinci periyot ise 90 gün devam etmiştir. Bu periyotta giriş KOİ değeri yaklaşık olarak 975 mg/l olan sentetik atıksu için HBS 48 saat olarak ayarlanmış olup bu periyotta ~86% KOİ giderimi elde edilmiştir. KOİ gideriminin bu aşamada yükselmesiyle beraber reaktör kararlı hale gelmiştir. Bu durumun ortaya çıkmasındaki en önemli faktörün reaktörün laboratuvar ortamında muhafaza edilmesi, sıcaklık, bakım onarım gibi faktörlerin saha şartlarına oranla daha az değişime uğraması olduğu düşünülmektedir. Bu süreçte KOİ verimi artmış, aynı zamanda verilerin standart sapmaları da azalmıştır. Çalışmanın son kısmında (ikinci aşama/ikinci periyot) KOİ giderimine ek olarak askıda katı madde (AKM)/uçucu askıda katı madde (UAKM) oranı ile bulanıklık giderim verimi de belirlenmiştir. Ortalama AKM/UAKM oranı 0,62, ortalama bulanıklık giderim verimi ise ~70% olarak gözlenmiştir.

Teknik ve operasyonel sorunlar, birinci ve ikinci aşama/birinci periyotta dalgalanmalara neden olmuş ve sorunlar nedeniyle KOİ giderme verimliliği yaklaşık% 50 seviyelerinde kalmıştır. Bununla birlikte, problemlerin üstesinden gelindikten sonra, yüksek KOİ giderimi gözlenmiş ve çalışma sonunda (ikinci aşama/ikinci



periyot) kararlı durum koşulları sağlanmıştır. İlerleyen zamanlarda tekstil atıksularında renk giderme konusu da araştırılacaktır.

Çalışmada gerçek koşulları daha iyi yansıtabilmek için pilot ölçekli sistem sahaya yerleştirilmiş, ancak bu durum kontrol edilemeyen birçok farklı probleme yol açmıştır. Bu nedenle daha kontrollü koşullar için laboratuvar şartlarında çalışmaların yapılması önerilmekte, optimizasyonlar yapıldıktan sonra uygulama açısından test için saha çalışmaları tavsiye edilmektedir.





## **1. INTRODUCTION**

The textile industry is one of the major industrial areas that highly affects human life. Both a wide range of products and job opportunities make this industry highly important. The variety of textile products is being increased due to technological developments. Due to environmental effects the textile industry is one of the most polluted industries.

The textile industry has various processes, such as manufacturing fibers or fabric, dyeing, bleaching, etc. Mainly, fiber is turned into yarn, and yarn turned into a fabric that is used to manufacture end products such as clothes, curtains, towels, etc. (Ministry of Environmental and Urbanization, CSB, 2013).

Because of using dyes, the appearance of color is a unique characteristic in many industrial wastewaters, including dye manufacturing, kraft mills, tannery, textile waste, and other industrial wastes (e.g. food and cosmetics). Dye usage is very common in the textile industry. It is possible to categorize dye into two main groups: natural dyes and synthetic dyes. The word 'natural dye' covers all the dyes derived from natural sources like plants, animals, and minerals.

Managing textile wastewater is not so easy because of the high concentration of pollutants, which were caused by various factors such as using dyes and auxiliaries or contamination from fabric (washing unit). Reusing textile wastewater is also not much applicable because of the high concentration of chemicals and dyes which also cause a serious effect on the environment in case of discharging without an efficient treatment. Even though some of the dyes are not toxic, they are harmful to the ecosystem where they are introduced because of their sunlight-blocking properties (Zagal, 2008; Calisir, 2010). That's why the treatment of textile wastewater became a priority of industry.

Many textile companies are looking for efficient and feasible wastewater treatment solutions during the investment period. This demand leads the researchers to investigate alternative treatment systems or modify traditional systems.

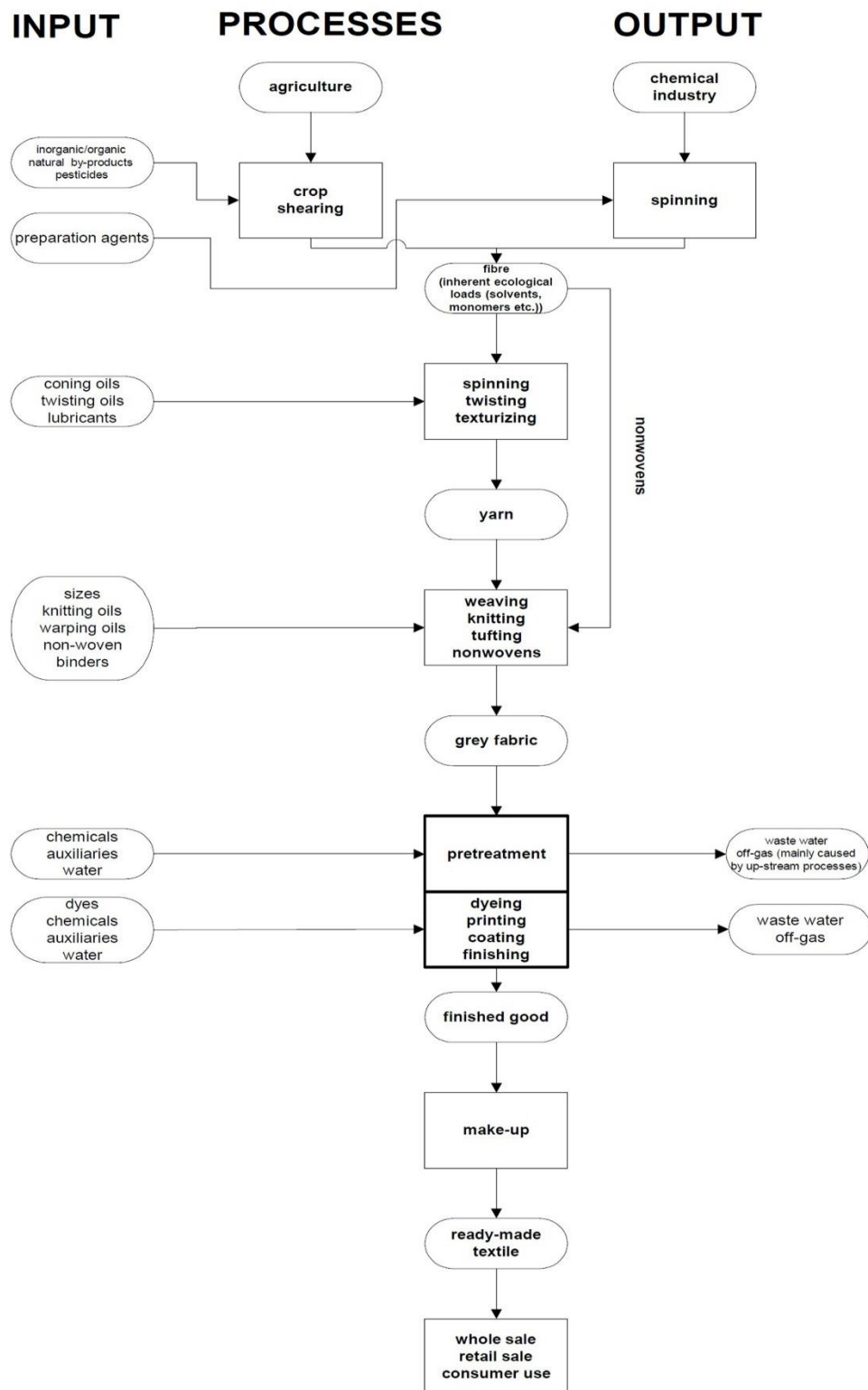
The purpose of this study is to investigate the treatability of synthetic textile wastewater by using a pilot-scale anaerobic completely stirred tank reactor (CSTR). However, technical and operational problems have occurred at the beginning of the study. For this reason, only the results of the start-up part was presented. Total duration of the study was 264 days. The study was conducted in two phases. The first phase was operated for 81 days to investigate COD removal of synthetic textile wastewater which has an average of 2.400 mg COD/l initial concentration with 24 h HRT. The second phase investigated under two periods by using similar synthetic wastewater with lower COD concentration and two different HRT. The average COD concentrations were 875 mg/l and 975 mg/l for phase two/period one (24 h HRT, 93 days operation) and phase two/period two (48 h HRT, 90 days operation), respectively.

## 2. LITERATURE SEARCH

Due to high COD levels, dye consumption in the textile industry has been always important for researchers who are interested in the environmental impact of textile industry. According to Desphande (2001), the data of dyes produced in the world is not available. It is estimated to be over 10.000 tons per year. Exact amounts of dyes discharged in the environment are also not known. Awareness of environmental protection in industrial production encourages the development of eco-friendly methods, reduced consumption of freshwater, and lower output of wastewater. In 2015, as the world production of man-made cellulosic fiber and cotton was  $90 \times 10^6$  Tone (Burkinhaw and Salihu, 2019). In addition to this, the amount of dye consumption is equal to 2% of total cellulosic fiber and cotton during the dyeing process (Desphande, 2001). These numbers show us; average dye consumption can be considered as  $1,8 \times 10^6$  tone/year. There are a lot of processes in textile industry. Flow chart of textile industry is shown in Fig. 2.1.

Due to the using a high amount of dye in textile wastewater, various methods such as; physical, chemical, and biological have been searched for color and COD removal from wastewater effluents. Although physical/chemical treatment methods reach considerable removal efficiencies, they are not economically feasible due to high energy and chemical needs, a high amount of sludge which causes disposal problems and complicated procedures (Saratale et al, 2010).

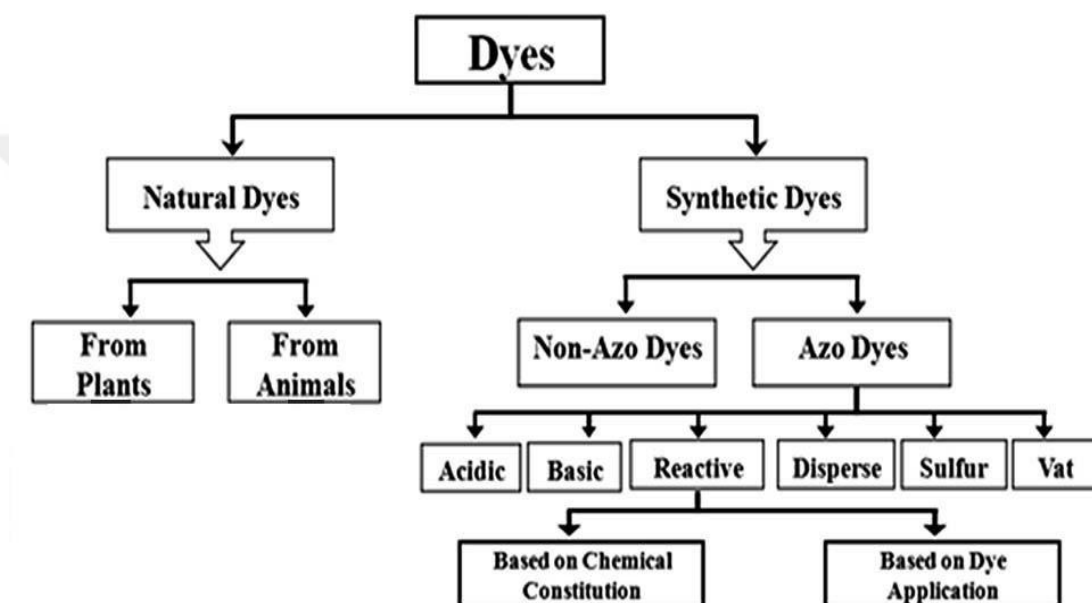
Biological methods have considerable advantages such as low operating costs and non-toxic end products. The various aspects of dye/color removal were investigated by Stolz (2001). In addition to traditional biological treatment systems, other methods such as using microorganisms derived from cattle manure for decolorization of Methyl violet and Rhodamine B and biofilms for decolorization of Acid Orange 7 have been employed (Forgacs et al, 2004).



**Figure 2.1.** Textile industry flow chart (OECD Environment Directorate, 2004).

## 2.1 Classification of Dyes

Aromatic compounds absorb electromagnetic energy. Only the ones which absorb the visible light (with wavelengths between 350-700 nm) are colored. Dyes contain auxochromes and chromophores. Usual chromophores are  $-C=C-$ ,  $-C=N-$ ,  $-C=O$ ,  $-N=N-$ ,  $-NO$ , and quinoid rings, while usual auxochromes are  $-NH_3$ ,  $-COOH$ ,  $-SO_3H$  and  $-OH$ . However, dyes are generally categorized into several groups and classes due to their structure, source, and fiber type with which they are most compatible as shown in Fig. 2.2.



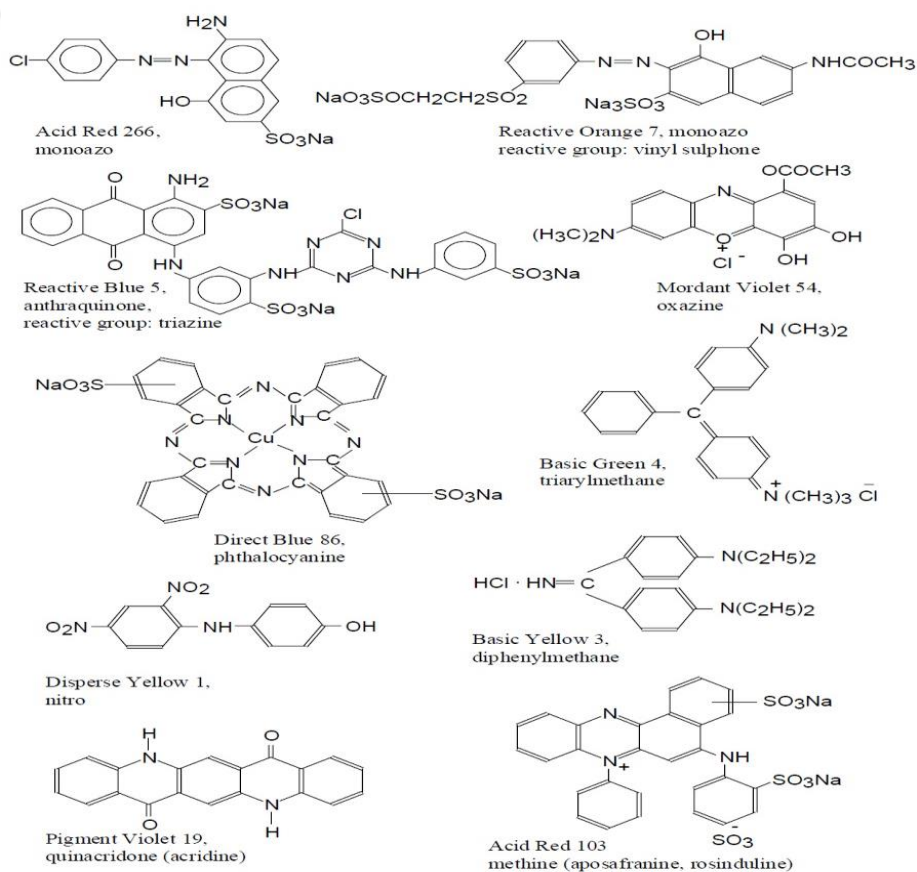
**Figure 2.2.** Dye classification based on dye chemical constitution and its application (Ajmal et al, 2014).

Natural dyes are mostly non-substantive and must be applied to textiles with the help of mordants, usually a metallic salt, having an affinity for both the coloring matter and the fiber (Samanta et al, 2009). That is why Synthetic dyes are extensively used in a wide range of industries amongst which textile processing industries are the major consumers (Keharia et al, 2003). Reactive dyes are the most common group of six classes of dye that can be used to dye cotton and other cellulosic fibers using immersion dyeing processes. Despite the very large global popularity of reactive dyes for cotton and other cellulosic fibers, their usage in immersion dyeing processes presents environmental challenges that arise because of the inherent inefficiency of the exhaust reactive dyeing process. In the textile industry, it is common to classify dyes

according to their solubility, usage areas, dyeing properties, and chemical structures (Birogul, 2012). Figure 2.3 shows the structural formulas of several different dyes (Zee, 2002).

Dye classes can be categorized under 6 major groups ;

- Acid dyes
- Basic dyes
- Vat dyes
- Disperse dyes
- Reactive dyes
- Sulfur dyes



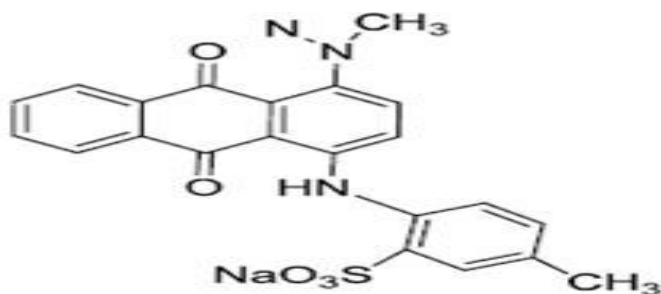
**Figure 2.3.** Structure of several dyes (Zee, 2002).

### 2.1.1 Acid dyes

Based on acid dyes' fastness characteristics, they can be used to dyeing several fiber types such as silk, nylon, and wool. The pH range for their application is 3-7. For decreasing the pH level of water consumed mostly acetic acid is used. Acid dyes contain metal complexes. The presence of a sulfonated group is the most important



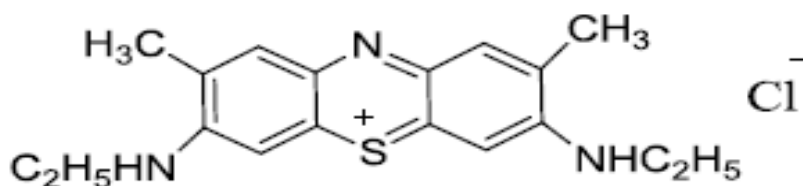
indicator to define acid dyes. In addition to this, the sulfonated group is the part that gives water solubility to acid dyes and colorful components are anions (Nunn, 1979). Basically, additional acid refers to the pH in dyebath more than the presence of sulfonated groups in the structure of acid dyes. The chemical structure of a common example of an acid dye; C.I. Acid Blue 24 is shown in Fig. 2.4.



**Figure 2.4.** Chemical structure of C.I. acid blue 24 (Nunn, 1979).

### 2.1.2 Basic dyes

Basic dyes are mostly used for dyeing acid group-containing synthetic polyacrylic fibers employing the cationic compounds which bind to an acid group of fibers in the structure of these dyes. They represent approximately 5% of all dyes listed in the Color Index (Zee, 2002). The basic dyes that have low migration that is why they are applied with retardants to have optimum dyeing efficiency. This low migration is due to the substrate's substantiality to the dye and diffusion speed at high temperatures (Benkhaya et al, 2007). The typical chemical structure of a common example of a basic dye; Basic Blue 22 is shown in Fig. 2.5.

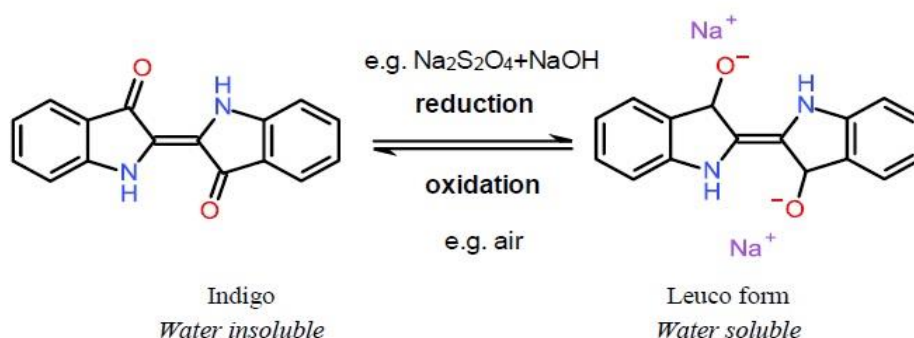


**Figure 2.5.** Chemical structure of basic blue 22 (Benkhaya et al, 2007).

### 2.1.3 Vat dyes

Indigo or indigotin is the most common natural vat dye found in various species of indigo plant *Indigofera*. Vat dyeing is a good option when bright and high color fastness is needed (Benkhaya et al, 2007).

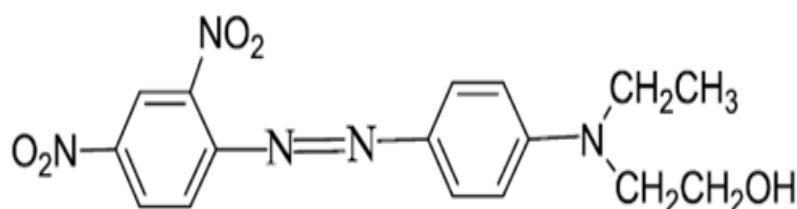
Vat dyes have water-insoluble characteristics mostly and particularly used for dyeing cellulosic fibers. Vat dyes are mostly used in their reduced (leuco) form that occurs with sodium dithionite in the dyeing process (Zee, 2002). The typical chemical structure of Indigo and leuco form are given in Fig. 2.6.



**Figure 2.6.** Chemical structure of Indigo and leuco form (Bagha et al, 2013).

#### 2.1.4 Disperse dyes

Disperse dyes are barely soluble dyes. It is very hard for them to interact with synthetic fiber such as polyester, acryl, cellulose acetate and etc. High temperature like over 120 °C is needed for the application of these dyes. The chemical structure of the common example of a disperse dye; Red 8 form is shown in Fig. 2.7.



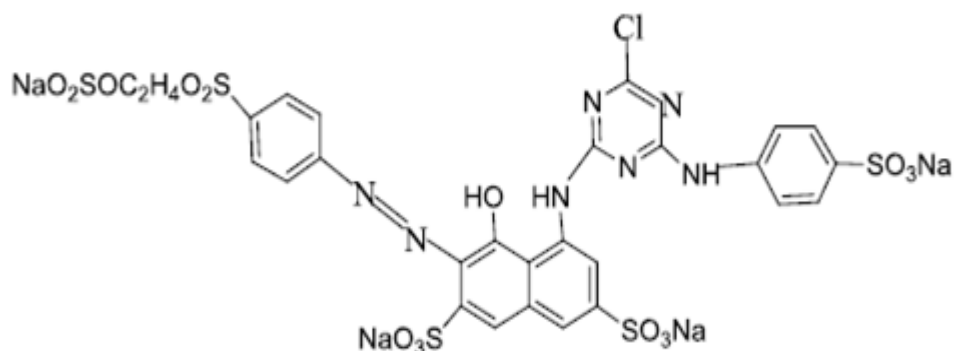
**Figure 2.7.** Chemical structure of disperse dye red 8 (Hunger, 2003).

#### 2.1.5 Reactive dyes

The reactive groups in reactive dyes form covalent bonds with OH-, NH-, or SH-groups in fibers. This interaction causes dyeing. Correspondingly, the issue of colored effluents is mainly associated with the use of reactive colors. The majority of reactive colors (approximately 80%) are azo or metal complex azo compounds (Zee, 2002).

The first commercial reactive dyes were in 1956 and they were produced based on a dichloro-s-triazine reactive group for cotton dyeing. Since 1956, various reactive group-based dyes have been developed and manufactured, especially in industrial

countries. (Ahmed, 1995; Shore, 1995; Zee, 2002 and Khatri et al, 2015). The chemical structure of a common example of a reactive dye; Reactive Red 198 dye is shown in Fig. 2.8.



**Figure 2.8.** Chemical structure of reactive red 198 (Benkhaya et al, 2007).

### 2.1.6 Sulfur dyes

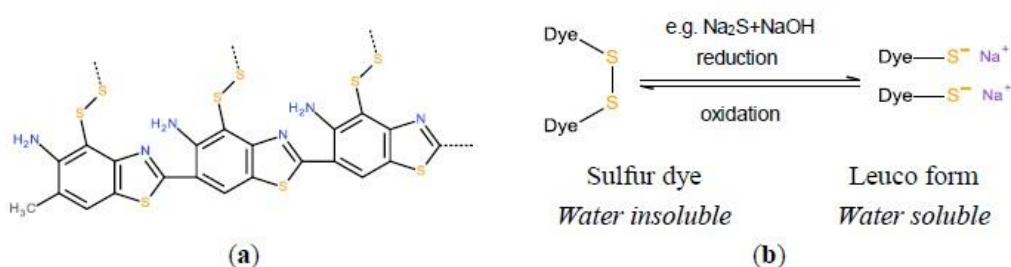
The first commercial sulfur dye was Cachou de Laval (C.I. Sulphur Brown 1) prepared by Croissant and Bretonnière in 1873 (Benkhaya et al, 2007). Sulfur dyes are mostly applied in dyeing for dark colors such as brown and black.

They have water-insoluble similarity with vat dyes. Due to this similarity sulfur dyes also need to be reduced to leuco form. For this reduction commonly sodium sulfide is used (Bagha et al, 2013). It has been confirmed that sulfur dyes represent 50% of all dyes used for cellulosic fibers dyeing (Wang et al, 2001).

On the other hand, according to some researches 9,1% of total US dye manufacturing are sulfur dyes, and 15,8 % of these dyes produced for dyeing cellulosic fibers and the world production was estimated at 110.000–120.000 tons per year (Benkhaya et al, 2007). Typical chemical structures of sulfur dyes and their reduced forms are shown in Fig. 2.9 and Fig. 2.10



**Figure 2.9.** Chemical structure of some sulfur dyes (Benkhaya et al, 2007).



**Figure 2.10.** Reduction of a sulfur dye (Benkhaya et al, 2007; Bagha et al, 2013).

(a) an example of a sulfur dye (b) The intensely colored and hydrophobic sulfur dye can be reduced to the water-soluble leuco form. The leuco form is oxidized back to the colored form.

## 2.2 Usage of Dyes in Textile Industry

One of the most important designing parameters of the textile industry is color that is why dyes are highly used therein. Although design and colors are the main factors for users, values of perspiration, good fixation, washing are taken into consideration by them as well. To supply all these features chosen dyes should be feasible, resistant to fading, and uniformly colored (Guaratini et al, 2000). Water is one of the fundamental demands for dyeing processes and the amount of it can change based on the type of machine employed, type of fiber used, methods, etc. (Burkinshaw, 2016).

According to Burkinshaw (2016), approximate water consumption corresponds to 18 l/kg-fiber. On the other hand, it was pointed out that 96 l/kg of water is consumed in traditional batches jet dyeing process (immersion dyeing of cotton with reactive dyes) (Huntsman, 2010).

Preparation is a very important step in which undesirable components which are harmful to the dyeing process are removed from the fabrics before dyeing. Detergents, alkaline substances and enzymes can be used for that purpose. As the last step of preparation, most fabrics are bleached by using chlorine-containing products - mostly hydrogen peroxide to extract the natural color from their body and the optical brightening agents are applied if the fabric is to be solid white and not colored.

Dyeing is the watery application of color to the material substrates, primarily utilizing engineered natural colors and as often as possible at raised temperatures and weights in a few of the steps (Reddy et al, 2008). During this progression, the colors and chemicals help such as alkali/bases, acids, surfactants, electrolytes, carriers, leveling operators, advancing operators, chelating operators, emulsifying oils, softening specialists, etc. are applied to the material to obtain a uniform profundity of color with the colorfastness properties appropriate for the conclusion utilize of the texture (Moore and Ausley, 2004). This preparation incorporates dissemination of the color into the fluid stage taken after by adsorption onto the external surface of the fibers, and at long last diffusion and adsorption on the inward surface of the fibers (Chequer et al, 2013). Depending on the usage area, a different type of fibers and dyes can be applied. For example, swimwear fabrics should be waterproof and fabrics used in cars should be durable against fadedness by sunlight. That is why different types of dyes and auxiliary products are used to reach the quality and properties desired (Moore et al, 2004).

### **2.3 Auxiliaries of Dyeing Process**

Dyeing processes demand auxiliaries that are used in other textile processes as well. Auxiliaries augment the dyeing process in specific ways such as fiber protection, dye balancing, fiber wetting, pH arranging, etc. Besides their primary duty, auxiliaries can have more than one role. Because of that, most commercial auxiliaries are mixtures that can contain several components such as acids, reducing and oxidizing agents, inorganic salts, lye (e.g. NaOH), polymers, etc. (Burkinshaw and Salihu, 2019). Some of the auxiliaries according to their application and components are shown in Table 2.1.

**Table 2.1.** Overview of auxiliaries employed in dyeing, their effects and chemical composition (OECD Environment Directorate, 2004).

Process	Auxiliary	Effect	Chemical Composition
Manufacturing of man-made fibers, coning, texturizing, spinning, twisting, winding, warping, weaving, knitting	Preparation agents (preparation agents for primary spinning, lubricants, conditioning agents, coning oils, warping oils, twisting oils, knitting oils)	Increasing processability, Protection of fibers/yarns; adjusting of friction properties; impart of anti-electrostatic properties	Mineral oils, common fatty acid esters, ethylene oxide-propylene oxide adducts, hindered fatty acid esters, polyesters, polyester-polyether carbonates, silicones, additives
Sizing	Sizing agents, sizing additives	Protection of warp yarns during weaving (Applied in weaving mills)	Macro-molecular natural or synthetic products (starch, modified starch, modified celluloses, polyvinyl alcohol, polyacrylates, polyesters) Additives
Scouring (kier boiling)	Scouring auxiliaries	Removal of fiber by-products (fats, waxes, inorganics etc.) from cellulose or synthetic fibers	Strong alkali; alkaline-resistant and electrolyte resistant surfactants (fatty alcohol ethoxylates, alkane sulfonates), complexing agents
Bleaching	Bleaching auxiliaries	Bleaching, whitening.	Peroxide, sodium chlorite, sodium hydroxide, dithionite, and dithionite derivatives, complexing agents, surfactants stable in acidic or alkali conditions, silicates,

**Table 2.1. (continued):** Overview of auxiliaries employed in dyeing, their effects and chemical composition (OECD Environment Directorate, 2004).

Process	Auxiliary	Effect	Chemical Composition
Carbonizing	Carbonizing auxiliaries	Removal of vegetable impurities with acid or acid salts	Strong sulfuric acid, acid-stable wetting agents (alkyl arylsulfatase, alkane sulfonates, fatty alcohol ethoxylates)
Dissolving of dyestuffs	Dyestuff solubilizing and hydrotropic agents, Dispersing agents, Protective colloids	Promotion of the dissolution of dyestuffs in water,	Naphthalene sulfonic acid formaldehyde condensates, naphthaline sulfonates, lignosulfonates, fatty alcohol ethoxylates, alkyl sulfonates, polyacrylates
Exhaust dyeing, padding processes	Wetting agents, De-aeration agents	Increase of wetting capacity of the dye liquors; improve dye penetration in padding processes; increase of dye absorption	Alkyl sulfates, alkane sulfonates, alkylaryl sulfonates, salts of sulfosuccinate acid esters, fatty alcohol ethoxylates, alcohols of higher valence, phosphoric acid esters,
Continuous dyeing, printing	Fixing acceleration for continuous dyeing and printing	Acceleration of dye fixation and diffusion, an increase of dyestuff yield	Aromatic ethers, fatty acid ethoxylates, polyglycols
After-treatment	After-treatment agents for fastness improvement	Improve rubbing fastness, wet fastness and lightfastness	Soaping after-treatment with detergents or dye-affinitive polymers. Cationic fixing agents for direct and reactive dyes. Polysulfonates for improvement of polyamide dyeing with anionic dyestuffs. Reducing agents for PES.

Auxiliary usage varies according to several factors, such as the particular dye-fiber system employed, depth of shade of the dyeing, machine type, liquor ratio employed (a detailed account of liquor ratio is presented above), etc., as illustrated in Table 2.2, which shows some of the amounts of auxiliary that can be employed in the different processes.

**Table 2.2.** Application of auxiliaries for different processes (OECD Environment Directorate, 2004).

Product	Process	Application Amount $Q_{\text{product}}$ (kg/t)
Preparation agents	Upstream processes to finishing	20 (2%)
Sizing agents	Weaving	100 (10%)
Basic chemicals	Finishing	varies strongly
Auxiliaries	Finishing, exhaust processes	20 (2%)
Auxiliaries	Finishing semi-continuous and continuous processes	30 (3%)
Auxiliaries	Padding liquors functional finishing	20 (2%)
Dyestuffs (powder form)	Dyeing, printing	50 (5%)
Dyestuffs (liquid)	Dyeing, printing	100 (10%)
Printing paste	Printing	750-1000 (75-100%)
Coating paste	Coating	>100 (>10%)

## 2.4 Countries Leading the Textile Industry in The World

Due to economical incomes of the textile industry, it became very important for countries all over the world. Turkey is also one of the leading textile exporting countries; As of 2012, Turkey ranks seventh in performing 3,8% of total world exports of textiles. Hong Kong, Japan, countries such as Indonesia and France are the main countries in both the textile export and imports. On the other hand, countries such as India and Pakistan, which have abundant raw materials, are textile exporters. Countries and exporting shares are shown in Table 2.3 (Turk, 2014).



**Table 2.3.** Textile Exporting Countries and Shares (Turk, 2014).

Countries	2005	2008	2009	2012	Share (%)
China	41,1	65,3	59,8	95,4	33,4
India	8,3	10,3	9,1	15,2	5,3
Germany	13,5	16,3	12,9	14,4	5,04
United States	12,4	12,5	9,9	13,4	4,7
Italy	14,8	16,1	11,8	13,1	4,5
Korea	10,4	10,3	9,1	11,9	4,1
Turkey	7,1	9,3	7,7	11,1	<b>3,8</b>
Hong Kong	13,8	12,2	9,9	10,5	3,6
Taiwan	9,7	9,2	7,8	10,2	3,5
Pakistan	7,1	7,1	6,5	8,7	3,04
Japan	6,8	7,3	6,1	7,8	2,7
Belgium	7,4	8,2	6,3	6,1	2,1
France	6,9	7,3	5,6	5,3	1,8
Netherlands	4	5,3	4,4	5,1	1,7
Indonesia	3,3	3,6	3,2	4,5	1,5
Total	-	-	-	232,7	81,4
World Total	-	-	-	285,6	100

## 2.5 Discharge Standards of Textile Wastewater

There are many types of research about characterization, and discharge limits of the textile industry. Countries' discharge limits for treated textile wastewater based on different parameters are given in Table 2.4.

**Table 2.4.** Discharge Standards of Textile Wastewater for Different Countries (Adapted from Dey and Islam, 2015; Wang et al, 2011; SKKY, 2004).

Parameter <sup>a</sup>	China (mg/L)	India (mg/L)	Pakistan (mg/L)	Bangladesh (mg/L)	Germany (mg/L)	USA <sup>b</sup> (kg/t)"	Turkey (mg/L)
pH	6-9	6-9	6-10	6-9	-	6-10	6-9
COD	100	156-400	150	200	160	163	250
BOD <sub>5</sub>	25	80-250	80	50	25	22,4	-
TSS	70	200	150	150	-	35,2	160
Total -P	-	-	-	-	-	-	-
Total - N	-	-	-	-	20	-	-
NH <sub>3</sub>	-	-	-	-	10	-	-
NH <sub>4</sub> - N	-	-	-	-	-	-	5
Nitrite	-	-	-	-	1	-	-
Oil and Grease	-	10	-	-	-	-	10
Total Ch-Cr	-	-	-	-	-	-	2
Total Sulfur	-	-	-	-	-	-	0,1
Sulphide - S	-	-	-	-	-	0,28	1
Phen Com - C <sub>6</sub> H <sub>5</sub> OH	-	1	-	-	-	0,14	-
Fish Bio-Ex (ZSF) (No Unit)	-	-	-	-	-	-	3
Color(Pt-Co)	-	-	-	-	-	-	280

<sup>a</sup> Parameter abbreviation: Total-P, total phosphor; Total Ch-Cr, Total Chromium Chrome; Sulphide-S, sulphide sulfur; Phen Com, phenolic compounds; Fish Bio-Ex, fish bio-experiment

<sup>b</sup> USA Limits: Half of given number must be reached in one-month average

## 2.6 Characterization of Textile Wastewater

Textile wastewater treatment should be focused on several parameters such as COD, BOD, TSS, pH, Color, etc. The concentration of these parameters differs due to the processes, fabric type, auxiliaries, dye type, etc. Textile/dyeing wastewater is invariably highly colored, contains various types of both organic/inorganic compounds (see Table 2.1 and 2.2 for chemicals that could be present), and displays typically high values of color, chemical oxygen demand (COD).

**Effluent COD:** Residual dyes coupled with the organic and inorganic auxiliary chemicals are thus responsible for color, dissolved solids, and at times very high COD and/or BOD values in textile/dyeing wastewaters. Table 2.5-2.7 show the effluent characteristics based on different dyes, processes, and manufacturing types. Tables also show that, characteristic of wastewater highly related to the type of dyes, fiber, processes, etc. Textile wastewaters contain a dyeing process that has a high color content, high COD, and BOD values.

**Effluent TDS and TSS:** TDS or TSS amount in textile wastewater depend on several factors during the processes in the textile industry. For instance, for dyeing cotton high-level pH is needed and to reach a high pH level high amount of salt is assigned which causes high-level TDS at wastewater (Table 2.5).

Another factor that affects TSS concentration is the usage of lint filters which keeps lint out of clothes. The factories which use lint filters have low-level TSS wastewaters (Tufekci et al, 2007).

**Effluent pH:** Textile/dyeing wastewaters have large pH intervals due to the type of dye, fiber, and machines established for the dyeing process. This interval can range from 3.2 to 11.8.

**Effluent Color:** Acid, basic and direct dyeing processes are applied in low acidic pH levels. On the other hand, reactive, naphthols, sulfur, and vat dyes also cause high color concentration at higher pH levels. Table 2.5 and 2.6 also show that fabric type is also a very important parameter affecting color concentration in textile/dyeing wastewater.

**Table 2.5.** Characteristics of dyeing wastewater based on dye and fiber type (Horning, 1978).

Dye	Fiber	Color ADMI	BOD (mg/l)	TOC (mg/l)	SS (mg/l)	DS (mg/l)	pH
Acid	Polyamide	4000	240	315	14	2028	5,1
Acid/Chrome	Wool	3200	135	210	9	1086	4
Basic	Acrylic	5600	210	255	13	1469	4,5
Basic	Polyester	1300	1470	1120	4	1360	5,0
Direct developed	Viscose	2730	12	55	13	918	3,2
Direct	Viscose	12500	15	140	26	2669	6,6
Direct after cooperable	Cotton	525	87	135	41	2763	5,0
Reactive (batch)	Cotton	3890	0	150	32	12500	11,2
Reactive (continuous)	Cotton	1390	102	230	9	691	9,1
Sulphur (continuous)	Cotton	450	990	400	34	2000	3,7
Vat	Cotton	1910	294	265	41	3945	11,8
Disperse (high temp.)	Polyester	1245	198	360	76	1700	10,2
Disperse (atm. Dyeing)	Polyester	315	234	300	39	914	7,8
Disperse	Polyester (carpet)	215	159	240	101	771	7,1
Disperse	Polyamide (carpet)	100	78	130	14	396	8,3
Disperse/Acid/Basic (continuous)	Polyamide (carpet)	<50	130	160	49	258	6,5
Disperse/Acid/Basic (batch)	Cotton	210	42	130	8	450	6,7
Disperse/Vat (continuous)	Polyester	365	360	350	9	691	9,1

**Table 2.6.** Characteristics of textile/dyeing wastewater based on different processes (Bisschop and Spanjer, 2003).

Parameter	Fiber	Desizing	Scouring	Bleaching	Dyeing	Printing
COD (mg/l)	Wool	-	5000-90000	-	7920	-
	Cotton	950-20000	8000	288-13500	1115-4585	-
	Synthetic	-	-	-	620	1515
BOD <sub>5</sub> (mg/l)	Wool	-	2270-60000	400	400-2000	-
	Cotton	-	100-2900	90-1700	970-1460	-
	Synthetic	-	500-2800	-	530	590
Color (ADMI)	Wool	-	2000	-	2225	-
	Cotton	64-1900	694	15	1450-4750	-
	Synthetic	-	-	-	1750	-
TS (mg/l)	Wool	-	28900-49300	910	-	-
	Cotton	-	-	2300-14400	-	-
	Synthetic	-	-	-	-	150-250
	Not specified	7600-42900	-	-	<50000	-
Sulphate (mg/l)	Cotton	-	-	-	1750-2690	-
Chloride (mg/l)	Not specified	-	-	90-100	26000	-
pH	Wool	-	7,6-10,4	6,0	4,6-8	-
	Cotton	8,8-9,2	7,2-13	6,5-13,5	9,2-10,1	-
	Synthetic	-	8-10	-	11,7	-
	Not specified	6,8	-	-	-	5-8,5

**Table 2.7.** Textile/dyeing wastewater characteristics due to manufacturing type (EPA, 1978).

Parameter	Raw Wool Scouring	Yarn and Fabric Manufacturing	Wool Finishing	Woven Fabric Finishing	Knitted Fabric Finishing	Carpet Manufacturing	Stock and Yarn Dyeing and Finishing
BOD <sub>5</sub> (mg/l)	6000	300	350	650	350	300	250
TSS (mg/l)	8000	130	200	300	300	120	75
COD (mg/l)	3000	1040	1000	1200	1000	1000	800
Oil and Grase (mg/l)	5500	-	-	14	53	-	-
Total Chrome (mg/l)	0,05	4	0,014	0,04	0,05	0,42	0,27
Phenol (mg/l)	1,5	0,5	-	0,04	0,24	0,13	0,12
Sulphide (mg/l)	0,2	0,1	8	3	0,2	0,14	0,09
Color (ADMI)	2000	1000	-	325	400	600	600
BOD <sub>5</sub> / COD	0,2	0,29	0,35	0,54	0,35	0,30	0,31
pH	8,0	7,0	10,0	10,0	8,0	8,0	11,0
Temp. (°C)	36	33	13	113	150	69	150

In the study of Tufekci et al. (2007), eleven different textile company's industrial wastewater were investigated and BOD<sub>5</sub>, COD, SS, TKN (Total Kjeldahl Nitrogen), TP (Total Phosphor) of influent and effluent of wastewater analyzed (Table 2.8). They also compared the results with Water Pollution Control Regulation (SKKY), this comparison shows that most of the companies can reach the limits.

**Table 2.8.** Characteristics of eleven different textile wastewater in Turkey (Tufekci et al, 2007).

Mill Parameter	A			B			C			D		
	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.
BOD <sub>5</sub> (mg/l)	293	42	86	370	26	93	600	152	75	420	30,3	93
COD (mg/l)	614	120	80	714	92	87	1200	518	57	980	200	80
SS (mg/l)	56	22	60	120	9	92	300	96	68	300	32	89
TKN (mg/l)	10	7,4	26	10	8	20	30	15,2	49	20	11,3	43
TP (mg/l)	1,3	0,7	46	2	0,8	60	2	0,34	83	4	3,6	10
Grease (mg/l)	34	4	88	40	4	90	50	13	74	40	6,7	83

Mill Parameter	E			F			G			H		
	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.
BOD <sub>5</sub> (mg/l)	1140	181	84	715	363	49	520	162	69	410	48	88
COD (mg/l)	1963	877	55	1130	780	31	1030	599	42	900	129	86
SS (mg/l)	653	247	62	420	109	74	670	431	36	230	10	95
TKN (mg/l)	60	49	18	43	27	37	37	17,6	52	19	14,6	23
TP (mg/l)	11	3	73	9	4	55	2,8	0,7	75	2,4	0,2	92
Grease (mg/l)	133	62	53	97	31	68	71	19,4	73	48	6	87

**Table 2.8. (continued):** Characteristics of eleven different textile wastewater in Turkey (Tufekci et al, 2007).

Mill Parameter	I			K			L		
	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.	Inf.	Eff.	Rem.
BOD <sub>5</sub> (mg/l)	974	186	81	615	242	61	280	112	60
COD (mg/l)	1740	363	63	1605	800	50	720	298	59
SS (mg/l)	600	77	87	470	288	39	180	33	82
TKN (mg/l)	11	1,8	84	92,5	53	43	17	9	47
TP (mg/l)	3	0,33	89	4	0,3	92	3	1	66
Grease (mg/l)	120	65	46	127	32	75	52	9,2	82

Countries have their discharge criteria depends on the discharge point and source of treated wastewater. Color is also always an important parameter that always has been taken into consideration. Turkish legislation have color limits based on drinking water quality or discharge quality of different countries (Turkish Ministry of Environment and Urbanization, 2013) (Table 2.9).

**Table 2.9.** Color concentration limits of countries (CSB, 2013).

Country	Discharge/ Water Environment	Color Standards <sup>a</sup>
EUROPEAN UNION	Discharge to recipient environment	7 SAC 436 <sub>min</sub> (m <sup>-1</sup> )
		5 SAC 436 <sub>min</sub> (m <sup>-1</sup> )
		3 SAC 436 <sub>min</sub> (m <sup>-1</sup> )
CANADA	Drinking water	15 TCU
	Residual color at wastewater	300 ADMI
CHINA	<u>Dyeing industry</u>	
	Discharge limits to A Class Water	50 ADMI
	Discharge limits to B Class Water	180 ADMI
	<u>Other Industries</u>	
	Discharge limits to A Class Water	50 ADMI
USA EPA	Discharge limits to B Class Water	80 ADMI
	Discharge recipient water quality	15 TCU
	Discharge to water source	70 Pt-Co
	Underground water	15 Pt-Co
	Discharge recipient water quality	200 ADMI (3WL)
USA Oklahoma	Discharge recipient water quality	225-600 ADMI
USA New York	Drinking water	15 TCU
USA Rhode Island		
USA Wisconsin		
USA Atlanta		
AUSTRALIA	Discharge to a recipient environment	No change in the discharged environment
UNITED KINGDOM	Water quality at the recipient environment	550 <sub>nm</sub> de 0,055 absorbance unit
	Drinking water	5 Hazen
	Drinking water if there is no alternative resource	25 Hazen
	Earth water resources	300 Hazen
	Surface water resources A Class	10 Hazen
INDIA	Surface water resources B Class	300 Hazen
	Surface water resources C Class	>300 Hazen
TAIWAN	Discharge to recipient environment	400 ADMI
SINGAPUR	Discharge to recipient environment	7 lovibond unit
	Controlled discharge to recipient environment	7 lovibond unit
KENYA	Discharge to urban wastewater system	40 Hazen
	Discharge to recipient environment	15 Hazen
	Water quality for recreation	100 TCU

**Table 2.9. (continued):** Color concentration limits of countries (CSB, 2013).

Country	Discharge/ Water Environment	Color Standards <sup>a</sup>
MALESIA	Water quality at water resources (I Class)	15 TCU
	Water quality at water resources (II Class)	150 TCU
DUBAI	Discharge to sea	50 Color unit
GUATEMALA	Discharge to urban wastewater system	500 Pt-Co
VIETNAM	Water resources	15 Pt-Co
	Underground water	5-50 Pt-Co

<sup>a</sup> Color Standards: SAC, spectral absorption coefficient; TCU, true color unit; ADMI, American dye manufactures institute unit.

## 2.7 Methods Applied for Textile/Dyeing Wastewater Treatment

Although textile/dyeing wastewater is subjected to some form of effluent treatment, because the wastewater from dyeing processes characteristically displays marked resistance towards biodegradation, such treatment is, typically, not only complex but also entails a substantial expenditure of time, energy and chemicals.

Treatment methods of textile/dyeing wastewaters could be classified as physical, chemical, and biological. Although many strategies have been explored for treating dyeing effluent, including both traditional treatment methods such as adsorption, filtration and coagulation, as well as oxidation, biological degradation, photocatalysis, biosorption and low cost adsorbents, no single treatment method has yet been developed which can deal with the complex and varied nature of textile/dyeing wastewater. Furthermore, the impact of dyeing auxiliaries on the effectiveness of wastewater decolorization and re-use has received attention as has the toxicity of auxiliaries used in reactive dyeing whilst the environmental impact of surfactants is a well-discussed area (Wang et al, 2002).

### 2.7.1 Physico-chemical methods

#### 2.7.1.1 Coagulation / Flocculation

Coagulation/Flocculation process has been widely used for the treatment of the different types of industries' wastewaters including the textile industry.

Removal efficiencies of different types of coagulants on textile wastewater collected from the balancing tank of the treatment plant were investigated (Mohamed et al,2014) (Table 2.10). This study shows that the efficiency of this method depends on initial concentration, pH, dosage amount and coagulant type. In addition, they showed that

dosage amounts are not very applicable alone for textile waste due to the high flow rate of the textile industry.

Tufekci et al. (2007) reported that the average wastewater flow rate of 11 different textile factories is 190 m<sup>3</sup>/day. The sludge disposal problem also can be a factor in the selection of the coagulation/flocculation process for wastewater color removal. To reach economically feasible and satisfying effluent color quality, the coagulation process should be combined with other techniques such as biological processes.

**Table 2.10.** Treatment of industrial textile wastewater with Alum, MgCl<sub>2</sub>, and PAC (Mohamed et al, 2014).

Coagulant	Dosage (mg/L)	pH	Color Removal		
			Initial	Final	% Reduction
Alum	3.000	5	12.424	6.336	49
	4.000	4,7	12.450	4.607	63
	5.000	4,3	12.450	3.113	75
	6.000	2,4	12.424	1.242	90
	7.000	4	12.450	1.370	89
PAC	400	5,5	12.750	5.228	59
	600	5,6	12.750	4.718	63
	700	4,9	12.750	2.805	78
	800	4,5	17.200	344	98
	1.000	4,3	12.700	127	99
MgCl <sub>2</sub>	2.000	4,1	12.250	0	100
	1.000	11,6	12.750	9.563	25
	2.000	10,1	12.700	1.270	62
	3.000	10,6	12.400	372	97
	4.000	10,4	17.233	173	99
	5.000	10,3	17.233	345	98

### 2.7.1.2 Chlorination

Chlorine or sodium hypochlorite has been used for decolorizing waste in textile, tannery, and dyeing industries, because of the on-site availability of these chemicals. Chlorination pretreatment may increase the biodegradability of the biologically resistant compounds. The efficiency of using these chemicals depends on the chemical dosage, type of dyes, and solution pH. The optimum pH, in turn, depends on the type of colored wastewaters, for example, low pH is better for basic dyes and high pH for a Kraft mill wastewater. Also, chlorination is ineffective for the decolorization of disperse dyes. The major problem for the chlorination technique is the production of halogen organics. For example, compounds are identified in the coagulation/chlorination process for the treatment of a dye manufacturing waste,

including chloroanilines, chlorophenols, and chloronitrobenzenes. Even with dechlorination or other treatment techniques, it is doubtful that these hazardous compounds could be eliminated (Hao et al, 2000).

### 2.7.1.3 Adsorption

Adsorption is one of the most efficient methods that has been widely used for several types of industrial wastewaters. Pollutants in wastewater adhere to the surface of a solid part which is also called adsorbent has an extremely porous surface structure. Pollutants are concentrated on this solid surface with the help of liquid-solid intermolecular forces (Kandisa et al, 2016). Many adsorbents have been used for the treatment of a different type of wastewater and also for the removal of color from textile wastewaters. Mainly used adsorbents are activated carbon, kaolin, and silicon polymers. By using activated carbon, it is possible to reach 92% color removal and 91% COD removal. Yet, there are some important disadvantages of using activated carbon for textile wastewater, including regeneration and investment costs. Due to high concentration dye in textile wastewater, activated carbon can not be directly used for the treatment of this wastewater. On the other hand, activated carbon adsorption can be applied as an advance treatment (Zongping et al, 2011). Economic reasons and desire of searching alternatives lead researchers to investigate the adsorption capacity of different types of feasible adsorbents. The adsorption capacity of the waste red mug has been investigated widely and the results of these studies were summarized in the study of Kandisa et al. (2016) (Table 2.11).

**Table 2.11.** Adsorption capacity of some dyes on waste red mud investigated by researchers (Kandisa et al, 2016).

Dye	Adsorption Capacity	Researchers
Congo red	4,05 mg/g	Namasivayam and Arasi,1997
Methylene Blue	$7,8 \times 10^{-6}$ mol/g	Wang et al, 2011
Rhodamine B	$1,16 \times 10^{-5}$ mol/g	Gupta, 2014
Phosphate	205,13 mg/g	Prajapati et al, 2016
Remazol Brilliant Blue	27,8 mg/ g	Ratnamala et al, 2012
Safranin-O	89,4 mg/g	Sahu and Patel, 2015
Acid Blue 113	83,33 mg/g	Shirzad-Siboni et al, 2014
Reactive Black 5	35,58 mg/g	Shirzad-Siboni et al, 2014
Lead (Pb)	38,2 mg/g	Kong, 2011

Different wastes' adsorption capacity also was investigated Oden et al. (2017) used dry-prepared pomace in order to examine color removal from synthetic wastewater which contains a certain type of dye - Everzol Yellow 3RS. According to results they



obtained, 0,6g/250ml (more than 80% color removal) adsorption capacity was observed at 25°C and 7,7 pH with 150 min 250 rpm.

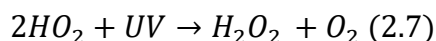
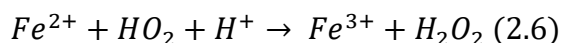
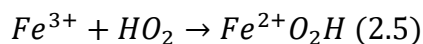
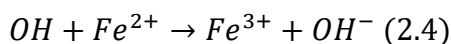
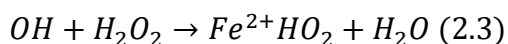
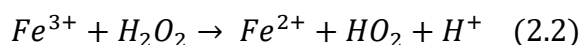
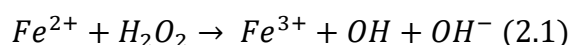
Some of the other alternatives also were investigated such as; a silica; rice husk, straw, mushroom, sulfonated coal, peat, hair, beet pulp, bentonite, sugar beet pulp, red mud, seaweed and bone chart, fly ash, palm-fruit particles, diatomite; teal wood balk (Hao et al, 2000).

#### **2.7.1.4 Advance oxidation processes (AOP)**

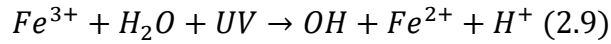
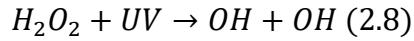
Recently, many AOPs, such as the Fenton's reagent [ $H_2O_2$  and Fe (II)], UV light with or without catalysis (e.g.,  $TiO_2$ ),  $H_2O_2$ , and  $O_3$ , have been evaluated for decolorization of wastewaters. The AOP processes are essentially based on the generation of highly reactive radical species, specifically, the hydroxyl radical (OH) to react with dye molecules.

##### ***Photo-fenton like oxidation;***

The photo-fenton process is an advance oxidation method which is found to be highly successful in removing pollutants. Iron is mostly used metal which are able to active  $H_2O_2$  reacts with  $Fe^{2+}$  to generate hydroxyl radicals in water. In the so-called Fenton process,  $H_2O_2$  reacts with  $Fe^{2+}$  to generate strong reactive species. The reactive species produced are traditionally recognized as hydroxyl radicals, though other substances such as iron ions are proposed. The classical Fenton radical mechanisms primarily involve the following reactions;



The photo-fenton process suggests same mechanism as Fenton process that defined between equation 2.1-2.7. Photo-fenton oxidation, in addition to the Fenton reactions the formation of hydroxyl radical also occurs by the reactions given below:



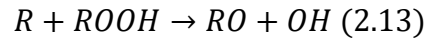
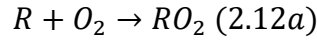
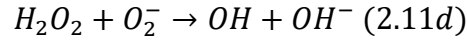
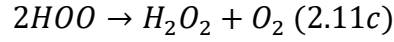
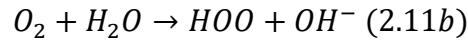
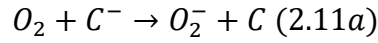
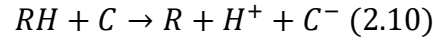
The naturally occurring form of iron is generally found as  $Fe^{3+}$  and additional  $Fe^{2+}$  tends to be oxidized to the  $Fe^{3+}$ . Hence,  $Fe^{3+}$  can be used as a source of iron which resulted in a process defined as photo-fenton-like (Park et al, 2018). A reactive blue dye-containing synthetic textile wastewater was examined by Kang et al. (2002). According to the results, 95% color removals observed in 5 min by Fenton process, which occurs mostly in the first stage of hydroxyl radical oxidation. Yet, the experiment showed that dosages of Fenton reagent are considerably high to reach an effective COD removal.

There are some important parameters which highly affect this method for COD and color removal. These are dosages of  $Fe^{2+}$  and  $H_2O_2$ , initial pH, dye concentration, and temperature. Ertugay ve Acar (2013) reached 94% COD and 51% color removal on Direct Blue 71 (DB71) containing synthetic wastewater by Fenton reagent method. In this study, optimum conditions were determined as  $Fe^{2+}$ = 3 mg/L,  $H_2O_2$ = 125 mg/L, and pH=3. In addition to this, increasing temperature from 20°C to 60°C positively affected efficiency.

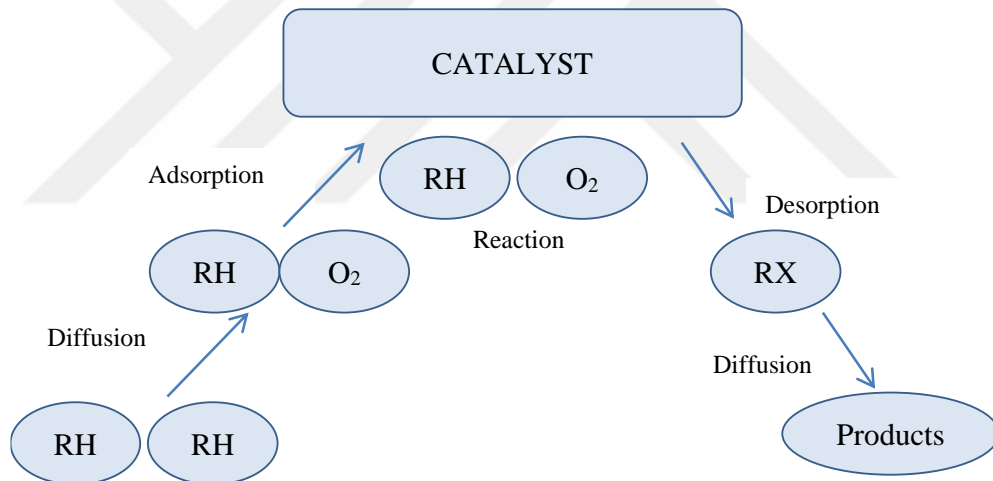
#### **2.7.1.5 Catalytic wet air oxidation**

When conventional treatment methods are insufficient for wastewater treatment, new and more efficient technologies are required. Therefore, studies on catalytic wet air oxidation (CWAO) increased. When this method is compared to the wet air oxidation; a higher oxidation rate due to the usage of the catalyst, low energy requirement, and more moderate oxidation conditions was observed (Levec and Pintar, 2007). The choice of catalyst to optimize temperature, pressure, and reaction time parameters is very important. Heterogeneous catalysts do not require an extra separation step after the reaction; therefore, they are more advantageous than homogeneous catalysts. Heterogeneous catalysts may be used without support, but the usage of an additional support material has certain advantages.

Support material increases catalyst stabilization and surface area (Bailie et al, 2001). The heterogeneous in CWAO reaction occurs on the surface of the catalyst.



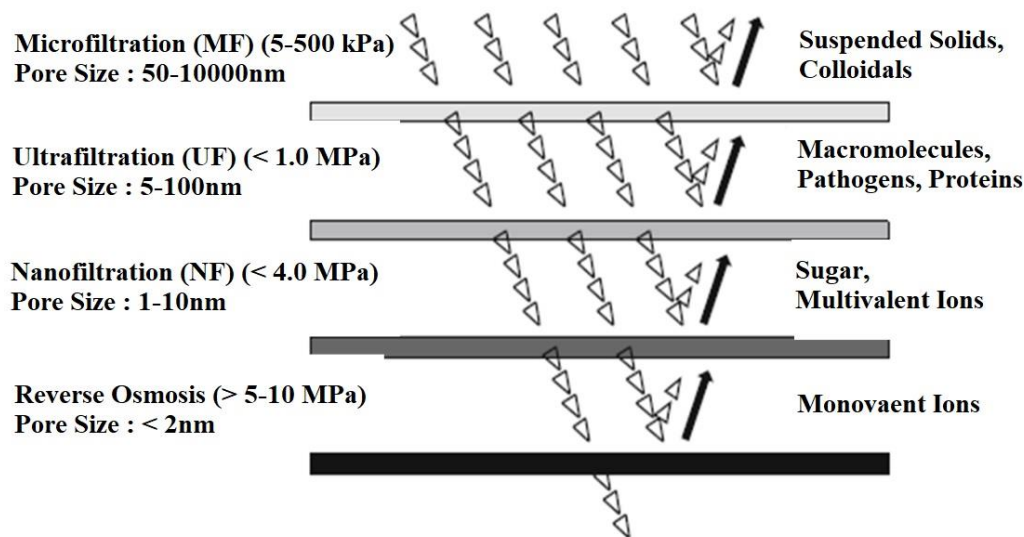
Reaction pathway of CWAO is shown in the Figure 2.11 schematically.



**Figure 2.11.** Reaction mechanism for heterogeneous CWAO (Heponiemi, 2015).

#### 2.7.1.6 Membrane applications

Membranes are microporous plastic barriers that are used for separating matters in suspensions. Membrane filters have wide application areas such as treatment of domestic or industrial wastewaters, desalination, treatment of drinking water. In addition to treatment applications, membranes also play an important role in the food industry, dairy industry, energy storage, etc. Membranes are considered as one of the most effective technology among wastewater treatment systems (Wang et al, 2011). Membranes types and properties are given in Figure 2.12.



**Figure 2.12.** Membranes types and properties (Wang et al, 2011).

### **Microfiltration (MF)**

Microfiltration membranes generally have 50-10.000nm pore sizes. They are mostly applied for eliminating colloidal particles, viruses, microorganisms. They can be run even under pressure 2 bar (Wang et al, 2011). For water recycling, microfiltration membranes conducted before reverse osmosis and nanofiltration units as a pre-treatment unit (Karaciray, 2019).

### **Ultrafiltration (UF)**

Since UF membranes allow the microparticles to take place in the permeate, the operating pressure is between 10-20 bars. UF membranes have a wide application area but it is not sufficient alone in wastewater treatment that is why it can be used for pre-treatment before RO systems and can be integrated into different systems (Baker, 2004)

### **Nanofiltration (NF)**

The pore size of nanofiltration membranes is in the range of 1-10nm. Since the pore size of NF membranes between RO and UF membranes, the operating pressure is between 10-20 bars (Wang et al, 2011).

NF membranes are also common in the industrial area. It serves to use salt removal, water recycling, treatment of whey, and color removal from textile wastewater. (Baker, 2004).

## Reverse osmosis (RO)

Due to its pore size under 2nm, RO membranes can separate almost all dissolved substances from solution. Because of its obligation to operate with high pressure (5-10MPa), its operating costs are relatively high. Its common application area is the treatment of drinking water. It is also used to be integrated with other membrane systems for the purpose of removing monovalent salts, water purification, salt recovery from seawater, and brine (Wang et al, 2011).

## Membrane applications in textile wastewater treatment

Suspended particles and biological molecules can be removed via MF and UF membranes. In the investigation of the treatment of a dyeing process, MF filtration followed by UF filtration was reported to be efficient (Uzal et al, 2009). In Japan, 82% of COD removal and 94% color removal were achieved by using UF membranes in a fabric bleaching factory (Rautenbach ve Albrecht, 1989). Yet, it was reported that UF membranes are not efficient for the removal of some dye types (Watters et al, 1991; Noel et al, 2000; Tang and Chen, 2006). NF membranes have been frequently applied in the dyeing industry. It was reported that the NF membrane can reach 99% color removal efficiency. Applying NF membranes in full-scale projects showed high efficiencies and short return-on-investment periods (Tang and Chen, 2006). Some studies were summarized in Table 2.12.

**Table 2.12.** Several membrane technologies applied in textile wastewater treatment (Adapted from (CSB, 2013).

Membrane	Waste Water	Dye	Color Removal (%)	References
UF + NF	Synthetic	n.m.	94-97	Alcaina-Miranda et al, 2009
UF + NF	Synthetic	n.m.	99 for NF+UF,	Fersi and Dhahbi, 2008
NF	Synthetic	Blue Bezaktiv	+99,6	Aouni et al, 2009
NF	Synthetic	SGLD 150 ve Black Novacron R	96	Khouni et al, 2011
MF + NF	Synthetic	Reactive and direct	100	Ellouze et al, 2012
RO	Synthetic	Azo dye	91,9-99,9	Nataraj et al, 2009

### **2.7.2 Biological methods**

There are some advantages of using microorganisms for the removal of dyes from textile wastewaters. The processes with microorganisms are relatively cheap to operate and end products are non-toxic that is also an advantage during the management of it (Forgacs et al, 2004).

Many researchers have managed to partially or completely remove the color from wastewater by using pure or mixed culture bacteria, fungi, and algae.

The first step of bacterial degradation of Azo dyes is the cleavage of -N=N- bonds. Dye degradation is also referred to as decolorization. Studies show that removal of dyeing textile wastewaters can occur under aerobic, anaerobic, and anoxic conditions by various groups of bacteria (Alabdraba and Albayati, 2014).

#### **2.7.2.1 Aerobic Treatment**

It is a well-known fact that traditional aerobic treatment systems are most suitable for certain types of industrial and municipal wastewaters. Due to the low biodegradability of some textile dyes (mostly reactive dyes) aerobic biological treatment is not always sufficient for color removal (Vilaseca et al, 2010). Although aerobic treatment methods for dye removal had a successful application in many studies and reports, a common conclusion is most of the azo dyes are non-biodegradable by traditional aerobic methods (Shore J, 1995).

#### **Bacterial treatment method**

In general, bacterial treatment of wastewater takes place in aerobic (in the presence of oxygen) and / or anaerobic conditions (in the absence of oxygen). The most important point in the biodegradability of dyes is the chemical structure of dyes.

The natural structure of the azo bond of dye molecules prevents its sensitivity to oxidative reactions. Although, azo dyes are resistant to biodegradation under aerobic conditions, some bacterial groups that reduce azo dye in aerobic conditions have been isolated in the last few years. Since most of them cannot use azo dye for growth and development, they need some organic carbon sources (Stolz, 2001). This shows that dyes are not used by aerobic bacteria as a source of carbon and energy, bacteria need an alternative carbon source. For example, *Bacillus subtilis* can break down p-aminoazobenzene in an aerobic environment only when another source of carbon and energy (glucose) is present (Zissi et al, 1997).

### **Fungal treatment method**

In scientific researches on biodegradation of dyes, the most commonly used pure microorganism cultures are white-rot fungi. This group of organisms is at the center of the global carbon cycle, as it plays an important role in the decomposition of lignin, a plant material with a complex polymeric structure. In addition to lignin, white rotting fungi play a role in the biodegradation of organic pollutants with a wide spectrum that undergoes difficult biodegradation.

### **Treatment by algae**

In many studies, it has been reported that algae can reduce azo dyes (Semple et al, 1999). Some algae (e.g. *Microcystis sp.*) species have been reported to be successful in removing color from paper industry wastewater. In two-month incubations of pure and mixed algae cultures, 70% color removal yields were observed (Lee et al, 1978). However, dyes in wastewater have not been completely removed in studies with algae, which is why it is not a recommended treatment application.

#### **2.7.2.2 Anaerobic treatment**

It has been reported by Forgacs et al. (2004) that many anaerobic treatment methods widely have been investigated to evaluate their color removal efficiency from dyeing or textile wastewaters. During the investigation of color removal from textile or dyeing wastewaters under anaerobic conditions, several anaerobic reactor types such as Upflow Anaerobic Sludge Blanket Reactor (UASB), Anaerobic Baffled Reactor (ABR) or Anaerobic Sequencing Batch Reactor (ASBR) have been evaluated (Sen and Denirer 2003). Due to some advantages of thermophilic UASB systems such as fast-high degradation and low HRT, UASB systems are much more applicable than mesophilic systems. This detail also applies to other anaerobic systems (Willettts and Ashbott 2000). On the other hand, these advantages should also be investigated according to energy costs (Garan and Celik 2018).

Decolorization of Black 2 HN and Orange 2 which are relevant with commercial azo dyes by using ASBR showed more than 99% dye removal with 400 mg/l initial dye concentration (Manu and Chaudhari 2002). Similarly, dye removal of synthetic wastewaters which have 100 mg/l initial concentrations of Reactive Red 24, Reactive Black 5 and Reactive Blue 49 dyes was investigated by using ASBR with different HRTs (Carliell et al., 1994). They reported 90-97% removal (for 32 h HRT) for

Reactive Red 24, 80-85% removal (for 4,5 h HRT) for Reactive Black 5 and 7-10% removal (2 h HRT) for Reactive Blue 49.

Dye removal of synthetic wastewater containing 500 mg/l Remazol Black B dye was investigated by using up flow anaerobic filter reactor and more than 95% color removal with 48 h HRT was obtained (Oxspring et al, 1996). Results of some studies are shown in Table 2.13.

**Table 2.13.** Color removal efficiency of different anaerobic systems (Adapted from D'Antoni et al, 2017).

Dye	Reactor	HRT	Color Removal (%)	References
Acid Red 42	UASB	16h	62	Goncalves et al, 1993
Direct Red 80			81	
Disperse Blue 56			0	
Acid Orange 7	Fluidized Bed	24h	90	Seshadri et al, 1994
Acid Orange 8		12h	98	
Acid Orange 10		12h	81	
Acid Red 14		24h	86	
Acid Yellow 17	UASB	8-20 h	20	An et al, 1996
Basic Blue 3			72	
Remazol Black B	Upflow Filter	48h	>95	Oxspring et al, 1996
Mordant Orange 1		8h	95	
Mordant Orange 1	UASB	8h	99	Donlon et al., 1997
Azodisalicylate		8h	98,9	
Azodisalicylate	UASB	24h	88,9	Razo-Flores et al, 1997
Maxilon Red BL-N	Upflow Filter	6-8,6h	99	Basibuyuk and Forester 1997
Pricion RED H-E7B	UASB	16h	55-77	O'Neill et al, 2000a
Textile Wastewater	ABR	20h	90	Bell et al, 2000
Textile Wastewater	UASB	8-10h	80	Huren et al, 1994
Textile Wastewater	Fluidized Bed	5,7h	59	Sen et al, 2003

### 2.7.2.3 Sequential and integrated anaerobic-aerobic systems

Combined/sequential systems involve separated sequential steps in which the anaerobic phase is followed by the aerobic phase for the complete treatment of textile/dyeing wastewaters. To understand the principle of these systems it is important to investigate reactions related to dye removal both under anaerobic and aerobic conditions. Dyes (mostly azo dyes) are biologically degraded into toxic aromatic amines which are mostly colorless under anaerobic conditions. These amines have structure rapidly degradable by aerobic bacteria (Hazrat, 2010).

In the study of Amaral et al. (2014), color removal efficiencies were noted respectively 52% and 94%, where UASB reactor is followed by a Submerged Aerated Biofilter



(SAB) for investigating decolorization of textile/dyeing wastewater. Decolorization of several combined / sequential anaerobic-aerobic systems are shown in Table 2.14.

**Table 2.14.** Combined/Sequential anaerobic-aerobic reactor systems (Adapted from Zee and Villaverde, 2005; Di'Antoni et al, 2017).

Anaerobic <sup>a</sup>		Aerobic <sup>b</sup>		Wastewater Characteristic			Color Removal		References
Type	HRT	Type	HR <sup>c</sup>	Type <sup>d</sup>	Concentration (mg/l)	Substrate <sup>e</sup>	Anaerobic	Aerobic <sup>f</sup>	
Filter	36	CAS	36	Synthetic	5-100	Glucose	90-100	+	Rajaguru et al, 2000
Filter	12-72	CAS	10	Synthetic	400-450	Molasses	60-100	+15	Kapdan et al, 2003
Filter	12-72	CAS	10	Synthetic	n.m.	Glucose & Nutrients	60-85	10	Kapdan and Alparslan, 2005
Filter	24	CAS	24	Denim Ww	n.m.	-	90	n.m.	Setiadi et al., 2004
Filter	6	Filter	7,7+ 8,6	Synthetic	25	Starch & Glucose	0	+	Basibuyuk and Forster, 1997
UASB	24	CAS	19	Synthetic	450	Starch & Acetate	64	11	O'Neill et al, 2000b
UASB	24	CAS	19	Synthetic	150-750	Starch & Acetate	38-59	6,82	O'Neill et al, 2000a
UASB	15-16,5	CAS	55-60	Synthetic	100-3200	Glucose	800-100	+	Sponza and Isik, 2005
UASB	86,4	CAS	432	Synthetic	3200	Glucose	81	13	Işık and Sponza 2004c
UASB	6-10	CAS	6,5	Synthetic	n.m.	-	70-80	+10-20	An et al, 1996
UASB	24	SBR	21,5-24	Synthetic	60-300	Glucose+Peptone	60-97	+	Ong et al, 2005
Rot. Disc	15	Rot. Disc	7,5	Synthetic	650-1300	Acetate & YE	90-95	-	Sosath et al, 1997
Rot. Disc	31	Rot. Disc	7,5	Synthetic	600	Acetate & YE	70	+	Sosath et al, 1997
Rot. Disc	15	Rot. Disc	7,5	Synthetic	530	Acetate & YE	100	-35	Libra et al, 2004
Rot. Disc	7-8	Rot. Disc	4,5-5	Synthetic	n.m.	PVA and LAS	60-85	n.m.	Zaoyan et al, 1992

<sup>a</sup> Anaerobic reactor type: UASB, upflow anaerobic sludge bed; Filter, anaerobic filter; Rot. Disc, anaerobic rotating disc

<sup>b</sup> Aerobic reactor type: CAS, continuous aerobic sludge; Filter, aerobic filter; Rot. Disc, aerobic rotating disc; SBR, aerobic sequential batch reactor

<sup>c</sup> HRT: Hydraulic retention time

<sup>d</sup> wastewater types: 1) Textile wastewater with added glucose and nutrients 2) Actual denim effluent 3) wastewater from a dye-manufacturing factory, mixed with simulated municipal ww 4) Textile dye wastewater with PVA and LAS as main COD

<sup>e</sup> Substrates, abbreviations: YE, yeast extract; PVA, polyvinyl alcohol; LAS, linear alkylbenzene sulfonate

<sup>f</sup> Aerobic color removal: positive values express the additional color removal as a percentage of the influent color, negative values express the development of color (autooxidation) as percentage of influent color. 'n.m.' not mentioned

Integrated anaerobic-aerobic systems also have been investigated. These systems are based on the fact that oxygen-tolerant anaerobic and aerobic microorganisms can coexist beneficially in a single environment (D'antoni, 2017). Some studies are summarized in Table 2.15.

**Table 2.15.** Integrated anaerobic-aerobic reactor systems (Adapted from Zee and Villaverde, 2005; D'Antoni et al, 2017).

Integrated System <sup>a</sup>	HRT	Wastewater	Concentration (mg/l)	Substrate <sup>b</sup>	Color Removal (%)	References
ESGB with oxygenation of recycled effluent	36-43 26-34	Synthetic	59-65 50	Ethanol n.m.	100 <100	Tan et al,1999; Tan, 2001
UASB with aerated upper part	1-100	Synthetic	50	Ethanol	40-70	Kalyuzhnyi and Sklyar, 2000
RAD	0,16-3	Synthetic	300	ME, peptone, YE, trout chow	18-97	Harmer and Bishop, 1992
RAD	2	Synthetic	n.m.	ME, peptone, YE, trout chow	20-90	Jiang and Bishop, 1994
Baffled reactor with anaerobic and aerobic compartments	48+18	Synthetic	500	Starch, PVA, CMC	84-88	Gottlieb et al, 2003

<sup>a</sup> Reactor types: EGSB, expanded granular sludge bed; UASB, upflow anaerobic sludge blanket; RAD, rotating annular drum.

<sup>b</sup> Substrates, abbreviations: YE, yeast extract; PVA, polyvinyl alcohol; ME, meat extract; CMC, carboxymethylcellulose.

#### 2.7.2.4 Membrane bioreactor (MBR) systems

There are many pilot-scale MBR systems. The first large-full scale MBR system was established at the beginning of the 1990's to treat a textile factory wastewater in the USA (Sutton, 2006; Mutamim et al, 2012). The major problem of applying MBR systems is fouling. Wastewater characterization, sludge properties, environment, and hydrodynamic conditions directly affect fouling problems (Meng et al, 2009; Drews, 2010; Gao et al, 2013).

MBR systems have been variously applied for decolorization of textile/dyeing wastewater. They can be also applied to both anaerobic and aerobic conditions. Although MBRs are mostly applied on their own, and applied sequential NF or UF process can increase efficiency. By using this sequential system, it is possible to reach

90-98% COD removal and 95-99% color removal. In addition to this, water reusing can be considerable (TSEKOKT, 2011).

In the study of Yigit et al. (2009), an MBR was applied to investigate COD and color removal of textile wastewater for 75 days and 98% color and 97% removal was observed.

Hoinkis et al. (2012) reached 60-75% color removal during their study which was conducted by using the MBR system to investigate real textile wastewater. In this study, even with the lowest HRT 90% COD removal was observed.

There are also anaerobic MBR studies in the literature. Khelifi et al. (2008) conducted an integrated continuous stirred tank reactor (CSTR) + anaerobic fixed-film bioreactor (AFFB) to investigate the treatment of real textile wastewater which has 11.185 mg/l initial COD concentration. As a result of this study 97,5% COD removal and 97,3% color removal were noted with 4 days HRT.

Some other studies which were conducted by using different type membranes under different anaerobic or aerobic conditions are summarized in Table 2.16.

**Table 2.16.** MBRs applied for treatment of textile/dyeing wastewater (Adapted from Karaciray, 2019; CSB, 2013).

Type and Properties	Wastewater	Dye	COD Removal (%)	Color Removal (%)	References
Aerobic Pore Size: 0,025µm Lab Scale	Synthetic	n.m.	97	72	Badani et al, 2005
Aerobic Pore Size: 0,04µm Pilot Scale	Synthetic	Mixed	97	97	Yigit et al., 2009
Aerobic Pore Size: 0,2µm Pilot Scale	Synthetic	n.m.	97	60-75	Hoinkis et al, 2012
Aerobic Pore Size: 0,4µm Lab Scale	Synthetic	Acid Orange 7 Azo Dye	60-80	94	Konsowa et al., 2011
Anaerobic Pore Size: 0,4 µm Lab Scale	Synthetic	Orange 16 Azo Dye	n.m.	91-95	Spagni et al, 2012
Anaerobic + Aerobic Pore Size: 0,04 µm Lab Scale	Synthetic	Reactive Orange 16 Azo Dye	90	50-90	Spagni et al, 2012

### 2.7.2.5 Important design parameters for biological dye removal

The parameters are given below should be considered for effective color removal from textile wastewater.

### ***Dye structure***

Dye structure plays an important role during color removal because of their bond's biodegradability, several color removal efficiencies were reported (Rajaguru et al, 2000; Lourenco et al, 2001; Isik and Sponza, 2004b).

### ***Hydraulic retention time***

The effect of HRT was investigated in many studies and the positive relation between HRT and color removal efficiency was noted (Kapdan et al, 2003; An et al, 1996).

### ***Biomass concentration***

Biomass concentration which was examined in the study of Lourenco et al. (2000). It is also an important parameter for color removal efficiency. In the case of decreasing biomass concentration from 2 to 1,2g VSS/l and SRT time from 15 days to 10 days decreased the efficiency from 90% to 30%.

### ***Alternative electron acceptors***

The reduction of azo dyes is an oxidation-reduction reaction. The study of Lourenco et al. (2000) shows that the presence of nitrate in textile wastewater causes to slow down decolorization. The presence of an alternative electron acceptor may compete with the azo dye for reducing equivalents.

### ***Primary substrate concentration***

Electron donors are a precondition for azo dye reduction. In theory, the required amount of electron-donating primary substrate is low, four reducing equivalents per azo linkage, i.e. 32mg COD per millimole monoazo dye.

On the other hand, Electron donors for other reactions will increase the required amount of primary substrate (Zee and Villaverde, 2005).

### ***Primary substrate type***

In one of study which was conducted with SBR, anaerobic color removal highly increased in the case of adding lactate to influent instead of starch as the main COD source (Albuquerque et al, 2005).

### ***Dye concentration***

As it is shown in Table 2.14 and 2.15, various dye concentrations have been performed in different reactor studies. It is usually reported that higher net color removal

efficiencies were achieved at lower dye concentrations (O'Neill et al, 2000a; Rajaguru et al, 2000; Sponza and Isik, 2005).

### ***Dye toxicity***

Dye toxicity was associated to some parameters such as high dye concentrations, the presence of heavy metals (metal-complex dyes) and/or the presence of non-hydrolyzed reactive groups (reactive dyes).

The benzidine azo dye Direct Black 38, when tested at a very high influent concentration (3.200 mg/l), was found to lower the anaerobic COD removal efficiency, whereas concentrations up to 1.600 mg/l did not seriously inhibit the process (Sponza and Isik, 2005).

## **2.8 Comparison of Treatment Systems**

In the study of Robinson et al. (2001), the advantages and disadvantages of several treatment systems were investigated (Table 2.17).

**Table 2.17.** Advantages and disadvantages of several applied treatment systems of textile wastewaters (Robinson et al, 2001).

Treatment process	Technique applied	Advantages	Disadvantages
Fenton reagents	Oxidation reaction using mainly $H_2O_2$ -Fe (II)	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Ozonation	Oxidation reaction using ozone gas	Application in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	Oxidation reaction using mainly $H_2O_2$ -UV	No sludge production Formation of by products	Photochemical Oxidation reaction using mainly $H_2O_2$
NaOCl	Oxidation reaction using $Cl^+$ to attack the amino group	Initiation and acceleration of azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	Oxidation reaction using electricity	Breakdown compounds are non-hazardous	The high cost of electricity
Activated carbon	Dye removal by adsorption	Good removal of a wide variety of dyes	Very expensive
Membrane filtration	Physical separation	Removal of all dye types	Concentrated sludge production
Ion exchange	Ion exchange resin	Regeneration: no adsorbent loss	Not effective for all dyes
Electro kinetic coagulation	Addition of ferrous sulfate and ferric chloride	Economically feasible	High sludge production

When designing of treatment plant advantages and disadvantages must be taken into consideration. In addition to this, the total cost of a treatment plant is the most important parameter and can be defined as investment cost + operating costs. Some parameters may help to choose a proper treatment system for textile wastewater:

- Dye type
- Characterization of wastewater
- Chemical demand
- Area demand and investment cost
- Operating costs
- End products and management problem

In the study of Ministry of Environment and Urbanization, 2013 some of the treatment systems were compared based on costs per m<sup>3</sup> (Table 2.18).



**Table 2.18.** Costs of treatment systems for textile wastewaters (Adapted from CSB, 2013).

Treatment System	Cost	Wastewater Type	Details	References
H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /UV	6,54 USD/m <sup>3</sup>	Textile -Dyeing	Only chemical consumption cost	Azbar et al,2004
Coagulation and O <sub>3</sub>	1,57 USD/m <sup>3</sup>	Dye manufacturing	Chemical demand is very low. This value is only for ozone electricity generator	Hsu et al, 1998
Adsorption and UV/H <sub>2</sub> O <sub>2</sub>	1,00 USD/m <sup>3</sup>	Everzol Black Reactive -GSP	Operating cost for %50 TOC removal	Ince et al, 2002
Sun-Fenton before biological treatment	22,00 USD/m <sup>3</sup>	5-amino-6-metil-2-benzimidazolone AMBI 0,4 g C/L	Investment (excluding area cost) and operating costs	Sarria et al, 2003
Advance H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /UV	0,85 USD/m <sup>3</sup>	Textile	Operating cost	Liao et al, 2000
Advance ozone(i) and membrane(ii)	(i)0,19 USD/m <sup>3</sup> (ii) 0,69 USD/m <sup>3</sup>	Textile-Dyeing	Investment and operating cost (i) 2000m <sup>3</sup> /day, (ii)1000 m <sup>3</sup> /day	Koyuncu et al, 2001
Coagulation, Fenton and active sludge	0,4 USD/m <sup>3</sup>	Textile	Operating cost (excluding sludge management cost)	Lin and Peng, 1995
Biological, sand filter and O <sub>3</sub> (recycling treated water)	0,13 USD/m <sup>3</sup>	Fiber manufacturing-Dyeing	Investment and operating costs (water recycling decreases the costs)	Ciardelli and Ranieri, 2001
Biological, sand filter and Membrane (MF-NF) (recycling treated water)	0,44 USD/m <sup>3</sup>	Dyeing	Investment and operating costs (water recycling decreases the costs- ROI is three years)	Marcucci et al, 2002
Biological, Membrane (MF-NF) and O <sub>3</sub> (recycling treated water)	1,69-1,95 USD/m <sup>3</sup>	Mixed %30 domestic + %70 textile wastewater	Investment and operating costs for 2.500m <sup>3</sup> /day	Rozzi et al,1999
Membrane bioreactor	0,273 USD/m <sup>3</sup>	Domestic wastewater	Investment and operating costs for 2.4m <sup>3</sup> /day	Yoon et al, 2004

ROI: Return of Investment





### 3. MATERIAL AND METHODS

#### 3.1 Reactor Design

Completely-sealed 55l anaerobic reactor which was made of plexiglass (height: 80 cm Diameter: 40 cm) was operated automatically by the PLC unit during the study (Figure 3.1). A funnel was located in the reactor as a settling tank. Two peristaltic pumps - one for the influent, one for transporting the anaerobic effluent to the effluent tank. The influent flow was regulated with the help of a level sensor installed in the reactor. The heating jacket was also used to maintain the temperature of the reactor at 35,5°C and magnetic stirrer was used for good mixing at 280 rpm. 120l PE plastic barrel was designated as equalization tank where synthetic wastewater was kept.



**Figure 3.1.** Anaerobic reactor.

**Other equipment were used during the study:**

- Peristaltic pump (EZ435, Shenzhen, China) x2 and accompanying tubing (Figure 3.2)
- Thermoreactor (CR3200, Weilheim, Germany) (Figure 3.3)
- Vacuum filtering device (Figure 3.4)
- Centrifuge (Rorofix 32 A, Tuttlingen, Germany) (Figure 3.5)
- Oven for TSS measurement (Elektro.mag M 6040 p, Istanbul, Turkey) (works at 105°C) (Figure 3.6)
- Ash oven (Lenton Furnaces ECF, Hope Walley, United Kingdom) for VSS measurement (Figure 3.7)
- Multimeter (Hanna HI2211, Bedfordshire, United Kingdom) (including probes for measuring pH, redox state, conductivity) (Figure 3.8)
- Turbidity meter (WTW 550 IR, Weilheim, Germany) (Figure 3.9)
- Sensitive lab scale
- Magnetic stirrer

**Samples were taken during the project:**

- COD samples (Figure 3.10)
- MLSS samples (Figure 3.11)
- MLSS and MLVSS samples (Figure 3.12)



**Figure 3.2.** Peristaltic pumps (EZA35).





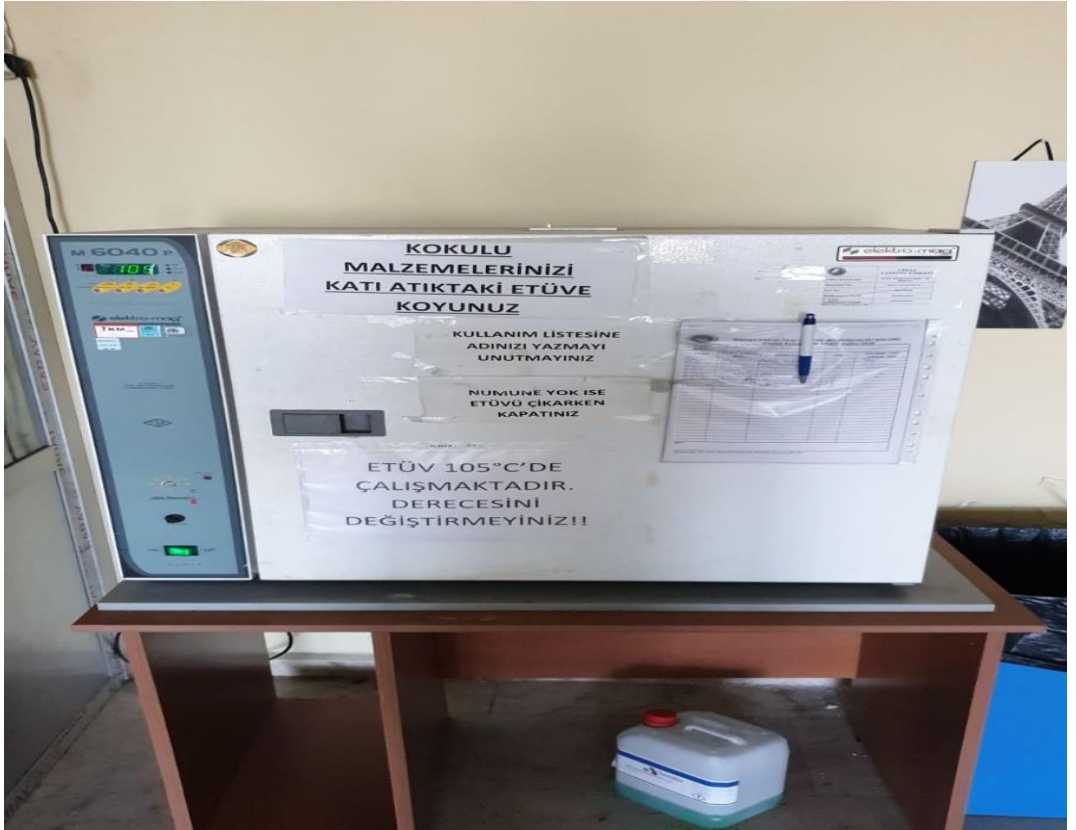
**Figure 3.3.** Thermoreactor (CR 3200).



**Figure 3.4.** Vacuum filtering device.



**Figure 3.5.** Centrifuge (Rotofix 32 A).



**Figure 3.6.** Oven (Elektromag M 6040 p).





Figure 3.7. Ash oven (Lenton Furnaces ECF).



Figure 3.8. Multimeter (Hanna HI 2211).



**Figure 3.9.** Turbidity meter (WTW Turbo 550 IR).



**Figure 3.10.** COD Samples.





**Figure 3.11.** MLSS samples.



**Figure 3.12.** MLSS and MLVSS samples.



### 3.2 Operational Conditions

System was operated in two phases using synthetic wastewater (Table 3.1 and 3.2) for 264 days. For inoculum, a mixed microbial culture obtained from Atakoy Advanced Biological WWTP was used. This facility is an advanced biological domestic wastewater treatment plant that was established to serve seven districts with a 2,5 million population in Istanbul, operated by the Istanbul Water and Sewerage Administration (ISKI). The temperature was set 35,5°C to have an optimum level for growing of anaerobic microorganisms to reach best removal efficiency (Mata-Alvarez, J, 2002). System was operated at mesophilic conditions and infinite sludge age by using PLC.

**Table 3.1.** Conditions in phases/periods.

Phases/ Periods	HRT (h)	Days	Wastewater
Phase one	24	1-81 (81 days)	Synthetic 1 (2000 mg COD/l)
Phase two Period one	24	82-174 (93 days)	Synthetic 2 (1000 mg COD/l)
Period two	48	175-264 (90 days)	Synthetic 2 (1000 mg COD/l)

**Table 3.2.** Composition of synthetic wastewaters were used during study (Ersahin et al, 2013; Cinar et al, 2008).

Chemical (mg/l)	Phase One (Synthetic 1)	Phase Two (Synthetic 2)
	(Cinar et al, 2008).	(Ersahin et al, 2013; Cinar et al, 2008).
NH <sub>4</sub> Cl	230	741
MnCl <sub>2</sub> .4H <sub>2</sub> O	0,5	0,5
ZnCl <sub>2</sub>	0,05	0,05
CaCl <sub>2</sub> .2H <sub>2</sub> O	-	13,55
MgSO <sub>4</sub> .7H <sub>2</sub> O	-	9,25
K <sub>2</sub> HPO <sub>4</sub>	37	420
KH <sub>2</sub> PO <sub>4</sub>	67	7,125
Na <sub>2</sub> SO <sub>3</sub> .5H <sub>2</sub> O	0,164	0,164
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> .4H <sub>2</sub> O	0,05	0,05
CuCl <sub>2</sub> .2H <sub>2</sub> O	0,038	0,038
FeCl <sub>3</sub> .6H <sub>2</sub> O	5	5
NiCl <sub>2</sub> .6H <sub>2</sub> O	0,09	0,09
CoCl <sub>2</sub> .6H <sub>2</sub> O	1	1
Sucrose	2.000 (as COD)	1.000 (as COD)

### 3.2.1 Phase one

The system was operated as CSTR under mesophilic conditions with two peristaltic pumps with 24 h HRT value. The inoculum was left for acclimation in phase one. During this phase, measurements were performed three times a week for one period.

In this phase, the reactor was located at Umit Boya dyeing factory name in Gungoren, Istanbul until day 154. The objective of locating the reactor in the factory was to mimic field conditions. However, this caused some problems such as electrical cut off which resulted discontinues operation and high temperatures.

### 3.2.2 Phase two

After the initial phase, the concentrations of macronutrients were increased, and the initial COD concentration was decreased according to Table 3.2. During phase two, 24 h and 48 h HRT were examined in two periods.

For the first period, system was run with 35,5°C temperature, ~7,3 pH, and 24 h HRT. Measurements were performed three times a week for these conditions for three months. For the second period, HRT value was increased to 48 h by keeping other conditions same. Measurements were performed two times a week under these conditions.

## 3.3 Analytical Methods

The frequency of the common analyses is presented in Table 3.3. Details of analytical methods given in the below sections.

**Table 3.3.** Analyses and their frequency.

Sample origin	Analysis	Frequency during Phase 1 (Number of Measurements Per Week)	Frequency during Phase 2, Period 1 (Number of Measurements Per Week)	Frequency during Phase 2, Period 2 (Number of Measurements Per Week)
Reactor influent	COD	3	3	2
	pH	3	3	2
Reactor effluent	COD	3	3	2
	pH	3	3	2
	Turbidity	-	-	2
	pH	3	3	2
	ORP	3	3	2
Inside of reactor	MLSS	3	3	2
	MLVSS	-	-	2
	Turbidity	-	-	2

### **3.3.1 pH measurements**

pH measurements were performed as specified in the standard methods (APHA, 2017), section 5130, respectively, by using a pH meter. For the measurements, pH meter was calibrated with proper calibration solutions.

### **3.3.2 ORP measurements**

ORP level was automatically measured by ORP probe located in the sealed reactor.

### **3.3.3 MLSS and MLVSS measurements**

MLSS/MLVSS samples were collected from different height levels of reactor to obtain a composite sample. Also, samples were taken from top of the reactor, without opening the lid in order to reach good anaerobic conditions. MLSS and MLVSS concentrations were measured according to standard methods section 2540 (APHA, 2017).

For this measurement, 5 ml composite sample was filtered with each filter paper and dried in the oven at 105°C for 60 min, then they were left in a desiccator for 30 min. To measure MLVSS values, measured samples were put in an ash oven at 550°C for 30 min, then again in a desiccator for 30 min, and finally measured again.

### **3.3.4 COD measurements**

For the COD measurements, samples were collected from the reactor feed and effluent and analyzed directly. COD measurement was performed with Closed Reflux Titrimetric Method as specified in the standard methods (APHA, 2017) section 5220.

Briefly, two samples for feed/influent, two samples for effluent and two blank/control samples were prepared for each analysis. Influent and effluent samples were centrifuged at 4.000 rpm for 10 minutes. The prepared samples were digested at 150°C for 120 minutes with sulfuric acid and silver as a catalyst and then measured titrimetrically.

#### Chemicals used during COD measurements:

- Potassium dichromate,  $K_2Cr_2O_7$  - 1,5 ml
- Silver sulfuric acid,  $Ag_2H_2SO_4$  – 3,5 ml
- Ferrous Ammonium Sulfate (FAS),  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$  (for titration)
- Phenolphthalein,  $C_{20}H_{14}O_4$  (for titration)

### **3.3.5 Turbidity measurements**

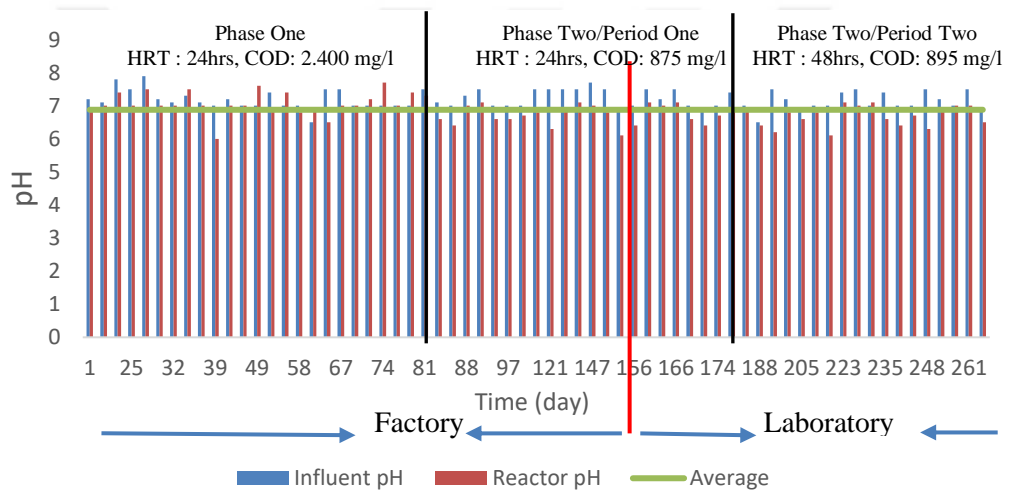
Turbidity measurements were performed as specified in the standard methods (APHA, 2017) section 4500, by using a turbidity meter.



## 4. RESULTS AND DISCUSSION

### 4.1 pH

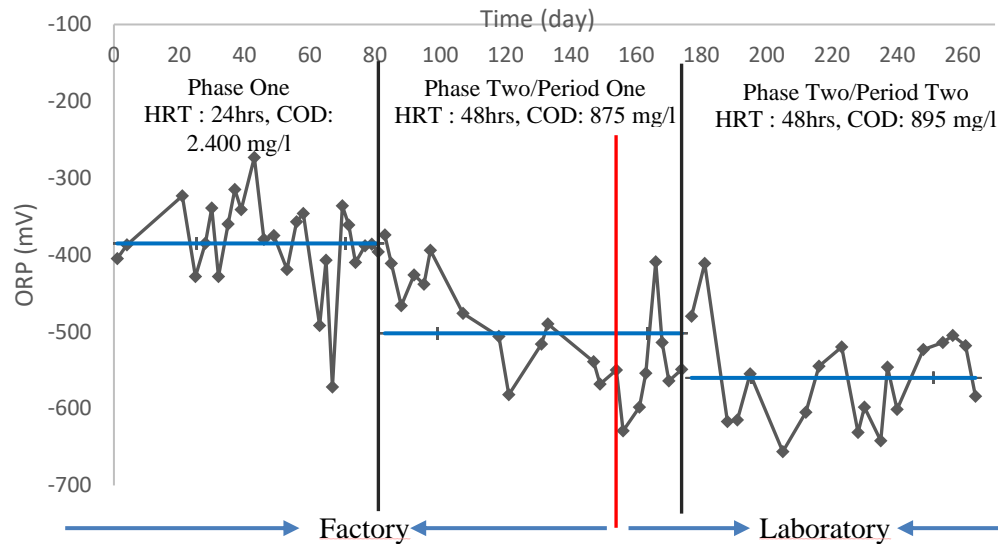
During study, the pH level was kept around 7 as aimed. The average pH level of study was 6,9 (Figure 4.1).



**Figure 4.1.** pH levels during the study.

### 4.2 ORP

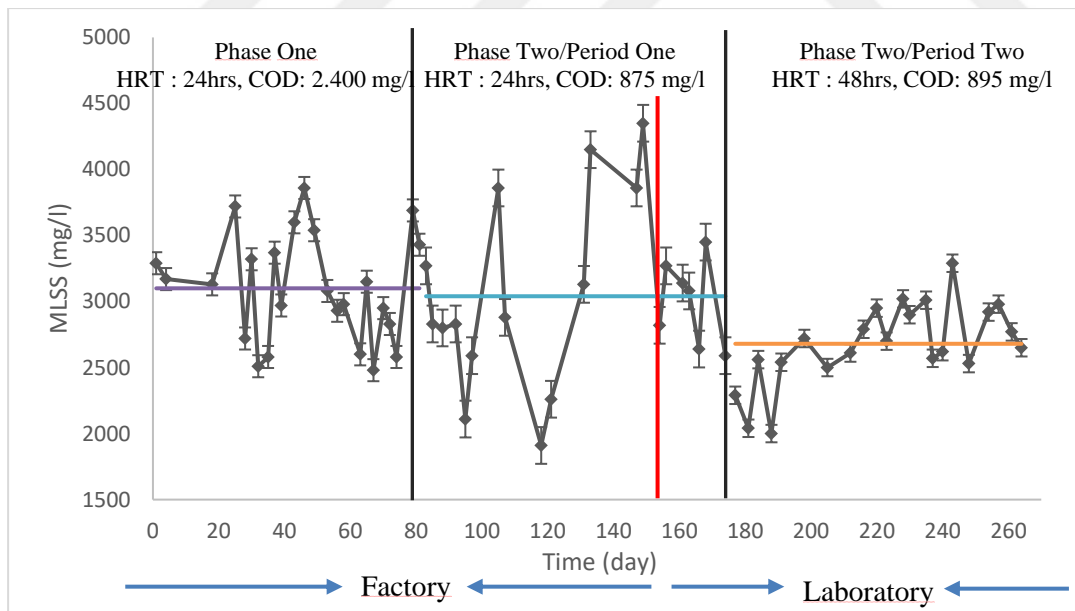
During phase one average ORP value was measured as -385 miliVolt (Figure 4.2). Average ORP values were -502 miliVolt and -560 miliVolt, respectively for period one and period two at phase two.



**Figure 4.2.** ORP levels during the study.

### 4.3 MLSS and MLVSS

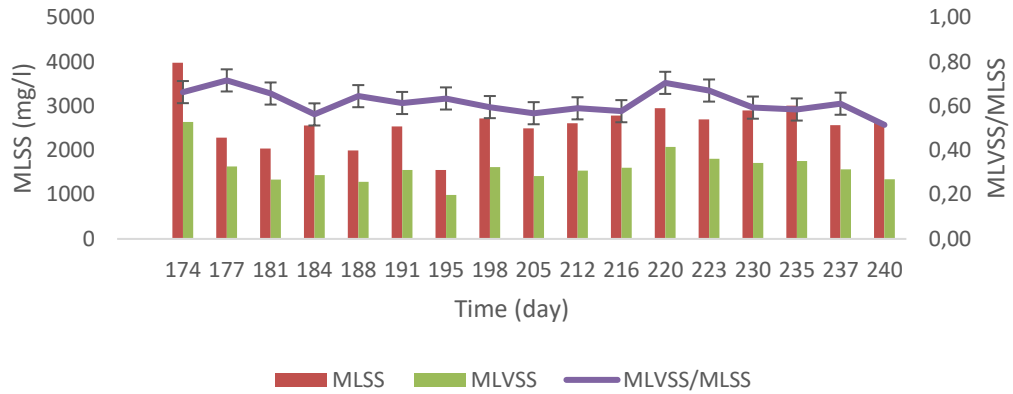
The average MLSS concentration in phase one was 3.100 mg/l (Fig 4.3). During the phase two, average MLSS concentrations were 3.040 mg/l and 2.465 mg/l for periods one and two, respectively (Fig. 4.3).



**Figure 4.3.** MLSS concentrations during the study.

In addition to MLSS, MLVSS was also measured in phase two/period two. The average MLVSS/MLSS ratio was calculated as 0,62 during this period (Fig. 4.4). MLVSS/MLSS ratio values are comparable with literature. Khalida et al. (2011) reported that MLVSS/MLSS ratio increased from 0,73 to 0,85 when COD

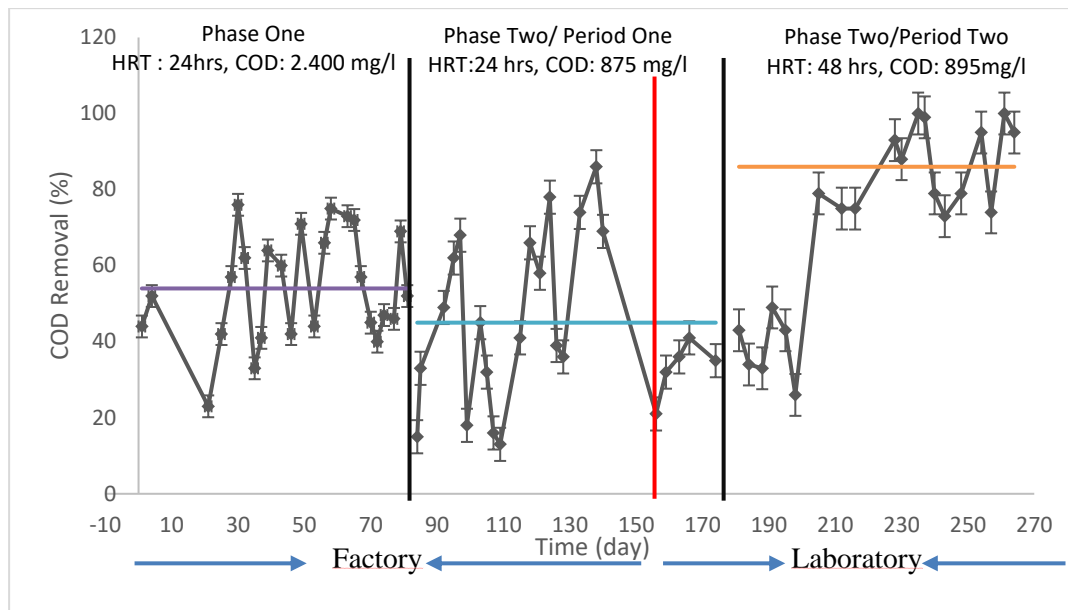
concentration increased from 600 mg/l to 800 mg/l at 24 h HRT. Yurtsever et al. (2015) operated an anaerobic MBR which was fed with 1.000 mg/l initial COD concentration. An increase in the MLVSS/MLSS ratio was reported in that study. They reported the MLVSS/MLSS ratio as 0,47 at the beginning and it reached to 0,53 at the end of the study.



**Figure 4.4.** MLSS & MLVSS concentrations and MLVSS/MLSS ratio during the phase two/period two.

#### 4.4 COD Removal

Average initial COD concentration was 2.400 mg/l during phase one (24 h HRT). The average COD removal efficiency of this phase was 54%. In phase two, initial COD concentration was decreased, on the other hand, initial macronutrient concentrations were increased. Average initial COD concentration was 875 mg/l during phase two/period one (24 h HRT). The average COD removal efficiency of this period was 45% (Fig. 4.5). Decreasing the initial COD concentration caused for a decrease on COD removal efficiency from ~54% (phase one) to ~45% (phase two/period one). However, these results are not reliable due to operational problems. During phase two/period two, average initial COD concentration was 895 mg/l and 86% average COD removal efficiency was observed (Fig. 4.5).



**Figure 4.5.** COD removal efficiencies during the study.

There were more fluctuations in phase one and phase two/period one and COD removal efficiency was approximately 50% due to problems. However, at the end of the study after fixing the problems 86% COD removal was achieved. This value is comparable with COD removal efficiencies reported in the literature. The summary of different studies for the treatment of synthetic textile wastewater using anaerobic reactors in literature was given in Table 4.1. In a study that was run by anaerobic and aerobic SBR sequentially at 24 h HRT, 70% COD removal was observed in the anaerobic phase with 3.000 mg/l initial glucose synthetic textile wastewater (Shoukat et al, 2019). However, at 48 h HRT, the maximum COD removal of 81% was reported for the same study. In the study of Khalida et al. (2011) an increase (from 91% to 94%) of COD removal efficiency was observed when the HRT was increased from 12 h to 18 h. They reported that when the initial COD was increased from 600mg/l to 800mg/l, the average COD removal efficiency increased from 84% to 91%. On the other hand, they also reported a decrease in COD removal from 94% to 91% when HRT was increased from 18 h to 24 h. Brus et al. (2005) reported an increase in COD removal efficiency from 77% to 92% when HRT was increased from 8 h to 24 h.



**Table 4.1.** Different studies for the treatment of synthetic textile wastewater using anaerobic reactors.

Reactor Type <sup>a</sup>	HRT (h)	Wastewater	Substrate <sup>b</sup>	Dye <sup>c</sup>	Initial Dye Concentration (mg/l)	Initial COD Concentration (mg/l)	COD Removal (%) <sup>d</sup>	References
CMAR	24	Synthetic	Sucrose	-	-	2400	~54	This study
	24					876	~45	
	48					895	~86	
AFBB	8	Synthetic	n.m.	Sulfur Dye, Reactive Dye, Disperse Dye	n.m.	n.m.	~50	Stern et al, 2003
ABFR	60	Synthetic	Starch	Remazol Red RR	100	65	~70 & 70	Punzi et al, 2015
	60				500	900	~67 & 71	
	60				1000	1288	~76 & 74	
ABFR	12	Synthetic	Glucose	Remazol Red RR, Remazol Blue RR,Remazol Yellow RR	100-300	1000	~82 & 78	Jonstrup et al, 2011
	24				100	1000	~82 & 82	
	36				100-2000	1000	~94 & 95	
	48				100	1000	~94 & 95	
	72				100	1000	~95 & 95	
	19				25	500	~88	
ASBR	19	Synthetic	n.m.	Reactive Red 195	n.m.	700	~95	Farabegoli et al, 2010
	19				n.m.	800	~92	
	19				40	800	~93	
	19				45	800	~78	
	19				50	800	~77	
	24				-	1800	>85	
	24				60	1800	~92	
	24				100	1800	n.m.	
UASB	24	Synthetic	Acetate	Acid Orange 7 & Direct Red 254	150	1800	n.m.	Brus et al, 2005
	24				300	1800	~67	
	8				60	1800	~76 & 75	
	8				150	1800	~84 & 82	

Reactor Type <sup>a</sup>	HRT (h)	Waste-water	Substrate <sup>b</sup>	Dye <sup>c</sup>	Initial Dye Concentration (mg/l)	Initial COD Concentration (mg/l)	COD Removal (%) <sup>d</sup>	References
SBR	24	Synthetic	Glucose	Cibacron Yellow, Cibaron	15	2200-2800	~69	Shoukat et al, 2019
	48			Blue, Methylene Blue.	15	2200-2800	~81	
SBR	12	Synthetic	Glucose, Acetate, Ethanol,	Sumifix Black EXA,	50	800	~90,7	Khalida et al, 2011
	18			SumifixNavy	50	800	~94,1	
	24			Blue EXF and	50	600	~84,4	
	24			Synozol Red K-4 (mix).	50	800	~90,7	

<sup>a</sup> Reactor type: CMAR, completely mixed anaerobic reactor; ABFR, anaerobic biofilm reactor; ASBR, anaerobic sequential batch reactor; UASB, anaerobic up-flow bed reactor

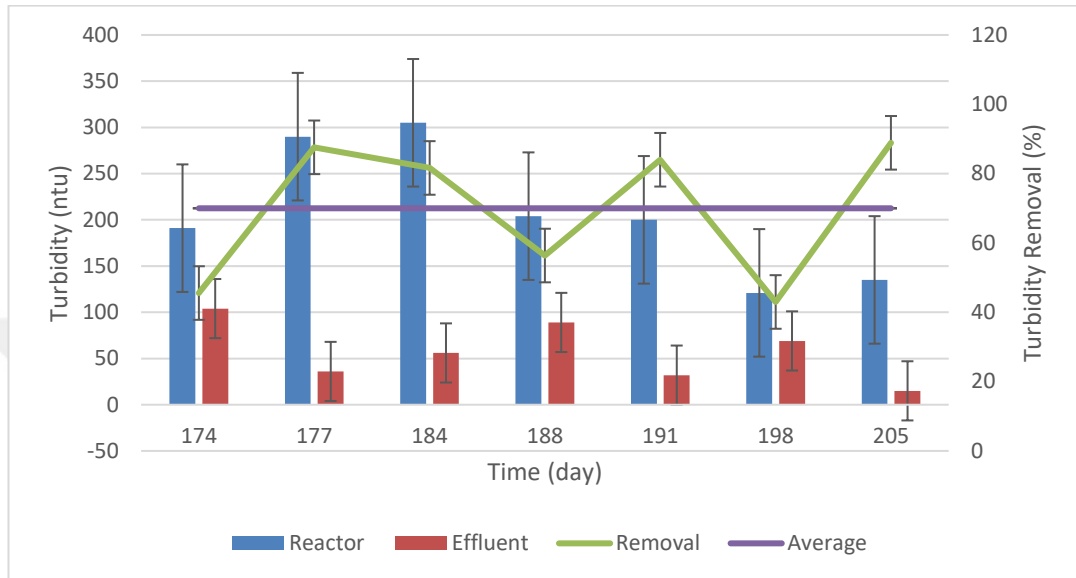
<sup>b</sup> Substrate: In the study of Khalida et al. (2011), equal ratio (based on the COD concentration) of glucose (0.5 g/l), ethanol (0.125 g /l) and sodium acetate (0.5 g/l) were used as carbon source.

<sup>c</sup> Dye: In the study of Brus et al. (2005) a mixed solution that has 35% Acid Orange 7 and 65% Direct Red 254 was used for 24 h HRT. However, dyes separately added for 8 h HRT and COD removal values are shown for Acid Orange 7 and Direct Red 254 respectively. Shoukat et al. (2019) and Muda et al. (2011) used a uniformly mixed solution used in the studies. In the study of Stern et al. (2003) a mixed solution that has 40% sulfur dye 35% reactive dye and 25 % disperse dye was used.

<sup>d</sup> COD removal: Regarding the study of Punzi et al. (2015), values are shown for two reactors (A&B) respectively. The reactors filled with carriers (poraver) were 0.340 l and 0.345 l for A and B respectively. Regarding the study of Jonstrup et al. (2011), values are shown respectively for two reactors (A&B). The reactors filled with poraver and kaldness as carriers for A and B respectively.

## 4.5 Turbidity

Turbidity measurements were only performed in phase two/period two, between days 174 and 205. The average turbidity removal efficiency of this period was 70% (Fig. 4.6).



**Figure 4.6.** Turbidity values and removal efficiency during phase two/period two.

It was expected to observe better turbidity removal. An inconvenience with design of reactor might have caused lower turbidity removal.



## 5. CONCLUSION

In this study, treatability of synthetic textile wastewater was investigated by pilot-scale anaerobic completely stirred tank reactor (CSTR). However, technical and operational problems were occurred at the beginning of the study. For this reason, only the results of the start-up part was presented.

The study was conducted in two phases for 264 days. The first phase was operated for 81 days with 2.400 mg/l initial COD concentration and 24 h HRT. The second phase was operated under two periods (93 and 90 days for period one and two, respectively) with approximately 900 mg/l initial COD concentration and two HRT (24 and 48 h for period one and two, respectively). The system was located at a dyeing factory until day 154 and it was transferred to a laboratory for better control.

The average pH was around 6,9 and average MLSS concentration was in between 2.500-3.000 mg/l during the study. At the last period (phase two/period two) of the study, average MLVSS/MLSS ratio was calculated as 0,62 and 86% COD removal was achieved. This COD removal efficiency is comparable with literature.

Technical and operational problems resulted fluctuations in phase one and phase two/period one and COD removal efficiency was approximately 50% due to problems. However, after overcoming problems high COD removal was observed and steady state conditions were achieved at the end (phase two/period two). In the future, color removal is going to be investigated.

Although it was aimed to locate systems in the field for better mimicking real conditions this resulted many different problems. It is suggested to use laboratory for better controlled conditions.



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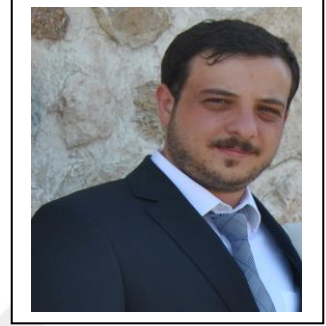
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## **CURRICULUM VITAE**



**Name Surname** : Cenk Ali BİLGİÇ  
**Place and Date of Birth** : Istanbul / 03.06.1985  
**E-Mail** : cenkalibilgic@hotmail.com

### **EDUCATION :**

- **B.Sc.** : 2010, Yıldız Technical University, Faculty of Civil Engineering, Environmental Engineering

### **PROFESSIONAL EXPERIENCE AND REWARDS:**

- 2011-Present, Yildiz Environmental Engineering & Consulting Co., General Director