

T.R.
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**TREATABILITY OF DYEING PROCESS WASTEWATER FROM
TEXTILE SECTOR BY CERAMIC MEMBRANE**

AHMED MUSTAFA SALIH ALBAHNASAWI
A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF ENVIRONMENTAL ENGINEERING

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PROF. DR. EBUBEKİR YÜKSEL

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MEMBRANLARLA ARITILABİLİRLİĞİNİN
ARAŞTIRILMASI

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SUMMARY

In this thesis, the ability of a sequential anoxic-aerobic batch reactor followed by a ceramic membrane for the treatment of wastewater from woolen textile industry was investigated. The investigated system was tested under three Internal Recycle ratios (IR) and the effect of IR on the removal of Total Organic Carbon (TOC), Total Nitrogen (TN), color, and Aromatic Amines (AAs) were investigated. Moreover, the influence of AAs physical-chemical properties on its fate and removal efficiency was examined. The result showed that the TN removal efficiency was 20.9%, 53.4%, and 71.7% under IR of 0.0, 0.5, and 2.0 while the color removal was 81%, 85%, and 88%, respectively was observed. However, the results showed high TOC removal, over 93%, which was independent of IR.

Most AAs possessing one aromatic ring and an Electron Donating Group (EDG) such as (-NH₂) and (-CH₃) are highly biodegradable under aerobic condition (above 80 %), whereas AAs with 2 aromatic rings and strong Electron Withdrawal Group (EWG), such as azo bond and (-Cl) exhibited low to moderate removal efficiency (below 75%). The $\sum$ AAs increased by 91% in the anoxic tank (IR=2.0), owing to the unique bacterial diversity under a high IR operation scheme. On the other hand, $\sum$ AAs in the anaerobic tank (IR=0.0) increased by 6.1%, while, the $\sum$ AAs in the aerobic tank remained constant at 50 ng/L in both cases. Most of AAs accumulated in sludge under reducing condition due to the refractory behavior of AAs in this environment, while hydrophobic AAs were slightly accumulated in aerobic sludge.

Key words: Anoxic-Aerobic, Aromatic Amines, De-colorization, Internal Recycle, Textile Wastewater.

ÖZET

Bu çalışmada, yünlü tekstil endüstrisi atıksularının arıtımında seramik membran ile entegre edilmiş ardışık kesikli anoksik/aerobik prosesin performansı araştırılmıştır. Proses, üç farklı dahili geri devir oranında işletilmiş ve geri devir oranının organik madde, toplam azot (TN), renk ve aromatik aminlerin (AAs) giderimi üzerine olan etkisi incelenmiştir. Ayrıca, aromatik aminlerin fiziksel ve kimyasal özelliklerinin arıtma verimi üzerine olan etkisi test edilmiştir. Geri devir oranı 0, 0,5 ve 2,0 iken sırasıyla TN giderimi %20,9, %53,4 ve %71,7 ve renk giderimi ise %81, %85 ve %88 olarak bulunmuştur. Ancak, %93'ün üzerinde giderim oranıyla, toplam organik karbon gideriminde geri devir oranının bir etkisinin olmadığı sonucuna varılmıştır.

Bir aromatik halka ve (-NH₂) ile (-CH₃) gibi elektron donör grubu bulunduran çoğu aromatik aminlerin aerobik koşullarda yüksek oranlarda biyolojik olarak bozunabildiği gözlemlenirken (%80'nin üzerinde), 2 aromatik halka ve azo-bağı ve (-Cl) gibi güçlü elektron alıcı grubu bulunduran aromatik aminlerin ise %75'in altında gideriminin olduğu gözlemlenmiştir. Bakteriyal çeşitliliğin fazla olduğu yüksek geri devir oranında (IR=2,0), anoksik tankta toplam aromatik amin konsantrasyonu %91 oranında artış göstermiştir. Diğer yandan, geri devirin olmadığı (IR=0,0) anaerobik tankta aromatik amin konsantrasyonu %6,1 artış gösterirken, her iki durumda da aerobik tanktaki aromatik amin konsantrasyonu 50 ng/L olarak sabit kalmıştır. Aromatik aminlerin çoğunluğu dirençli yapılarından dolayı çamurda birikim gösterirken, hidrofobik yapıli aromatik aminlere aerobik çamur içerisinde az da olsa rastlanmıştır.

Anahtar kelimeler: Anoksik/Aerobik reaktör, Aromatik aminler, Renk giderimi, İçsel geri devir, Tekstil Atıksuyu.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>and Acronyms</u>	
AAs	: Aromatic Amiens
ADMI	: American Dye Manufacturer's Institute
BOD	: Biological Oxygen Demand
CE	: Capillary Electrophoresis
COD	: Chemical Oxygen Demand
DO	: Dissolved Oxygen
EDG	: Electron Donating Group
EWG	: Electron Withdrawing Group
GC	: Gas Chromatography
HRT	: Hydraulic Retention Time
IR	: Internal Recycle (internal volume recycle)
LC	: Liquid Chromatography
LMH	: Litter per Meter square per Hour
MBR	: Membrane Bioreactor
MF	: Micro-Filtration
MLSS	: Mixed Liquor Suspended Solids
MS	: Mass Spectrometry
NF	: Nano-Filtration
OMPs	: Organic Micropollutents
ORP	: Oxidation Reduction Potential
RO	: Reverse Osmosis
SPE	: Solid Phase Extraction
SRT	: Sludge Retention Time
SS	: Suspended Solids
TKN	: Total Kjeldahl Nitrogen
TLC	: Thin Layer Chromatography

TMP	: Transmembrane Pressure
TN	: Total Nitrogen
TOC	: Total Organic Carbon
TP	: Total Phosphorus
UF	: Ultra-Filtration
UHPLC	: Ultra High Pressure Liquid Chromatography
UV	: Ultraviolet–Visible Spectrophotometry

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1. INTRODUCTION

1.1. Background

The textile industry is considered one of the most important and fast-developing industrial divisions in Turkey. It has an enormous impact on the environment, as it consumes significantly high amounts of water and discharges high polluted wastewater. As a result, feasible treatment methods are required to protect the environment in Turkey [Neşe et al., 2007].

The textile industry uses many types of chemical dyes and releases huge quantities of vastly colored wastewater as the fabrics uptake of these dyes are small leaving a vast majority of dyes discharge to throw the wastewater effluent. The World Bank estimations are 17–20% of water pollution caused by industry is subsidized by the industry of textile. Growing up the release of such stream without efficient measure has affected the soil, rivers, lakes and environments harmfully [Kant, 2012]. This textile wastewater adversely disturbs the photosynthetic process in the plant. Besides, it has impacted aquatic ecosystem due to low oxygen consumption and light intrusion [Frijters et al., 2006]. Nowadays, the focus is not on dye removal technologies, but on technologies that increase water reuse, mineralize aromatics, eliminate toxicity, do not produce toxic sludge, and possibly zero rejection [Verma, 2017].

To date, many physical-chemical remediation methods have been developed and used to deal with the threats of pollution of dye that involve oxidation, adsorption, coagulation, membrane separation, and ion-exchange [Field et al., 1995]. However, these methods are beleaguered with technical and economic difficulties, for example, the production of huge volumes of sludge (resulting in hard treatment and disposal), high operating/energy costs and creation of harmful byproducts. It is important to note that the majority of the conventional methods are costly and consume a huge amount of chemicals as well as energy [Parmar and Shukla, 2018].

The biological method for the full biotransformation of wastewater from textile industry has advantages, for instance (a) less sludge production, (b) low cost, (c) eco-

friendly, (d) consume less water compared to oxidative and physical methods (e) may achieve full mineralization of pollutant [Ayed et al., 2017].

The importance of using membrane technologies as an option for textile wastewater treatment has increased. Membrane separation methods have developed the effective process that may be implemented for full-scale treatment plants possessing the advantages such as high removal efficiency, environmentally friendly and modest energy consumption [Samaei et al., 2018].

The core difficulty that textile wastewater treatment plant designer must deal with is the removal of dye from wastewater. Nevertheless, elimination of color from textile wastewater has been a huge challenge during the last years, and yet no economically and single feasible measures that may efficiently remove dyes has been recognized, and the need for novel, effective, environmentally friendly and economically wastewater treatment technologies that can de-colorized dyes is pressing [Parisi et al., 2015], [You and Teng, 2009].

Recently, azo dyes and AAs are heavily adapted in textile dyes manufacturing. The stable and complex structure of dyes make the biodegradation of dyes hard in any complex environmental matrix. The mineralization of dyes, organic loading and the hazardous material produced by textile industry and pigment manufacturing waste is an essential issue and ecological threat. Therefore, full understanding and devolving innovative waste treatment technology is pressing issue toward sustainability in textile industry [Holkar et al., 2016].

AAs structure ranging from the simplest aniline with one aromatic ring and one amino substituent to complex structures with multiple aromatic rings and vary substituents are being produced from textile industrial besides non-industrial sources. Synthesis azo colorants and sometimes byproducts of azo dyes degradation are the main sources of AAs. Almost, all AAs including toluidine, benzidine and chloramines are toxic in nature with carcinogenic effects on both humans and ecosystems. Moreover, they are soluble in water. Consequently, they have thermodynamic stability. However, effluent quality assessment based only on color and Chemical Oxygen Demand (COD) removals, without includes AAs in assessment, appears rather inadequate with respect to the risk of environmental toxicological [Schmidt et al., 2019].

In the present time, physical, chemical and biological approaches are used to treat textile wastewater, among those, biological treatment is a preferable option for its low cost, effectiveness and less environmental effect. In addition, it is used by most textile wastewater treatment plants. However, with this method, AAs are frequently observed in the effluent of textile wastewater treatment plants. Therefore, the biodegradation process must be enhanced to deal with AAs. However, limited studies investigated the effect of redox condition on color removal as well as AAs removal [Zhu et al., 2018]. In addition, the most of results showing the degradation of AAs after the cleavage of the azo bond have usually been generalized, leading to reports that after dye reduction to AAs, they are readily removed in the aerobic condition [Libra et al., 2004], [Spagni et al., 2010]. Consequently, until now limited understanding of AAs biotransformation under anaerobic/anoxic and/or aerobic environments. Moreover, the AAs removal efficiency in these conditions has been focused by a few numbers of studies recently [Mathematik, 2017], [Tony et al., 2009].

The doubts about the aerobic fate of AAs reveal the need to find a better understanding of the matter. Future investigation should focus on (i) assessment of the degree of mineralization, (ii) the detection of AAs and their degradation and (iii) determination of the structure and hazardousness of non-biodegradable recalcitrant dye [Ito et al., 2016], [Mathematik, 2017], [Schmidt et al., 2019], [Van Der Zee and Villaverde, 2005].

Using Ceramic membrane for textile wastewater treatment has been examined as an easy, efficient and economic method with an important elimination method of organic pollutants. Nevertheless, the removal of AAs from textile wastewater is not investigated until now [Popli and Patel, 2015].

The treatment of woollen textile by the membrane is challenging due to the high content of fatty materials which increase the fouling of membranes, especially the polymer-based membrane. Therefore, using the ceramic membrane in woollen textile may seem a promising solution to prevent the fouling on the membrane surface.

In this study, the woollen dyeing process wastewater which is an important waste source was treated by sequential anoxic-aerobic batch reactor followed by tertiary

treatment using ceramic membrane. Their efficiency in the removal of organic matter, nitrogen color and AAs were assessed.

1.2. Aims and Objectives

The main goal of this research is to investigate the treatability of woollen textile wastewater by enhanced sequential anoxic-aerobic batch reactor. The objectives of this research are:

- Investigate, for the first time in Turkey, the applicability of using the ceramic membrane in woollen textile wastewater treatment.
- Investigate the impact of different redox potentials on full-color removal.
- Understanding the fate of AAs (sorption and biotransformation) in the sequential anoxic-aerobic batch reactor.
- Determine the dye and AAs biotransformation in anoxic and aerobic tanks,
- Full understanding of how different redox environment affect the dye and AAs biotransformation pathways and removal efficiency to a better understanding of the fate of AAs under different redox condition.
- Evaluate wastewater contaminant removal, mainly nutrients and COD using the sequential anoxic-aerobic batch reactor.
- Determine the degradable degree of dyes that degraded biologically and what remains after the treatment.
- Evaluate different biological operating conditions for their capability to remove dyes and AAs.
- From the results, try to understand and develop a novel textile wastewater treatment method which can effectively remove color and AAs at low cost and no-environmental impact.
- Try to understand the sorption and biotransformation of organic micropollutants in innovative biological wastewater treatment technologies depending on the physical-chemical properties and the operation conditions.

1.3. Significance

This thesis offering a new treatment approach where the sequential anoxic-aerobic batch reactor is used for dyes biotransformation and toxicity removal. This study is used the anaerobic/anoxic biological treatment to split the azo bonds of the dyes while the next aerobic reactor removes the AAs that are not removable in anaerobic degradation.

This study contributes towards sustainable development in the textile wastewater industry by enhancing the water quality of treated textile wastewater which helps to decrease freshwater consumption and pollutant release.

This study recognizes to be a forward step involving new factors influencing AAs elimination, particularly, the effect of redox condition on AAs removal and the influence of the AAs physical chemical characteristics on their co-metabolic removal under different redox conditions and biotransformation has been investigated. This thesis implicates that different redox condition may be an essential factor that may affect the biotransformation of a persistent AAs and achieve full mineralization of dye.

This study investigates for the first time in Turkey, the using of the ceramic membrane in woollen textile wastewater treatment, which considers a challenge due to high content of fatty materials that influence the fouling behaviour of the membrane.

The use of ceramic membrane instead of polymer membrane has many advantages such as; narrow and well-defined pore size distribution, higher porosity, better separation and a higher flux; higher thermal, mechanical and chemical stability and longer membrane lifetimes; and higher hydrophilicity, high fluxes at low pressures and lower fouling. Therefore, in this study the ceramic membrane has been used.

This study is trying to understand the following:

- The relation between internal recycle and the removal efficiency of the quality parameter such as COD, TOC, TN and micropollutant.
- Role of redox conditions on full dye mineralization.
- Overall aqueous phase organic pollutant removal.
- The importance of the anoxic-aerobic bioreactors.
- Overall fate of the AAs.

2. LITERATURE REVIEW

2.1. Introduction

Wool is gradually becoming the preferred lifestyle option for fashion and interior design among consumers. As a result, fashion designers are increasingly asking textile manufacturers about origins, and sustainability. Sustainability along the supply chain from farm to fashion as well as textile wastewater treatment is an increasingly significant element in areas regarding corporate social responsibility [Qurashi and Sahu, 2015]. Different industries have their own importance. However, with increasing industrialization, there are also certain drawbacks, in particular environmental problems. In all branches, the wool industry also contributes significantly to the increase in pollution as well as foreign income [Metcalf and Eddy., 2013].

The textile manufacturing sector is the major producer of the colored wastewater due to the huge water usage for the various production phases. These wastewaters contain harmful chemicals such as heavy metals, dyes, alkalis, starch, hydrogen peroxide, surfactants dispersing agents and detergent of metals which have a harmful effect on the environment. The textile manufacturing is often consuming water intensively more than any other industrial sector. In addition, worldwide and virtually all textile wastewater effluents are vastly contaminated. Typical sized textiles fabric needs around 200 L of water for each kg of cloth produced daily [Kant and Kant, 2012]. According to the World Bank, the textile industry and its related industries is sharing about 20 % of wastewater discharged from industry [Holkar et al., 2016], [Kant and Kant, 2012].

The discharge of chemical pollutants into water bodies can causes a plethora of serious environmental problems as well as for human [Chhetri et al., 2017], [Işik and Sponza, 2003], [You and Teng, 2009]. Among a massive number of industrial pollutants, azo dyes which are used in a varied range of industries, especially textile industry, are considered the largest industrial pollutants [Ito et al., 2016], [Ye et al., 2018].

Different physicochemical treatment methods have been implemented and applied for textile wastewater treatment. These include; ion exchange, adsorption, oxidation, coagulation, and membrane separation. Nonetheless, these options are obstructed by technical and economic barriers such as the production of harmful byproduct, formation of a massive amount of sludge (disposal and handling problems) and high operating/energy costs. It is worthful to said that the majority of conventional treatment methods are greatly costly, energy consumption is high and many chemicals are added to treatment process [Siddique et al., 2017]. Among textile wastewater treatment options, biological methods are considered a promising technology to deal with colored wastewater. The biological treatment has many advantages such as eco-friendly, less sludge production, full mineralization, cost effective and less consumption of water [Holkar et al., 2016]. However, studies on combining multi redox conditions in hybrid systems for color removal are still scarce [Zhu et al., 2018].

The combination of anoxic-aerobic and the IR stream from aerobic rector to anoxic one leads to 1)enhanced mixing/mass transfer, 2)dilution of media, 3)transport of dissolved oxygen from aerobic tank, and 4) supply of nitrate [Li et al., 2012], [Phan et al., 2016]. Moreover, IR between anoxic and aerobic tanks may form conditions that promotes the development of specific bacterial community distributed between two redox environments, which serve the central function of the anoxic-aerobic bioreactor systems [Luo et al., 2015], [Xue et al., 2019], [Zhang et al., 2018].

AAs are ranging from the simplest structure with one aromatic ring connected to one amino group to complex structure with multiple aromatic rings with multiple substituents [Juárez et al., 2015], [Rani and Shanker, 2017]. AAs are an important category of the ecosystem and water pollutants as many of AAs are highly toxic, allergic and carcinogenic [Dados et al., 2004], [Juárez et al., 2015], [Wei et al., 2019]. Studies have shown that AAs including benzidine, chloroanilines and toluidine are highly hydrophilic and are toxic for both humans and ecosystem and having thermodynamic stability [Dai et al., 2018]. As AAs are polar compounds, they are more soluble in water than azo dyes. Moreover, the AAs widespread distribution in the aquatic ecosystem can be attributed to AAs high mobility. Hence, a recognizable concentration of AAs can be found in aquatic ecosystems like lakes, rivers and wastewater [Casero et al., 1997],

[Luongo, 2015], [Rani and Shanker, 2017]. Like other Organic Micropollutants (OMPs), sometimes, Azo dyes metabolites such as AAs are even more toxic than the parent compounds [Özkan et al., 2019], [Wei et al., 2019].

The removal of AAs from wastewater can be accomplished in various forms including adsorption on activated carbon, extraction, microbial or oxidation and electrochemical techniques [Bhatia et al., 2017], [Casero et al., 1997], [Zhu et al., 2018]. The need for feasible and environmentally friendly full dye removal processes led to the study of different biological wastewater treatment systems. Commonly, the azo dye is stable to aerobic biodegradation whereas it can be reduced under anaerobic biodegradation and form AAs, which in the contest, biodegradable in aerobic condition and non-biodegradable in anaerobic biotreatment [Dai et al., 2018], [Franca et al., 2019], [Ning et al., 2015], [Xiao et al., 2018]. Thus, the biological remediation of textile wastewaters is typically achieved by integration anaerobic for decolorization with aerobic conditions for AAs mineralization [Libra et al., 2004], [Spagni et al., 2010].

2.2. Processes in Textile Industry

Dyeing is the process in which textile fabrics are colored. This process includes several phases which can be done together or alone process [Luongo, 2015]. De-sizing, printing, sieving scouring, washing, rinsing, bleaching, mercerizing, dyeing, carbonization and finishing are the main processes in the textile industry.

2.2.1. Textile Dying Process

The main composition of textile wastewater is generated mostly from the dyeing, painting and washing. The main stages in textile industry are summarized in Table 2.1 [Vigo, 2002].

Table 2.1: Textile Dying Process Description.

Process	Disruption
Singeing	Get rid of protruding by passing fibres on flame
Sizing	Protecting fibre by coating yarn to reduce the damage of fabric in weaving process.
De-sizing	Removal of chemical which used in sizing phase to prepare the fabric to following process.
Scouring	Cleaning fabrics from impurities.
Bleaching	Removing the original colours of fabrics.
Mercerization	Preparation of fabrics to dying process.
Dyeing	Process which dye use to colour the fabric.
Printing	Using pigments and/or dyes in the pattern form to produce decorating textile.
Finishing	Improving the look, performance of fabric to be ready for using.

In addition to the previous process, the washing process is used after almost all previous process to remove the chemical used in those process as well as the non-fixed dye in the dying process [Vigo, 2002].

2.2.2. Dyes Types

The purpose of dyes is to color the fabrics; therefore, many types of dyes are used next to the preparation phases of textile. The dyes are considered a significant section of the worldwide chemical industry trade. Mostly all used dyes are prepared synthetically. The coal tar and petroleum-based products are the raw material for synthetic dyes. The developments in textile industry are responsible for the frequently changed the type of the textile materials such as fabric. In addition, the demand for dyes is highly increased as the population numbers are grown up; therefore, the production of textile fabrics should meet the demand. Consequently, the enormous amount of textile wastewater has been produced, which usually increases the pollution in environmental systems [Elnemr, 2012].

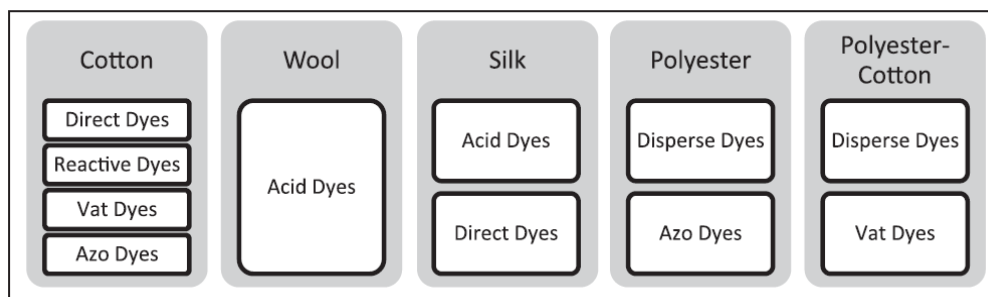


Figure 2.1: Dyes for Different Fibers.

Figure 2.1 shows the main kinds of dyes which are used for dyeing different categories of fiber [Holkar et al., 2016]. However, even natural based dyes are not capable to fix completely on fabrics during the dyeing process resulted in a massive amount of residual dyes are released in wastewater. For instance, the fixing range for reactive dyes which use in the cotton color process is 20-50 % [Mughal et al., 2013].

2.2.3. Environmental Concerns of Textile Wastewaters

The discharge of wastewater which contains complex pollutant such as dye and other used chemicals in the textile industry is considered the main concerns related to the environment. Moreover, sludge which produced during the treatment of textile wastewater is considered a threat due to containing many chemicals, Besides the polluting effects, consumption of energy sources, such as fuel, water and electricity increase greenhouses gases which causes global warming [Alkaya and Demirer, 2014], [L et al., 2015].

Severe environmental problems are presented by colored textile effluents as many kinds of synthetic dyes have been used in textile industry. These effluents contain various chemical compositions with a high concentration of inorganic and organic compounds. Many studies reported that more than 100 thousand usable fabrics pigment are available in dyes trade. Furthermore, million tons of pigment are manufactured annually whereas 280 thousand tons of dye are released from textile manufactory to the environment every year via effluents produced [Katheresan et al., 2018], [Samaei et al., 2018]. Table 2.2 shows the consumption of water, energy and chemicals for production

1 kg of colored fabric [Parisi et al., 2015]. The dying and painting process are usually consuming most of the water consumption that uses in textile dyeing process. The water usage depends on fabric type and generated waste streams are loaded with a high concentration of residual dye from the dyeing processes [Dilaver et al., 2018]. It is estimated that every 1 kg of fabrics needs around 220 L of water during the production [Arslan et al., 2016], [Kant, 2012].

Table 2.2: Consumption of Water, Energy and Chemicals for Production of 1 kg of Colored Fabric.

Unit	Input	Consumption
Pre-treatment	water	20 L
	chemical	120 Kg
	Gas	-
	energy	0.13 Kwh
Dyeing	water	20 L
	solvent	20.98 Kg
	Dyestuff	10 g
	Auxiliary	25 g
	energy	3.82 Kwh
Washing	water	10 L
	Washing agents	5 g
	energy	0.16 Kwh
Drying	Energy	0.04 Kwh
	Gas	0.27 Kwh

Besides the massive water consumption by the textile industry, the wastewater from this industry has become a major environmental issue due to its highly polluted and toxic properties [Majewska, 2010], [Makertihartha et al., 2017]. As a consequence of progressively strict restriction on the pollutant content of textile wastewater. Elimination of hazardous materials from textile wastewater before discharge to ecosystems is necessary to protect the environment [Yin et al., 2018].

The highly colored wastewater has an impact on photosynthetic function in plant. In addition, colored wastewater harmfully affects the aquatic life because textile water affects the sunlight penetration and increase the oxygen utilization. Furthermore, textile wastewater contains metals and chloride that may be harmful to particular aquatic species [Cheng et al., 2018], [Holkar et al., 2016]. Also, dye degradation products such as aromatic amines have a toxic and carcinogenic effect on the ecosystem [Alventosa et al., 2014], [Hai, 2010], [Puvaneswari et al., 2006]. Precisely, discharge of highly polluted stream without decent and sufficient remediation has adversely affected soil, water bodies, soil and ecosystems [Holkar et al., 2016], [Oliveira et al., 2018].

2.2.4. Discharge Standards for Textile Wastewater

Friha et al [2015] discussed the wastewater properties which discharged from six textile dyeing plants (Table 2.3) [Friha et al., 2015]. Due to the toxicity effects of effluent from those plants, standards for discharging textile wastewater into the environment and/or water bodies has been regulated in many regions; therefore, dyeing houses are banned from discharging their wastewater into environment without proper treatment.

Table 2.3: Characteristics of Real Textile Wastewater.

Parameters	C1	C2	C3	C4	C5	C6
pH	10.95	12.48	12.60	12.34	11.78	11.26
EC (mS/cm)	5.12	5.32	13.22	11.76	6.41	8.26
COD (mg/L)	3089	1916	1838	1463	2220	1871
BOD ₅ (mg/L)	300	900	600	900	1375	1250
BOD/COD	0.1	0.47	0.33	0.62	0.62	0.67
TOC (mg/L)	898	686	563	614	439	629
TSS (g/L)	0.46	1.07	0.22	1.21	0.67	0.21
Ions (mg/L)						
Calcium (Ca)	6.94	1.34	9.33	10.88	11.9	7.64
Potassium (K)	1.13	8.13	68.84	90.84	110.8	17.13
Sodium (Na)	100.4	162.4	142.4	226.0	118.0	142.4
Magnesium (mg)	10.39	40.39	40.13	34.13	40.13	8.39
Heavy metals (mg/L)						
Copper (Cu)	0.003	0.001	-	0.011	-	-
Zinc (Zn)	0.092	0.018	0.106	0.104	0.179	0.012
Nickel (Ni)	-	-	0.027	-	-	-
Chrome (Cr)	-	-	-	-	-	-
Cadmium (Cd)	0.008	0.008	-	-	-	-
Container	-	-	-	-	-	-

In Table 2.4, the discharge limits for textile wastewater are presented. The direct discharge limits illustrate the limits that be must followed when textile wastewater discharge to water bodies whereas the indirect discharge limits when discharging into the sewer system.

Table 2.4: Discharge Limits of Textile Factory Effluents.

Parameters	Limit value (max)		Monitoring Location
	Direct discharge	Indirect discharge	Wastewater total outfall from factory
pH	6-9	6-9	
COD	100 mg/L	200 mg/L	
BOD5	25 mg/L	50 mg/L	
TSS	60 mg/L	100 mg/L	
Color (dilution ratio)	70	80	
Ammonia nitrogen	12 mg/L	20 mg/L	
N total		30 mg/L	
	20 mg/L	50 mg/L	
	35 mg/L (batik industry)	(batik industry)	
P total	1.0 mg/L	1.5 mg/L	
Chlorine dioxide	0.5 mg/L	0.5 mg/L	
AOX	15 mg/L	15 mg/L	
Sulfide	1.0 mg/L	1.0 mg/L	
Anilines	1.0 mg/L	1.0 mg/L	
Antimony total	0.10 mg/L	0.10 mg/L	
Chromium VI	0.50 mg/L		Wastewater outfall from factory workshop of production facility

2.3. Treatment Processes of Textile Industry Wastewaters

Textile wastewater treatment, especially color removal, has been a great challenge during the last decades because there is no single and economically attractive technology for dye decolorization [Haiming et al., 2017]. In addition to color, a conventional textile industry wastewater is characterized by COD, BOD [Ozdemir et al., 2013]. Following dyeing process, a massive amount of unfixed active dye usually withdraws the dye houses with other additional chemicals which used in dying process, consequential in wastewater that is heavily contaminated with non-biodegradable chemicals, which should be removed before being discharged into the environment [Arslan et al., 2016], [Cheng et al., 2018], [Xiao et al., 2018]. To tackle this problem, the physical, chemical and biological treatment methods are mostly used in textile wastewater treatment plants [Xue et al., 2019]. Even though some of the physical and chemical processes have been shown to be effective, their application is hindered due to the extensive usage of chemicals, generation of a huge amount of sludge with a disposal problem, high cost of installation as well as maintenance and operating costs and high sensitivity of a variable textile wastewater influent [Balapure et al., 2015], [Murali et al., 2013], [Zhu et al., 2018].

2.3.1. Conventional Physical and Chemical Processes

The most common physical and chemical treatment methods which use in textile wastewater treatment plant are adsorption, coagulation/flocculation, ion exchange, oxidation and membrane separations [Haiming et al., 2017]. Regarding the wastewater properties and discharge standards, more than one method can be used in an integrated or hybrid way to achieve the final discharge limits [Holkar et al., 2016].

2.3.1.1 Coagulation/Flocculation

Removing dyes from wastewater by coagulation is an effective method. This approach uses iron sulfate and iron chloride as coagulants, which can be used to remove dyes directly [Huang et al., 2014]. Nevertheless, coagulation is inefficient for acidic and reactive dyes [Ahmad et al., 2015], [Yeap et al., 2014]. Furthermore, from an economic

perspective, coagulants are costly materials which restrict the applicability for a huge amount of textile wastewater [Robinson et al., 2001]. In addition, production of a large amounts of sludge seems impractical in terms of sludge handling and disposal hindered the feasibility of this [Huang et al., 2014], [Yeap et al., 2014].

2.3.1.2 Adsorption

The attention has been attracted towards adsorption methods as an effective approach to treat textile wastewater due to their high color removal efficiency for textile wastewater containing a many dyes category [Ahmad et al., 2015], [Liu et al., 2018]. The most important characteristic that must be taken in consideration when selecting the proper adsorbate are the capability for the adsorbent regeneration and high affinity [Ayati et al., 2016], [Jadhav and Srivastava, 2013]. However, the sludge generation, regeneration and / or dumping and a high price of the adsorbent are the main obstacles for a wide application of adsorption methods. Like all adsorbents, dye removal by activated carbon is considered an efficient way for various dyes. The high cost and regeneration problems are the main problems which hinder the effective use of activated carbon as adsorbant [Ahmad et al., 2015], [Galán et al., 2013], [Vikrant et al., 2018]. Figure 2.2 shows the physical chemical and biological methods for the degradation of dyes in textile wastewater [Holkar et al., 2016].

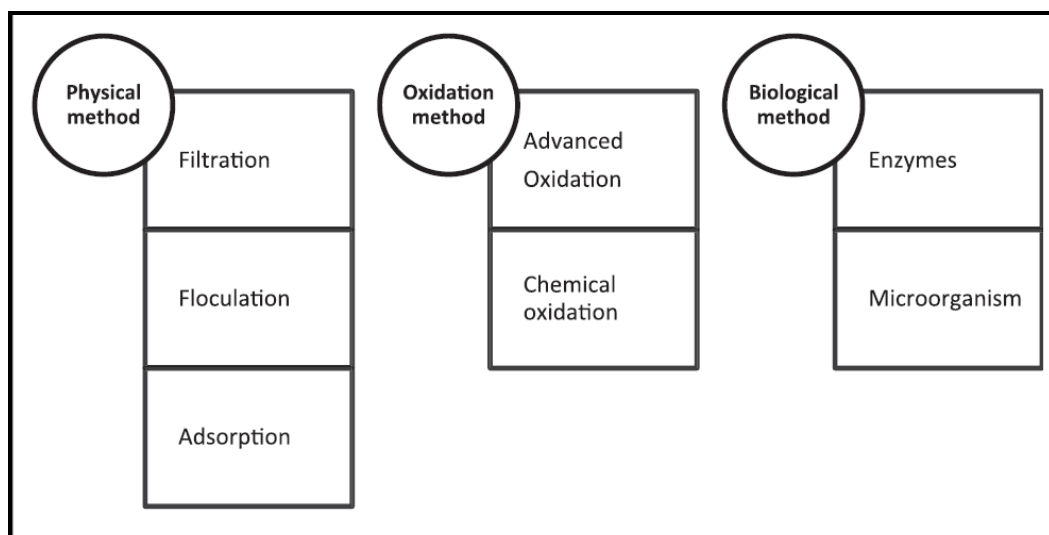


Figure 2.2: Methods for Textile Wastewater Treatment.

2.3.1.3 Ion Exchange

The dyes used in the textile industry contain chromophores and auxochromes, which are considered typical anionic groups. Therefore, commercially available anion exchange resins can be used in the treatment of textile wastewater to remove dye residues [Vikrant et al., 2018]. However, the ion exchange methods generally used in industrial wastewater treatment are implemented in fixed beds which are expensive and have a flow restriction [Hassan and Carr, 2018].

In the ion exchange process, dye-containing textile wastewater is passed through an ion exchange bed containing resin until all available sites for the exchange in the resin are replaced [Robinson et al., 2001]. However, the expensive operation and the associated ineffective measures make it a less practical choice of treatment for disperse dyes [Ahmad et al., 2015], [Robinson et al., 2001]. Ion exchangers as a dye treatment method have not been used actively and extensively for the treatment of textile wastewater since the range of dyes which they can handle is moderately small [Murali et al., 2013], [Robinson et al., 2001].

2.3.1.4 Oxidation

Oxidation methods are very effective and practicable for the degradation of the dye in textile wastewater only if the volume of textile wastewater is low. This has hindered the use of oxidation methods [Asghar et al., 2015]. The methods of oxidative discoloration of textile wastewater mainly use a chemical methodology for the removal of dyes [Ahmad et al., 2015]. The method is simple; therefore, it is very popular. The division of the aromatic cycle in dye molecule is considered to be the main driving mechanism used by the oxidation of the dye to treat textile wastewater. [Pan et al., 2017]. Hydrogen peroxide (H_2O_2) has been recognized as the main oxidative chemical method in oxidation methods. However, activation step using ultraviolet light, for example, must be used to activate H_2O_2 before using it as an oxidation agent [Robinson et al., 2001]. Many diverse oxidation methods (such as ozonation, photochemical, Fenton's reagent, electrochemical destruction, and sodium hypochlorite ($NaOCl$)) have been implemented in this domain [Pan et al., 2017], [Robinson et al., 2001]. Most of these oxidation processes have been described to give good results in the treatment of dyes. However, almost most of them have major disadvantages, such as the production of large amounts of sludge (extremely difficult to handle and dispose of), the formation of toxic by-products (e.g. the formation of AAs) carcinogenic due to the implementation of ($NaOCl$) and the consumption of energy and chemicals [Ahmad et al., 2015], [Robinson et al., 2001].

2.3.1.5 Membrane Processes

Membrane process separation of dyes effective due to its many advantages of limited maintenance needs, simple operation and installation, no usage of chemicals and a small place is required [Rondon et al., 2015]. The mechanism of the dye separation process is controlled by the partial pressure difference between the two sides of the membrane (permeate and feed) of the membrane [Vikrant et al., 2018]. Many advanced membranes have been developed to enable the selective process of dye molecules [Ahmad et al., 2015], [Robinson et al., 2001], [Rondon et al., 2015]. However, certain defects, such as clogging (fouling) of the membrane, such as a large capital investment

and the removal of concentrated residues, limit its spread as an effective method for removing dyes [Rondon et al., 2015]. The inability of membranes to influence large amounts of dyes and their uncertainty under high pressure also require further investigation [Karisma et al., 2017]. Recently, when small quantity of textile wastewater is produced, the membranes process is seen as an effective way to recycle a small amount of water [Robinson et al., 2001].

Many membranes types such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF), classified according to the pore size, have been used for treatment, recovery and reuse of water from textile wastewater. It's important to take into consideration the temperature of textile wastewater during the selection of the membrane type [Chollom et al., 2015]. However, the fouling of membrane is a significant drawback which affects detrimentally the cost of operation and maintenance. In addition, generation of concentrate stream is needed further treatment [Koyuncu and Güney, 2013].

Samaei et al [2018] investigated the hollow fiber nanofiltration membranes for the treatment of textile wastewater treatment on both laboratory and pilot scale. Various operating conditions such as conductivity, pH values and temperature were examined. In the study, high salt concentrations were investigated, therefore, salt accumulation on the membranes surface was observed due to polarization which had severe effects on flux. Samaei et al suggested using the antic-scaling solution for periodical washing of the membrane surface to prevent flux. In case of dyes removal, the removal of dye was above 98% in the study, which means that the applicability for dye recovery as well as wastewater reuse [Samaei et al., 2018]. Table 2.5 summarized the drawbacks of previous conventional treatment methods used for textile wastewater treatment [Vikrant et al., 2018].

Table 2.5: The Disadvantages of Different Textile Wastewater Treatment Methods.

Textile Wastewater Treatment Method	Disadvantages
Oxidation	• Produce huge volume of sludge. • Toxic by-products formation. • High costs of energy and chemicals.
Adsorption	• Ineffectiveness in terms of cost. • Retention time is long. • Side reactions occurrence.
Coagulation	• Inefficient for acidic dyes. • High cost of coagulant specially when dealing with huge amount of wastewater. • Produce huge volume of sludge.
Membrane Separation	• Capital investment is high, • Fouling problem, • Generate considerable volume of concentrate stream.
Ion-exchange	• Regeneration problems due to large volume of wastewater.

2.3.2. Biological Processes

Biological treatment techniques have attracted the attention of the scientific researcher in the past ten years. Due to many advantages over conventional methods (e.g. in terms of environmental compatibility, cost efficiency, non-generation of sludge and simple and safe operation), biodegradation has been identified as a method for the prospective treatment process of dyes under different conditions [Ghosh et al., 2017], [Ito et al., 2016]. The biological treatment is flexible in terms of design and operating conditions since it mixes with naturally occurring microorganisms in order to biodegrade harmful materials (e.g. dyes under anaerobic/aerobic conditions) into harmless products (e.g. carbon dioxide and water) [Ito et al., 2016].

The biological treatments for the full mineralization of textile wastewater have advantages such as less sludge production, cost-competitive, eco-friendly, less water consumption compared to physical/oxidation methods, ending with harmless products or full mineralization [Hayat et al., 2015], [Jonstrup et al., 2019]. According to the growth system, biological treatment systems can be divided into suspended growth and attached growth system. Figure 2.3 shows the biological treatment systems.

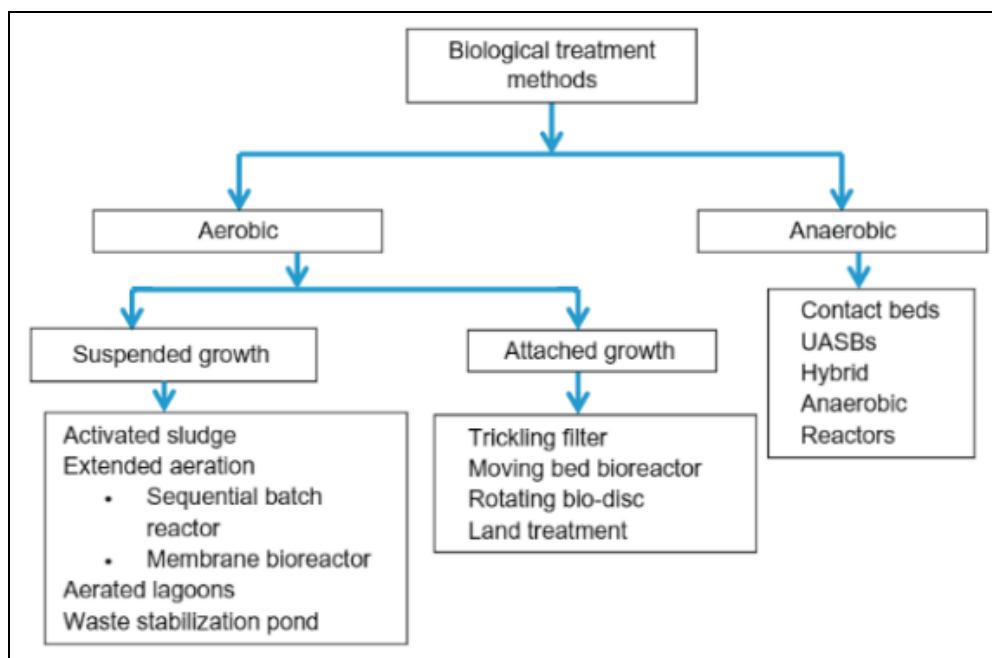


Figure 2.3: Biological Treatment Methods.

Biological processes can probably be carried out under aerobic conditions (in the presence of molecular oxygen as an electron acceptor), anoxically (in the absence of oxygen, but in the presence of nitrate as an electron acceptor), or under anaerobic conditions (in the absence of oxygen and nitrate, and organic matter is the electron acceptor [Bhatia et al., 2017]. Different redox conditions can promote the growth of different microbial cultures and promote the excretion of different enzymes, which leads to a high degree of complex biotransformation of organic substances. Besides, redox environments can significantly influence the properties of sludge, which increases the biosorption of harmful organic substances [Phan et al., 2014]. Since textile wastewater contains complex, toxic and difficult to biodegradable compounds. Aerobic, anoxic and

anaerobic biological processes and their combinations have been used effectively by treating textile wastewater [Padrón et al., 2016].

2.4. Ceramic Membrane for Textile Wastewater

Two types of materials that are commonly used to construct the membranes are polymeric and ceramic. Ceramic membrane is usually used by industrial wastewater which has a good performance in filtration compared to polymer due to its high chemical resistance, inert and easy to clean. The chemical stability depends not only on the materials used but also the size of pore where it reduces the stability of the membrane when the structure is too fine. Ceramic also has higher hydrophilic ability due to the water contact angle. However, the main issue of ceramic membrane is it is very expensive to fabricate and is fragile [Mutamim et al., 2012].

The advantages of ceramic membranes have been recognized for a long time. Process stability and minimum need for support and maintenance are the main features demanded by plant engineers and plant operators. As a result, the benefits offered by flexibility in chemical cleaning, ease of use and general robustness and reliability outweigh the energy penalty for many low-flow applications [Meabe et al., 2013], [Samaei et al., 2018].

Membrane technologies have broad applications in the removal of contaminants from drinking water and wastewater. In recent decades, ceramic membrane has made rapid progress in industrial/municipal wastewater treatment and drinking water treatment owing to their advantageous properties over conventional polymeric membrane. The beneficial characteristics of ceramic membranes include fouling resistance, high permeability, good recoverability, chemical stability, and long lifetime, which have found applications with the recent innovations in both fabrication methods and nanotechnology [Li et al. 2020].

Ceramic membranes are mostly applied in MF and UF, on some occasions in NF and RO. Compared to polymeric membranes, ceramic membranes have the technical advantages including narrow and well-defined pore size distribution, higher porosity, better separation and a higher flux; higher thermal, mechanical and chemical stability

and longer membrane lifetimes; and higher hydrophilicity, high fluxes at low pressures and lower fouling [He et al., 2019].

For ceramic membranes in water and wastewater treatment, there are two fundamental configurations, namely, flat-sheet type and tubular type (Figure 2.4) and both of them are with multi-channels. Compared to flat-sheet membranes, tubular membranes have attracted great interest due to their high surface-to-volume ratio. Both flat-sheet and tubular ceramic membranes could be employed in different applications, such as, removal of natural organic matter from drinking water source, treatment of oil-field produced water, cleaning of dyeing wastewater, reuse of car-washing wastewater and desalination. In general, ceramic membranes for water and wastewater treatment are asymmetric in microstructure with a denser active layer on top of a more porous and larger particle substrate [He et al., 2019].

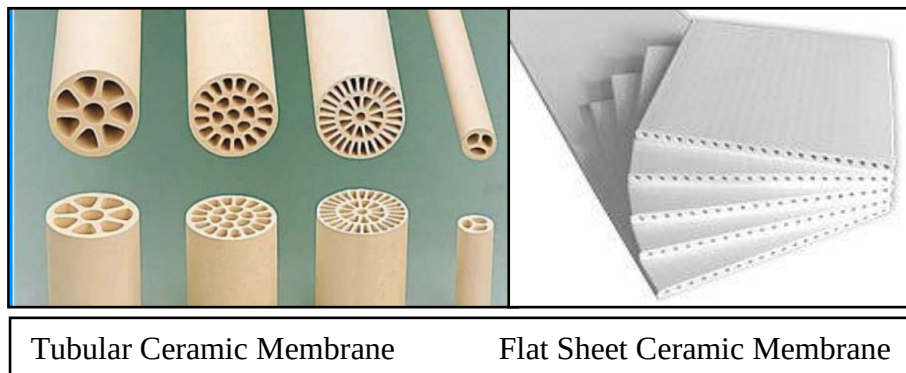


Figure 2.4: Ceramic Membrane Configurations.

Advantages and disadvantages of ceramic membrane Compared with the organic membranes that are currently used more industrially, ceramic membranes have the following advantages [Feng et al., 2018]:

- Good chemical stability, acid and alkali resistance and organic solvents, good oxidation resistance.
- High mechanical strength, no deformation under high pressure or large pressure difference, abrasion resistance, erosion resistance, high pressure back pressure can be used to regenerate the film.
- Strong anti-microbial ability and good antibacterial effect. It is suitable for medical and biological engineering.
- High temperature resistance. Generally, it can be operated at 400°C. The maximum operating temperature is up to 800°C.
- The pore size distribution is narrow, and the separation efficiency is high.
- Non-toxic, suitable for food and drug treatment.

2.4.1. Ceramic Membrane for Textile Wastewater Treatment

The textile industry has a large amount of water, and the generated wastewater contains suspended substances, COD, residual bleaching agents, heavy metal substances, various types of pulp and other substances. There are many pollution components, and it is difficult to handle with conventional methods. Ceramic membrane technology Wastewater treatment is better. Feng et al [2018] used alumina microfiltration membranes to treat textile wastewater. The study found that the removal of suspended solids and organic matter was very good. The removal rate of insoluble dyes was more than 98%. At the same time, soluble dyes could be removed by adding some surfactants. The rate is greater than 97% [Feng et al., 2018].

2.5. Biological Treatments Mechanism

Dye removal can be done in two ways; either sorption on microbial biomass or biotransformation of dyes by cells. Sorption divided into adsorption and biosorption. The adsorption of dyes can occur on living / growing microbial cells as well as on dead

cells and occurs due to the ion exchange [Robinson et al., 2001], [Tsai and Chen, 2010]. The molecular structure of the dye remains during biosorption whereas the original molecular structure of the dyes is changed in the biotransformation and the pollutant is destroyed in segments by the microbial cells, sometimes complete mineralization being achieved, for example, the conversion of the organic substance into CO₂, inorganic and biomass. Biosorption of dyes does not solve the problem, since the pollutant is not converted into harmless material, but is captured in the medium of the adsorbent (microbial biomass) [Khan et al., 2013].

Textile wastewater treatment is normally carried out by various groups of bacteria with a view to biological treatment under anaerobic, anoxic and aerobic conditions. A single microbial culture or mixed microbial cultures can be used. The mixed microbial population may be more efficient due to the increased production of enzymes compared to the individual microbial culture [Hameed and Ismail, 2018]. The decomposition process includes the process by which the microbial culture attacks the structure of the dye at different locations in the bonds by different strains and the coexisting strains can benefit from the more numerous decomposition processes. This is important for the complete mineralization of organic substances. However, the remaining toxic organic substance can have a toxic effect on the environment [Katheresan et al., 2018].

2.5.1. Redox Conditions for Azo Dye Treatment

Recently, many studies have investigated the feasibility of using redox conditions for micropollutant removal [Luo et al., 2014], [Phan et al., 2014]. Redox combination, especially anoxic and aerobic, in biological treatment to enhance microbial diversity can increase the bio-transform organic micropollutants, meanwhile, the removal of micropollutant such as organic carbon and nitrogen is not affected [Alvarino et al., 2018]. IR between aerobic and anoxic tanks probably produce a unique environment that enhance the growth of a specific bacterial culture distributed between aerobic and anoxic reactors. This common community usually responsible for the advantages of anoxic-aerobic systems [Phan et al., 2016]. Many studies investigate the removal of OMPs in different redox condition, especially denitrification process. The result revealed that such

system increases the removal efficiency of many OMPs, such as aproxen, ibuprofen, roxithromycin and celestolide [Alvarino et al., 2018], [Suárez et al., 2012].

Decolorization occurred in anaerobic compartments, while the mineralization of the resulting AAs mainly occurred under aerobic conditions [Kokabian et al., 2013], [Olivares et al., 2016], [Ozdemir et al., 2013]. Many studies investigated the removal of azo dye under redox condition. The results showed that the removal efficiency of azo dye under aerobic condition was low whereas the removal of azo dye is high under reduction environment. However, the azo dye reduction resulting in the formation of AAs which considered highly toxic compounds. Fortunately, AAs is removable under aerobic condition, therefore, the combination of anaerobic/anoxic and aerobic is essential to full mineralization of azo dye. Figure 2.5 illustrates the treatment of azo dye under anaerobic/aerobic systems [Franca et al., 2019], [Lin et al., 2010], [Spagni et al., 2010], [Xu et al., 2018], [Zhu et al., 2018], [Zuriaga et al., 2010].

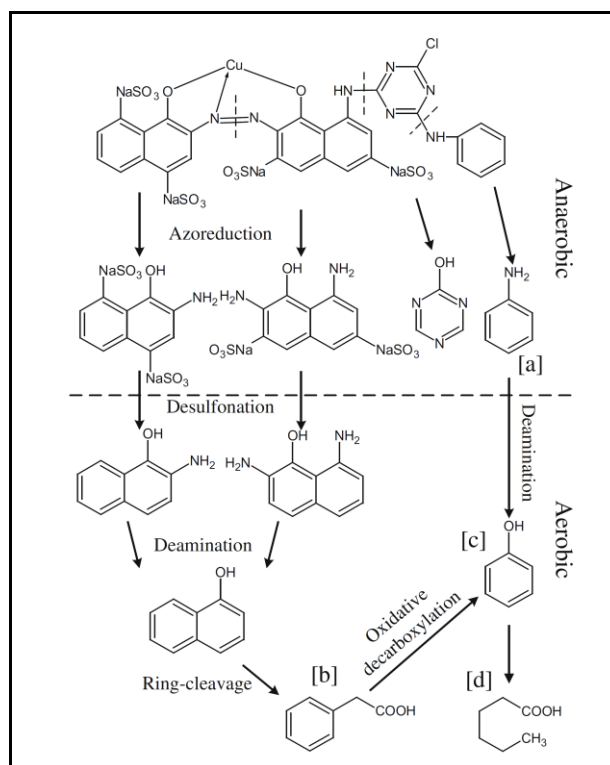
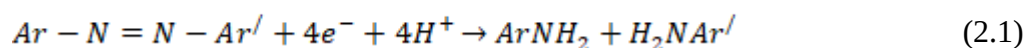


Figure 2.5: Azo Dye Treatment Path Under Anaerobic/Aerobic Treatment.

2.5.2. Anaerobic Decolonization of Azo Dye

The reduction of azo dye under anaerobic biological treatment is a biochemical reaction. The availability of electron acceptors is the most important factor in the decolorization of azo dye under anaerobic condition. The azo dye is acting as a final electron acceptor in the anaerobic microbial chain [Santos et al., 2007], [Van der Zee et al., 2001].

The mechanism of azo dye reduction under anaerobic condition includes the cleavage of azo bond, which resulted in formation of AAs, by the help of azoreductase enzyme [Robinson et al., 2001], [Van Der Zee and Villaverde, 2005]. Equation (2.1) shows the reduction path of azo dye [Luangdilok and Panswad, 2000].



2.5.3. Anoxic Decolorization of Azo dye

The core function of the anoxic tank is increasing the nitrogen removal. The removal of nitrogen in biological treatment systems includes two processes: nitrification and denitrification. Nitrification is the process of oxidize ammonia (NH_3) to Nitrite (NO_2) by ammonia-oxidizing bacteria, then NO_2 is going to further oxidizing by nitrite-oxidizing bacteria to end by Nitrate (NO_3). Both ammonia and nitrite-oxidizing Bactrian are autotrophic aerobic bacteria. On the other hand, Denitrification is the process of reduction of nitrite and nitrate to nitrogen gas. The process is accomplished by heterotrophic bacteria which use NO_2 and NO_3 as the electron acceptor [Alzate et al., 2016]. Besides the nitrogen removal, the role of the anoxic tank is accomplished by the IR from aerobic reactor to anoxic reactor which increases the possibility of growth of specific bacterial culture shared between anoxic and aerobic tank leading to the excretion of diverse enzymes [Phan et al., 2016].

The anoxic-aerobic biological method is a suitable choice to achieve the biological elimination of nitrogen by denitrification in an anoxic reactor and aerobic nitrification. It is able to increase the efficiency of eliminating micropollutants as well as macropollutants. AAs are considered the main contribution of OMP pollutants in textile wastewater. As a result, the anoxic-aerobic system is very attractive for the treatment of chemically intensive industrial wastewater [Lin et al., 2010].

Yun et al [2006] studied the anoxic-aerobic sequence for textile wastewater treatment. The removal efficiency was compared between anoxic and aerobic reactors. The removal efficiency of COD was 27% and 94% when Dissolve Oxygen (DO) was 0.3 mg/l and 6.0 mg/L, respectively. While the color removal efficiency raised from 72.9% to 86.6% with lowering the dissolved oxygen for 6.0 to 0.3 mg/L, the results showed that the anoxic environment was better than aerobic in terms of color elimination [Yun et al., 2006].

2.5.4. Role of Aerobic in Azo Dye Treatment

Both the aerobic and anaerobic microbial culture can be used for textile wastewater treatment due to enzymes with azoreductase ability which can be found in

both environments [Punzi, 2015]. However, the organic material due to dye is not often removed under the anaerobic reactor because of the AAs resulting from the reduction of azo dye in anaerobic tank which are non-biodegradable under anaerobic condition. However, they may be biodegradable under aerobic condition [Van Der Zee and Villaverde, 2005]. Hence, the main role of the aerobic environment which follows anaerobic condition is removal both the remaining dye and the dye reduction by-products such as AAs [Bonakdarpour et al., 2011], [Libra et al., 2004].

The sequential batch reactor is a developed activated sludge treatment system which can be used to treat a wide range of wastewater, e.g. industrial wastewater, landfill leachate, domestic wastewater as well as biological and nitrogen removal, due to its advantages such as low construction and maintenance, flexibility in operation and compact layout [Khan et al., 2019]. Anaerobic-aerobic sequencing batch reactors have been suggested for complete biotransformation of azo dyes, owing to color removal in anaerobic condition and the intermediate AAs mineralization in the subsequent aerobic condition [Franca et al., 2015].

The combination of anaerobic-aerobic systems for reducing the toxicity of textile wastewater have been widely examined. Sponza and Isik investigated the toxicity of direct red 28 azo dye through a continuous anaerobic-aerobic sequential reactor by using the anaerobic toxicity assay and specific methanogenic activity for anaerobic culture, where (respiration/inhibition test) bacteria and *Daphnia Magna* were used for aerobic reactor. Their results showed a reduction of toxicity in anaerobic toxicity assays of respiration/inhibition and *Daphnia magna* tests [Sponza and Isik, 2005].

2.5.5. Factor Affecting Azo Dye Decolorization

The decolorization of azo dye is influenced by different parameter. Those parameters are the level of agitation, temperature, oxygen, pH, dye concentration, adding external carbon and nitrogen, redox mediator and electron acceptor. Table 2.6 shows those factors and how they influence the decolorization of azo dye. Determining the impact of each component on the microorganism is significant to make the process more effective, faster and practically applicable [Khan et al., 2013].

2.6. Aromatic Amines

Azo dyes contain one or more azo bonds linking phenyl or naphthyl radicals usually substituted with diverse of following functional groups: sodium salt of sulfonic acid ($-\text{SO}_3\text{Na}$), methyl ($-\text{CH}_3$), hydroxyl ($-\text{OH}$), nitro ($-\text{NO}_2$), chloro ($-\text{CL}$) and amino (NH_2) [Martin et al., 2005], [Shanker et al., 2017]. Azo dyes are composed of 50-70 % of all dye types that use in the textile industry. Having the functional group $\text{R}-\text{N}=\text{N}-\text{R}$, azo dyes could be reductively reduced by anaerobic environment by different bacteria into AAs that are carcinogenic [Ayed et al., 2017], [Kadoya et al., 2018], [Shanmugam et al., 2018], [Haiyuan et al., 2019]. AAs are a large group of environmental pollutants that stable thermodynamically. Recently, the AAs have received more attention worldwide due to their toxicity and calling for emerging treatment technology development has been needed [Rani and Shanker, 2017]. Consequently, many governmental authority's has forbidden the use of azo dyes in food and textile products as they can release carcinogenic chemicals [Sen et al., 2019], [Yang et al., 2017], [Ye et al., 2018].

Table 2.6: Factors Influencing Degradation of Synthetic Dyes.

Factors	Descriptions
pH	As decolourization of azo dye is accomplished by bacteria, the pH is considered an essential factor. The optimum pH value for colour removal is between 6.0 and 10.0.
Temperature	Hence, all process associated with bacterial culture is temperature dependent, the temperature is an important factor for dye decolourization.
Dye concentration	The dye material is considered a toxic substance for bacteria. Therefore, increasing the concentration of dye gradually may decrease the removal efficiency of azo dye due to the toxic effects as well as to deactivate the azoreductase by blockage the active spots.
Carbon and nitrogen sources	Generally, dyes are not containing enough nutrient such as carbon and nutrient for bacterial growth. As a result, without adding supplementary of carbon and nitrogen, the decolourization process is difficult.
Oxygen and agitation	As cleavage of azo bond is a reductive reaction, the reduction environment is essential for decolourization of azo dyes whereas the oxidative environment is important for oxidizing AAs.
Dye structure	The dye structure plays important role in decolorization process as simple structure and lower molecular weight show high removal efficiency, whereas the lower removal is related to dyes with EWG such as (CL), (SO ₂ NH ₂) and (SO ₃ H).
Electron donor	The presence of electron donors such as acetate ions or glucose enhances the removal efficiency of bioreactor especially under reduction condition in the anaerobic biological reactor.
Redox mediator	As the split of the azo bond is a reductive process, adding redox mediator may improve the reduction of azo dye under anaerobic condition.

2.6.1. AAs Structure

The structure of AAs includes one or more aromatic rings attached to one or more amino groups (-NH_2). The simplest aromatic amine is aniline (see Figure 2.6) [Luongo, 2015]. Beside to (-NH_2) AAs may be substituted with various combinations of the following functional groups: chloro (-Cl), methyl (-CH_3), hydroxyl (-OH), sodium salt of sulfonic acid ($\text{-SO}_3\text{Na}$) and nitro (-NO_2) [Martin et al., 2005], [Snyderwine et al., 2002].

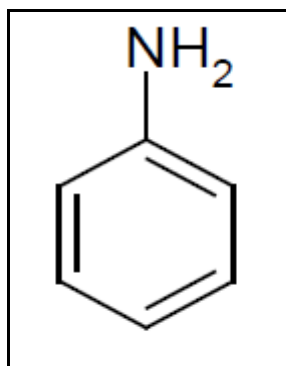


Figure 2.6: Aniline Structure.

The environmental and health effects of AAs is highly dependent on the structure of AAs; the number of aromatic rings and the substituents. The AAs sources can be diesel engine exhaust, refining processes, synthetic polymers, hair dyes, textile industry, pesticides, rubber and pharmaceuticals [Juricek et al., 2015], [Kahl et al., 2011], [Manzetti, 2012].

2.6.2. Environmental Effect of AAs and Health Effect

Recently, due to AAs adverse effect on the environment, they have received more attention. Even though the environmental composition of AAs has been widely investigated, studies on the unplanned release of AAs from expected sources is insufficient to regulate the total emission of AAs [Jurado et al., 2012], [Shabbir et al., 2015]. The main concern related to AAs is the ability of the amino group to cause damage of DNA and portions which make AAs metabolically activated. Thus, AAs are well thought out mutagens [Özkan et al., 2019], [Patel et al., 2018]. Figure 2.6 illustrates

the mechanism of the mutagenic pathway of AAs. The N- hydroxylamines can also non-enzymatically form the nitrenium ion under mildly acidic conditions by NO cleavage (represented by the dotted arrow) [Mathematik, 2017].

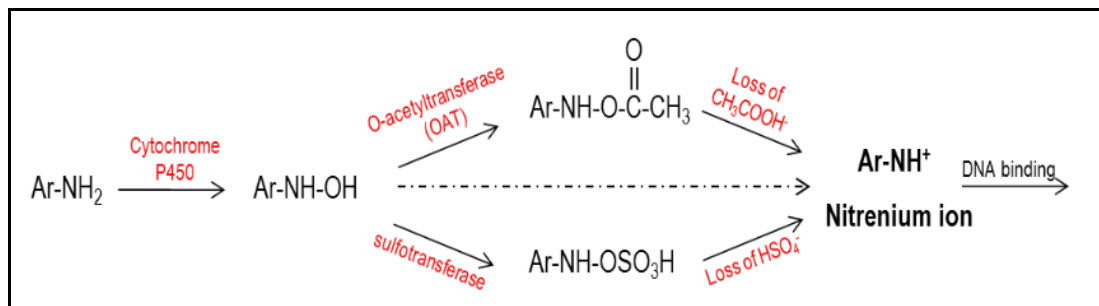


Figure 2.7: Mutagenic Pathway of AAs.

The high polarity of AAs in water contributes to their high mobility, which leads to the widespread of AAs in water bodies, therefore, high level of carcinogenic AAs may be found in environmental matrices such as lake, rivers and wastewater [Plum and Rehorek, 2005], [Singh et al., 2003].

2.6.3. Health Concerns Related to AAs

In early time the bladder cancer was reported as a negative health impacts related to AAs. Workers exposed to 4-chloro-o-toluidine, benzidine, naphthylamine and 4-aminobiphenyl were correlated to bladder cancer by Ludwing Rehn [Donaldson et al., 2019], [Fishbein, 1984], [Safavi and Momeni, 2012], [Talaska, 2003]. As AAs are used in the manufacture of dyes that are more complex than AAs, the metabolized of dyes may re-produce AAs [Brüschweiler and Merlot, 2017], [Landler and Worfel, 1976]. However, the body skins bacteria is capable to cleavage azo bond to produce AAs, causing a severe risk to human body health [Pinheiro et al., 2004], [Platzek et al., 1999]. Moreover, many studies have suggested O-toluidine as highly related to be a bladder carcinogen. Occupational health and safety experts stated that exposure to o-toluidine and 4,4'-methylene bis(2-methylaniline) increases the balder cancer risk by 62-fold [Ferrís et al., 2013], [Gadaleta et al., 2016], [Golka et al., 2004], [Rubino et al., 1982], [Tauber et al., 2008].

The international agency for cancer research has categorized a number of AAs which use in azo dye production as a potential carcinogen [Schreiber et al., 2010]. The European Union has also identified 22 AAs as potential carcinogens. They have therefore banned the use of azo dyes that can release these AAs in textile materials above a threshold concentration of 30 mg/kg [Mortensen et al., 2005], [Muz et al., 2017].

2.6.4. Method of AAs Detection

Many methods have been used to detect AAs in textile wastewater before, during and after the treatment processes. The ultraviolet (UV) method has been used to detect azo dyes and AAs as the aromatic structure can absorb light in UV. Therefore, it is applicable to track the degradation of azo dyes and AAs by measuring the absorbance of light by UV, as every dye has a particular absorbance spectrum. For example, Figure 2.8 shows the azo dye Remozal Red, which has an absorption spectrum with two characteristic peaks at 290 nm and 516 nm. In case of the wavelength cannot be tracked, the degradation of AAs can be predicted by measuring the absorbance at 254 nm. However, this method normally used to monitor the presence of AAs compounds in water [Punzi, 2015].

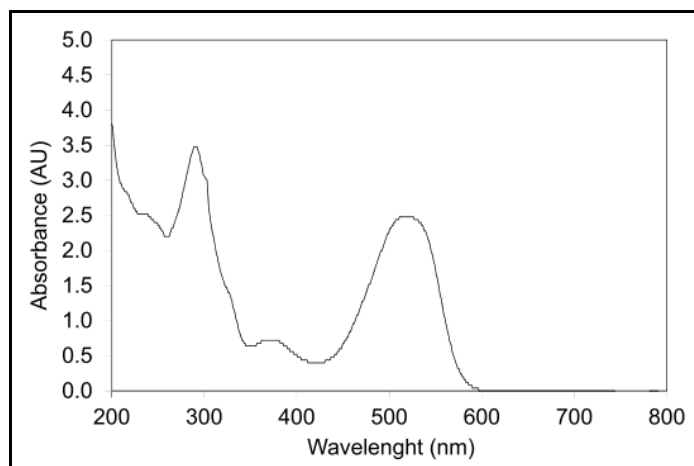


Figure 2.8: UV Spectrum for Azo Remozal Red.

The other way to detect and measure the AAs compound is using high analytical methods such as gas chromatography–mass spectrometry (GC–MS), as thin layer

chromatography (TLC), capillary electrophoresis (CE), liquid chromatography–mass spectrometry (LC–MS), and ultra-high-performance liquid chromatography (UHPLC) [Popli and Patel, 2015]. Those techniques involve sample conditioning, reductive cleavage of the azo bond, extraction of AAs and chromatography technology instrumental determination. Figure 2.9 shows the example of LC-MS/MS for 2,5-diaminotoluenem 2,6-diaminotolene, 2,4-diaminotoluene and 3,4-diaminotoluene determination [Kämpfer et al., 2019].

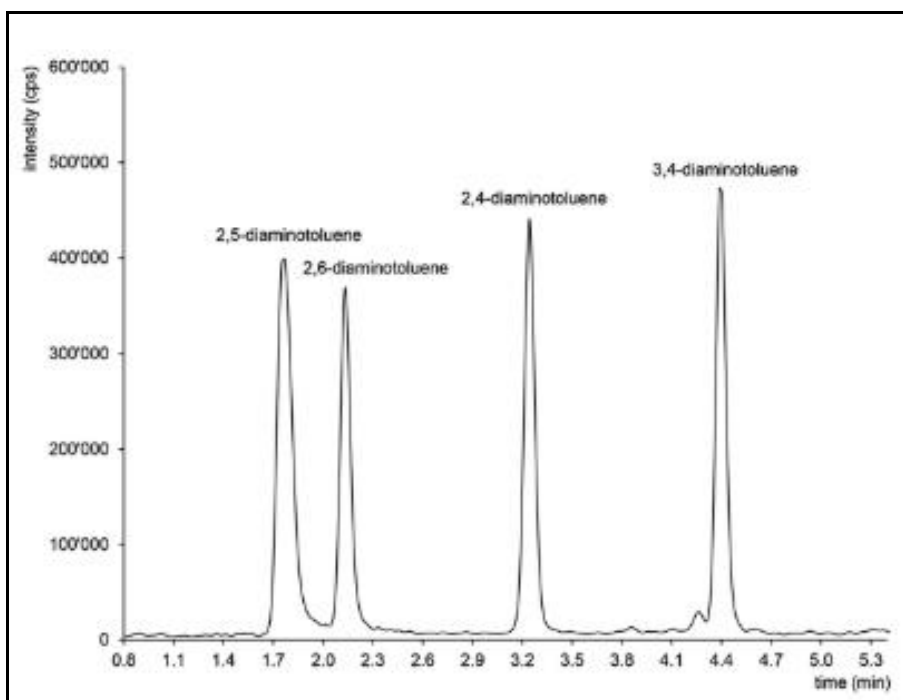


Figure 2.9: LC-MS/MS Chromatogram for Four AAs.

2.6.5. AAs Removal in Aerobic Process

Many physical, chemical and biological treatment methods are used for the removal of AAs from textile wastewater in the textile-dyeing industry [Robinson et al., 2001], [Van der Zee and Villaverde, 2005]. The removal efficiency range of AAs is between 35% and 100% according to Van der Zee and Villaverde [2005] when the anaerobic-aerobic sequential reactor was used. However, it's obvious that full removal of AAs cannot be accomplished through the anaerobic-aerobic biological treatment

system because of the high tendency of AAs to sorption by biomass [Vasudevan et al., 2013].

Under the aerobic condition, there are two ways for molecular oxygen to oxidize the AAs. In the first way, oxygen is combined in the aromatic ring by means of mono and dioxygenases prior to ring-fission. Secondly, oxygen serves as the terminal electron acceptor of the reducing equivalents generated during the oxidation of the aromatic molecule [Field et al., 1995].

Several studies state that aerobic treatment can be used to remove AAs which is produced after azo dye degradation in anaerobic treatment [Frijters et al., 2006], [Maria et al., 2013], [Kapdan and Alparslan, 2005]. The main idea is that aerobic bacteria has the ability to produce oxidative enzymes that are able to oxidize the aromatic rings in AAs produced during anaerobic treatment. However, the chemical structure of AAs and the produced enzymes in the system determine the aerobic biotransformation of the AAs. On the other way, the degradation process may occur or not, consequently, some toxic organic substance may release in the effluent [Silva et al., 2012], [García et al., 2008] those organic substances can be AAs, carboxylic acids and other organic matter [Işik, 2004], [Michael et al., 1999], [Ozdemir et al., 2013]. In other cases, in aerobic treatment, AAs may also endure autoxidation and return into color compounds [Michael et al., 1999], [Neill et al., 2000], [Rehorek and Plum, 2006].

2.7. Research Contribution

In this study, the process of dyeing wastewater from the wool textile sector, which is an important source of waste, was treated by sequential anoxic-aerobic batch reactor followed by Ceramic membrane for tertiary treatment. In line with the research gaps mentioned above, this study aimed to determine the extent of color removal under various redox conditions that are common in textile wastewater treatment processes. The sequential anoxic-aerobic batch reactor was used to treat real textile wastewater under various redox conditions. The removal of carbon, nitrogen and color was assessed in each reactor to determine the effect of the different redox regimes. The results of this study underline the importance of the redox environment for the removal of colors.

The first approach to considering AAs elimination in wastewater treatment projects is to understand better their elimination mechanisms, including the impact of physico-chemical properties and operating conditions on AAs elimination [Punzi, 2015]. Recently, studies have been published on systems that combine anaerobic-aerobic treatments for textile wastewater [Salter et al., 2016], [Sarayu and Sandhya, 2012], [Tauber et al., 2008], [Xu et al., 2018]. However, there is still a lack of knowledge about their ability for removing AAs [Phan et al., 2014]. Fewer studies on eliminating AAs under anoxic/aerobic conditions have been conducted compared to anaerobic-aerobic conditions. As a result, understanding of AAs degradation under anoxic-aerobic conditions is still rather limited. Moreover, the performance of combined anoxic-aerobic reactors has only been the subject of a limited number of recent studies, and conflicting reports are often found in the literature [Rani and Shanker, 2017].

This work focuses on the investigation of the sorption and biotransformation of a selected group of 22 AAs during the biological treatment of textile wastewater. In general, information on the combination of different redox potentials in hybrid systems is still rare. A better understanding of the effects of redox conditions on metabolic pathways and biodegradation rate beside the influence of AAs physical chemical characteristics are required to predict the fate of AAs during the treatment of textile wastewater.

3. METHODOLOGY

3.1. Material

3.1.1. Wastewater Samples

The textile wastewater was collected from textile dyeing factory located in Istanbul-Turkey. The collected wastewater was kept at 40⁰ C to eliminate biological growth. A summary of the influent characteristics is shown in Table 3.1. The dying factory produces two types of colored fabrics: woollen (70%) and polyester (30%). As polyester fabrics are produced from this factory, it is expected that azo dyes are used to color polyester fabrics. In addition, the primary characterization of the raw wastewater sample proved the presence of AAs which is considered the main chemical in azo dyes production.

Table 3.1: Characteristics of the Textiles Wastewater.

Parameter	Value
COD (mg/L)	750
BOD (mg/L)	350
TOC (mg/L)	200
TN (mg/L)	47
PH	7.82
Color (ADMI unit) *	480
Conductivity (ms)	3680
Alkalinity (mg/L)	435
Chloride (mg/L)	89.84
Nitrate -N (mg/L)	8
Sulfate (mg/L)	394.6
Ammonia-N (mg/L)	35
TKN (mg/L)	39
Organic N (mg/L)	4
TP (mg/L)	0.161

* American Dye Manufacturer's Institute (ADMI) color unit.

3.1.2. AAs Agent

Twenty-two AAs were used in this study. Table 3.2 shows the physical chemical characteristic of investigated AAs. A 300 mg/L mix slandered was used in calibration. The chemical standards were obtained from O2si Smart Solutions (Charleston, SC, USA).

Table 3.2: Physical Chemical Characteristic of Targeted AAs.

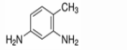
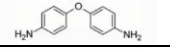
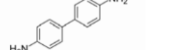
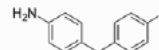
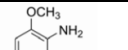
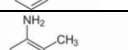
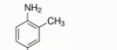
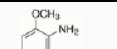
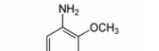
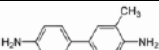
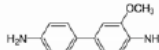
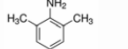
Component	P _{ka}	log k _{ow}	MW	Molecular formula	Cas #	Structure	Log D at pH=8
2,4-Diaminotoluene	5.35	0.14	122	C ₇ H ₁₀ N ₂	95-80-7		0.139029
4,4'-Diaminodipheny	3.96	1.36	200	C ₁₂ H ₁₂ N ₂ O	101-80-4		1.35996
Benzidine	4.3	1.34	184	C ₁₂ H ₁₂ N ₂	92-87-5		1.339913
4,4'-Diaminodiphenylmethan	4.83	1.59	198	C ₁₃ H ₁₄ N ₂	101-77-9		1.589706
o-Anisidine	4.53	1.18	123	C ₇ H ₉ NO	90-04-0		1.179853
o-Toluidine	4.48	1.32	107	C ₇ H ₉ N	95-53-4		1.319869
2,4-Dimethylaniline	4.89	1.68	121	C ₈ H ₁₁ N	95-68-1		1.430497
2,4-Diaminoanisole	5.15	0.5	138	C ₇ H ₁₀ N ₂ O	120-71-8		0.499387
2-Methoxy-5-methylaniline	4.66	1.74	137	C ₈ H ₁₁ NO	120-71-8		1.739802
o-Tolidine	4.59	2.34	212	C ₁₄ H ₁₆ N ₂	119-93-7		2.339863
o-Dianisidine	3.3	1.81	244	C ₁₄ H ₁₆ N ₂ O ₂	119-90-4		1.809991
2,6-Dimethylaniline	3.95	1.84	121	C ₈ H ₁₁ N	87-62-7		1.839961

Table 3.2: Continuation.

Component	pKa	log k _{ow}	MW	Molecular formula	Cas #	Structure	Log D at pH=8
4,4'-Methylene-di o-toluidine)	4.48	1.32	226	C ₁₅ H ₁₈ N ₂	838-88-0		1.319869
2-Naphthylamine	4.16	2.28	143	C ₁₀ H ₉ N	91-59-8		2.279937
2,4,5-Trimethylaniline	5.09	2.27	135	C ₉ H ₁₃ N	137-17-7		2.269466
4,4'-Thiodianiline	4.55	2.18	216	C ₁₂ H ₁₂ N ₂ S	139-65-1		2.179846
4-Chloro-2-methylaniline	3.85	2.27	142	C ₇ H ₈ ClN	95-69-2		2.269969
4-Aminobiphenyl	4.35	2.86	169	C ₁₂ H ₁₁ N	92-67-1		2.859903
4,4'-Methylene-bis(2-chloroaniline)	3.1	3.91	267	C ₁₃ H ₁₂ Cl ₂ N ₂	101-14-4		3.909995
3,3'-Dichlorobenzidine	1.6	3.51	253	C ₁₂ H ₁₀ Cl ₂ N ₂	91-94-1		3.51
4-Aminoazobenzene	2.82	3.41	197	C ₁₂ H ₁₁ N ₃	60-09-3		3.409997
o-Aminoazotoluene	3.01	3.92	225	C ₁₄ H ₁₅ N ₃	97-56-3		3.919996

3.2. Methods

3.2.1. Sampling Process and Sample Preparation

3.2.1.1 Aqueous Phase Extraction

The wastewater samples were collected from anoxic, aerobic and membrane tank. The collected samples were sampled into a 1.0 L polypropylene plastic bottle (Figure 3.1). All samples were filtered using 0.45 μm glass paper and stored at 4⁰ C. Prior to the determination of AAs concentrations, solid phase extraction (SPE) was conducted using Dionex SolEx C18 column (6 mL, 1000 mg, Thermo Fisher, USA). The SPE cartridges were preconditioned with 5 mL methanol, followed by 5 mL ultra-pure water at a flow rate of 3.0 mL/min (Figure 3.2). On completion of SPE, cartridges were dried under vacuum for 30 min. For elution, the target AAs possibly retained in the SPE cartridges were eluted first by 10 mL methanol. Then, 10 mL of the resulting extract was further used as the solvent to elute target AAs absorbed onto C18 cartridge. The final eluates were dried under a gentle stream of nitrogen at 35⁰ C. Finally, the dried extracts were dissolved again with 1 mL of a mixture of methanol-Ultra pure water (25:75, v/v). The final aliquots were transferred into 2 mL amber vials (Figure 3.3) and stored at -20⁰ C until UHPLC-MS/MS analysis.



Figure 3.1: Collected Samples.



Figure 3.2: Solid Phase Extraction.

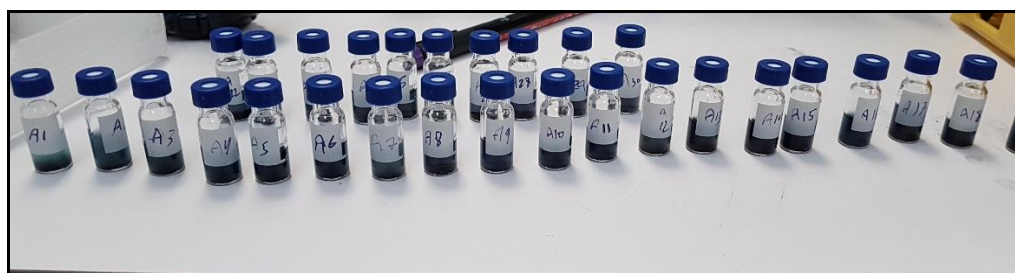


Figure 3.3: Final Extracted AAs samples were Ready to LC-MS/MS Analysis.

3.2.1.2 Sludge Extraction

The collected sludge samples from anoxic and aerobic tanks were centrifuged at 4000 rpm for 10 minutes. Following that, it was dried and saved at -20°C . The dried sludge (1 g) was grounded to powder and extracted successively with 10 mL methanol by ultrasonic solvent extraction for 10 min at 40°C . The solvent was then evaporated using nitrogen gas. The dried extracts were dissolved again with 1 mL of a mixture of methanol-Ultra pure water (25:75, v/v). The final aliquots were transferred into 2 mL amber vials and stored at -20°C until UHPLC-MS/MS analysis.

3.3. Experimental Setup and Procedure

In this study, the sequential anoxic-aerobic batch reactor followed by ceramic membrane unit was used. The anoxic tank and the aerobic were separated, therefore, the two sludge were produced 1) anoxic sludge 2) aerobic sludge. The working volume of 15 L was used in each separate reactor (Figure 3.4). The membrane consisted of a flat ceramic membrane module (Chembrane - Denmark) with a nominal pore size of 0.1 μm and an effective membrane surface of 0.528 m^2 , which was immersed in a tank installed next to it. A pressure/pressure vacuum pump (BEM20, Priom Teknik, Turkey) was used using 10-minute suction cycles followed by 2-minute backflushing to avoid clogging the membrane module. A certain volume of water was returned from the aerobic tank to the anoxic tank. The IR was then calculated as the ratio of the volume of the recycled water to the volume of the feed. As the investigated system was operated in batch mode, the IR term present the ratio of recycled volume. The aerobic reactor and the ceramic membrane tanks were continuously ventilated via air nozzles connected to an air pump. The mixed liquor from the anoxic tank was stirred with an air laboratory mixer (Mtops MS 5010, Kore) to ensure a homogeneous distribution in the tank. The membrane system was operated with a constant flow of 25 LMH. The total hydraulic residence time (HRT) of 24 h (12 h for anoxic and 12 h aerobic) was used. Aeration in each reactor was controlled to achieve the desired redox conditions. The DO concentration in the aerobic reactor and membrane tank was kept at 3 to 5 mg /L, while the DO for the anoxic reactor was kept at about 0.12 mg /l. The redox potential (ORP) for the anoxic and aerobic reactors was -115 ± 25 mV and 130 ± 16 mV, respectively.

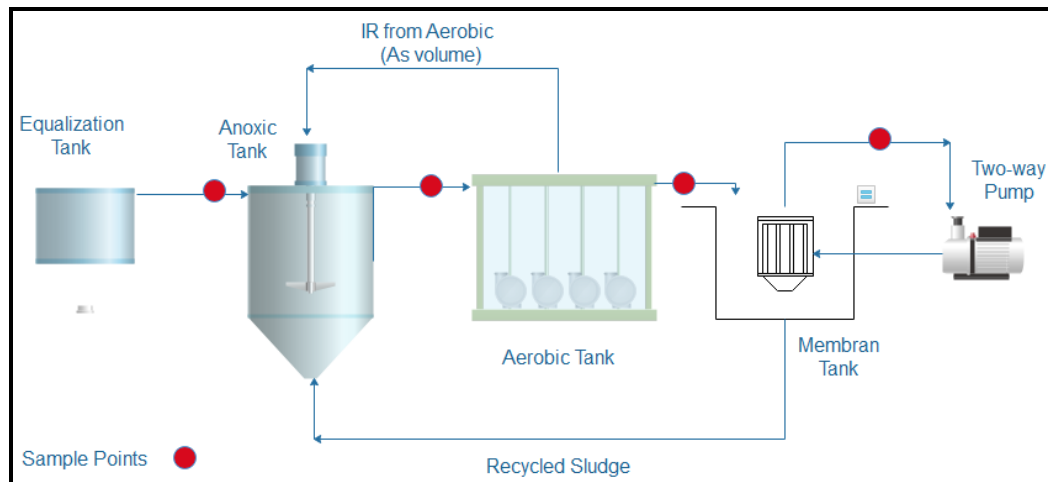


Figure 3.4: Schematic Diagram of the Anoxic-Aerobic Membrane System.

3.4. System Operation Condition

The anoxic-aerobic system was first sown with activated sludge from an industrial biological sewage treatment plant in Dilavosi, Turkey. In total, it ran for 103 days, in the first 33 days without internal volume recycle ($IR = 0.0$) and without sludge removal. This condition allowed the sludge to acclimatize and stabilize to remove TOC, color and TN. The system was then used with $IR = 0.5$ for 35 days to examine the relationship between IR, carbon, nitrogen and color removal. In the last 35 days, the system has been operated with $IR = 2.0$. As showed in Table 3.3, The cycle started by filling the anoxic tank and operate it for 11.125 hr. Following that, the mixer was closed to allow the settlement of the sludge in anoxic tank. After that, the wastewater transferred to aerobic tank by gravity and operated for 11 hr. Following that, the aeration was closed to allow the sludge in aerobic tank to settle. After settlement, the wastewater from aerobic tank was transferred by gravity to polishing stage in membrane tank which took 75 minutes. In addition, the IR volume was transfer from aerobic tank manually to the anoxic tank.

Table 3.3: Operating Cycles for Sequential Anoxic-Aerobic Batch Reactors.

Activity	Anoxic	Aerobic	Filtration by Membrane model
Cycle duration (h)	12	12	12
Filling (min)	0.5	7	7
Reaction time (h)	11.125	11	-
Settling time (min)	45	45	-
Emptying time (min)	7	7	75

3.5. Analytical Methods

3.5.1. Basic Parameters

Samples for analyses were collected from influent, anoxic, aerobic and membrane tanks. The chemical oxygen demand (COD) was measured according to Standard methods (American Public Health Association) [APHA, 1997].

The TOC and TN were analyzed using (IL550 and IL530 TOC-TN Analyze, Hach, Germany), ammonia was measured using Ammonia-Selective Electrode (Standard method: 4500-NH₃ D), Thermo Orion model 710 A+ meter and Orion 9512 electrode (Thermo Fisher Scientific, USA). The Nitrate was measured using Nitrate Electrode (Standard method: 4500-NO₃⁻ D), the 9707BNWP Nitrate Combination Electrode was used compatible with Thermo Orion 710 A+ meter [Federation, 1999]. Color was measured according to Standard method: 2120 F by using DR 5000, Spectrophotometer, Germany. The analytical procedure was repeated three times and the average data was reported. All chemicals used in the experiments were of analytical grade.

3.5.2. Aromatic Amines Analysis

To determine the ability of the cultures to cleavage of azo dye and produce aromatic amines under anaerobic/anoxic condition and to assess the degradability of AAs under aerobic condition under the cyclic conditions imposed, UHPLC measurement

techniques were used. The target AAs were analyzed by means of Ultimate 3000 UHPLC/TSQ Fortis triple quadrupole mass spectrometer (Thermo Fisher Scientific, USA) according to the DIN EN ISO 17234-1 method. In positive ion mode (Figure 3.5).



Figure 3.5: UHPLC- MS/MS.

Chromatographic separation was achieved with a Accucore aQ C18 Polar End capped (length 100 mm; diameter 2.6 mm; particle size 2.6 μm) (Figure 3.6) supplied by Thermo Fisher (USA). Separation and detection of the analytes followed a procedure based on a modification of the methods described by [Macherey, 2018]. The column temperature was thermostated at 40 $^{\circ}\text{C}$. The injection volumes were 2 mL. The mobile phase A was (HPLC ultra-pure water +0.1% (v/v) formic acid) and mobile phase B was (HPLC grade methanol +0.1% (v/v) formic acid). The flow- rate was 1 mL/min. The eluent gradient was in 10 min from 5 % to 95 % B, hold for 4.0 min, in 1 min to 5 % B, hold 5% B for 5 min. The detection limit of this analytical method was from (1-50) ng/L for targeted AAs. A Detailed description of the UHPLC–MS/ MS settings is available elsewhere [Macherey, 2018].



Figure 3.6: Chromatographic Separation Column.

The HPLC System Settings and Chromatographic Conditions are showed in Table 3.4. The calibration curve was plotted using 8 concentration points ranged from 1- 500 ng/. the calibration curves for all investigated AAs were showed in Appendix C.

Table 3.4: UHPLC-MS/MS Settings.

UHPLC System Settings (Ultimate 3000 UHPLC)	
Analytical column	Accucore aQ C18 Polar End capped (length 100 mm; diameter 2.6 mm; particle size 2.6 μm)
Column temperature	40 $^{\circ}\text{C}$
Injection volume	2 μL
Mobile phase	- mobile phase A was (HPLC ultra-pure water +0.1% (v/v) formic acid). - mobile phase B was (HPLC grade methanol +0.1% (v/v) formic acid).
Run time	16 min
Flow rate	0.3 ml/min
MS/MS settings (TSQ Fortis triple quadrupole mass spectrometer)	
Ion source type	H-ESI
Spray voltage	static
Positive ion voltage	3500 v
Vaporize temperature	350 $^{\circ}\text{C}$
Ion transferee tube temperature	350 $^{\circ}\text{C}$

In Figure 3.7 an exemplary LC-MS/MS chromatogram of the amine mix under the given chromatographic conditions with 22 compounds is shown.

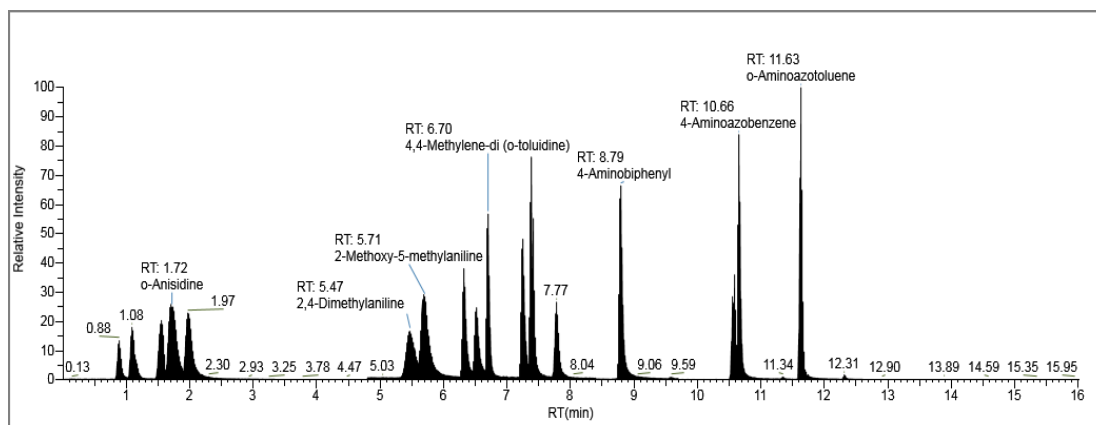


Figure 3.7: LC-MS/MS Chromatogram for the Amine Mix.

The recovery rate of investigated AAs was ranged from 6% to 103% as showed in Table 3.5

Table 3.5: LC-MS/MS Parameters.

Compound	Recovery rate (%)	Retention Time (min)	RT Window (min)	Precursor (m/z)	Product (m/z)	Collision Energy (V)	Min Dwell Time (ms)
2,4-Diaminotoluene	5.4928	1	2	123.1	77.1	28.88	69.771
4,4'-Diaminodiphenyl	96.7902	1.3	2	201.1	80.1	32.17	69.771
Benzidine	88.3386	1.5	2	185	99.043	55	69.771
4,4-Diaminodiphenylmethan	91.3322	2	2	199.1	77.1	47.84	69.771
o-Anisidine	15.6128	2.14	2	124.1	80.1	29.68	69.771
o-Toluidine	10.6096	2.34	2	108.1	91.1	18.27	69.771
2,4-Dimethylaniline	46.215	5.8	2	122.1	77.071	27.75	40.003
2-Methoxy-5-methylaniline	43.2308	6	2	138.1	65.054	42.66	40.003
2,4-Diaminoanisole	43.7606	6	2	139.1	93.125	22.02	40.003
o-Tolidine	103.2326	6.3	2	213.1	123.011	13.85	40.003
o-Dianisidine	68.3876	6.4	2	245.1	187.079	32.46	40.003
2,6-Dimethylaniline	17.5634	6.6	2	122.1	77.071	28	40.003
4,4-Methylene-di (o-toluidine)	92.1926	6.7	2	227.1	77.071	51.76	40.003
2-Naphthylamine	42.1314	7.2	2	144.1	77.071	36.72	40.003

Table 3.5: Continuation.

Compound	Recovery rate (%)	Retention Time (min)	RT Window (min)	Precursor (m/z)	Product (m/z)	Collision Energy (V)	Min Dwell Time (ms)
2,4,5-Trimethylaniline	58.1652	7.4	2	136.2	91.125	23.28	40.003
4,4-Thiodianiline	84.2236	7.4	2	217.09	80.125	39.96	40.003
4-Chloro-2-methylaniline	28.3168	7.7	2	142	106.029	26.06	40.003
4-Aminobiphenyl	61.1766	8.7	2	170.1	152.029	29.43	81.674
4,4-Methylene-bis(2-chloroaniline)	65.917	10.54	2	267	139.975	26.1	98.335
3,3-Dichlorobenzidine	58.7966	10.57	2	253	182.15	27.75	98.335
4-Aminoazobenzene	47.4	10.6	2	198.1	93.1	21.89	98.335
o-Aminoazotoluene	57.5834	11.6	2	226.1	121.046	21.89	98.335

4. RESULT AND DISCUSSION

This study was carried out with real textile wastewater in a pilot plant in batch mode using the sequential anoxic-aerobic batch reactors followed by ceramic membrane for tertiary treatment. The observed concentration of suspended solids in the mixed liquor (MLSS) was 5.2 to 5.8 g/L for the aerobic tank and 2.5 to 2.7 g/L for the anoxic tank (Figure 4.1). The MLVSS / MLSS ratios for the anoxic and aerobic reservoirs were stable at 0.68 ± 0.04 and 0.71 ± 0.03 . The pH of the mixed liquor for the aerobic tank was stable at 8.15 ± 0.65 , while that of the anoxic tank was 7.25 ± 0.05 .

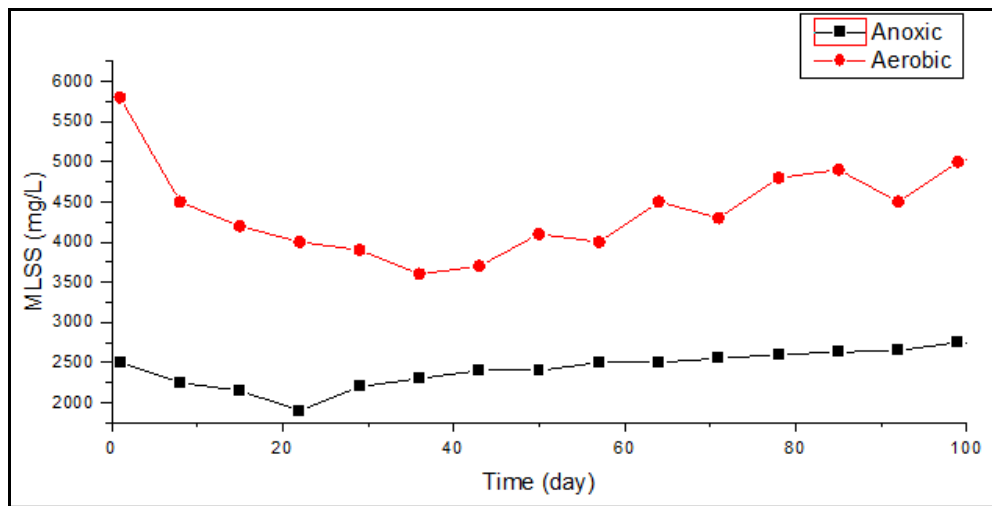


Figure 4.1: MLSS Concentration Throughout the Studied Period.

4.1. Organic Matter Removal (TOC)

In this study, TOC is used as indicator of organic matter contamination. TOC analysis is specific to organic compounds and theoretically measures all the covalently bonded carbon in water. In all the countries, the analysis of TOC is recognized as the most suitable index for the control of civil and industrial wastes [Visco et al., 2005]. The TOC removal of the sequential anoxic-aerobic batch reactors during the 103 days operation time is presented in Figure 4.2. As can be seen, average TOC removal of 93% (6 - 22 mg/L residual TOC) was observed in the system, far below the Turkish national discharge standard of effluent from Textile industry (COD<200 mg/L). The results also

indicate potential of wastewater treatment for reuse applications, if appropriate farther refining such as nanofiltration and reverse osmosis are applied. Notably, the aerobic tank served as an efficient treatment step for TOC with a small variation in TOC removal with IR ratios due to the dilution effects. In addition, effluent TOC concentration was not affected by increase in IR ratio. This indicates stability of the system for TOC removal. The results of this study agree with those of Sun et al. Agreed where more than 85% of the absorption of organic substances for the treatment of wastewater from textile auxiliaries has been recorded under IR of 0.5, 1.5 and 5 2.5. In addition, Sun et al. In the same study, the COD concentration in the wastewater was not affected when the recycling ratio increased from approximately 0.5 to 2.5 [Sun et al., 2015].

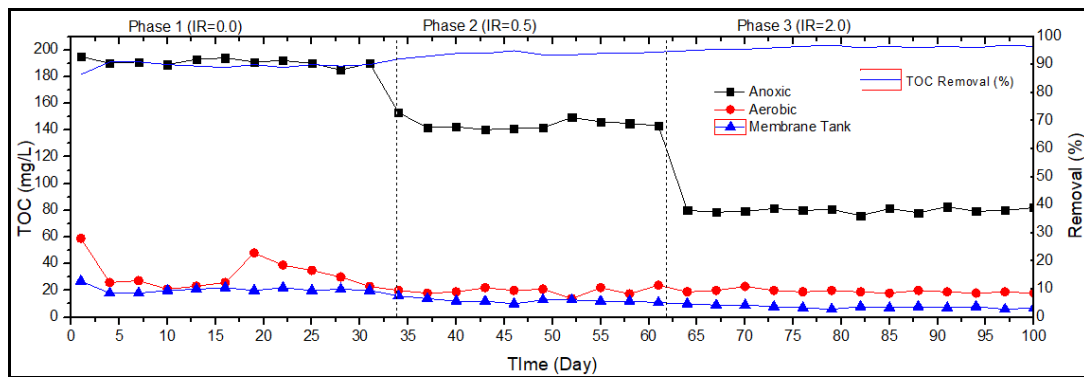


Figure 4.2: TOC Removal Efficiency.

4.2. Nitrogen Removal

An overview of the TN concentration and the removal efficiency for the entire operating period is shown in Figure 4.3. The 103-day operating period was divided into three phases depending on the IR ratio implied. Phase one lasted for 31 days with zero IR. Phase two lasted 35 days with 0.5 IR ratio and phase three lasted 35 days with 2.0 IR ratio. In order to better understand the removal of nitrogen, analyzes of the concentrations of TN, $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ were carried out in the three phases.

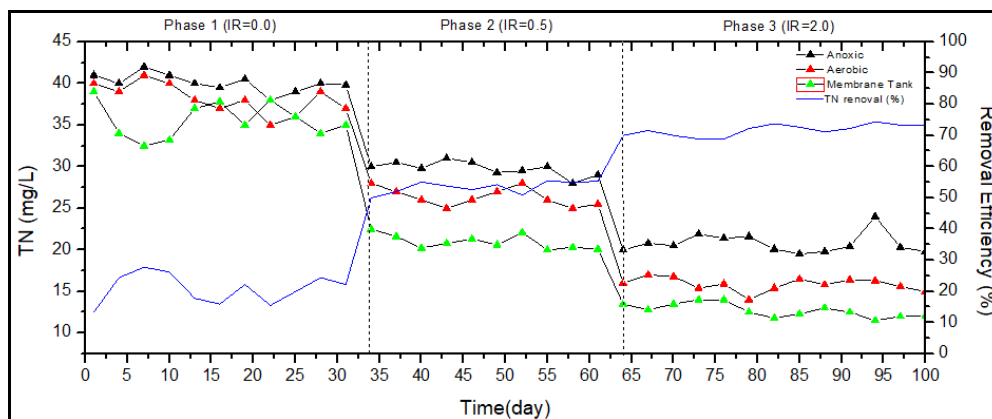


Figure 4.3: TN Concentration and Removal Efficiency.

Stable performance in the removal of $\text{NH}_3\text{-N}$ and TN from the sequential anoxic-aerobic batch reactors was observed 7 days after start of operation. As shown in Figure 4.4, nitrification occurred in the aerobic reactor and the effluent $\text{NH}_3\text{-N}$ concentration was 7 mg/L, which shows that 94% of $\text{NH}_3\text{-N}$ was oxidized. During the first phase, with an average influent TN concentration of 35 mg/L-N, removal efficiency of about 20% was recorded.

The concentration of TN in the anoxic reactor, aerobic reactor and membrane tank was 40 ± 2 , 38 ± 2 and 36 ± 2 mg/L, respectively, which indicates that TN was mainly removed in anoxic reactor as $\text{NO}_3\text{-N}$. To improve TN removal, the IR was increased from 0.0 to 0.5, which ensured increased the nitrate loading in the anoxic reactor in phase 2 (32–61 days). When $\text{NH}_3\text{-N}$ concentration of anoxic reactor was only 23 ± 2 mg/L due to the dilution of the raw wastewater, the effluent concentration from recycled mixed liquor from aerobic reactor was 3 mg/L. During stable operation, the final effluent concentration of $\text{NH}_3\text{-N}$ in the aerobic reactor remained less than 2 mg/L, while the $\text{NO}_3\text{-N}$ concentration averaged 20 mg/L. TN concentration in the effluent from anoxic reactor, aerobic reactor and membrane tank were 28 ± 2 , 26 ± 3 and 20 ± 4 mg/L, respectively. Despite increasing IR ratio to 0.5 in phase 2, the observed TN removal efficiency at this phase was around 53%. Finally, increasing the IR ratio to around 2.0 in phase 3 (62nd–100th day) resulted into effluent $\text{NH}_3\text{-N}$ concentration in the sequential anoxic-aerobic batch reactors of less than 1 mg/L and the TN concentration in the final effluent of 12 ± 3 mg/L. This indicates that TN has decreased mainly in anoxic and aerobic reactors due to the elimination of recycled $\text{NO}_3\text{-N}$. The results showed that

increasing the recycling rate from 0.5 to 2.0 increased the TN elimination percentage to approximately 71%.

For a pre-denitrification system, it is known that the recycling flow of the internal mixed liquor from aerobic zones to anoxic zones plays an important role, which influences the elimination efficiency of TN. Tan and Ng reported a TN removal efficiency of domestic wastewater of 57%, 74%, 72% and 61% at a recycling rate of 1, 3, 5 and 10, respectively [Tan and Ng, 2008]. Similarly, Baeza et al [2004] reported TN removal efficiencies rates of 67%, 72% and 80% for recycling rates of 0, 2 and 5, respectively [Baeza et al., 2004]. Under anoxic conditions, the denitrification performance could be improved by the availability of readily biodegradable organic material, enough HRT and a low DO concentration in the recycling stream. In this study, HRT was held for 12 hours for all three phases in the anoxic reactor, which is sufficient for anoxic denitrification [Kim et al., 2008].

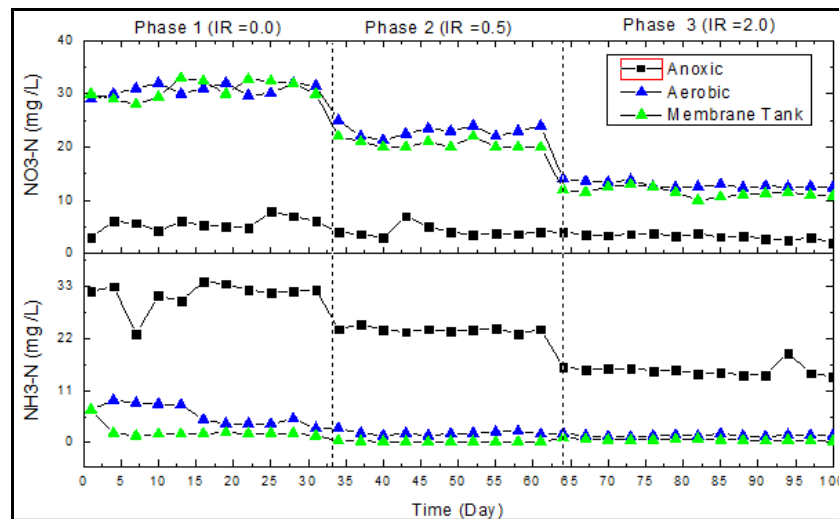


Figure 4.4 : NO₃-N and NH₃-N Concentration.

4.3. Color Removal

Differences in bacterial communities developed under / without IR conditions not only explain the differences in the nutrient removal performance of the system, but also provide insight into the differences in color removal under different redox conditions, as shown in Figure 4.5. The average color removal yields in the sequential anoxic-aerobic

batch reactors system were 81%, 85% and 88% for (IR = 0.0), (IR = 0.5) and (IR = 2.0), respectively, resulting in a high system efficiency. Color removal ranged from 78% to 82% with an IR ratio of 0.0. Increasing the IR ratio to 0.5 and 2.0 increased the color removal by 3% and 6%, respectively. The improvement in color removal under different IRs between anoxic and aerobic reactors could be attributed to the development of an environment that is adapted to the bacterial community shared between these two redox regimes and the possible excretion of different enzymes that are responsible for the central function of the integrated anoxic-aerobic function [Mallick and Chakraborty, 2019], [Phan et al., 2016]. In addition, due to the low oxygen content in the system, an alternative electron acceptor is required for anoxic treatment. The azo bond can act like this electron acceptor, which leads to discoloration due to the cleavage of the azo bond. Integrated anoxic-aerobic treatment processes can remove the color of the reactive azo dye more effectively from the wastewater than conventional aerobic processes. Biomass can be sustainably and efficiently developed in anoxic and aerobic environments. The anoxic phase shows both a higher color elimination percentage and a higher color elimination rate than the aerobic phase [Khehra et al., 2006], [Rass et al., 2007], [Venkata et al., 2007].

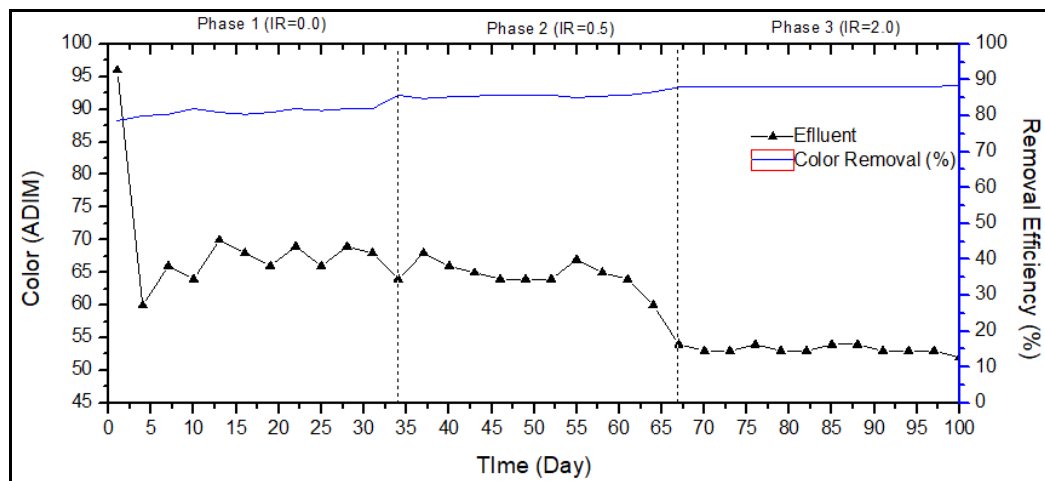


Figure 4.5: Color Removal Efficiency.

4.4. Aromatic Amines Removal

4.4.1. Aqueous Phase Aromatic Amine Removal

In this study, 12 AAs out of the 22 investigated AAs were detected. In this section the influence of the physical chemical properties and the operating condition on the removal efficiency of investigated AAs is discussed [Albahnasawi et al., 2020].

4.4.2. Effect of AAS Physical Chemical Characteristics

In the following section, the physical and chemical characteristic such as distribution coefficient (Log D at pH=8), dissociation constant (pKa), Molecular structure, octanol-water distribution coefficient (Kow) have been examined with respect to removal efficiency of the AAs in the proposed system.

4.4.2.1 Effect of Distribution Coefficient (log D)

Log D depends on the octanol-water distribution coefficient (Kow) and the acid dissociation constant (pKa). Compounds with high log D values, generally above 2.28, are readily sorbed onto sludge at specific pH. Consequently, high removal efficiencies were achieved [Alvarino et al., 2018]. The Log D value of the compound at a specific pH determines the absorption property of the micropollutants to the sludge. Results from this study showed that four AAs (2,4-Diaminoanisole, o-Toluidine, 4,4'-Diaminodiphenyl and 2,4-Dimethylaniline) showed over 90% removals (Figure 4.6). Although these compounds possess low hydrophobicity (log D at pH=8 <2.27), the significant removals could be attributable to the presences of strong EDG and the absence of EWG. Presence of the amino group (-NH₂) in 2,4-Diaminoanisole, o-Toluidine, 4,4'-Diaminodiphenyl and 2,4-Dimethylaniline increased the biodegradability of these AAs. On the other hand, the removal efficiency of high hydrophobic AAs (log D at pH>2.27) was 37-76 %. 3,3-Dichlorobenzidine and 2-chloroaniline consist of one or more (-Cl) group which is a strong EWG. In addition, AAs possessing an azo bond in their structure such as 4-Aminoazobenzene and o-Aminoazotoluene showed moderate removal efficiency of 52-68 % despite the high hydrophobicity (log D at pH >2.27).

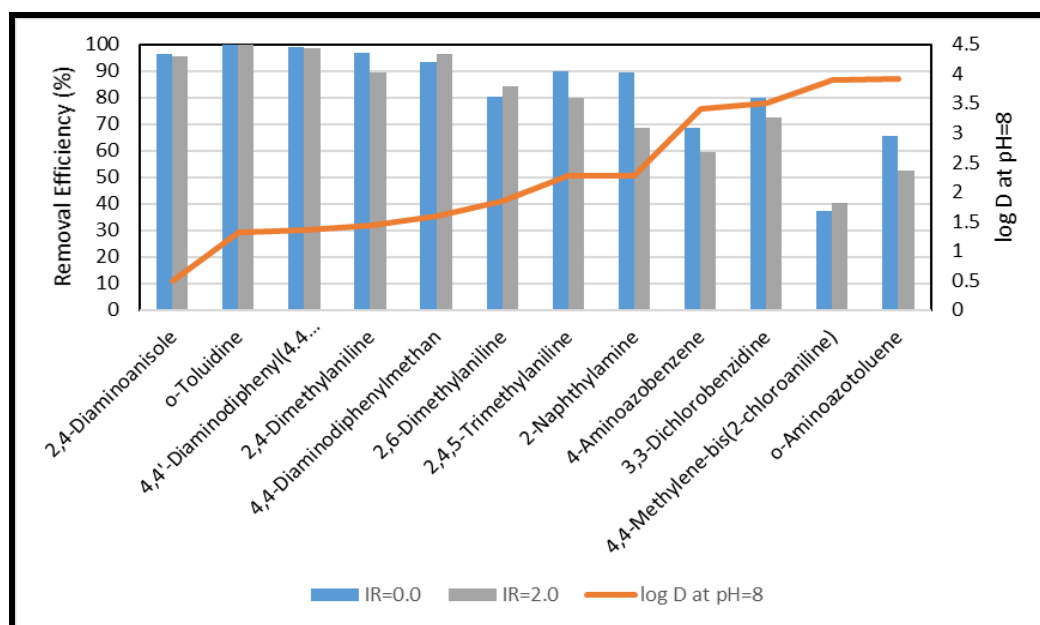


Figure 4.6 : Relation Between Log D (at pH=8) and Removal Efficiency.

Due to the limited studies on the effect of distribution coefficient (log D at pH=8) on fate and removal efficiency of AAs, the findings of this research were compared with Hop et al [Phan et al., 2014] who investigated the effect of physical-chemical properties of a wide range of OMPs removal in anoxic-aerobic conditions. They noted that in the presence of strong EDG and EWG, no generalization can be stated for the OMPs removal based on their hydrophobicity, these results are similar to the findings of our study [Phan et al., 2014].

4.4.2.2 Molecular Structure

Molecular structure plays a significant role in AAs removal. It has been noted in this study that removal efficiency is affected by the number of aromatic rings contained in AAs. Generally, AAs with 2 aromatic rings showed lower removal efficiencies compared to AAs with a single aromatic ring. For instance, the removal efficiency of 2-Naphthylamine, 4-Aminoazobenzene, 3,3-Dichlorobenzidine, 2-chloroaniline and o-Aminoazotoluene ranged between 37% and 76%, whereas for AAs possessing a single aromatic ring, over 80% removals were recorded. However, 4,4-

Diaminodiphenylmethan and 4,4'-Diaminodiphenyl (4,4 oxydianline) have 2 aromatic rings in their structure, the removal efficiency of these two compounds is still above 90%. This can be attributed to the absence of strong EWG in their structure and presence of strong EDG. Figure 4.7 presents the effect of the number of aromatic rings on AAs removal efficiency.

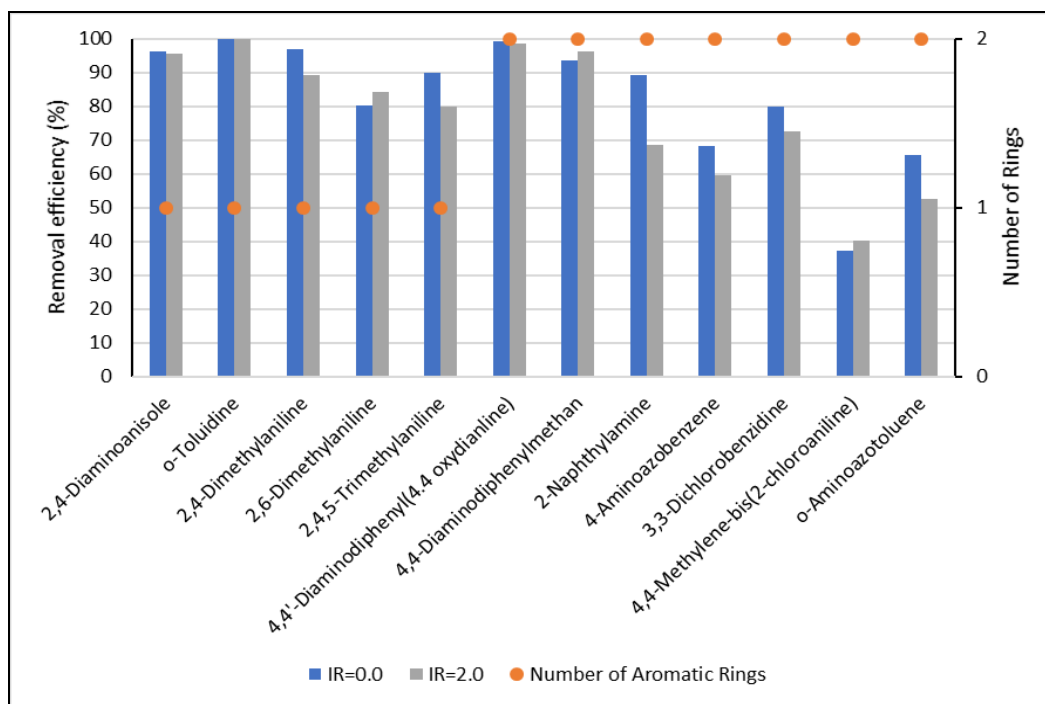


Figure 4.7: The Influne of the Number of Aromatic Rings.

Similar to this study, Field et al [1995] demonstrate that complex AAs may show recalcitrant behavior depending the number of aromatic rings possessed. This behavior may mostly occur because AAs with complex structures have less bioavailability instead of an intrinsic deficiency in biotransformation ability of oxygenases [Field et al., 1995].

In wastewater treatment plants, the accessibility of micropollutants to the population of the activated sludge can be defined in terms of external and internal bioavailability. External bioavailability rather defines the accessibility of the substance to microorganisms, while internal bioavailability is limited to the uptake of the compounds into the internal cell compartment. In general, bioavailability consists of the combination of physico-chemical aspects related to phase distribution and mass transfer, and of physiological aspects related to microorganisms such as the permeability of their

membranes, the presence of active uptake systems, their enzymatic equipment and ability to excrete enzymes and biosurfactants. Higher bioavailability and thus, potential for biological degradation of pollutants depend mostly on the solubility of these compounds in aqueous medium [Cirja et al., 2008].

Wang et al [2012] found that indigenous bacteria readily degrade AAs containing fewer aromatic rings, compared to AAs with more aromatic rings owing to the hydrophobicity, thermal stability and strong adsorption affinity. The complex AAs are not able to diffuse into the merorganization cell therefore, the kinetics go down, consequently the bioavailability was decreased [Wang et al., 2012].

4.4.2.3 Substitution Group

Besides the presence of EDG and EWG, the number of substitution groups strongly affect the removal efficiency of AAs. For instance, 2,4,5-Trimethylaniline, 2,6-Dimethylaniline, 2,4-Dimethylaniline, o-Toluidine and 2,4-Diaminoanisole, which containing two or more EDG and at the same time possess no EWG in their structure, showed high removal efficiency, mainly above 80%. Meanwhile, the removal efficiency of AAs possessing both EDG and EWG was in the range of 37-68%. In addition, although 4,4-Diaminodiphenylmethane structure contains two aromatic rings, its removal efficiency was 99% because it possesses two amino groups which are considered strong EDG [Khatiwada et al., 2018]. Figure 4.8 shows the effect of the possessed EDG and EWG groups on the removal efficiency of AAs investigated.

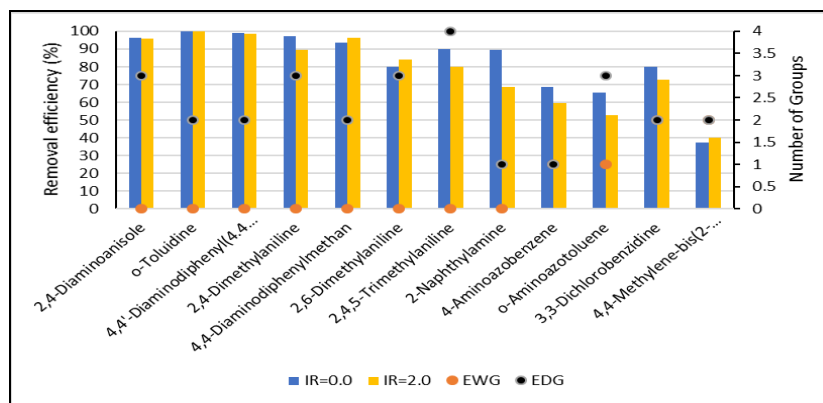


Figure 4.8: Effect of Substitution Groups.

Besha et al [2017] demonstrated that chemicals containing functional groups like nitriles, aromatic alcohol and esters may increase the biotransformation, whereas functional groups such as nitro, iodide, sulfo, azo aromatic amine and halogen decrease biological depredation [Besha et al., 2017]. The rate-determining step for biodegradation of most organic chemicals is considered as the initial electrophilic attack of the oxygenases by aerobic bacteria. Consequently, the attached EWG functional groups cause an electron deficiency and decrease the compounds ability to oxidize. Figure 4.9 illustrates the effect of having EWG in AAs structure on the removal efficiency. On the other hand, EDG functional groups enhance the biodegradation of organic compounds by improving the electrophilic attack of aerobic bacteria [Khatiwada et al., 2018].

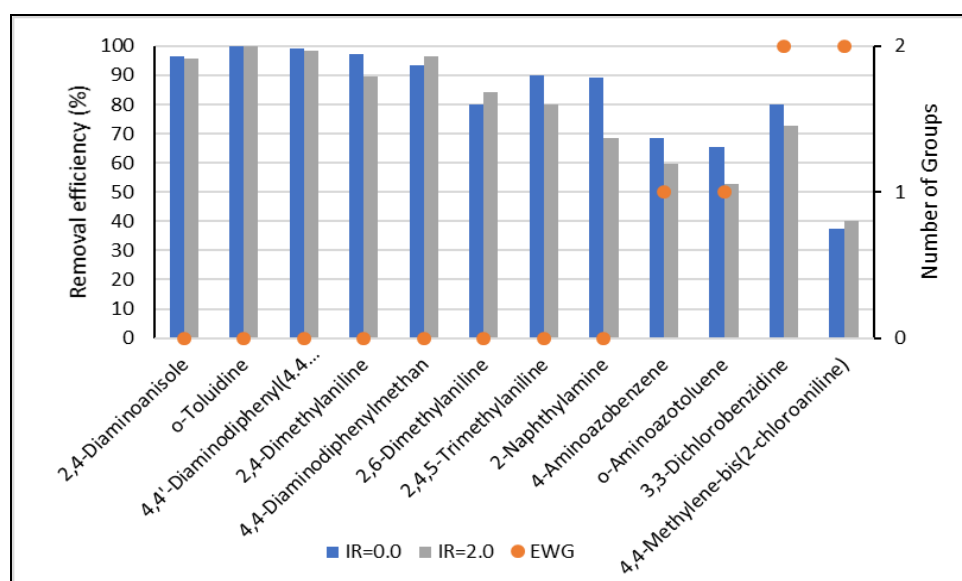


Figure 4.9: Effect of EWG.

4-Aminoazobenzene and o-Aminoazotoluene have the same backbone structure. Therefore, the observed similarity in their removal efficiency (65 and 67%) could be attributed to the presence of a similar backbone structure and their hydrophobic nature [Gebreyohannes et al., 2017].

AAs containing EWG and more than one aromatic ring in their structure were less capable of oxidizing under aerobic condition, while AAs with EDG and 1 aromatic ring in their structure were effectively removed under aerobic condition. Khatiwada et al [2018] found that EWG functional groups such as nitro ($-\text{NO}_2$), Azo ($-\text{N}\equiv\text{N}-$) and chloro

(Cl) in AAs, decrease the ability of anilines for oxidation by rising the standard reduction potential. In contrast, the Amino (-NH₂) EDG functional group improve the biodegradability of organic compounds by decreasing the standard reduction potential [Field et al., 1995], [Khatiwada et al., 2018].

Though it is not easy to relate the removal efficiency and molecular structure of AAs, it was generally concluded that simple AAs and compounds containing EDG like (-NH₂) and (-CH₃), show high removal efficiency, whereas, complex AAs and compound possessing EWG such as (-Cl) and azo bond demonstrate moderate removal efficiency [Joss et al., 2006], [Tadkaew et al., 2011].

4.4.2.4 Acidic Strength Coefficient (pKa) and Log Kow

All pKa values for the investigated AAs in this study were below the pH of the wastewater, which means that these molecules mainly existed as protonated species. As a result, an accelerating repulsion occurred between the protonated species and the negatively charged surface of microorganism/sludge, hindering adsorption, and hence reduction in the removal efficiency [Luo et al., 2014]. For instance, 4-Aminoazobenzene, o-Aminoazotoluene, 3,3-Dichlorobenzidine and 4,4-Methylenebis(2-chloroaniline) with pKa values of 2.82, 3.01, 3.2 and 3.1, respectively exhibited lower removal rates (37-76%) than AAs with high pKa values such as 2,4-Diaminoanisole (pKa = 5.15), 2,4-Dimethylaniline (pKa = 4.89) and o-Toluidine (pKa = 4.49), which showed high removal efficiency (95-99%). Figure 4.10 shows the relationship between removal efficiency of investigated AAs and pKa values [Salter et al., 2016].

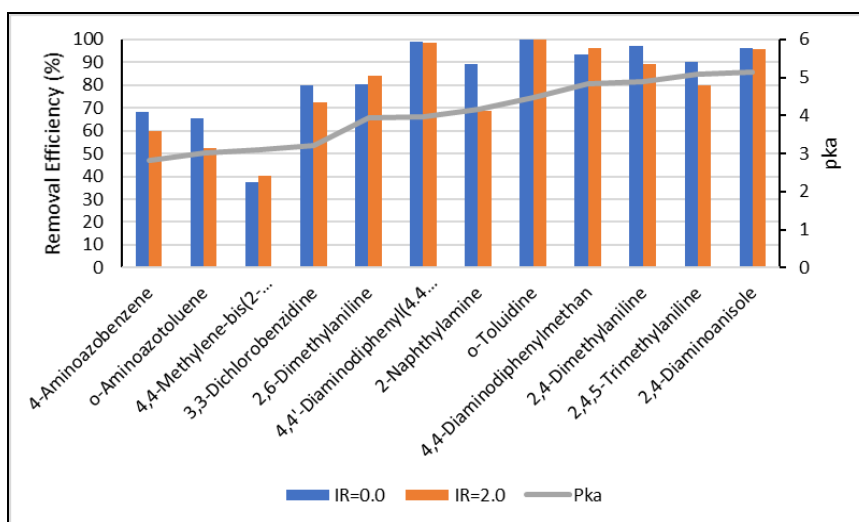


Figure 4.10: Effect of Pka Value.

The overall average removal efficiencies of the studied AAs were plotted against their physicochemical Log Kow as is shown in Figure 4.11. Hydrophilic compounds (Log Kow <2.27), o-Toluidine, 2,4 Diaminoaniso, 4,4'-Diaminodiphenyl(4.4 oxydianline), 4,4-Diaminodiphenylmethan, 2,4Dimethylaniline, 2,6-Dimethylaniline and 2,4,5-Trimethylaniline showed high removal efficiency (80-99%) while hydrophobic compounds (log Kow>2.27), 2-Naphthylaminem, 3,3-Dichlorobenzidine, 4-Aminoazobenzene, 4,4-Methylene-bis(2-chloroaniline) and oAminoazotoluene showed medium removal efficiency (37-78%). This can be explained by the tendency of hydrophilic compounds to readily biodegrade due to their high solubility [Sahar et al., 2011].

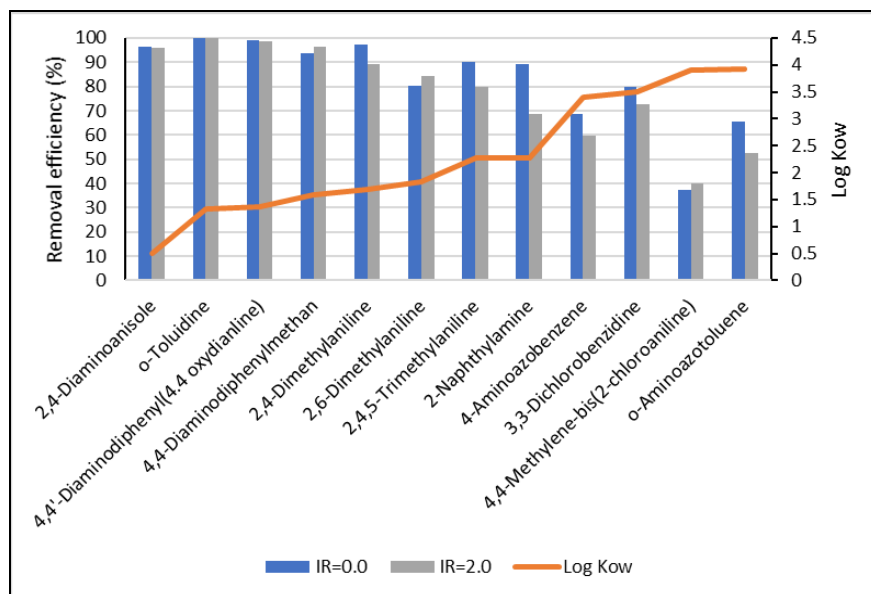


Figure 4.11: Effect of Log Kow value.

4.4.2.5 Summary

Generally, two observations were noticed regarding the physical chemical properties, Firstly, the hydrophobic AAs did not highly adsorb into sludge as expected, consequently, the low removal efficiency was noted. This is attributed to operation at $\text{pH} > \text{pKa}$ of the investigated AAs, which resulted in high protonation tendency and high negative charge, hindering sorption to sludge. Hydrophilic AAs witnessed high removal efficiency mostly above 80% due to their high solubility and $\text{pKa} < \text{pH}$ of the wastewater. Hollender et al [2018] found that negatively charged and neutral OMPs compounds with low log Kow values can only be removed by biotransformation. On the other hand, the OMPs compounds with high Kow and positive or neutrally charged may adsorb to organic matter which is usually slightly negatively charged [Hollender et al., 2018]. Secondly, it was concluded that simple AAs and compounds possessing EDG like ($-\text{NH}_2$) and ($-\text{CH}_3$) show high removal efficiency, whereas complex AAs and compound possessing EWG like ($-\text{Cl}$) and (azo bond), could exhibit moderate removal efficiency.

The physicochemical properties and molecular structure are highly related to the removal of organic micropollutants. However, it's difficult to relate the molecular structure and the removal efficiency of AAs, generally, it was concluded that simple

AAs and compounds possessing EDG are readily biodegradable, whereas, more complex AAs and compounds possessing electron EWG could be difficult to biodegrade. Moreover, the hydrophobic AAs did not adsorb into sludge due to the high protonation tendency ($pK_a < pH$), whereas the hydrophilic AAs showed high removal efficiency due to high solubility.

4.4.3. Operation Condition

Azo dyes are most commonly used to dye clothes. In general, the process of biodegrading azo dyes by microbes is done in two stages. As shown in Figure 4.12, the first step involves the reductive cleavage of the bonds ($R_1-N=N-R_2$) under anaerobic / anoxic conditions, which leads to the formation of AAs; These compounds are generally colorless but still toxic. In the second step, aerobic microorganisms convert these amines into organic acids or into CO_2 and H_2O [Amaral et al., 2014], [Chen et al., 2018], [Kadoya et al., 2018], [Olivares et al., 2016], [Ozdemir et al., 2013], [Van Der Zee and Villaverde, 2005].

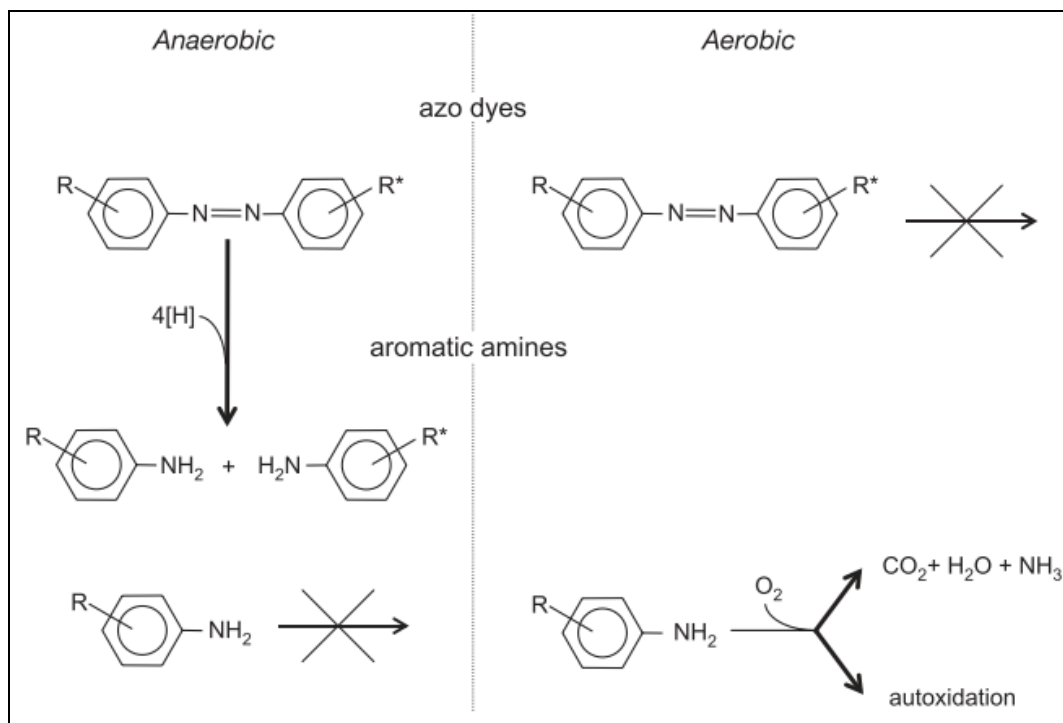


Figure 4.12: Azo Dye Degradation Pathway.

4.4.3.1 Anaerobic Condition

Results of the present study demonstrate that the concentration of some AAs in anaerobic (IR of 0.0) tank increased due to azo dye reduction. Many studies have shown that azo dyes are readily cleaved via a four-electron reduction mechanism at the azo linkage to generate AAs under anaerobic conditions [Hosseini et al., 2011], [Ong et al., 2017]. The decolorization of textile wastewater occurs when the enzymatic breakdown of azo bond is triggered in the presence of an electron donor [Bhatia et al., 2017].

As shown in Figure 4.13, the concentration of o-Toluidine, 4-Aminoazobenzene, 2,6-Dimethylaniline, 4,4'-Diaminodiphenyl, o-Aminoazotoluene, 4,4-Methylene-bis(2-chloroaniline) and 2,4-Dimethylaniline were increased. Markedly, the concentrations of o-Toluidine, 2,6-Dimethylaniline, and 4,4'-Diaminodiphenyl in the influent were 42, 50 and 33 ng/L respectively, whereas their respective concentrations in the anaerobic tank were 103, 75 and 47 ng/L, representing increases of 141, 50 and 40 %. On the other hand, removals of some AAs such as 3,3-Dichlorobenzidine, 2,4-Diaminoanisole, 2,4,5-Trimethylaniline, 2-Naphthylamine and 4,4-Diaminodiphenylmethan occurred in the anaerobic tank with a removal efficiency of 16-76%. The partial removal of some AAs in the anaerobic tank may be attributed to the long HRT of 12 hr used in this study. The high HRT allowed adequate contact time between AAs and sludge which increased the adsorption rate.

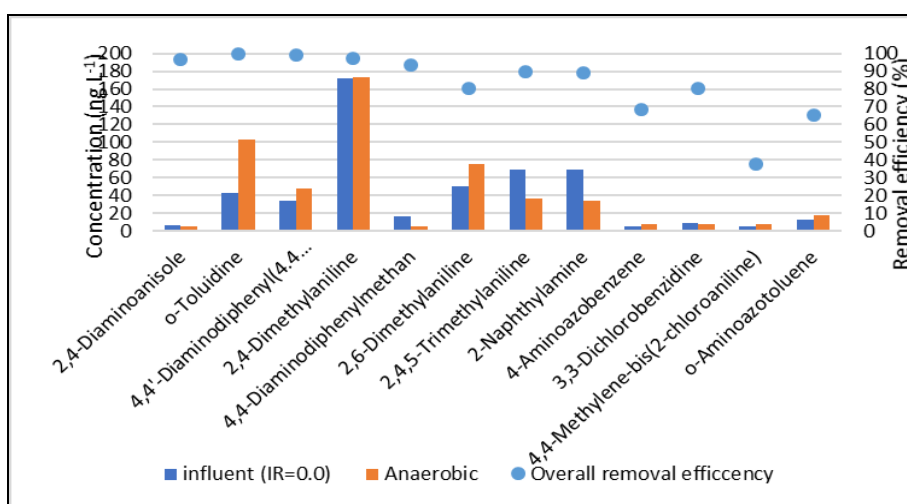


Figure 4.13: Effect of Anaerobic Condition on Azo Dye Removal.

The chlorinated amines slowly decomposed to form species that could not be converted back into the parent compound. The reaction rates of the pharmaceuticals with combined chlorine (i.e., chloramines) were significantly slower, and transformation of the compounds would not be expected under the conditions encountered during chloramination [Pinkston & Sedlak, 2004].

4.4.3.2 Anoxic Condition and IR Role.

It is obvious from Figure 4.14 that the concentrations of the most investigated AAs in this study increased in the anoxic tank. Strikingly, the concentration of 2,6-Dimethylaniline increased from around 40 ng/L to about 180 ng/L in the anoxic tank. Reducing conditions can induce the ring cleavage of the azo bond which in turn releases AAs. The significant difference in concentration of AAs in the presence and the absence of internal recycle observed in this study suggests that the reduction of the azo dye by an anoxic bioreactor is determined not only by the specific redox condition but also by other conditions resulting from the microbial diversity in the anoxic tank. The fundamental benefits of internal recycle from aerobic to anoxic bioreactor are; improved mixing/mass, dilution of the media, transfer of a portion of dissolved oxygen and supply of nitrate. These facilitate a unique environment which promotes aerobic degradation within the anoxic tank [Phan et al., 2014].

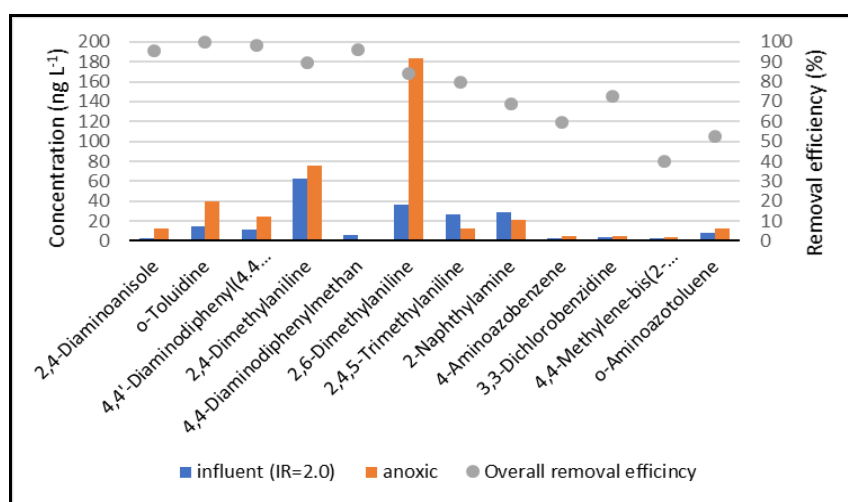


Figure 4.14: AAs Concentrations and Overall Removal Efficiency (IR=2.0).

Another reason for the enhanced degradation of azo dye in the anoxic tank may be attributed to the development of bacterial cultures. During the long run of the sequential anoxic-aerobic batch reactors a highly functionalized bacterial community for pollutant removal may develop because of sludge exchange between the aerobic and the anoxic tank [Phan et al., 2014].

Besides all these factors, strong evidence relating to the presence of nitrate in reducing condition was observed in this study, the increase of AAs concentration in anoxic tank was higher than observed in the anaerobic tank. These results are further confirmed by the higher color removal efficiency in the anoxic conditions than was observed in the anaerobic tank, an indication that more azo dye reductions occurred in the anoxic tank, producing more AAs [Albahnasawi et al., 2020]. Noticeably, the concentration of 2,4-Diaminoanisole, 2,6-Dimethylaniline, o-Toluidine and 4,4'-Diaminodiphenyl increased by 469%, 407%, 175% and 108%, respectively, while in the anaerobic tank these increases were 20%, 50%, 141% and 40%, respectively. In general, the Σ AAs increased by 91% (from 205.1 to 393.7 ng/L) in the anoxic tank (IR=2.0), owing to the unique bacterial diversity under high IR operation scheme. On the other hand, Σ AAs in the anaerobic tank (IR=0.0) increased by 6.1% (from 489.26 to 519.1 ng/L). Moreover, the Σ AAs in the aerobic tank remained constant, almost around 50 ng/L-1 in the two cases. Table 4.1 shows the difference in concentration between the anaerobic and the anoxic tank. Wang et al [2014] investigated the Reactive Black 5 azo dye fate and transformation of in a sequence anaerobic/aerobic and anaerobic/anoxic/aerobic batch reactor. Similar to our study they found that the combined anoxic/aerobic process can be effectively used to completely degrade azo dye-in wastewater [Wang et al., 2014]. In another study, Reddy et al [Reddy et al., 2018] reported that biodegradation pathways of the azo dye in anoxic/aerobic system was initiated by the azoreductase enzyme, which is formed by microbiomes. This enzyme catalyzes the cleavage of the azo bond under reducing condition using redox mediators or various reduced metabolites [Reddy et al., 2018]. Similarly, Santhanam et al [Santhanam et al., 2019] stated that anoxic process followed by aerobic conditions is effective for color removal [Santhanam et al., 2019]. Kherhra et al investigated the efficiency of anoxic/aerobic sequencing bioreactor for the decolorization of Acid Red 88

and showed that the proposed system achieved complete decolorization, whereas COD removal of up to 98% was noted for synthetic dye wastewater containing 100 mg/L of C.I. Acid Red 88 dye [Khehra et al., 2006].

Table 4.1: Role of IR in AAs Presence in Anaerobic and Anoxic Condition.

Compound	IR=0.0		IR=2.0	
	Influent (ng/L)	Anaerobic (ng/L)	Influent (ng/L)	Anoxic (ng/L)
2,4-Diaminoanisoole	5.63	4.48	2.23	12.75
o-Toluidine	42.70	103.18	14.23	39.18
4,4'-Diaminodiphenyl (4.4 oxydianline)	33.87	47.66	11.53	24.02
2,4-Dimethylaniline	171.92	173.21	62.66	76.09
4,4-Diaminodiphenylmethan	15.96	4.47	5.45	1.105
2,6-Dimethylaniline	50.38	75.70	36.10	183.27
2,4,5-Trimethylaniline	68.42	35.90	26.33	12.63
2-Naphthylamine	68.49	34.45	28.85	20.53
4-Aminoazobenzene	5.15	7.748	2.91	4.45
3,3-Dichlorobenzidine	9.02	7.54	3.80	4.38
4,4-Methylene-bis(2-chloroaniline)	5.26	6.96	3.02	3.17
o-Aminoazotoluene	12.40	17.78	7.97	12.16

4.4.3.3 Aerobic Condition

Despite the apparent difference in AAs concentration in the preceding anaerobic and anoxic tank (due to IR variation, the concentration of AAs in the aerobic effluent did not significantly differ (The $\sum$ AAs in influent remained around 50 ng/L), which indicates the significance of aerobic tank in AAs removal. Many studies have indicated the effectiveness of aerobic treatment in mineralization of AAs [Amaral et al., 2014], [Jonstrup et al., 2011], [Menezes et al., 2019], [Ong et al., 2017]. AAs were aerobically degraded via hydroxylation and cleavage of the ring by oxidative enzymes such as laccase, phenoloxidase and peroxidase. The aerobic biological treatment of AAs can lead to auto-oxidized products and/or complete mineralization, which leads to the formation of CO₂, NH₃ and/or biosorption and volatilization [Olivares et al., 2017], [Popli and Patel, 2015]. Oxygen plays two major roles in the aerobic processes. Firstly,

it acts as the terminal electron acceptor during the oxidation of the aromatic molecules. Secondly, oxygen is incorporated in the aromatic ring by means of mono- and dioxygenases prior to ring-fission [Field et al., 1995]. AAs requires an aerobic microenvironment for its degradation via hydroxylation and ring cleavage reactions by non-specific enzymes [Reddy et al., 2018]. Supplementary Table 4.2 and Table 4.3 show the concentration of detected AAs and the overall removal efficiency under IR =0.0 and IR=20.

Table 4.2: AAs concentration and Removal Efficiency (IR=0.0).

Component	Concentration (IR=0.0)			Removal Efficiency (IR 0.0)		
	influent (ng/l)	Anoxic (ng/l)	aerobic (ng/l)	Anoxic (%)	Aerobic (%)	overall (%)
2,4-Diaminoanisole	5.63	4.48	0.20	20.54	95.40	96.34
o-Toluidine	42.70	103.18	0.00	-141.62	99.99	99.99
4,4'-Diaminodiphenyl(4.4 oxydianline)	33.87	47.66	0.40	-40.68	99.14	99.14
2,4-Dimethylaniline	171.92	173.21	5	-0.74	97.11	97.11
4,4-Diaminodiphenylmethan	15.96	4.47	1.03	71.96	76.81	93.49
2,6-Dimethylaniline	50.38	75.70	15.12	-50.26	80.18	80.18
2,4,5-Trimethylaniline	68.42	35.90	6.81	47.52	81.00	90.03
2-Naphthylamine	68.49	34.45	7.31	49.68	78.75	89.31
4-Aminoazobenzene	5.15	7.74	2.44	-50.40	68.41	68.41
3,3-Dichlorobenzidine	9.02	7.549	1.80	16.35	76.12	80.02
4,4-Methylene-bis(2-chloroaniline)	5.26	6.96	4.36	-32.31	37.44	37.44
o-Aminoazotoluene	12.40	17.78	6.13	-43.38	65.49	65.49

Table 4.3: AAs Concentration and Removal Efficiency (IR=2.0).

Component	Concentration (IR=2.0)			Removal Efficiency (IR 2.0)		
	influent (ng/l)	Anoxic (ng/l)	aerobic (ng/l)	Anoxic (%)	Aerobic (%)	overall (%)
2,4-Diaminoanisoie	2.23	12.75	0.54	-469.55	95.76	95.76
o-Toluidine	14.23	39.18	0.00	-175.23	99.99	99.99
4,4'-Diaminodiphenyl(4.4 oxydianline)	11.53	24.02	0.364	-108.24	98.48	98.48
2,4-Dimethylaniline	62.66	76.09	8.04	-21.42	89.43	89.43
4,4-Diaminodiphenylmethan	5.45	1.105	0.20	79.73	81.91	96.33
2,6-Dimethylaniline	36.10	183.27	28.96	-407.63	84.19	84.19
2,4,5-Trimethylaniline	26.33	12.63	5.28	52.03	58.13	79.91
2-Naphthylamine	28.85	20.53	9.04	28.82	55.98	68.67
4-Aminoazobenzene	2.91	4.45	1.80	-52.80	59.62	59.62
3,3-Dichlorobenzidine	3.80	4.38	1.20	-15.03	72.61	72.61
4,4-Methylene-bis(2-chloroaniline)	3.02	3.17	1.90	-5.10	40.18	40.18
o-Aminoazotoluene	7.97	12.16	5.76	-52.47	52.59	52.59

4.4.4. AAs Accumulation on Sludge

Many researchers reported that AAs cannot be completely removed from wastewater by sorption to sediment and soil via physical and chemical processes [Ning et al., 2015], [Van der Zee and Villaverde, 2005]. In this study, 19 out of the 22 AAs investigated were detected in sludge samples unlike aqueous phase analyses in which only 12 were detected. This finding is supported by numerous studies published in the literature, which have clearly shown that anilines are easily and quickly linked to humic substances. These results indicate that the sorption of AAs plays a significant role in their removal. However, there is a lack of detailed research on the sorption of AAs into sludge. Humic substance offer numerous sites for covalent and adsorbent interactions with xenobiotics, in particular free anilines, via functional groups such as -COOH, C=O, phenolic and enolic OH groups, aromatic rings and radical units. These interactions vary between sub-fractions of humic substances; therefore, there are usually several mechanisms for sorption of AAs [Yuan et al., 2017]. Mechanisms of association between anilines and humics are covalent bonds, H-bonds, Van der Waals forces and hydrophobic partitioning among others [Cheng et al., 2018]. Table 4.4 shows the AAs concentration in sludge from anoxic and aerobic reactors under IR (0.0). The concentration of AAs was increased through the study period because no sludge withdrawal was done.

AAs sorption initially occurs through a rapid reversible equilibrium, followed by a slower and irreversible sorption process. The rapid sorption stage has generally been attributed to electrostatic interactions, hydrophobic distribution, and the formation of labile amine-carbonyl adducts, although Bhatia et al [2017] recently reported that the initial rapid sorption can also be irreversibly dominated by covalent bonds. The slower process has been attributed to irreversible covalent bonding through nucleophilic addition of the amino functional group to electrophilic sites (i.e. carbonyl residues) or oxidative mechanisms that lead to the formation of radical species which pair with radicals associated with sediments [Bhatia et al., 2017].

Table 4.4: Detected AAs Concentration in Sludge (IR=0.0).

Component	Pka	log kow	Influent (ng/L)	Anoxic (ng/g)	Aerobic (ng/g)
2,4-Diaminotoluene	5.35	0.14	0	22.69	1.74
2,4-Diaminoanisole	5.15	0.5	5.64	4.11	2.04
o-Anisidine	4.53	1.18	0	0	0
o-Toluidine	4.48	1.32	42.71	0	5.69
4,4-Methylene-di (o-toluidine)	4.48	1.32	1.43	0.57	1.87
Benzidine	4.3/3.3	1.34	0	0.99	4.29
4,4'-Diaminodiphenyl	3.96	1.36	33.88	0.94	0
4,4-Diaminodiphenylmethan	4.83	1.59	15.97	2.17	1.9
2,4-Dimethylaniline	4.89	1.68	171.92	15.3	43.71
2,6-Dimethylaniline	3.95	1.84	50.38	22.39	39.45
4,4-Thiodianiline	4.55	2.18	0	0	0.01
4-Chloro-2-methylaniline	3.85	2.27	5.72	0.58	0.02
2,4,5-Trimethylaniline	5.09	2.27	68.42	1.78	1.29
2-Naphthylamine	4.16	2.28	68.49	0.22	0.39
Σ AAs (ng/g) Hydrophilic (Log Kow <2.28)				71.74	102.4
4-Aminobiphenyl	4.35	2.86	4.35	0	0
4-Aminoazobenzene	2.82	3.41	5.15	1.54	1.26
3,3-Dichlorobenzidine	1.6/3.2	3.51	9.03	2.42	4.44
4,4-Methylene-bis(2-chloroaniline)	3.1	3.91	5.27	1.58	3.15
o-Aminoazotoluene	3.01	3.92	12.4	2.91	1.87
Σ AAs (ng/g) Hydrophobic (Log Kow >2.28)				8.45	10.72
Σ AAs (ng/g)				80.19	113.12

In this study, the concentration of hydrophobic AAs (log Kow >2.28) in aerobic tank increased by 23%, from 65 ng/g to 80 ng/g, whereas the hydrophilic AAs (Log Kow <2.28) decreased by 18.58%. As a result, total summation of AAs in aerobic tank was around 119 ng/g. On the other hand, the total summation of AAs in anoxic tank increased significantly by 140 %. The increase of AAs in anoxic tank can be attributed to the refractory behavior of AAs in reduction environment. This observation is at

tandem with Gebreyohannes et al [2017] who stated that the concentration of hydrophobic AAs in sludge seems to be higher than hydrophilic. A case in point is the removal mechanisms of hydrophobic compounds that are mainly governed by biosorption of the trace contaminants to the activated sludge, whereas those of hydrophilic compounds are governed by biodegradation [Gebreyohannes et al., 2017]. In addition, Ning et al [2015] confirmed that the concentration of AAs in sludge from anoxic tank was higher than observed in aerobic tank due to the refractory behavior of AAs under reducing environments [Ning et al., 2015].

For the anoxic tank, the two compounds accumulated in sludge at significant concentrations (64.88 and 78.22 ng/g) were 2,4-Dimethylaniline and 2,6-Dimethylaniline, respectively, and the summation of AAs after 100 days was 271 ng/g. Similarly, these two compounds (2,4-Dimethylaniline and 2,6-Dimethylaniline) accumulated in aerobic tank sludge, at significant concentrations (39.58.71 and 30.43 ng/g). The high sludge sorption of these three compounds was attributed to high their concentration relative to other AAs investigated. Table 4.5 show the AAs concentration in sludge from anoxic and aerobic reactors under IR (2.0).

Table 4.5: Detected AAs Concentration in Sludge (IR=2.0).

Component	Pka	log kow	Influent (ng/L)	Anoxic (ng/g)	Aerobic (ng/g)
2,4-Diaminotoluene	5.35	0.14	5.5	45.11	8.25
2,4-Diaminoanisole	5.15	0.5	4.83	16.05	2.29
o-Anisidine	4.53	1.18	0	1.96	0.8
o-Toluidine	4.48	1.32	29.54	2.82	5.09
4,4-Methylene-di (o-toluidine)	4.48	1.32	1.33	1.2	3.31
Benzidine	4.3	1.34	0	6.05	2.53
4,4'-Diaminodiphenyl	3.96	1.36	22.63	8.69	0.33
4,4-Diaminodiphenylmethan	4.83	1.59	10.93	4.74	1.95
2,4-Dimethylaniline	4.89	1.68	120.46	64.88	39.58
2,6-Dimethylaniline	3.95	1.84	52.87	78.22	30.43
4,4-Thiodianiline	4.55	2.18	0.83	0	3.95
4-Chloro-2-methylaniline	3.85	2.27	4.46	0.59	0.96
2,4,5-Trimethylaniline	5.09	2.27	48.62	2.04	1.8
2-Naphthylamine	4.16	2.28	48.71	0.37	0.54
Σ AAs (ng/g) Hydrophilic (Log Kow <2.28)				232.72	101.81
4-Aminobiphenyl	4.35	2.86	3.92	1.14	1.44
4-Aminoazobenzene	2.82	3.41	5.34	2.47	1.78
3,3-Dichlorobenzidine	3.2	3.51	6.81	6.49	8.51
4,4-Methylene-bis(2-chloroaniline)	3.1	3.91	4.76	15.89	3.88
o-Aminoazotoluene	3.01	3.92	9.68	12.9	1.92
Σ AAs (ng/g) Hydrophobic (Log Kow >2.28)				38.89	17.53
Σ AAs (ng/g)				271.61	119.34

4.5. Overall Fate of the AAs

Generally, the results showed that all the investigated AAs were biodegradable under aerobic condition. Hydrophilic AAs (Log Kow>2.28) such as 4-Aminobiphenyl, 4-Aminoazobenzene, 3,3-Dichlorobenzidine, 4,4-Methylene-bis(2-chloroaniline), 2,4-

Diaminotoluene, o-Anisidine, 4,4-Methylene-di (o-toluidine), 4,4-Thiodianiline, o-Toluidine, 2,4,5-Trimethylaniline, 2,4-Dimethylaniline and o-Aminoazotoluene were accumulated in sludge despite their biodegradability under aerobic condition. Meanwhile, the concentration of most of the investigated AAs increased under the anaerobic and the anoxic condition owing to the reduction of azo bond. Notably, the rate of increase in AAs in the anoxic tank (IR of 2.0) was higher than observed in the anaerobic tank (IR of 0.0) owing to the unique bacterial culture, facilitated by IR between aerobic and anoxic tank. In addition, most of AAs were accumulated in sludge under reducing environment due to the recalcitrant behavior of AAs under Anaerobic/Anoxic conditions.

4.6. Toxicity Assessment

Correlating conventional parameters such as COD with effluent toxicity responses could provide support for effluent management when toxicity testing is not possible. The high COD, TOC and color removal efficiencies observed in this research suggests the absences of toxicity in the treated effluent. This suggestion supported by the study of Liang et al [2018], which investigated the relationship between the conventional indicators and the toxicity of the influent and the effluent of four textile wastewater treatment plants. Their results indicated that the high COD removal (above 90%) helped to remove toxic substances from the textile wastewater. Particularly, the membrane filtration unit facilitated the removal of toxic compounds. Toxicity to *V. fischeri* or *D. subspicatus* was found to be positively correlated with certain conventional indicators such as TOC, COD, TP, colour, and MLVSS in different textile dyeing effluents ($R^2 > 0.84$) [Liang et al., 2018].

4.7. Ceramic Membrane Performance

The scope of this study is to assess the performance of the sequential anoxic-aerobic batch reactor coupled with ceramic membrane, for tertiary effluent treatment, in terms of product quality. However, the excellent performance of the ceramic membrane was noted. The pilot-scale was operated for 103 days without chemical or physical

cleaning resulted in steady-state operation with longer constant and stable flux (Figure 4.15). The MLSS concentration in the membrane tank was varied between 250-500 mg/L.

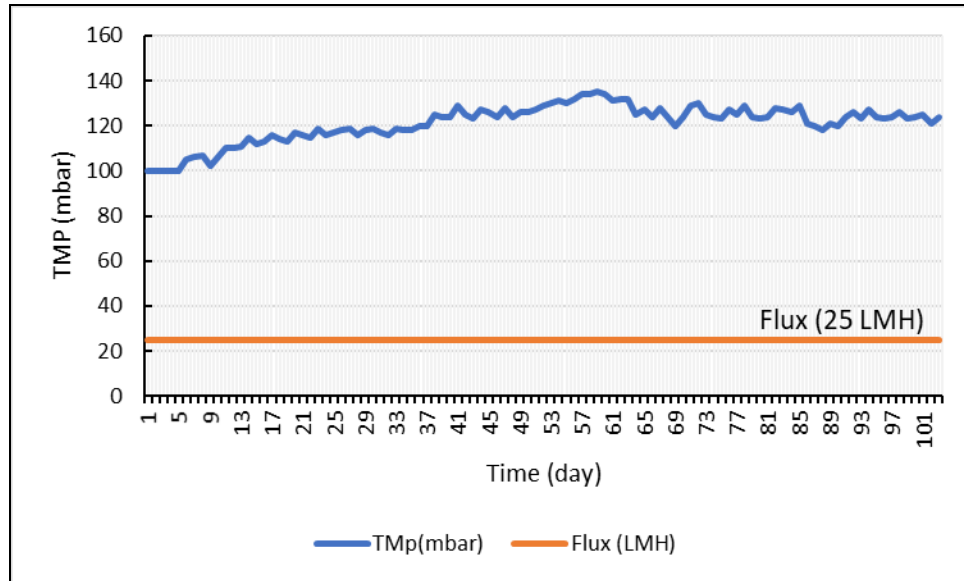


Figure 4.15: The Flow Diagram of Ceramic Membrane.

The flux was 25 LMH where the operating cycle was 10 minutes production following by 2 minutes backwash. The Transmembrane Pressure (TMP) was started at 100 mbar at the beginning, gradually increased to 135 mbar in the first 45 days before it fixed at around 120 mbar for the rest of the operating period. The ceramic membrane module was operated for 1.5 hr per cycle. Interestingly, though the ceramic membrane was stopped for around 22 hr, the membrane performance (flux vs TMP) not affected in the following cycle. Moreover, the performance of the ceramic membrane in this study indicate that the use of ceramic membrane guarantees the reliability, robustness and stability of the process generally demanded by textile wastewater treatment applications. Figure 4.16 demonstrate the performance of the sequential anoxic-aerobic batch reactor at IR 2.0.

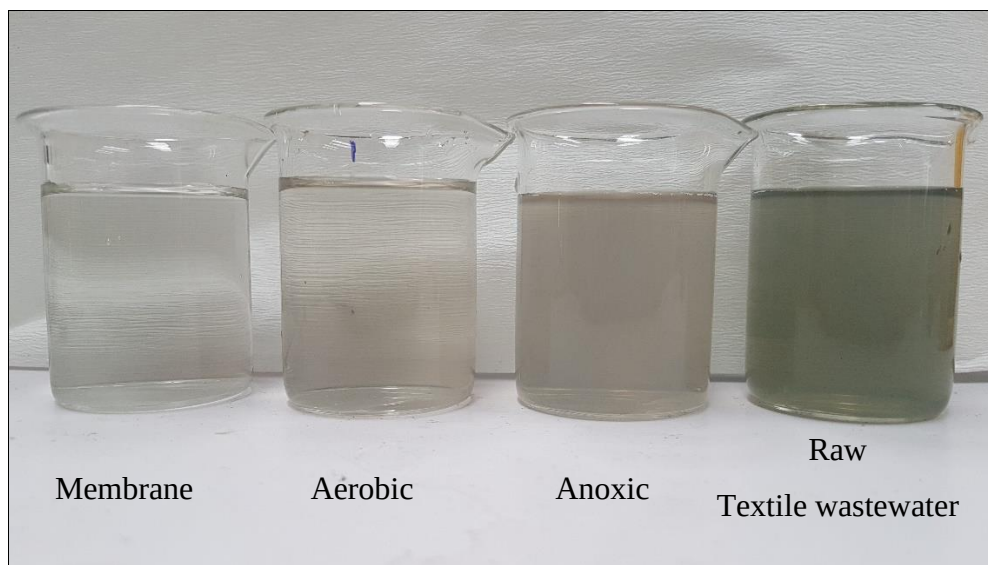


Figure 4.16: The performance of Sequential Anoxic-Aerobic Batch Reactors.

4.8. Summary

Beside the conventional pollutant, this study investigated the bioavailability of 22 AAs in each reactor and tracked those AAs through the system under different redox condition. In this study; AAs removal efficiency highly depend on physical chemical characteristic. AAs contain one aromatic ring are highly removed by the proposed system (above 80%) whereas AAs possesses 2 aromatic rings in their structure were moderately removed (35-75 %). As pKa values of investigate AAs below the pH value of wastewater, the electrostatic repulsion hindered the adsorption of AAs to sludge. Posing EWG such as (-CL) and azo bond decrease the removal efficiency while having EDG such as (-NH₂) in AAs structure increases the removal efficiency.

In this study, the results showed that color removal under anoxic condition was higher than anaerobic condition resulting in more AAs in anoxic tank compare to anaerobic tank. However, the aerobic tank is an effective way to remove the generated AAs in anoxic/anaerobic reactor.

In this study, the results show that AAs have a high ability to absorb into biomass under reduction environment which can be attributed to the recalcitrant behavior of AAs under anaerobic/anoxic condition and the high reactivity of aromatic ring. Therefore, more AAs were clearly detected in sludge than in aqueous phase.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The results from this research indicate that the use of ceramic membrane guarantees the reliability, robustness and stability of the process generally demanded by woollen textile wastewater treatment applications.

Simultaneous organic matter, TN, color and AAs removal in woollen textile wastewater treatment by sequential anoxic-aerobic batch reactors was examined. The study demonstrates that a system comprising of sequential anoxic-aerobic batch reactors and ceramic membrane is effective for the woollen textile wastewater treatment.

Organic matter removal was generally higher than 93 %. The use of an anoxic reactor was effective in TN and color removals which reached values higher than 70% and 85%, respectively. The IR between anoxic and aerobic tanks demonstrated a significant role in TN and color removal due to development of bacterial community under various IR. Nevertheless, the TOC concentration was not affected by IR ratio. Further research is needed to investigate the bacterial communities responsible for color degradation under different IR ratios, in addition, investigation of IR effect on elimination of generated aromatic amines is required.

AAs removal efficiency highly depends on physical chemical characteristic. AAs contain one aromatic ring are highly removed by the proposed system (above 80%) whereas AAs possesses 2 aromatic rings in their structure were moderately removed (35-75 %). As pKa values of investigate AAs below the pH value of wastewater, the electrostatic repulsion hindered the adsorption of AAs to sludge. Posing EWG such as (-Cl) and azo bond decrease the removal efficiency while having EDG such as (-NH₂) in AAs structure increases the removal efficiency.

The results showed that color removal under anoxic condition was higher than anerobic condition resulting in more AAs in anoxic tank compare to anerobic tank. However, the aerobic tank is an effective way to remove the generated AAs in anoxic/anerobic reactor.

In this study, the results show that AAs have a high ability to absorb into biomass under reduction environment which can be attributed to the recalcitrant behavior of AAs under anerobic/anoxic condition and the high reactivity of aromatic ring. Therefore, more AAs were clearly detected in sludge than in aqueous phase.

5.2. Recommendation for Future Work

Determine the microbial diversity in the reactors; anaerobic anoxic and aerobic is essential to get an over-review of the variety of biological culture. Understanding of the functional microorganism community is important for the elimination the azo dye from the wastewater using a biological method which considers a complicated process as it involves decolorization and mineralization. Nevertheless, there is little understanding of the functional microbial community involved in the entire dye degradation process. Using sophisticated technology such as DNA analysis for microbial diversity and structure can give a full understanding of specific microbial community that involve on dye degradation.

For discharge and reuse; it's essential to assess the effluent quality of treated textile wastewater by eco-toxicity analysis. Dyes and their by-product such as AAs are mutagenic. Therefore, eco-toxicity studies must be held to examine the influence of treated textile wastewater that would have on environment and aquatic ecosystem. Complex matrix such as textile wastewater is not assessable in terms of toxicity by chemical analysis, as a result toxicity test is needed.

Life Cycle Assessment is needed to evaluate the environmental effects of proposed system conversation of the environment and ecosystem. Moreover, suggesting methods to increase water recycle without damage to aquatic ecosystem and humans.

Finally, although this study investigated 22 AAs, many AAs still not investigated. Farther studies are needed to fully understand the extent of AAs's mineralization. It's necessary to study in details different redox condition for AAs memorialization.

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BIOGRAPHY

Ahmed M.S ALBAHNASAWI earned his B.S. in Civil Engineering at the Islamic University of Gaza, Palestine in 2010. Albahnasawi joined a water resources engineering master's program at the Islamic University of Gaza in 2011, studied the applicability of using Nano-filtration membrane for nitrate removal from Gaza strip groundwater. Albahnasawi received his MSc in JUNE 2013. In 2016, After Albahnasawi won the full PhD scholarship from The Presidency for Turks Abroad and Related Communities (YTB), he started his PhD research at Gebze Technical University, School of Engineering in the Department of Environmental Engineering in the SUMMER laboratory. Albahnasawi's graduate work focused on the investigation of the treatability of the sequential anoxic-aerobic batch reactors followed by ceramic membrane for textile wastewater treatment. Based on Albahnasawi PhD research, he published two Sci Expanded index journals and participated in two international conferences.

APPENDICES

Appendix A: Publications in the Scope of the Thesis Study.

Albahnasawi A., Yuksel E., Gurbulak E., Duyum F., (2020),” Fate of Aromatic Amines Through Decolorization of Real Textile Wastewater Under Anoxic-Aerobic Membrane Bioreactor”, Journal of Environmental Chemical Engineering, 8 (5), 104226.

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Albahnasawi A., Yuksel E., Eyvaz M., Gurbulak E., Polat E., Arslan S., (2019). “Integrated Anoxic-Aerobic Membrane Bioreactor for Textile Wastewater Treatment”, 4th Eurasian Conference on Civil and Environmental Engineering (ECOCEE), Double Tree by Hilton Istanbul-Avcılar, 17-18 June 2019, İstanbul, Turkey.

Appendix B: TOC, TN, NO₃, NH₃ and MLSS.

Table B1.1: TOC, TN and Color Concentration and Removal Efficiency (IR=0.0).

Time (Day)	Influent			Anoxic		Aerobic		Membrane			Rmoval Eficincy (%)		
	TOC (mg/L)	TN (mg/L)	Color (ADMI)	TOC (mg/L)	TN (mg/L)	TOC (mg/L)	TN (mg/L)	TOC (mg/L)	TN (mg/L)	Color (ADMI)	TOC	TN	Color
1	200	45	450	195	41	59	40	27	39	96	86.5	13.33	78.66
4	200	45	450	190	40	26	39	18	34	60	91	24.44	86.66
7	200	45	450	191	42	27.3	41	18	32.5	66	91	27.78	85.33
10	200	45	450	189	41	21	40	20	33.2	64	90	26.22	85.77
13	200	45	450	193	40	23.3	38	21	37	70	89.5	17.78	84.44
16	200	45	450	194	39.5	26	37	22	37.8	68	89	16	84.88
19	200	45	450	191	40.5	48	38	20	35	66	90	22.22	85.33
22	200	45	450	192	38	39	35	22	38	69	89	15.56	84.66
25	200	45	450	190	39	35	36	20	36	66	90	20	85.33
28	200	45	450	185	40	30	39	21	34	69	89.5	24.44	84.66
31	200	45	450	190	39.8	23	37	20	35	68	90	22.22	84.88

Table B1.2: TOC, TN and Color Concentration and Removal Efficiency (IR=0.5).

Time (Day)	Influent			Anoxic		Aerobic		Membrane				Rmoval Eficincy (%)	
	TOC (mg/L)	TN (mg/L)	Color (ADMI)	TOC (mg/L)	TN (mg/L)	Timme (Day)	TOC (mg/L)	TN (mg/L)	Color (ADMI)	TOC (mg/L)	TN (mg/L)	Timme (Day)	TOC (mg/L)
34	200	45	450	153	30	20	28	16	22.5	64	92	50.00	85.78
37	200	45	450	142	30.5	18	27	14	21.6	68	93	52.00	84.89
40	200	45	450	142	29.8	19	26	12	20.2	66	94	55.11	85.33
43	200	45	450	140	31	22	25	12	20.8	65	94	53.78	85.56
46	200	45	450	141	30.5	20	26	10	21.3	64	95	52.67	85.78
49	200	45	450	142	29.3	21	27	13	20.6	64	93.5	54.22	85.78
52	200	45	450	149	29.5	14	28	13	22.1	64	93.5	50.89	85.78
55	200	45	450	146	30	22	26	12	20	67	94	55.56	85.11
58	200	45	450	145	28	17.4	25	12	20.3	65	94	54.89	85.56
61	200	45	450	143	29	24	25.5	11	20.1	64	94.5	55.33	85.78

Table B1.3: TOC, TN and Color Concentration and Removal Efficiency (IR=2.0).

Time (Day)	Influent			Anoxic		Aerobic		Membrane				Rmoval Efficiency (%)	
	TOC (mg/L)	TN (mg/L)	Color (ADMI)	TOC (mg/L)	TN (mg/L)	Timme (Day)	TOC (mg/L)	TN (mg/L)	Color (ADMI)	TOC (mg/L)	TN (mg/L)	Timme (Day)	TOC (mg/L)
64	200	45	450	80	20	19	16	10	13.5	60	95	70.00	86.67
67	200	45	450	79	20.8	20	17	9	12.8	54	95.5	71.56	88.00
70	200	45	450	79	20.5	23	16.8	9	13.5	53	95.5	70.00	88.22
73	200	45	450	81	21.9	20	15.4	8	14	53	96	68.89	88.22
76	200	45	450	80	21.4	19	15.9	7	14	54	96.5	68.89	88.00
79	200	45	450	81	21.6	20	14	6	12.5	53	97	72.22	88.22
82	200	45	450	76	20.1	19	15.4	8	11.8	53	96	73.78	88.22
85	200	45	450	81	19.5	18	16.5	7	12.3	54	96.5	72.67	88.00
88	200	45	450	78	19.8	20	15.8	8	13	54	96	71.11	88.00
91	200	45	450	83	20.4	19	16.4	7	12.5	53	96.5	72.22	88.22
94	200	45	450	79	24	18	16.3	8	11.5	53	96	74.44	88.22
97	200	45	450	80	20.3	19	15.6	6	12	53	97	73.33	88.22
100	200	45	450	82	19.8	18	15	7	12.1	52	96.5	73.11	88.44

Table B1.4: TN, NH₃-N and NO₃-N Concentration (IR=0.0).

Time (Day)	Influent			Anoxic			Aerobic			Membrane			Rmoval Efficiency (%)
	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN
1	45	35	10	41	32	3	40	7	29	39	7	30	13.33
4	45	35	10	40	33	6	39	9	30	34	2	29	24.44
7	45	35	10	42	23	5.7	41	8.4	31	32.5	1.5	28	27.78
10	45	35	10	41	31	4.2	40	8.2	32	33.2	1.8	29.4	26.22
13	45	35	10	40	30	6	38	8	30	37	1.8	33	17.78
16	45	35	10	39.5	34	5.3	37	4.87	31	37.8	1.9	32.4	16.00
19	45	35	10	40.5	33.6	5	38	4	32	35	2.1	30	22.22
22	45	35	10	38	32.2	4.8	35	4	29.7	38	1.9	32.7	15.56
25	45	35	10	39	31.8	7.8	36	4	30.1	36	2	32.4	20.00
28	45	35	10	40	32	7	39	5	32	34	2	31.9	24.44
31	45	35	10	39.8	32.3	6	37	3	31.5	35	1.5	30	22.22

Table B1.5: TN, NH₃-N and NO₃-N Concentration (IR=0.5).

Time (day)	Influent			Anoxic			Aerobic			Membrane			Rmoval Efficiency (%)
	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN
34	45	35	10	30	24	4	28	3	25	22.5	0.434	22	50.00
37	45	35	10	30.5	25	3.6	27	2	22	21.6	0.28	21	52.00
40	45	35	10	29.8	23.9	3	26	1.5	21.3	20.2	0.22	20	55.11
43	45	35	10	31	23.4	7	25	2	22.5	20.8	0.18	20	53.78
46	45	35	10	30.5	24	5	26	1.5	23.5	21.3	0.17	21	52.67
49	45	35	10	29.3	23.5	4	27	1.9	23	20.6	0.2	20	54.22
52	45	35	10	29.5	23.8	3.5	28	2	24	22.1	0.2	22	50.89
55	45	35	10	30	24.1	3.8	26	2.3	22	20	0.2	20	55.56
58	45	35	10	28	23	3.6	25	2.4	23	20.3	0.2	20	54.89
61	45	35	10	29	24	4.1	25.5	1.8	24	20.1	0.2	20	55.33

Table B1.6: TN, NH₃-N and NO₃-N Concentration (IR=2.0).

Time (day)	Influent			Anoxic			Aerobic			Membrane			Rmoval Efficiency (%)
	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	N03- N	TN (mg/L)	NH ₃ -N (mg/L)	NO ₃ -N (mg/L)	TN (mg/L)	NH ₃ -N (mg/L)	N03- N	TN (mg/L)
64	45	35	10	20	16	4	16	2	14	13.5	1	12	70.00
67	45	35	10	20.8	15.4	3.5	17	1.5	13.6	12.8	0.7	11.5	71.56
70	45	35	10	20.5	15.6	3.4	16.8	1.3	13.4	13.5	0.6	12.5	70.00
73	45	35	10	21.9	15.8	3.6	15.4	1.2	13.8	14	0.5	13	68.89
76	45	35	10	21.4	15.2	3.8	15.9	1.5	12.6	14	0.6	12.5	68.89
79	45	35	10	21.6	15.3	3.2	14	1.6	12.4	12.5	0.7	11.5	72.22
82	45	35	10	20.1	14.6	3.7	15.4	1.4	12.5	11.8	0.8	10	73.78
85	45	35	10	19.5	14.9	3.1	16.5	1.9	13	12.3	0.6	10.6	72.67
88	45	35	10	19.8	14.3	3.2	15.8	1.4	12.4	13	0.5	11	71.11
91	45	35	10	20.4	14.2	2.8	16.4	1.3	12.7	12.5	0.4	11.3	72.22
94	45	35	10	24	19	2.4	16.3	1.6	12.5	11.5	0.6	11.5	74.44
97	45	35	10	20.3	14.7	3	15.6	1.6	12.6	12	0.4	11	73.33
100	45	35	10	19.8	14	2	15	1.5	12.4	12.1	0.3	10.8	73.11

B1.7: MLSS, MLVSS and MLSS/MLSSV values.

Time (day)	MLSS (mg/L)		MLVSS (mg/L)		MLVSS/MLSS	
	Anoxic	Aerobic	Anoxic	Aerobic		
1	5010	5893	3352	4060	0.669	0.689
8	4503	4514	3058	3155	0.679	0.699
15	4312	3006	2951	2104.2	0.684	0.700
22	3826	3283	2556	2240	0.668	0.682
29	2996	3524	2015	2450	0.673	0.695
36	2808	3674	1876	2520	0.668	0.686
43	2460	3836	1635	2660	0.665	0.693
50	2436	4167	1645	2870	0.675	0.689
57	2504	4310	1683	3017	0.672	0.700
64	2543	4594	1689	3150	0.664	0.686
71	2559	4613	1763	3220	0.689	0.698
78	2643	4887	1740	3360	0.658	0.688
85	2635	4926	1780	3430	0.676	0.696
92	2654	4875	1820	3409	0.686	0.699
99	2758	5036	1900	3500	0.689	0.695
106	2741	5265	1890	3640	0.690	0.691

Other Appendices (CD)