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SCIENCE AND ENGINEERING



M.Sc. THESIS

**DECOLORAZITION AND DETOXIFICATION OF TEXTILE
WASTEWATER BY ION-EXCHANGE PROCESS**

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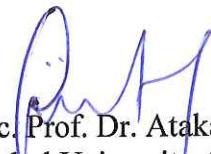
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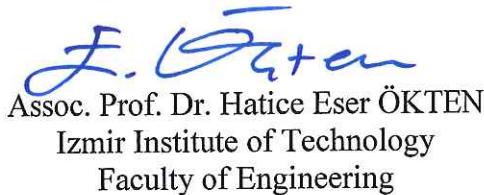
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FOREWORD

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TABLE OF CONTENTS

	Page
FOREWORD	iv
TABLE OF CONTENTS	v
LIST OF FIGURES.....	ix
LIST OF TABLES.....	xi
LIST OF SYMBOLS AND ABBREVIATIONS.....	xii
ÖZET	xiii
SUMMARY	xiv
1. INTRODUCTION	1
1.1. THE PURPOSE AND SCOPE OF THE THESIS	2
1.2. TEXTILE INDUSTRY	2
1.3. TEXTILE INDUSTRY PROCESSES	4
1.3.1. Fiber preparation	4
1.3.2. Spinning.....	4
1.3.3. Weaving.....	5
1.3.4. Singeing.....	5
1.3.5. Designing.....	5
1.3.6. Scouring.....	5
1.3.7. Bleaching	5
1.3.8. Mercerizing.....	6
1.3.9. Dyeing	6
1.3.10. Printing	6
1.3.11. Finishing	6
1.4. TEXTILE INDUSTRY WASTEWATERS	7
1.4.1. Characterization.....	7
1.4.2. Water usage	9
1.5. DISCHARGE STANDARDS	10
1.6. CONVENTIONAL TREATMENTS OF TEXTILE EFFLUENTS	10
1.6.1. Primary treatment	11
1.6.2. Secondary treatment	11
1.6.3. Advanced treatment.....	12

1.7. MEMBRANE TECHNOLOGY	13
1.7.1. Microfiltration	14
1.7.2. Ultrafiltration (UF)	14
1.7.3. Nanofiltration (NF).....	14
1.7.4. Reverse Osmosis (RO)	14
1.8. ADVANCED TECHNOLOGY	15
1.8.1. Oxidation	15
1.8.1.2. <i>Ozonation</i>	15
1.8.2. Adsorption	15
1.8.2.1. <i>Activated carbon (AC)</i>	16
1.9. APPLIED ADVANCED ION EXCHANGE PROCESS (IE) AS A PRETREATMENT METHOD	16
1.10. RESIN TYPES	18
1.11. THE MECHANISM OF ION-EXCHANGE PROCESS (IE)	20
1.12. THE ADVANTAGES OF APPLY ION – EXCHANGE PROCESS (BATCH PROCESS)	21
1.13. REGENERATION OF ION EXCHANGE RESIN	22
1.14. CHALLENGES IN SUSTAINABLE PROCESSING OF TEXTILES	24
2. MATERIALS AND METHODS	25
2.1. CHEMICALS AND SAMPLES	25
2.2. EXPERIMENTAL SET-UP OF ION-EXCHANGE PROCESS	25
2.2.1. Ion -exchange Process for the Treatment of RTWW	26
2.2.2. Ion -exchange Process for the Treatment of Black Azo dyes	27
2.2.3. Ion -exchange Process for the Treatment of BTTWW.....	27
2.2.4. Preparation of Black azo dyes	27
2.3. CHARACTERIZATION	28
2.3.1 .UV–Vis Spectrophotometer	28
2.3.2. pH	28
2.3.3. Chemical Oxygen Demand (COD)	28
2.3.4. Total Organic Carbon Analyzer (TOC).....	28
2.3.5. Chlorine	28
2.3.6. Toxicity Tests	29
2.3.6.1. <i>Daphnia Magna</i>	29
2.3.6.2. <i>Microtox</i>	29
2.3.7. Regeneration procedure.....	30

2.3.7.1. <i>Apply regeneration for Anion ion -exchange process</i>	30
3. RESULTS	32
3.1. DECOLORIZATION OF TEXTILE WASTEWATER AS A PRETREATMENT METHOD	32
3.1.1. Decolorization of Raw textile wastewater (RTWW)	32
3.1.1.1. <i>pH</i>	35
3.1.1.2. COD Removal of Raw textile wastewater.....	35
3.1.1.3. TOC Removal of Raw textile wastewater	36
3.1.1.4. Detoxification of Raw textile wastewater as a pretreatment method.	37
3.1.1.4.1. <i>Detoxification of Raw textile wastewater (RTWW) By using Daphnia magna</i>	37
3.1.1.4.2. <i>Detoxification of Raw textile wastewater (RTWW) By using Microtox</i>	38
3.2. DECOLORIZATION OF SYNTHETIC DYES AS A PRETREATMENT METHOD	39
3.2.1. Decolorization of Black Azo dyes.....	39
3.1.2.1. <i>Optimization of different concentration from Black azo dyes.</i>	42
3.2.2. pH	43
3.2.2. COD Removal of Black azo dyes.....	43
3.2.3. TOC Removal of Black azo dyes.	44
3.2.4. Detoxification of Synthetic dyes as a pretreatment method.	45
3.2.4.1. <i>Detoxification of Black azo(RB5) dyes by using Microtox</i>	45
3.3. DECOLORIZATION OF BIOLOGICAL TEXTILE WASTEWATER (BTTWW).	46
3.3.1. Decolorization of BTTWW	46
3.3.1.1. <i>pH</i>	49
3.3.2. COD Removal of Biological treated textile wastewater.	50
3.3.3. TOC Removal of BTTWW.	51
3.3.4. Detoxification of BTTWW by using Microtox as a pretreatment method.....	52
3.4. REGENERATION OF ANION RESIN (OH ⁻).	53
3.4.1. Regeneration with Chlorine and <5% NaOH at 20 ⁰ C.....	53
3.4.2. Regeneration with the same reagent (Chlorine and <5% NaOH at 40 ⁰ C).	54
3.4.3. Decolorization of Raw textile wastewater after regeneration with the same reagent.....	55
3.4.3. COD Removal of Raw textile wastewater after regeneration.....	57
3.4.4. TOC Removal of Raw textile wastewater after regeneration.....	58
3.4.5. Detoxification of Raw textile wastewater after regeneration.....	59

4. DISCUSSION.....	61
5. CONCLUSION AND RECOMMENDATIONS.....	65
REFERENCES	67
APPENDICES.....	73
CURRICULUM VITAE	80



LIST OF FIGURES

	Page
Figure 1.1: Textile industry processes.....	7
Figure 1.2: Primary treatment.....	11
Figure 1.3: Secondary treatment	12
Figure 1.4: Advanced treatment.....	13
Figure 1.5: Schematic of Ion -Exchange process.....	18
Figure 1.6: Types of resins.....	20
Figure 1.8: Mechanism of Ion Exchange process (Batch process).	21
Figure 1.9: Advantages of Ion -Exchange process	22
Figure 1.10: Schematic of Regeneration system by anion resin (OH ⁻).....	23
Figure 2.1: The anion resin (OH ⁻).....	25
Figure 2.2: Ion Exchange process (IE).....	26
Figure 2.3: Black azo dyes (RB5).....	27
Figure 2.4: Microtox device.....	30
Figure 2.5: Applying regeneration for anion ion -exchange process by using a mixture of Sodium hypochlorite and > 5 % of Sodium hydroxide at 40 C°.....	31
Figure 3.1: Decolorization of Raw textile wastewater by applying IE process.....	33
Figure 3.2: Color removal of Raw textile wastewater after IE, 25 ml of anion resin (OH ⁻) at pH 5.65.....	34
Figure 3.3: Absorbance measurements before and after IE.....	34
Figure 3.4: pH before and after IE process.....	35
Figure 3.10 : Absorbance measurements before and after IE.....	41
Figure 3.11: Optimization of different concentration from Black azo dyes.....	42
Figure 3.12: Correlation between different concentration and absorbance.....	42

Figure 3.13: pH before and after IE process.....	43
Figure 3.14: COD values of RB5 before and after IE.....	44
Figure 3.15: TOC values of RB5 before and after IE.....	45
Figure 3.16: Acute toxicity before and after IE by using Microtox.....	46
Figure 3.17: Decolorization of biological textile wastewater by IE process.....	48
Figure 3.20: The pH values of BTTWW before and after IE process.....	50
Figure 3.21: COD values of BTTWW before and after IE.....	51
Figure 3.22: TOC values of BTTWW before and after IE.....	52
Figure 3.23: Detoxification of BTTWW before and after IE by using Microtox.....	53
Figure 3.24: Apply Regeneration with Chlorine and NaOH at (20 $^{\circ}$ C) and (40 $^{\circ}$ C)	54
Figure 3.25: The anion resin (OH $^{-}$) before and after Regeneration with Chlorine and <5% NaOH at 40 $^{\circ}$ C.....	55
Figure 3.26: Performance of the 25 ml of anion resin (OH $^{-}$) used after regeneration (8 regeneration) with Chlorine and <5% NaOH at 40 $^{\circ}$ C.....	56
Figure 3.27: Color removal performance of the anion ion exchanger (25 ml) after 8 generations in untreated textile wastewater with chorine and <5% NaOH at 40 $^{\circ}$ C.....	56
Figure 3.28 : The performance of depleted anion resin (25ml) with Raw textile wastewater after 8 regenerations in untreated textile wastewater with chorine and <5% NaOH at (40 $^{\circ}$ C) for COD Removal.....	59
Figure 3.29: The performance of depleted anion resin (25ml) with Raw textile wastewater after 8 regenerations in untreated textile wastewater with chorine and <5% NaOH at (40 $^{\circ}$ C) for TOC Removal.....	59
Figure 3.30: Detoxification of depleted anion resin (25ml) with Raw textile wastewater after 8 regenerations in untreated textile wastewater with chorine and <5% NaOH at (40 $^{\circ}$ C).....	60

LIST OF TABLES

	Page
Table 1.1: Characteristics of typical untreated textile wastewater[29].....	8
Table 3.1: Characterization results of Raw textile wastewater.	32
Table 3.2 : Characterization results of Black azo dyes.	39
Table 3.3: Characterization results of BTTWW.....	47
Table 4.1: The optimum operational condition determination for the removal of color, COD, TOC and the removal of toxicity of treated samples	63

LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Explanation
AC	: Activated carbon.
AOPs	: Advanced oxidation processes.
BTTWW	: Biological treated textile wastewater.
BOD	: Biological oxygen demand.
COD	: Chemical oxygen demand.
EC	: Effective concentration.
ED	: Electrodialysis.
EU	: European Union.
GDP	: Gross Domestic product.
IE	: Ion – Exchange.
NF	: Nanofiltration.
RTWW	: Raw textile wastewater.
RO	: Reverse osmosis.
SAC	: Strong acid cation.
SBA	: Strong base anion.
TDS	: Total dissolved suspends.
TOC	: Total organic carbon.
UF	: Ultra filtration.
WAC	: Weak acid cation.
WBA	: Weak base anion.

ÖZET

YÜKSEK LİSANS TEZİ

İYON DEĞİŞİTİRİCİ PROSESİ İLE TEKSTİL ATIK SULARINDAN RENK VE TOKSİSİTE GİDERİMİ

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Küresel su kullanımı, nüfus ve ekonomik faaliyetlerin büyümesi nedeniyle artmaktadır. Bu zorlukların üstesinden gelmek için, geleneksel atık su arıtma sistemlerinden kaynak geri kazanım odaklı ve çevre dostu teknolojilere geçiş olmaktadır. Tekstil endüstri çok yüksek hacimde su tüketen bir endüstridir olup teksti ıslak proseslerinde toksik boyalar, kimyasallar ve çok farklı kimyasal katkı maddeleri kullanmaktadır. Azo boyalar pamuklu tekstil endüstrisinde en çok kullanılan sentetik boyalar olup kanserojen ve mutajenik etkileri ile bilinmektedirler. Organik ve inorganik kirletici maddelerin uzaklaştırılması için ileri oksidasyon ve membran ayırmaları yaygın olarak kullanılmaktadır. Ancak, bu arıtma sistemlerinde arıtılmış atıksuda veya membran konsantresinde geriye kalan organik, inorganik ve boyalı kirleticilerin yanı sıra her iki sürecin de yatırım ve işletme maliyetleri yüksektir. Buna karşılık, iyon değiştiriciler (İD) basit, çevre dostu ve ekonomik olmalarından dolayı geniş bir alanda kullanılmaktadırlar. Bu çalışmada, tekstil atıksularından anyonik reaktif boyaların giderilmesi için iyon değiştirme yöntemi uygulanmıştır. İD prosesinin tekstil atıksuyundan renk ve toksisite giderimi üzerindeki performansı, Microtox toksisite testi, renk, kimyasal oksijen ihtiyacı (KOİ) ve toplam organik karbon (TOK) parametreleri ile izlenmiştir. Çalışmada anyonik reçinelerin rejenerasyonu için yeni hidrotermal klorlama metodu geliştirilmiştir.

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Anahtar kelimeler: İyon değişimi, Tekstil atıksuları, Reaktif azo boyaları, Microtox testleri

SUMMARY

M.Sc. THESIS

DECOLORAZITION AND DETOXIFICATION OF TEXTILE WASTEWATER BY ION-EXCHANGE PROCESS

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Global water use is increasing due to population and economic activities growth. To tackle these challenges, a shift from conventional wastewater treatment systems to source recovery oriented and eco-friendly technologies is taking a place. Textile processes are water intensive industry, and many different toxic dyes, chemicals and additives are used in the wet textile processes. Reactive azo dyes, the most used synthetic dyes in synthetic-cotton textile industries, are known to have carcinogenic and mutagenic effects. Advanced oxidation and membrane separation processes are widely used for removal of organic and inorganic pollutants. However investment and operational costs of both processes are high. Additionally due to the remaining organic, inorganic, dyes in the treated samples or membrane brine. In contrast ,Ion exchange system is highly considered to be widely used due to its simplicity ,eco-friendly and cost effective. In this study ion exchange method was applied to remove anionic reactive dyes from textile wastewater. The performance of IE processes on the decolorization and detoxification of textile wastewater was evaluated by following toxicity (Microtox test), color, chemical oxygen demand (COD), and total organic carbon (TOC) parameters. In the study a new hydrothermal chlorination method was developed for regeneration and reuse of exhausted anionic resins.

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Keywords: Ion exchange, Textile wastewater , Reactive azo dyes ,Microtox tests.

1. INTRODUCTION

Recently, due to rapid urbanization, Scarcity of water and the compression on water resources. Wastewater reuse has become one of the biggest challenges facing the world[1]. The universal changes have associated with the increasing of industrial activities, although it is essential to the progress of the economy, have an environmental influence on water resources. However, industrialization plays an essential role in the evolution of many countries worldwide. As industrialization has increased in many countries, the use of water will be increased by sundry factors, which leads to increasing the pressure on water resources[2]. The textile industry has considered as one of the industries that consume enormous quantities of water. Industrial wastewater varies widely in composition, flow and volume and strength depending on the sort of industry[3]. Textile industries that produce huge amounts of wastewater comprise different substances some of them inorganic and the others of these substances that considered as organic matters. The effluents from these industries can be include compounds that resist biological degradation or may be toxic components that may be intervene with the operation of the wastewater treatment plant and leads to environmental problems[4]. Textile wastewater can be defined as a combination of liquid substances or wastewater that detached from these industrial establishments and contains a lot of chemicals, dyes and toxic substances[5]. In addition, they may contain a high load of waste that requires oxygen, organic substances, pathogens, nutrients that stimulate plant growth, inorganic chemicals, sediments, minerals and others[6]. It can be also comprising toxic compounds. In recent decades there has been increasing concern about pollution that can be effect on the aquatic environment[7]. The wastewater of textile industries can contribute a significantly of water degradation and have a negative impact on the ecosystem. Thus, universal textile industries are the sectors that need recycling of water and the minimization of waste to conserve the ecological system. Nowadays, the treatment of textile effluents Subject to many discussions in numerous of countries around the world[8]. Wastewater from textiles has been one of the trickiest sorts of wastewater treatment due to the huge number of dyes, chemicals and toxic substances[9]. Numerous of these dyes which can cause the color of effluent have been found to be have carcinogenic or mutagenic effects as well as harmful to aquatic life. Advanced textile wastewater treatment methods can be used to

achieve of treatment required. The ultimate goal of wastewater treatment should be managing wastewater effectively, economically, and ecologically[10-13].

1.1. THE PURPOSE AND SCOPE OF THE THESIS

The aim of this study is to use the ion exchange process (IE) that can be applied to the removal of the color from the wastewater generated by the textile industry and the application of anion resin from the ion exchange system to achieve the highest treatment efficiency and conduct remedial studies on it. Samples of different textile wastewater from cotton fabric industry. By utilizing the innovation that ion exchange technology brings to textile wastewater treatment, this new technology will explore the performance of wastewater treatment fabric. Thus, it would be possible to make the waste water of textile waste harmless, and to eliminate it in a more controlled manner by avoiding harmful environmental impacts that may arise. This study aims to apply IE and EIE treatment methods to remove color and toxicity from the Raw textile wastewater (RTWW), Synthetic dyes (Black azo dyes) and biologically treated textile wastewater(BTTWW) for the development of practicable safe and cost-effective wastewater reuse options. The consequence of IE based treatment processes on the decolorization and detoxification of (RTWW), (RB5) and (BTTWW) that evaluated in this study by following toxicity Microtox toxicity tests and daphnia magna in the treated effluents. Treatment performances of enhanced ion exchange method will be evaluated by monitoring color removal, chemical oxygen demand (COD), and total organic carbon (TOC) parameters.

1.2. TEXTILE INDUSTRY

The main exporter of the color in wastewater of textile industries are the dyes used. Reactive azo dyes are particularly associated with the contaminated wastewater that are used to stain fibers in the textile industry[10]. These dyes can form make up about 30% of the total pigments. The azo dyes that are applied for a long time in numerous industries such as weaving, dyeing, printing, photography, cosmetics and other industries. The textile industry is one of the most compliant and multifaceted industries[11]. It is an enormous consumer of water and therefore produce large amounts of colored wastewater. Throughout textile industry, up to 10-60% of effluent dyes, which are considered as a major source of water pollution, are released into effluents. Most of these dyes are xenobiotic complexes due to the existence of (N = N) bonds and other groups such as aromatic rings which are not facilely to degrade. Using of dyes in

textiles has considered as one of the most vital ecological problems worldwide in these day[12]. The existence of very high concentrations of dyes in wastewater from textiles has very clear and indisputable as well as diminish of the breakthrough of light while the photosynthesis[13]. In addition, some of these dyes are either mutagenic or carcinogenic and also has a very toxic effectes. This waste water from textile industries may also containing predominant chromatography is not only toxic to the biological world, but leads to serious problems of the ecosystem[14]. The discharge of these industries into effluents can leads to the significant environmental pollution through water enrichment in the aquatic ecosystem and severe health risk agents during bioaccumulation. Many of these toxic chemicals remain in effluents even after several methods of treatment such as chemical or biological methods[15]. Recently, strict ecological regulations have been carried out for the control of various of toxic compounds that used in textile wastewater and also water shortages in several areas like arid and semi-arid areas have obliged the textile industry to employ novel technologies and develop new cost-effective treatment approaches for the recycling of wastewater during water discharge of these factories. In order to meet discharge requirements, textile wastewaters are often treated by chemical or biological treatment processes. However, the effluents of textile wastewater secondary treatment plant that also needs further treatments for reclamation of water and can applied sustainable development[16]. Many industries have started to applying new methods on the recycling of wastewater to achieve sustainable development by preserving of water resources for future generations. Nowadays, several advanced treatment methods are applied for this purpose, such as membrane separation, ozonation, catalytic oxidation, Fenton reagent, electrochemical processing, adsorption, coagulation and Ion- Exchange process (IE) have been attempted to eliminate the remaining contaminants in textile wastewater treatment plant . Thus, general standards for water treatment should be developed for each process to reduce the costs of water recovery systems and enhancing the economic and environmental performance of these plants.

1.2.1. Textile Industry in Turkey

Turkey is the foremost country around the world by 3.7% in world trade of textiles and among the most competitive countries including India, China and South Korea in terms of marketing and raw materials[17]. Moreover, Turkey that can be considered as the second country in export of textiles to European Union countries and has ranked the seventh in cotton production and

also the fourth in cotton consumption. Turkey has considered the leader in cotton production around the world. The EU, which accounts for 75% of Turkey's total exports, is Turkey's most significant export market. The textile industry in Turkey has always been observed as a water intensive sector which relies on ground water. One of the major environmental Concerns about is therefore the amount of water discharged and the chemical load it carries. Turkish industrial sector, textile and garment industry is accountable for 15% of water consumption, which makes it the 2nd largest, industrial water consumer[18].

1.3. TEXTILE INDUSTRY PROCESSES

Textile industry has considered to be an intensive water consuming sector and that need the use of a large amounts of water and chemicals, and also contains natural fibers such as cotton, fabrics, silk, wool and other textile products[19].Textile industry is one of the greatest prevalent and ancient industrial activities around the world. The textile industry, which comprise of several processes like washing, Scouring, bleaching, dyeing, and finishing not only needs a huge amount of water, but also expend a considerable amount of varied hazardous chemicals such as diverse dyes, sulfur, metals, various organic halogens, enzymes, and a lot of other plugins. Many of these Chemicals are subject to be toxic which are stay in liquids even after biological or chemical treatment[20-22].

1.3.1. Fiber preparation

Normal fibers are always need to be very clean before production. This condition is the most intensive fiber that are implicates around 20-40 % of impurities.In order to eliminate these substances, large amounts have to be used of hot water that may containing non-ionic detergents and inorganic salts. During this step from the production of synthetic fibers, a number of interactive species and a wide range of chemicals can be used at this stage.

1.3.2. Spinning

Bleaching agents and hypochlorite, such as percutic acid and H_2O_2 , can be used at this stage. In order to obtain the white tissues, it is significant to eliminate natural colored materials from the fabric by bleaching process.

1.3.3. Weaving

At this stage woven weaver yarn is woven-taught, parallel warp yarns. Warp threads are subject to stress during weaving as the weft yarn is inserted between them in a great Speed. In order to diminish the damage that can produced by numerous of contacts, the shed should be established during chemical preparation. Thus, it diminishes the friction, that can be interfere with the fabric process. As a result, the scaling agents such as helper are widely used, especially for cotton.

1.3.4. Singeing

Basically, raw material has exposed to a gas flame in order to get rid of protrusion that caused by fibers. Fibers that protrude can caused none of dye absorption. The advantage of this process is that the chemical agents are not needed. However, dust and organic compounds are still an issue.

1.3.5. Designing

During this process, the elimination of Impurities carried out before dying. This technique depends on the size that can applying. Only the volume of water that soluble or insoluble may need enzymatic or chemical degradation.

1.3.6. Scouring

Natural fibers comprise impurities substances, and they require to be detached. Thus, sodium hydroxide at high temperature can be used. In addition, organic solvents can be utilized for scouring wool.

1.3.7. Bleaching

During this process, the tissue has to be exposed to bleaching agents. Generally, for treatment of tissue, (H_2O_2) can be applied. In addition, there are other chemicals that used such as formic acid, caustic soda and natural coloring materials. The process is stimulated by washing the cloth with water. Then, utilizing sodium diphosphate and diluted acid. As a result, this process can cause pollution, which is 10-30% of the total pollution[21].

1.3.8. Mercerizing

This process is especially used for cotton fabrics. This process progresses capability for dyes adsorption. Through this process, sodium hydroxide solution(NaOH) are utilized. After using the solution, (NaOH) can be reused again during other several processes.

1.3.9. Dyeing

One of the most essential parts of the textile industry in terms of the environment is Dyeing. Because of this process, several sorts of dyes and chemicals are used at this stage. There are a wide range of dyes such as exotic dyes, basic dyes, dispersive dyes, acid dyes, direct dyes, advanced dyes, fluorescent dyes, and based dyes.

1.3.10. Printing

In contrast to the dying process, printing process can allow an assortment of colors to be utilized. Commonly, this process needs between 5 and 10 pastes to create a single pattern. In order to obtain color, dyes are used.

1.3.11. Finishing

Finishing process has to be the last stage in the textile industry. As the fabric is washed to eliminate the dyes that are not installed. After that, it ought to be treated using starch to finish the fabric. This process produces very high pollution to the environment. Figure 1.1 shows Textile industry process.



Figure 1.1: Textile industry processes.

1.4. TEXTILE INDUSTRY WASTEWATERS

1.4.1. Characterization

The "wastewater characteristics" expression refers to the organic and inorganic substances, total phosphorus, total nitrogen etc. In the textile industries, there is a huge quantity of wastewater from each process refers to these substances[22].In spite of the fact that the structure of wastewater may be different even for the same process, there are general values to grant a better understanding of pollution.The variety in the production of the textiles also can damage the characterization of wastewater.Due to the textile industry includes a several processes, the characteristics of wastewater are so different and extensively. The textile wastewater is truly colored and toxic because of the existence of many substances that considered to be harmful to the environment.In addition, the high volume of wastewater that comes with organic and inorganic matter has to be the root of environmental problems.The characteristics of the characteristic textile wastewater is given in Table 1.1.

Table 1.1: Characteristics of typical untreated textile wastewater[29].

Parameter	Range
pH	6-10
Total dissolved solids (mg/L)	8.000-12.000
Total Suspended Solids (mg/L)	15-8.000
COD (mg/ L)	150-12.000
Oil & grease (mg/ L)	10-30
Free ammonia (mg/ L)	<10
Chlorine (mg/ L)	1000-6000
Free Chlorine (mg/ L)	<10
Sodium (mg/ L)	70%
So ₄ (mg/ L)	600-1000
Silica (mg/ L)	<15
Total Kjeldahl Nitrogen (mg/ L)	70-80
Color (pt, co)	50-4000

The textile Wastewater has contained of the many materials. The textile industry process has to be characterize that a high consuming of water. These industries may cause the increasing of water shortage problem in many countries of the world. The major pollutant parameters that characterize the textile wastewater can be included during the textile industry as color, chemical oxygen demand (COD), Biological oxygen demand (BOD), total organic carbon (TOC), toxic substances, suspended solids, oils and grease[23].

1.4.2. Water usage

The textile industry uses a great amount of water during all operations of processing. All dyes and chemicals are almost utilized to textiles. Most of fabric preparation steps, including scouring, bleaching, mercerizing and dyeing that use a vast quantity of water and each one of these steps should be followed by a thorough washing of the fabric to eliminate all chemicals that are utilized. The amount of water that is utilized in this industry, are depending on processes operated at the plant, equipment used, and prevailing management concerning the use of water[24]. The extensive use of water throughout textile processing operations are used. Almost all dyes, specialty chemicals are applied to textile substrates from water bodies. additionally, most of fabric preparation steps, including fiber preparation, desizing, scouring and mercerizing, that used aqueous systems. Textile operations vary greatly in water consumption. Wool and fabrics processes are more water intensive than other processing subcategories. Since there is a massive amount of water can be employed in the textile industry processes, wastewater treatment for these processes is of great essential. The water utilized is often returned to our ecosystem without any treatment. This leads to causes pollution at the groundwater and caused a lot of problems. As the pollution increases, the foremost thing that happens is that the amount of useable water declines.

1.4.3. Environmental Effects of Textile Wastewater

The discharge of textile industry can lead to contaminate water into the aquatic environments. Therefore, it has a great significant in controlling of pollution due to the consumption of water and can affects the environment. It seems that in recent days the textile wastewater fabric from the production leads to severe ecological problems[25]. Discharge of these industries into the aquatic environments without any treatment this leads to defect of the ecological balance. Even if the dye concentration is lower than to (1mg /L).

1.4.3.1. Color

It is usually utilized in textile industry azo dyes and 12 Chronographs in fabrics. Treatment of textile wastewater in three different categories according to the type of wastewater. Discharge with a strong color is the result of the use of the reaction of the dye[26]. Since the resistance of dye, azo dyes are separated through the air inside of the activated sludge system.

1.4.3.2. Toxic substance

There are many studies that are conducted to determine the effects of wastewater toxicity on the water quality. With the addition of various azo dyes in activated sludge, the demand for chemical oxygen is reduced by 10-30% or less. The illegal discharge of organic solvents used in each process is considered as a toxic and harmful to the sludge and water[27].

1.5. DISCHARGE STANDARDS

The standard values of the direct discharge of textile wastewater into the receiving water environments that have been brought from the Water Pollution Control Regulation regarding are the limit values that should not be exceeded in the composite wastewater samples that are taken. For industries such as textile industry the Increasing of water request around the world can brings with it the limitation of water in many countries.Stringent controls are faced these industries this leads to increase the cost of water for removal the pollutants from these industries. The textile sector has the forefront of sectors with the highest water consumption. Therefore, textile industries that are widespread around the world and requires for recycling and minimization of pollution that caused by wastewater.Textile wastewater which contain many of chemicals. These waters may vary over time and include dyes, compounds, solvents and inorganic salts depending on the sort of these processes. Although textile wastewaters can be treated in activated sludge systems to meet permitted discharge standards, treated wastewater is not suitable for reuse. The effluent waste disposal rules have been enforced by environmental bodies around the world to protect the environment from pollution caused by the textile industry[28].

1.6. CONVENTIONAL TREATMENTS OF TEXTILE EFFLUENTS

Treatment of textile industries is subject to biological treatment and many chemical methods such as ozonation, flocculation biological treatment and ion- exchange are used for the removal of organic matter and toxic substances. The disadvantages of biological treatment are the toxic heavy metals in effluents that affect the growth of microorganisms and most of these dyes are not degradable in nature. In addition, its required long time to treat effluents. Since the wastewater in the textile industry contains a high level of COD. Due to a wide range of inorganic and synthetic organic pollutants, it becomes very difficult to process these industries.

Treatment of textile effluents involves three treatment processes: primary, secondary and Advanced treatments[29].

1.6.1. Primary treatment

The major phase in the treating of textile wastewater is to eliminate suspended solids. This treatment contains processes that minimize the floating solids in wastewater. In primary treatment, sediment tanks are usually used. Other process is the mechanical sintering process that involves mixing of liquid wastes that combine particles[22]. After that, the stable blister molecules are removed. The disadvantage of this process is that the flow formation is tricky to control as shown in Figure (1.2).

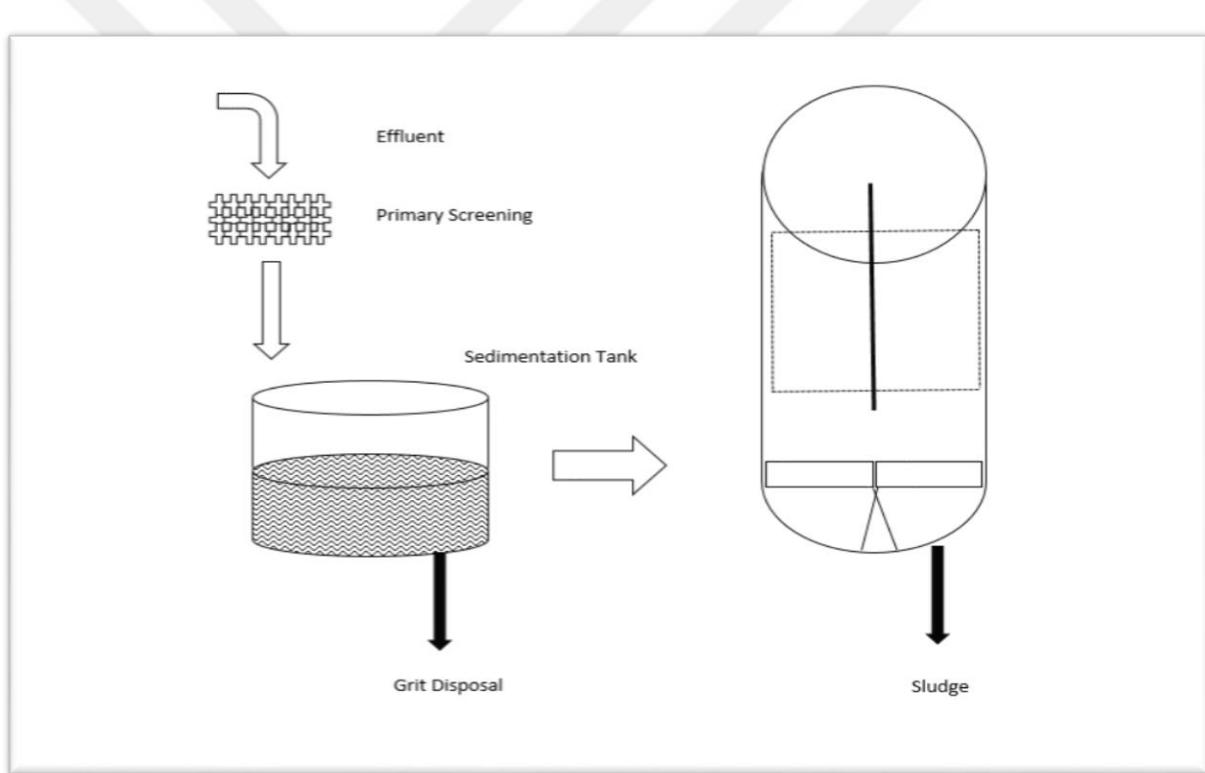


Figure 1.2: Primary treatment[29].

1.6.2. Secondary treatment

The secondary processing process is mainly performed to minimize biological oxygen demand in wastewater. This can be done with the micro-organisms in aerobic or anaerobic conditions. They oxidize dissolved organic matter to CO₂ and water and dissolve organic matter nitrogen

to ammonia. The activated sludge systems and the air lakes are among the pneumatic systems used for secondary treatment as shown in Figure (1.3).

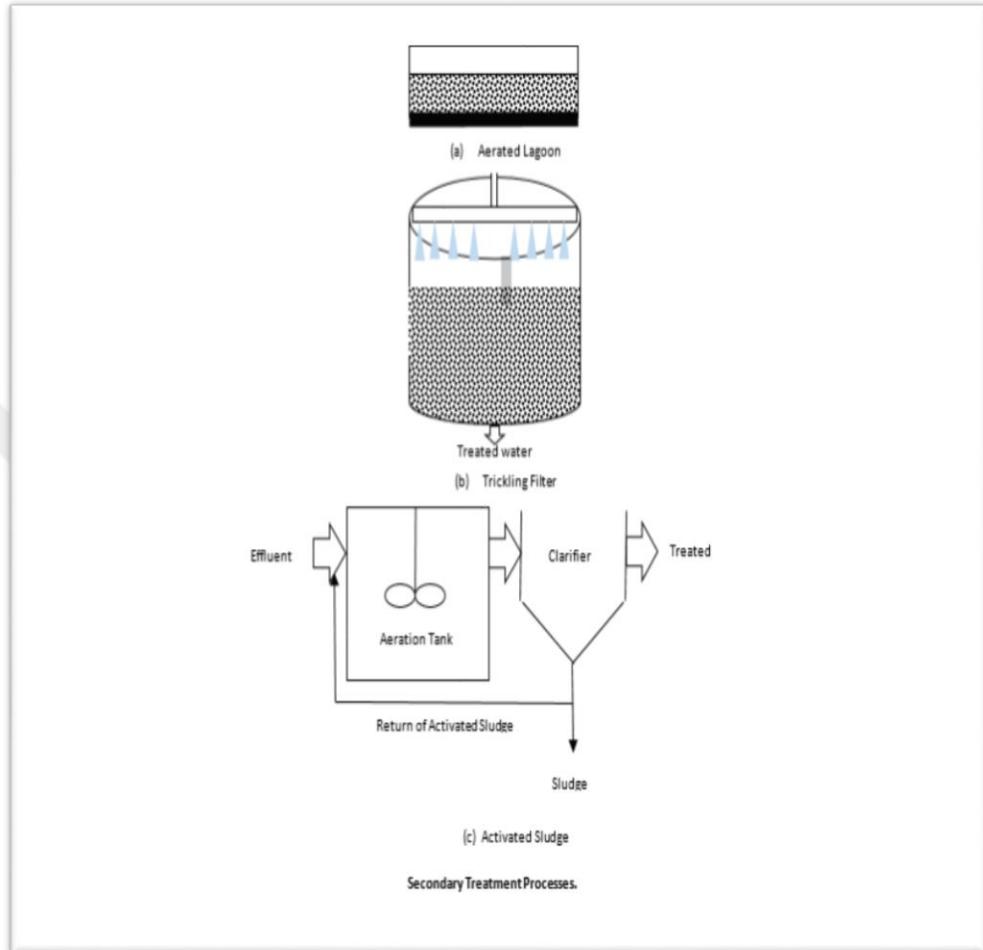


Figure 1.4: Secondary treatment[29].

1.6.3. Advanced treatment

There are several techniques that applied in advanced treatments inclusive electrolysis, reverse osmosis and ion exchange. Electrodialysis is the process of passing electro ions through liquid waste using fabric electrodes. As a result of electrical chemical reactions, the dissolved metal ions accumulated with particles in the solution. One of the disadvantages is that consuming a long time until the discharge of cathode. Reverse osmosis is a method that can remove the dissolved solids content. Moreover, the Ion-Exchange method is known as the mostly method can be used as an enhanced process due to it has a high efficiency more than 70 % for

decolorization of effluents and reducing the COD levels and other parameters[29].All of these methods are shown in Figure 1.4.

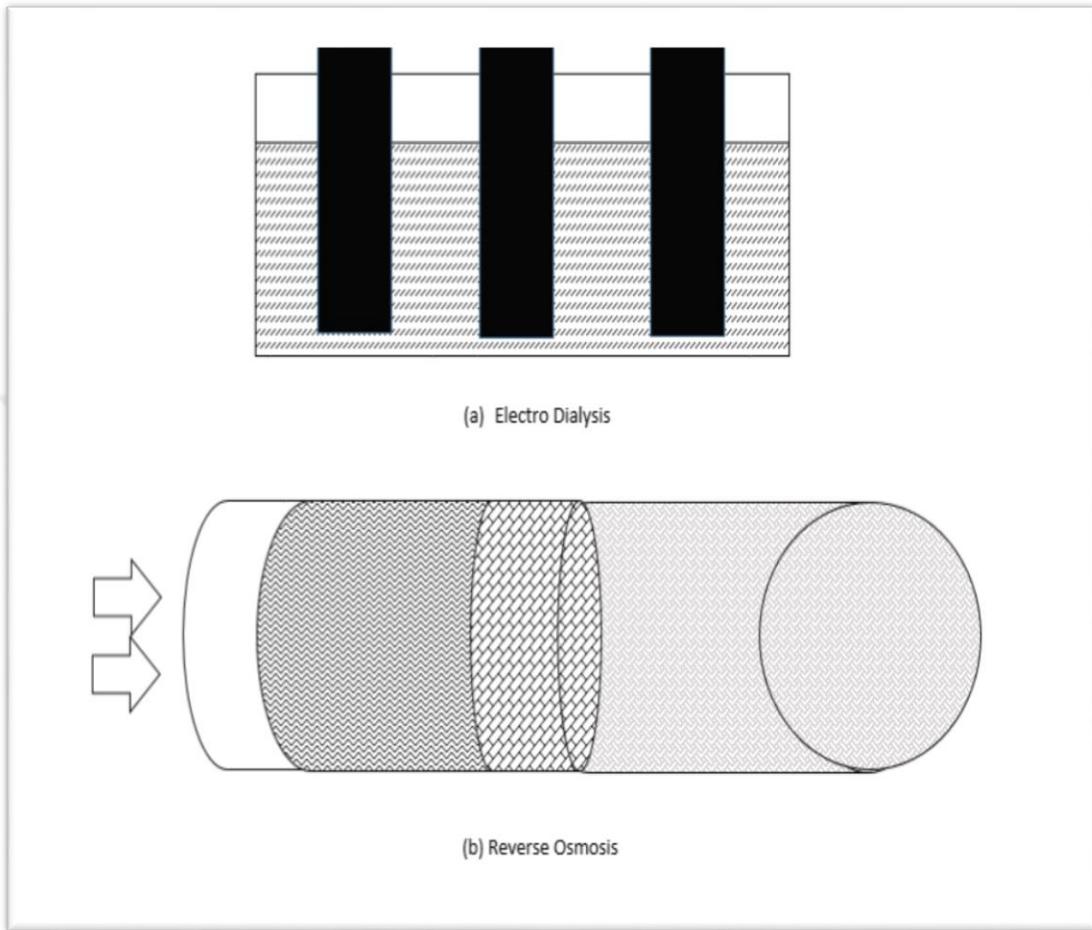


Figure 1.5: Advanced treatment[29].

1.7. MEMBRANE TECHNOLOGY

Membrane technology has been implemented as part of separation technologies[30].The variation in filtration membranes according to the size of the particles. Membranes are usually made from organic polymers such as cellulose acetate, polyamide and polycarbonate are the most commonly utilized and have high flexibility in separation properties. Microfiltration, Ultrafiltration (UF), Nanofiltration (NF), Reverse osmosis (RO) and Electrodialysis (ED) are applied for full scale treatment and recovery of water and chemicals.

1.7.1. Microfiltration

This method has used in the purification of particles. the disadvantages of this method that a high renovation costs which reduces the flow of time. The filtration membranes, reverse osmosis and ultrafiltration are operated by low pressure with high pH and high thermal solutions, which has antioxidant resistance[31].

1.7.2. Ultrafiltration (UF)

Ultrafiltration (UF) is defined as a low-pressure membrane filtration process[32].This process operates in limits between $0.005\text{ }\mu\text{m}$ and $0.1\text{ }\mu\text{m}$. Although the membranes are classified due to the size of the components by molecular weights. It can be used either to treat surface water or wastewater, as well as reverse osmosis before it can be used as a pretreatment method[33].

1.7.3. Nanofiltration (NF)

Nanofiltration (NF) is one of the vastly used membrane processes for wastewater treatment in addition to other applications such as desalination[34].NF has replaced reverse osmosis (RO) membranes in many applications due to lower energy consumption and higher flux rates[35].

1.7.4. Reverse Osmosis (RO)

RO membrane is essentially non-porous, and it preferentially passes in liquid and most of the solutes including ions has retained in it[36].The RO has characterized by high operating pressure and it can retains ions, and low molecular weight organics. It has significantly higher water permeability than that of RO membrane and operates at lower pressure.

1.7.5. Electrodialysis (ED)

In this technique, salt water has used and pumped into a low pressure between several parallel apartments, and the ionic membranes are assembled. Membranes that allows the cations to pass through permeable membranes[37].This electricity ions can separated through the membranes and concentrates between each pair of alternative membranes[38].

1.8. ADVANCED TECHNOLOGY

1.8.1. Oxidation

Over the past decades, it has attracted advanced oxidation processes (AOPS) as a wastewater treatment much attention from researchers[39]. It is known that as this method the most advanced technology, which has destruction of the organic content of pollutants and total toxic water[40]. This process has been utilized for a long time, and it has turned out to be an easy process can be used widely used.

1.8.1.1. *Fenton Treatment*

It is known as a very beneficial technique for wastewater treatment. It has very effective to removal of dyes and to reduce COD levels[41]. Besides many advantages, this process also has limitations. Sludge produced by this process contains many impurities and requires proper disposal of land that is not easy to handle. These Sludge contains phosphate that can be removed and making sludge less harmful[42].

1.8.1.2. *Ozonation*

Ozone is being used for the wastewater treatment since a long time[5]. In this process, the usual application is the use of sodium hypochlorite that has the ability to break azo bond. The shortcoming of this process is that it is readily decomposed in water having a life span of just 20 min. It also has a limitation that releases amine compounds and these can cause cancer. In addition, the cost of this method very high than others[43]. Each method has an advantages and disadvantages .However, in textile wastewater treatment have to apply the best methods that has a good performance ,low in cost and ecofriendly.

1.8.2. Adsorption

Adsorption has been shown to be as one of the most extensively methods can used for the removal of both inorganic and organic substances from polluted industrial wastewater[1].The major disadvantages of these processes are that they have a short lifetime and also the high cost thus be included in any analysis of their economic viability. In accordance with data, adsorption has to be one of the most common methods for the removal of pollutants from wastewater since proper design of the adsorption process will be produce a high-quality for treated effluent[44].

This process can provided an alternative method for the treatment of contaminated wastewater,especially if the sorbent is inexpensive and does not demand an additional pre-treatment step before its application[45].This method has founded to be one of famous techniques for treatment of textile wastewater in terms of flexibility and ease of operation and insensitivity to toxic pollutants[46]. Dyes can be removed from industrial wastewater by several methods such as Adsorption. Because of a lot of advantages like ease of operation, high efficiency and so on. Activated carbon has to be a big potential for the treatment. Other treatment applications such as Ion-Exchange process can be operated during the process of wastewater for removal of dyes with some advantages such as low cost, high efficiency, operation system[47-50].

1.8.2.1. Activated carbon (AC)

This method has widely used to treat wastewater from industrial activities but it has some limitations like the high cost of investment of treatment and also it is very difficult to remove the color continuously by this method[46].On the other hand, there is no significant change in the salinity of water passing through activated carbon. Therefore, activated carbon is usually used as a pre-treatment method[15].

1.9. APPLIED ADVANCED ION EXCHANGE PROCESS (IE) AS A PRETREATMENT METHOD

The recycling of textile wastewater components requires strong and effective separation process[27].Ion exchange (IE) process is very effective method for using in separation applications such as power generation and water treatment. Moreover, it can provide cleaner and more energy-efficient for these applications[47].Over the past 50 years, ion exchange has used in several applications such as fuel cells, wastewater treatment. In addition (IE) process has a lot of advantages and high efficiency[48].In order to develop more environmentally competitive technologies all, the focus on reducing the costs of Ion - exchange process. In this area has a big challenge to find a method has the lowest cost with excellent characteristics.IE has become a commercial competitive in terms of industrial activities due to the significant reduction in the costs without sacrificing of execution[49]. The IE method has still the simplest to applicable among all other applications for recycling of textile wastewater due to a lot of advantages such as low cost of its implementation.

Batch process are chemical reactions to eliminate dissolved ions from solution and substitute them with other ions that has a similar charged[50].In addition, IE has mostly used to soft the water where magnesium and calcium ions are removed from water[51]. There are two sorts of IE process. The first one is cation exchange process, that has positive charged ions and these ions can exchanged on the surface of the resin with the ions that has the same charged obtainable on the resin surface, and the second one of these types of IE is anion exchange process, that has ions with a negative charged and can exchanged on the surface of the resin with the same negative charged of ions[52].The resins and ions of the polymers has that associated with the resin. One of the most common applications that used by this process treatment of wastewater and water softening by using cations exchange resin[53].However, it is usually utilized for color removal from industrial wastewater such as textile wastewater effluents and other dissolved ionic species[54].Batch process has applied in several applications and also supply a method of separation in many non-water processes. It has a special utility in medical research, chemical synthesis, mining food processing, agriculture and a variety of other areas[55].The utility of Batch process rests with the ability to employ and reuse the ion exchange material. A Schematic of Ion - Exchange process is shown in Figure (1.5).

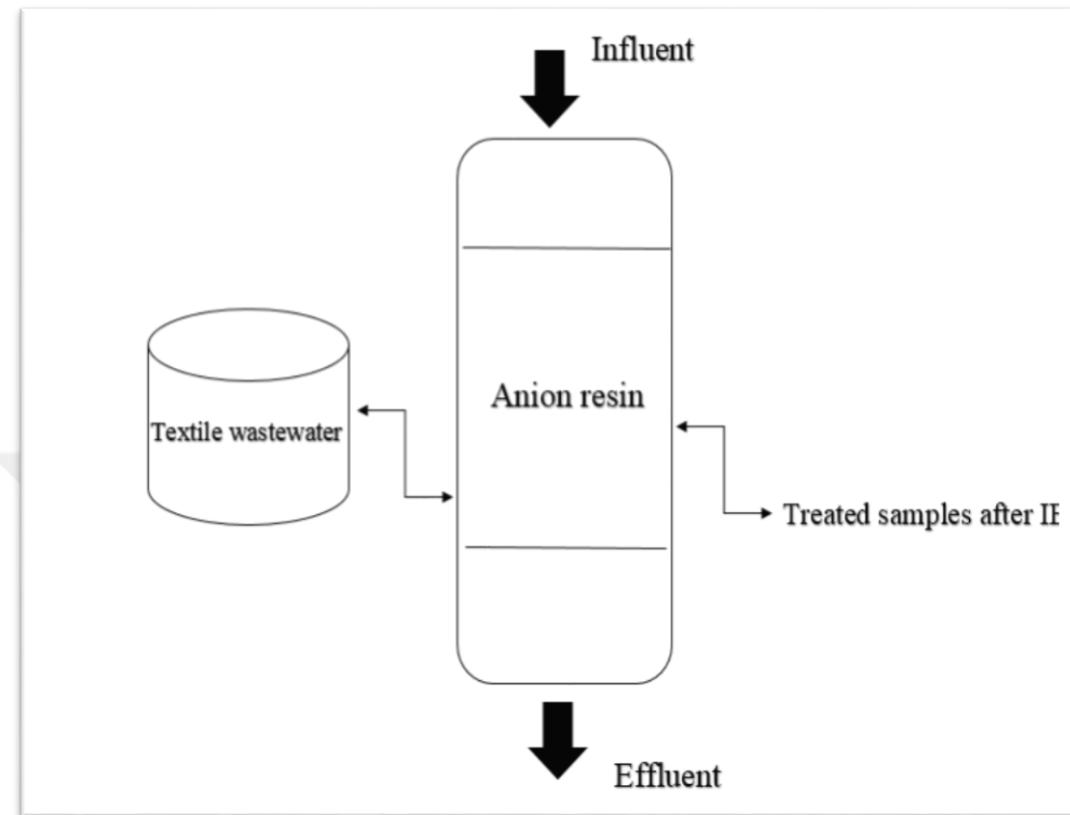


Figure 1.6: Schematic of Ion -Exchange process.

The earliest report of IE process date back to 1850, There are many studied the adsorption of ammonium ions to soils[55].Other studies published in 1947 with describing practical methods for separation of the rare earths by displacement ion-exchange chromatography and numerous of analytical methods which are utilized for metal ions that based on the separation of negative ions by using anion exchange resin[56]. Recently, using of thid process technique has been increased due to it allows analysis of wide range of molecules. The popularity of this process has been applied for many years in order to separate the various of ionic complexes.

1.10. RESIN TYPES

The resins of Batch process are polymers that has an ability to exchange ions within the polymer in the solution. Synthetic resins have been utilized for water purification and also for other applications to separate different elements[46].The materials of Batch process are unsolvable substances that contains of ions has an ability to exchange with other ions that has the same

charged[57]. These materials are carried out without any modification in material of these ions. furthermore, these exchangers are also soluble acids or bases with insoluble salts, which let them to exchange ions that has a negative charged or positive charged[58]. A several of natural substances like proteins and cellulose that offer the properties of batch process which play a significant role in the reduction of organic materials by utilizing cation and anion exchange resins[59].The resources of synthetic ion exchange were founded at the first time introduced on the basis of phenol and carbon resin for using in industrial activities during the 1930s. After a few years, the polystyrene resins have created with sulfonate groups in order to form the positive exchangers or the amine groups to compose the progressive anionic exchangers. These two sorts of the resin are still the most common resin until these days. IE resins are classified as a catalytic exchanger, which consist of the positive and negative charged ions that are available for exchange[60].The two types of resin are created from the same basic organic polymers. Resins can be widely categorized as strong or weak exchangers of positive or strong or weak base negative exchangers.The cations and anions are replaced in a water with changeable ions from the same charge in the ion exchange resin. Strong acid cation (SAC) are composed of a polymer matrix to which anionic functional groups are bound, such as sulphonate (SO_3^-).In contrast, Weak acid cation (WAC) resins are typically employ the carboxylic acid functional groups (RCOO^-). However, the Strong base anion (SBA) exchange resins are also obtainable in numerous varieties. Each type of resin can offer a unique set of that has a several advantages[61].On the other hand, the Weak base anion (WBA) exchange resins are the only major sort of resins that have not the ability for exchangeable ions. These resins can adsorb the mineral ions like Cl^- and SO_4^- . WBA resins have amine functional groups and can be regenerated with sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3). The resins of IE have been utilized in numerous fields such as water treatment, natural resource recoveries, medicine and so on. Moreover, the resins have also been usually applied in the laboratory for the separation applications and concentration of small species as a pre-treatment of chemical quantification.

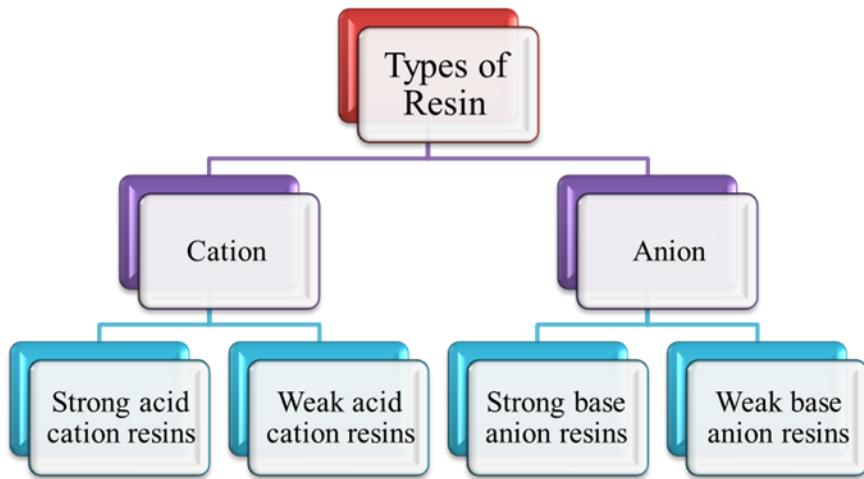


Figure 1.7: Types of resins.

The cation resins have a high capacity for the alkaline metals that associated with alkalinity and also these resins have a high affinity for the hydrogen ions. Therefore, it can be regenerated with strong acids very easily[57]. There is no significant salt that occurs with other materials. However, while the resin has not protonated, the softening can be applied, even in the presence of a high salt concentration[62]. These materials have many characterizations due to their ability for exchanger. These resins have an ability to absorb the strong acids with high capacity[63]. It is therefore in particular that has an effective used with anion base resins and it can be provided an overall high operating capacity and the high ability for applying regeneration. Figure 1.6) illustrates the types of resins[64].

1.11. THE MECHANISM OF ION-EXCHANGE PROCESS (IE).

Batch process are especially designed to distinct the variation of compounds, and consists of the phases one of them fixed and the other one has a mobile phase similar to other forms of columns that founded chromatography[65]. The mobile phases are containing of an-aqueous system that can dissolved in the mixture. On the other hand, the stationary phase has typically made from an inorganic matrix in which is chemically with ionizing of the functional groups[62]. These ions are in equilibrium between the mobile and fixed phases this leads to two possible forms are referred to as anion exchange as (Na^+ , K^+ and Cl^-), mono-atomic monomers (Ca^{2+} , Mg^{2+}) and multiple inorganic ions (SO_4^{2-}), as well as organic bases (H^+), hydroxide (OH^-) and acids (COO^-). The separation on the basis of obligated that can analyze of

positive or negative charge to a fixed phase which is in balance with the free counter ions in the mobile phase according to variation in the surface charge[66].The Batch process has comprised of the separation of ionic by utilizing the chromatographic supports derivatized with the ionic process groups that have a same charge as shown in Figure (1.8) [67].

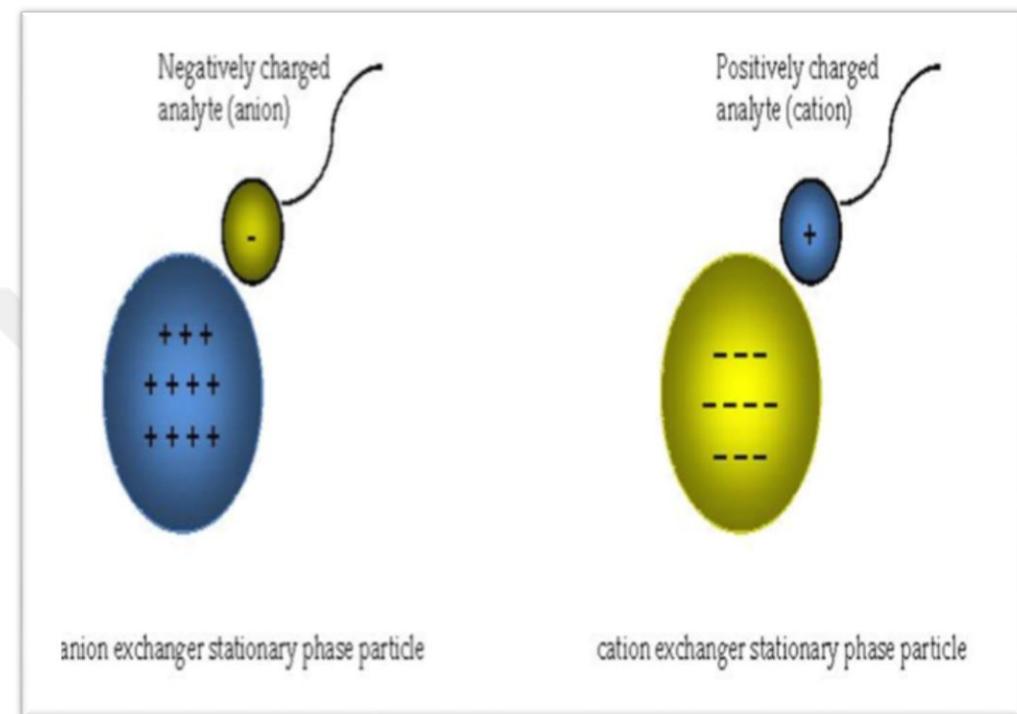


Figure 1.8: Mechanism of Ion Exchange process (Batch process).

Over time, the batch process becomes the most and best method for many applications in these days[68]. As we mentioned before, the anion resin has a good performance and high affinity for separation between ions. In addition the anion resin can be regenerated several times with the same efficiency for treatment applications of textile wastewater.

1.12. THE ADVANTAGES OF APPLY ION – EXCHANGE PROCESS (BATCH PROCESS)

Ion exchange process (IE), which is also known as adsorption chromatography, is a useful and popular method as shown in Figure (1.9) due to its:

- Widely used for wastewater treatment.
- Re-usable (Can Regeneration).
- Cost effective.

- Environment friendly.
- Easily collectable.
- Efficient technique.
- Quick separation.
- Provide high flow rate of treated water.

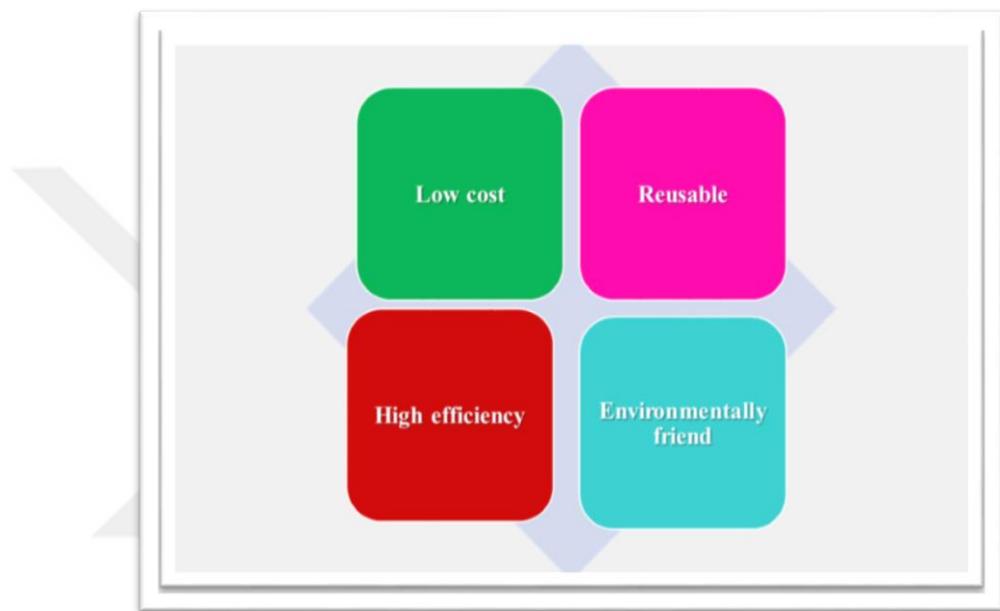


Figure 1.9: The Advantages of Ion -Exchange process.

1.13. REGENERATION OF ION EXCHANGE RESIN

The application of regeneration of ion exchange resins has a significant compound in numerous applications, such as in water treatment, industrial wastewater treatment such as Textile industry and in separation of heavy metal. Although the ion exchangers need a great volume of acid and base solutions for their regeneration. Because of this, there are several new methods of regeneration of resins have been studied. During operations, liquid waste has been imparted to a purified bed[69]. In addition, IE method has cost-effective implementation is to ensure that resins can be work effectively and easily renewed in order to ensure their operation for as many possible applications. In the regeneration step the resin is returned to its original state and the ions that have been exchange in to the solution. cationic resins are typically replenished by utilizing concentrated solutions and anionic resins with using of base[70]. For many materials,

such as heavy metals that has usually used at the first step in the recovery process. For others, it is just a focus before the final disposal occurs. There are many famous ions which is usually used such as Hydroxide (OH^-) which is the strongest one, chloride (Cl^-), hydrogen ion (H^+) and sodium (Na^+). As well as are the most generally utilized ions in anion exchange and cation exchange reactions, respectively, because they speedily exchange with ions contaminants. Different regenerate solutions have been used for cation and anion exchangers such as Hydrochloric acid solutions are used to regenerate strong ion exchange acid ions. Also, a series of positive cation resins are utilizing hydrochloric acid solutions. On the other hand, NaOH solutions are commonly used for anion exchange resin regeneration. A new method has been used in this research to regenerate the Anion resin (OH^-) as shown in Figure(1.10). For the first time a mixture of NaOH with NaOCl solution was used with a slight increase in temperature ranging from $30-40^\circ\text{C}$. This method is very effective and with the frequency of activation is then use only chlorine and thus this method is one of the most appropriate methods of optimization because of its quality and cheap price.

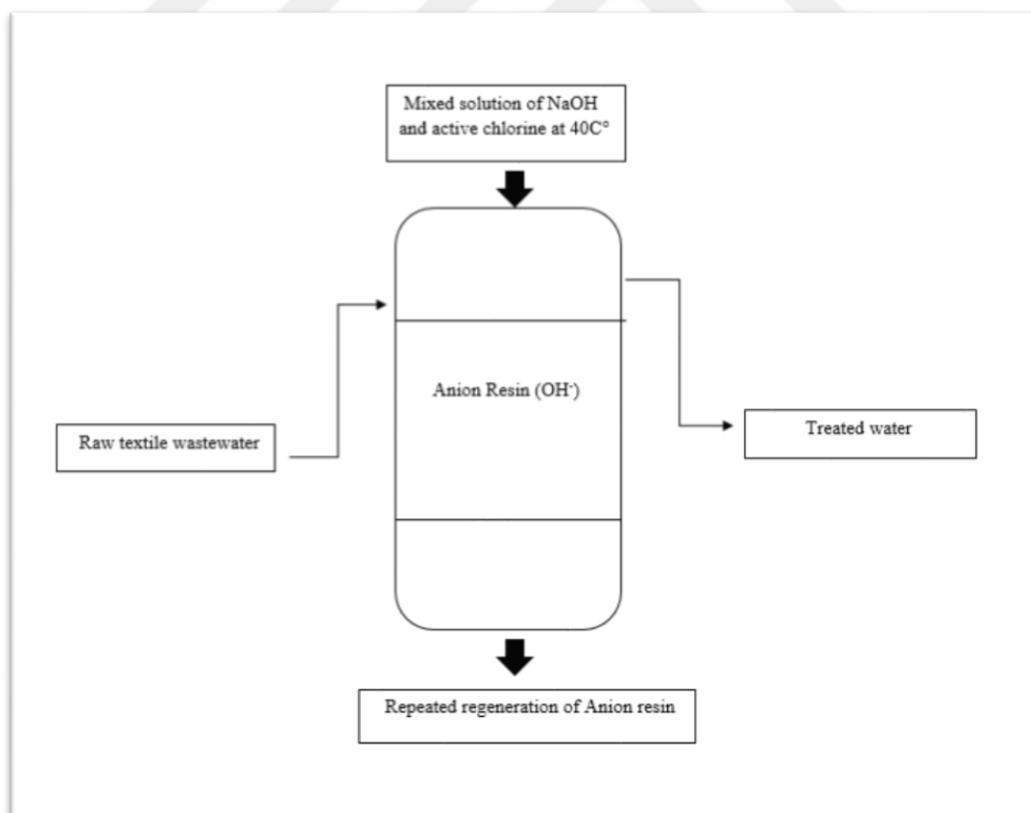


Figure 1.10: Schematic of Regeneration system by anion resin (OH^-).

1.14. CHALLENGES IN SUSTAINABLE PROCESSING OF TEXTILES

New ecological regulations of textile products and increased wastewater with limiting discharge that permit the of reclamation of water that treated before. These difficulties led to intensive research on advanced processing technologies, some of which are now accelerating. Today, the stringent environmental regulations for the control of several hazardous compounds has a consideration for researchers who care about protection of ecology. In environments with wastewater, the textile industry has been forced to applied a new technology that have a low cost and good performance of treatment for wastewater. In order to meet the requirements of discharge, textile wastewater is usually treated with biochemical and active biological processes. However, the effluents of secondary textile wastewater have need more treatments for reuse. The Color, (COD), (TOC) and Toxicity in the secondary treated textile wastewater are some of significant parameters limiting the reuse of treated wastewater in the textile industry processes. Nowadays, many advanced treatment applications, such as ozonation, Coagulation and advanced IE process, have been attempted for the removal of pollutants in the textile wastewater. Currently, Batch process is one of the only known advanced treatment methods to eliminate the remaining pollutants that have negative impacts on the environment. Textile materials are treated with various dyes, finishing chemicals and toxic substances that used as a carrier to be discharged at the end of each process. This discharged water is essentially very contaminating because it contains of residual chemicals and requires extensive treatment before disposal. Increasing demand for these industries has increased the amount of wastewater from textile processing and is compressing on the world's scarce freshwater resources. Using of several of hazardous chemicals in processing has a severe impact for the ecosystem and human health. Therefore, attempts have been made to reuse of effluents from textile industry in order to minimize the demand for fresh water. The water challenge for the textile industry is to conserve water resources and ensuring that contaminated wastewater has treated with in an environmentally friendly manner. a number of solutions are available for several textile processing operations which can significantly reducing the detrimental impact on the environment. However, there are still many challenges and many promising technologies that require further development to make them an applicable alternative. Similarly, many efforts are needed for the developments.

2. MATERIALS AND METHODS

2.1. CHEMICALS AND SAMPLES

Textile wastewater samples such as Raw textile wastewater (RTWW), Synthetic dyes as Azo dyes (Black azo dyes) and biological textile wastewater (BTTWW) which were used in this study are taken from Gümüşsu Aritma corporation located at Denizli, Turkey. It was worked under laboratory conditions of treatability with Ion-Exchange system, Ion-Exchange column, Anion resin (OH^-), Black azo dyes (RB5) as a powder, Sodium hydroxide (<5% NaOH), Sodium hypochlorite (6-14 % NaOCl), Sulphuric acid (H_2SO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), Ferroin acid (HgSO_4), all the stock solutions were prepared using deionized water.

2.2. EXPERIMENTAL SET-UP OF ION-EXCHANGE PROCESS

The ion -exchange consisted of glass column of length 50 cm and diameter 2.5 cm as shown in Figure (2.1). It was plugged with cotton at the bottom for free flow of the treated textile wastewater and to hold the anion resin (OH^-) intact .Figure (2.2) shows the anion ion-exchange procedure used for the separation of anions.



Figure 2.1: The anion resin (OH^-).



Figure 2.2: Ion Exchange process (IE).

2.2.1. Ion -exchange Process for the Treatment of RTWW

25 ml of anion ion-exchange resin was utilized for the separation of anions with RTWW after filtration of the samples to evaluate the efficiency before and after IE process .

2.2.2. Ion -exchange Process for the Treatment of Black Azo dyes

25 ml of anion ion-exchange resin was used for the separation of anion with 1g from RB5 was diluted by 100 ml of distilled water after filtration of the samples to estimate the efficiency before and after ion -exchange process.

2.2.3. Ion -exchange Process for the Treatment of BTTWW.

25 ml of anion ion-exchange resin was used for the separation of anions with BTTWW samples to appraise the performance of mnjthe IE process.

2.2.4. Preparation of Black azo dyes

A solution of 1 g black-azo dyes was added slowly in 100 ml of distilled water in a flask with a strong stirring for 15 minutes as shown in Figure (2.3) .



Figure 2.3: Black azo dyes (RB5).

2.3. CHARACTERIZATION

In this context, physical and chemical characterization of Raw textile wastewater effluents (RTWW), synthetic dyes (Black azo dyes) and biological textile wastewater(BTTWW) have been revealed.

2.3.1 .UV-Vis Spectrophotometer

UV-vis spectrophotometer was employed for recording UV-vis scan in wavelength in the range of 200–700 nm, and also applied for the measurement of color as Pt-Co at 465 nm.

2.3.2. pH

The pH of the samples were characterized by utilizing pH-meter, which was also used for measurement of Conductivity, Salinity, Total dissolved solid (TDS) and wastewater parameters were analyzed according to Standard Methods.

2.3.3. Chemical Oxygen Demand (COD)

The analytical methods of the COD of all textile wastewater samples were determined by the closed reflux method, after digestion of the samples in a COD digester over 2 hr at 150°C according to METU 5220 B given in Standard Methods.

2.3.4. Total Organic Carbon Analyzer (TOC)

TOC experiments were conducted with Shimadzu TOC-VWP instrument with diluted samples if they are very concentrated.

2.3.5. Chlorine

The chlorine of textile wastewater samples was measured according to DPD method in standard methods by used (Colorimeter) giving to standard iodometric method.

2.3.6. Toxicity Tests

2.3.6.1. Daphnia Magna

The Performance of textile wastewater before and after treatment was evaluated by using a plant plankton (*Daphnia magna*) as an indicator to study the adverse effects of the treated textile wastewater samples on the aquatic ecosystem. Experiments were carried out quadruplicate and five daphnids were used in each test beaker with 50 ml of effective volume. Results were evaluated on the basis of immobilization percentage obtained by dividing the number of immobilized animals by total animals.

2.3.6.2. Microtox

Acute toxicity of textile wastewater before and after IE process was measured using microtox Figure (2.4). The short-term luminescent bacteria assay was done according to the Basic test protocol was described in the manual of the Microtox Model 500 analyzer. In this study bacteria *Vibro fischeri* has utilized as an indicator for toxic substances and after 5 and 15 min exposure the device has calculated the effective concentration after that the results showed the removal of toxicity after applying IE process.



Figure 2.4: Microtox device.

2.3.7. Regeneration procedure

The basic aim of resin regeneration is to restore the exhausted resin back to its proper form for using again. Before the first regeneration, the resins must be thoroughly backwashed to eliminate any undesirable particles from the resin bed.

2.3.7.1. Apply regeneration for Anion ion -exchange process

In order to regenerate the exhausted ion exchanger, in the case of conventional (OH⁻) resins, active chlorine was added with (<5%) NaOH with a slight increase in temperature up to 40°C in order to facilitate the reaction speed and increase the resins efficiency Figure(2.5). This method was applied for (RTWW), and it was repeated for 8 times in order to see the resin efficiency. Before the first regeneration, the resins must be thoroughly backwashed to remove from the resin bed any particles .If demineralized water is available, the first regeneration is

identical to a normal regeneration, except for the quantity of regenerate that must be twice the normal amount. In such a case, the simplest way is to double the injection time for each regenerate, and the same volume of textile wastewater was recovered with the almost the same color removal efficiencies have been achieved.

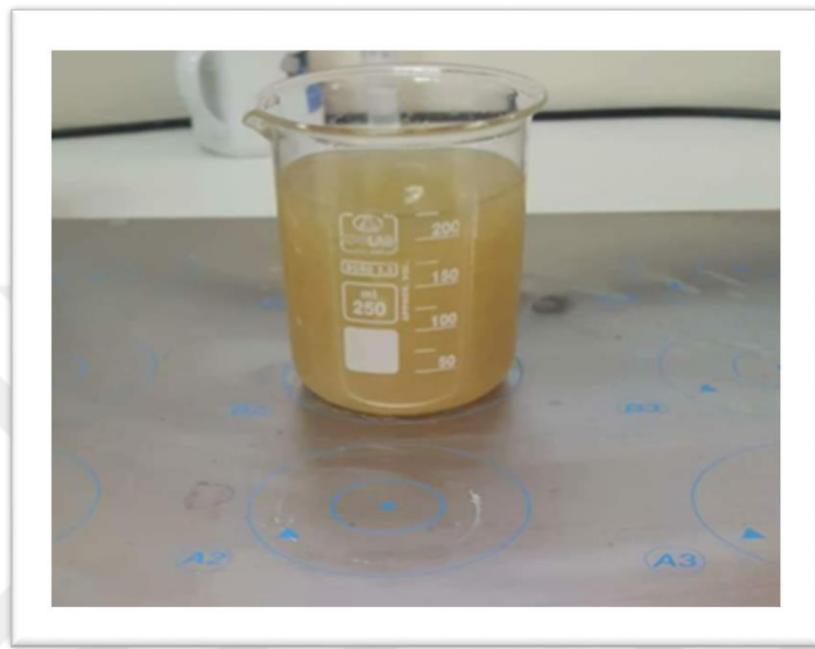


Figure 2.5: Applying regeneration for anion ion -exchange process by using a mixture of Sodium hypochlorite and > 5 % of Sodium hydroxide at 40 C °.

3. RESULTS

3.1. DECOLORIZATION OF TEXTILE WASTEWATER AS A PRETREATMENT METHOD

3.1.1. Decolorization of Raw textile wastewater (RTWW)

In order to observe the effect of color removal on the Ion-Exchange system, the Raw textile wastewater was taken from Gümüşsu Arıtma are located at Denizli, Turkey . It was treated with the IE process by eliminating the color at the exit of the treatment after this process and measuring the absorbance by the UV-Spectrophotometer immediately afterwards. Different parameters were performed to analyses results of treated textile wastewater after IE process. Characterization studies have been carried out for RTWW from textile factories that are touched by the wastewater used in the treatability studies. The results obtained in this work are given in Table 3.1. According to wastewater characterization experiments, the pH of the Raw textile wastewater was 7.25, The color removal was shown in Figure (3.1) , The COD of the Raw textile wastewater was 711 mg/L and after applying IE process in the range of 400 mg/L, TOC of Raw textile wastewater was 20 mg/L before apply IE process (Batch process), and It was 8 mg/L after applying IE Process.

Table 3.1: Characterization results of Raw textile wastewater.

Parameter	Range
pH	5.65-7.75
Conductivity (µs/cm)	6.71-7.65
Salinity (mg/L)	3.80-4.90
TDS (mg/L)	3.66-4.10
Color (pt, co)	800-3250

The Color was measured before and after applyied IE process ,and the absorbance measurements were performed on the Batch process after the run and the color removal values were given in Figure (3.2). Absorbance was obtained before and after applying IE process by utilizing UV-visible spectrophotometer in the wavelength range between 200 - 700 nm as shown in Figure (3.3). According to these results, it is observed that at the effluent, it is significantly removed in the color of the (RTWW).



Figure 3.1: Decolorization of Raw textile wastewater by applying IE process.

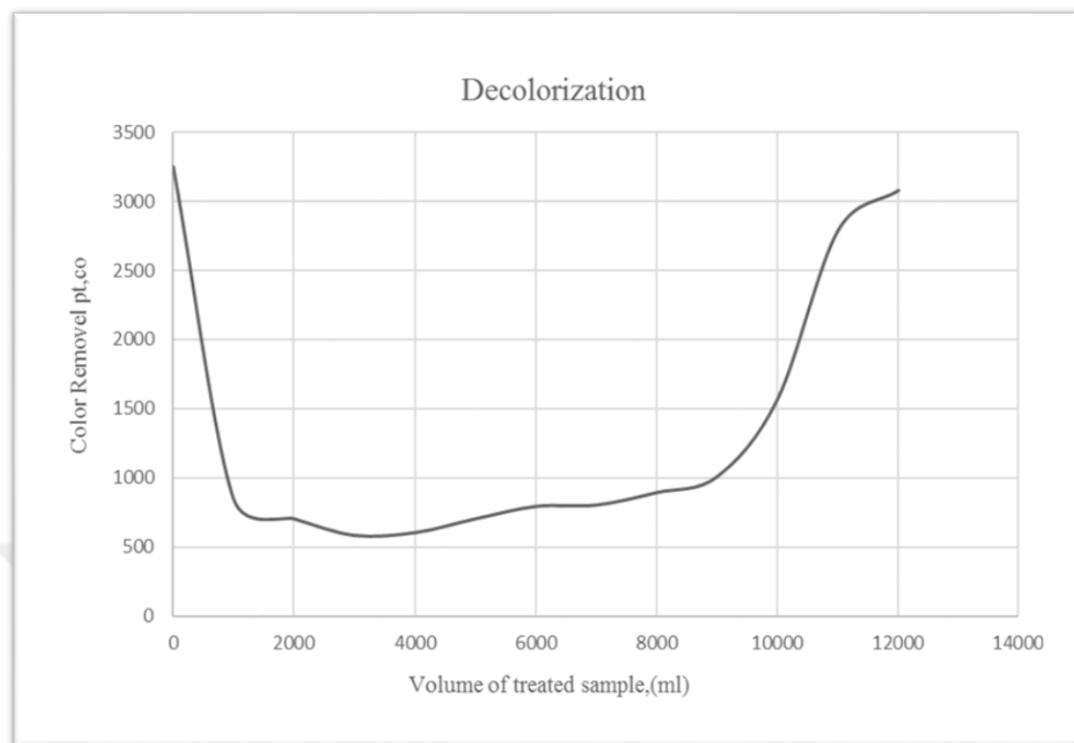


Figure 3.2: Color removal of Raw textile wastewater after IE, 25 ml of anion resin (OH^-) at pH 5.65.

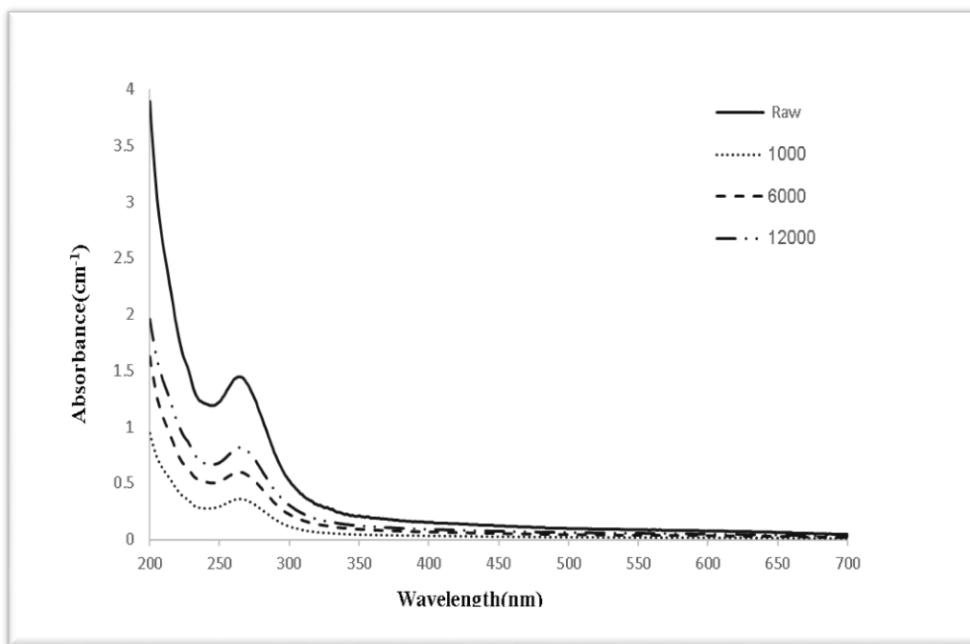


Figure 3.3: Absorbance measurements before and after IE.

3.1.1.1. pH

pH values of (RTWW) were continuously monitored during IE system as shown in Figure (3.4). At the end of the study, the pH value of the RTWW was increased to 7.75.

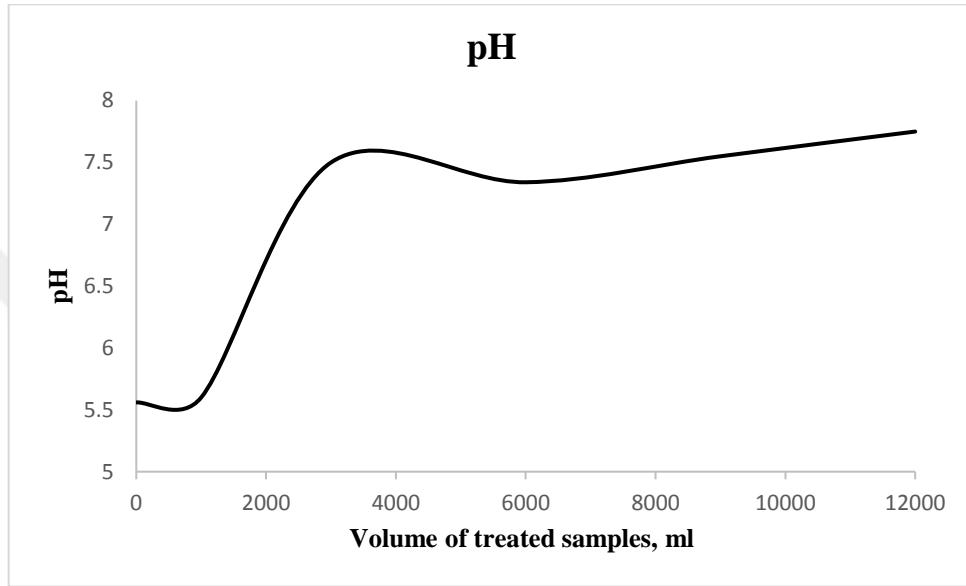


Figure 3.4: The pH before and after IE process.

3.1.2. COD Removal of Raw textile wastewater

The Chemical Oxygen Demmand (COD), is an indicative measure amount of oxygen that can be consumed by reactions in a measured solution. (COD) was measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time. A commonly utilized oxidant in COD assays was potassium dichromate ($K_2Cr_2O_7$) which was used in combination with boiling sulphuric acid (H_2SO_4). Because this chemical oxidant is not specific to oxygen-consuming chemicals that are organic or inorganic, both of these sources of oxygen demand are measured in a COD assay. Figure 3.5 shows the COD of RTWW before and after IE with 25 ml of anion resin (OH^-) at pH 5.65.

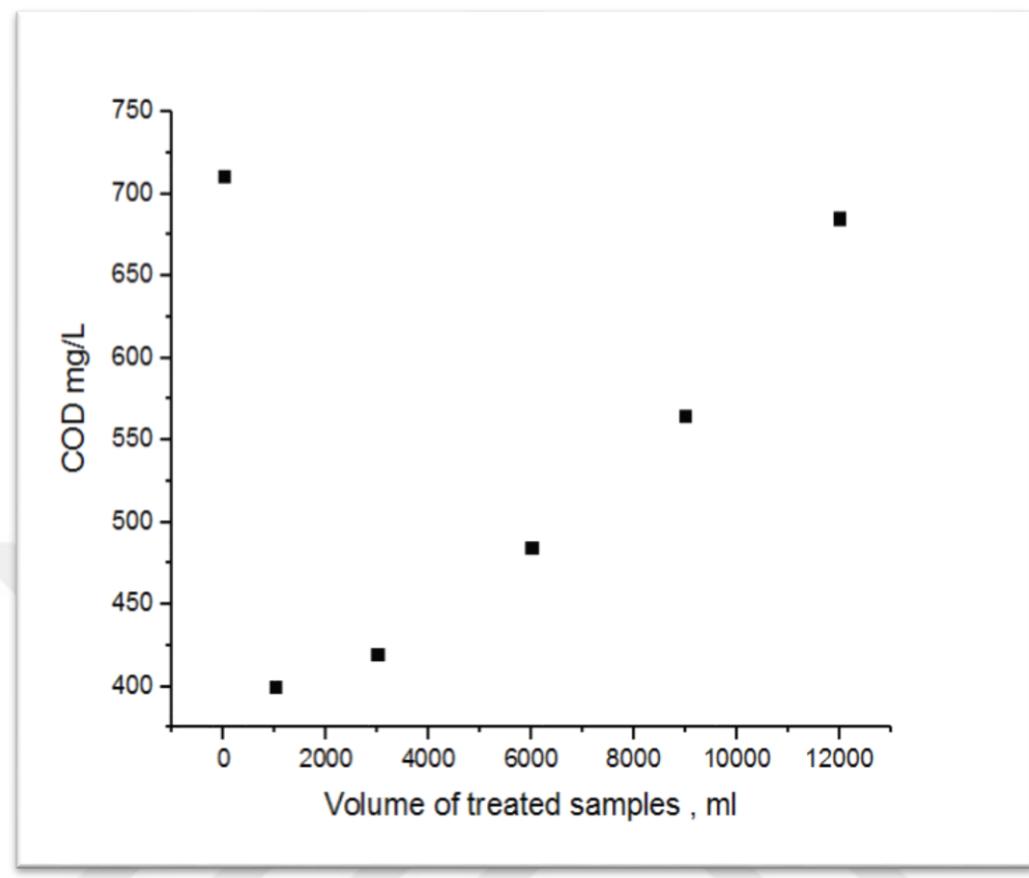


Figure 3.5: COD of Raw textile wastewater before and after IE with 25 ml of anion resin.

3.1.3. TOC Removal of Raw textile wastewater

Total organic carbon (TOC) was conducted with Shimadzu TOC-VWP instrument with diluted samples. The effluent of Raw textile wastewater are often accompanied high values of TOC due to the presence of associated dye chemicals. Several methods are available for decolorizing textile wastewater, including Ion Exchange. Results showed the Batch process was very effective as a pre-treatment method for TOC reduction to textile wastewater. TOC levels was reduced after applying IE process to 6.18 mg/L. Figure (3.6) shows TOC of RTWW before and after IE with 25 ml of Anion resin (OH^-) at pH 5.65.

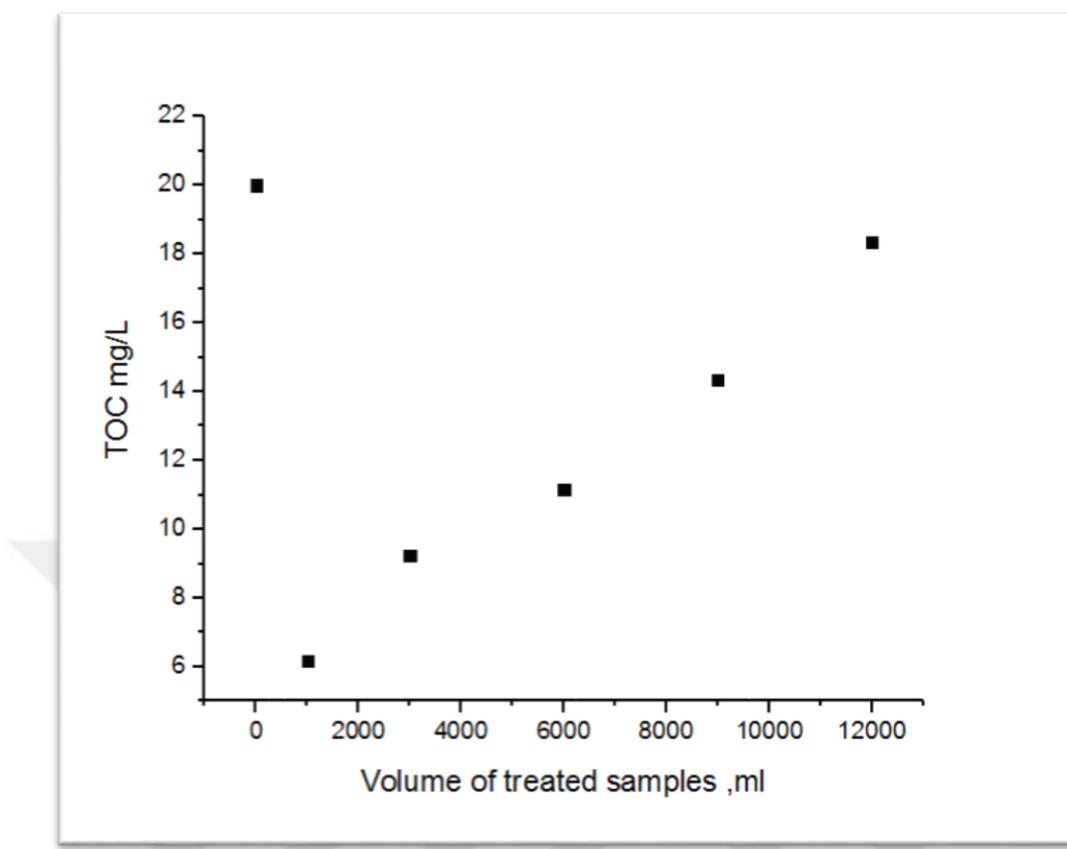


Figure 3.6: TOC of Raw textile wastewater before and after IE with 25 ml of anion resin.

3.1.4. Detoxification of Raw textile wastewater as a pretreatment method.

3.1.4.1. *Detoxification of Raw textile wastewater (RTWW) By using Daphnia magna.*

The toxicity of Raw textile wastewaters (RTWW) was tested using of 24 h born *Daphnia magna* at diffrent concentration as described in Standard Methods. All solutions were prepared in budi stilled water at pH 8. Toxicity experiments were carried out with five daphniids utilized in each test beaker with 50 ml of effective volume. The results were assessed on the basis of paralysis obtained by dividing the number of fixed animals on total animals. The toxicity of wastewater samples was described as toxic when paralysis was higher than 50%. *D. magna* water flea has been evaluated as a good object to test the toxicity of effluents in wastewater and dyes. Toxicity assays, *D. magna* are standardized and reliable while biodegradability depends heavily on the biomass selected and the results obtained are usually difficult for other researchers to reproduce. The effectiveness of the processes is measured by the number of

plankton that died before and after applying IE process. Results were expressed as a percentage of immobilized animals after 24 h and 48 h. During toxicity removal experiments, the toxicity of the treated effluent was performed at 25 and 50% dilution before and after applying this process. RTWW resulted that has not a big different in toxicity even at 50% dilution because of this the toxicity test will be evaluated by Microtox.

3.1.4.2. Detoxification of Raw textile wastewater (RTWW) By using Microtox.

The toxic response of commonly used non-ionic surfactants with different bioluminescence inhibition assays Microtox was established. The 50% effective concentration (EC₅₀) values were determined for every standard substance using each assay, together with toxicity units. The (EC₅₀) was calculated by device as shown in Figure (3.7).

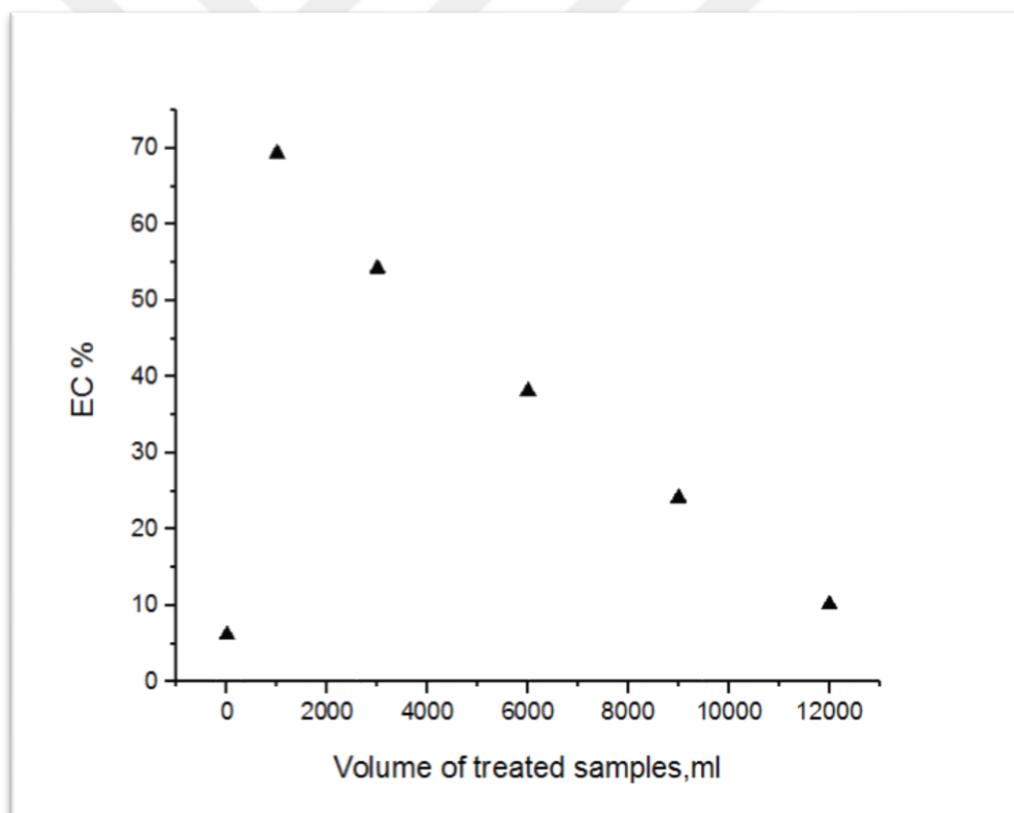


Figure 3.7: Detoxification of Raw textile wastewater before and after IE with 25 ml of anion resin (OH⁻), pH 5.65.

When the EC levels are high, this means that the textile wastewater is low in toxicity. In contrast, the water is highly toxic when the EC values are low. In this study the RTWW and the toxicity study before and after the application of IE we observed that the Raw textile wastewater was low in toxicity.

3.2. DECOLORIZATION OF SYNTHETIC DYES AS A PRETREATMENT METHOD

3.2.1. Decolorization of Black Azo dyes.

Pre-treatment with anion resin(OH⁻) was practical to eliminate of color from Black azo dyes. (IE) was applied for different samples. Pre-treatment of the textile wastewater is carried out using Batch process. The final treatment effluent has thus been carried out. The results of analyzes before and after IE process are summarized in Table 3.2. There is not much change in conductivity, pH, TDS and salinity. The color value was reduced to 75 % for 465 nm by IE process as shown in Figure (3.8). The results obtained after apply IE process shows a good performance of this process for decolorization from synthetic Black azo dyes.

Table 3.2 : Characterization results of Black azo dyes.

Parameter	Range
pH	9.25-13.5
Conductivity (μs/cm)	7.80-8.90
Salinity (mg/L)	4.88-5.65
TDS (mg/L)	4.17-4.21
Color (pt, co)	1000-4000

The Color was measured before and after applying IE process as shown in Figure (3.9) and absorbance measurements were achieved on the Batch process effluent after the run and the absorbance scan values were given in Figure(3.10). According to these results, it is practical that at the effluent, it is knowingly detached in the color of the RB5. The performance of this process is very effective for removal color from synthetic dyes and reduced the color value to 1000 pt, co.



Figure 3.8: Decolorization of Black azo dyes by IE process.

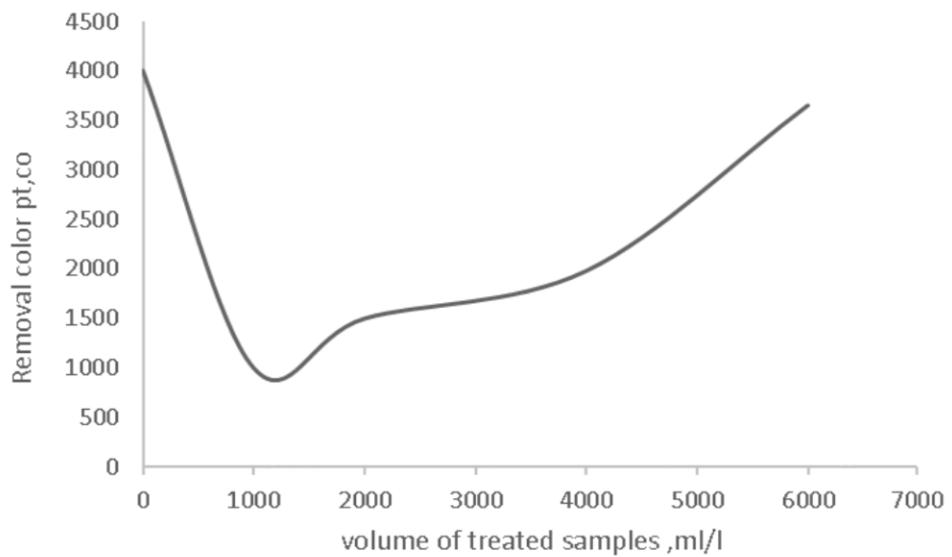


Figure 3.9 : Color removal from Black azo dyes by IE process.

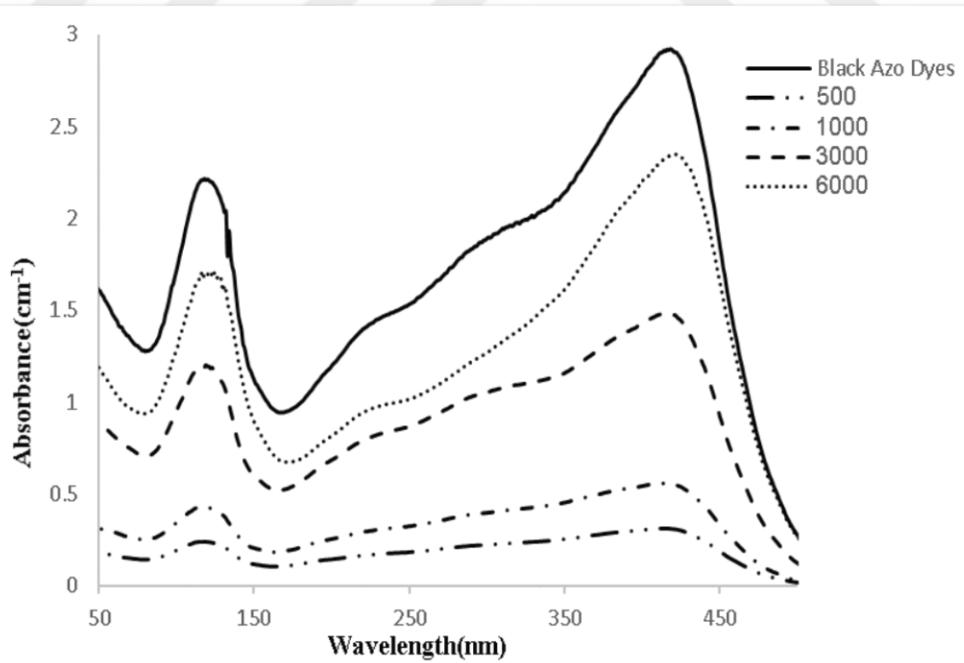


Figure 3.6 : Absorbance measurements before and after IE.

3.1.2.1. Optimization of different concentration from Black azo dyes.

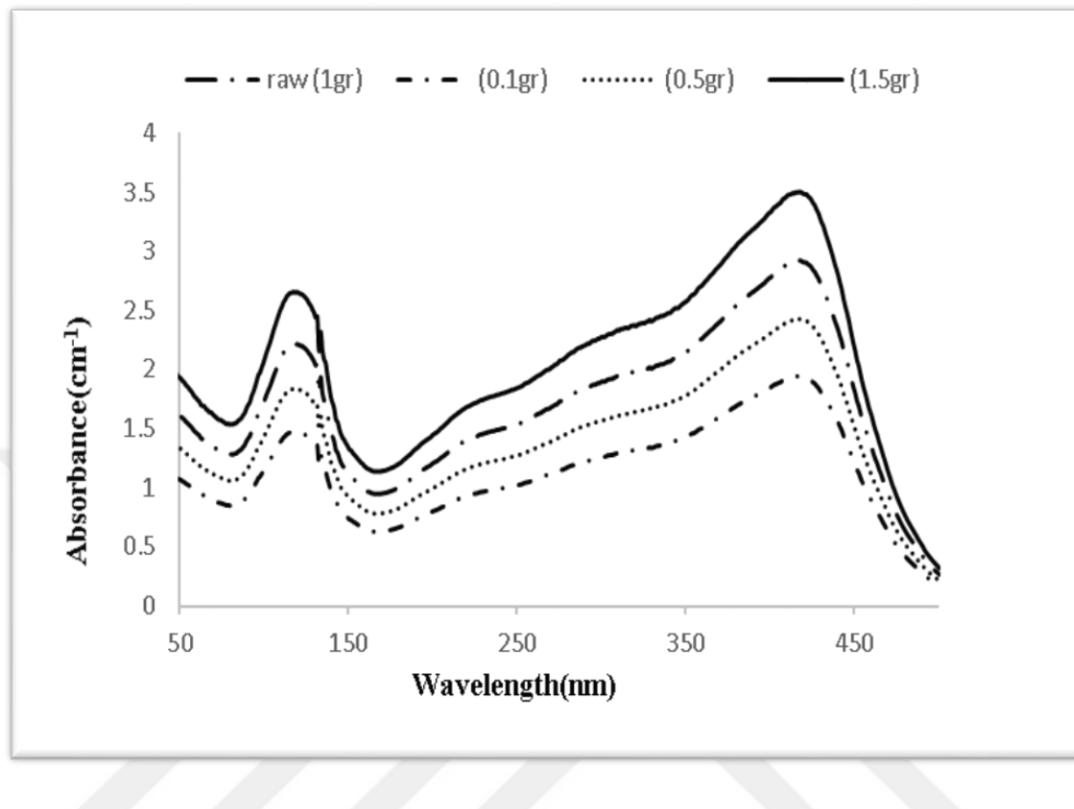


Figure 3.7: Optimization of different concentration from Black azo dyes.

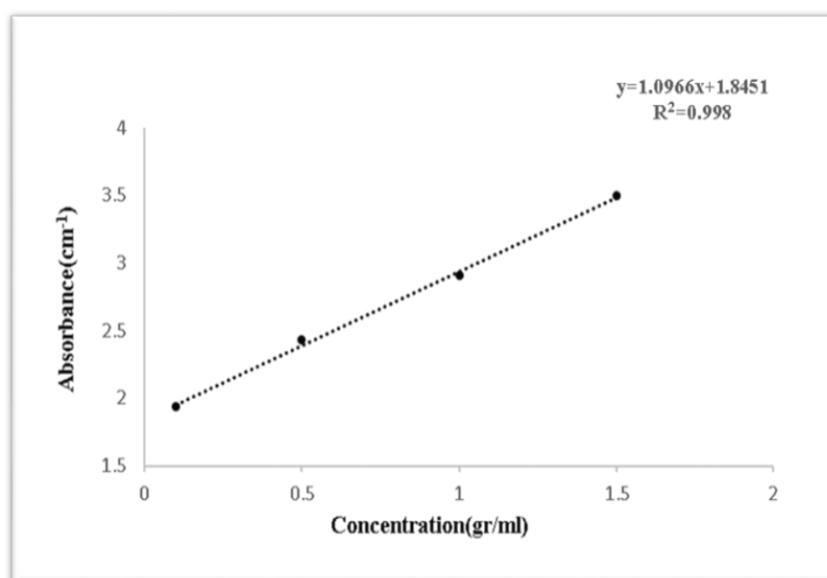


Figure 3.8: Correlation between different concentration and absorbance.

3.2.2. pH

The pH values of Black azo dyes were continuously monitored during IE system (Batch process). At the end of the study, the pH value of the synthetic dyes was increased to 13.5 this is because of anion resin as shown in Figure (3.13).

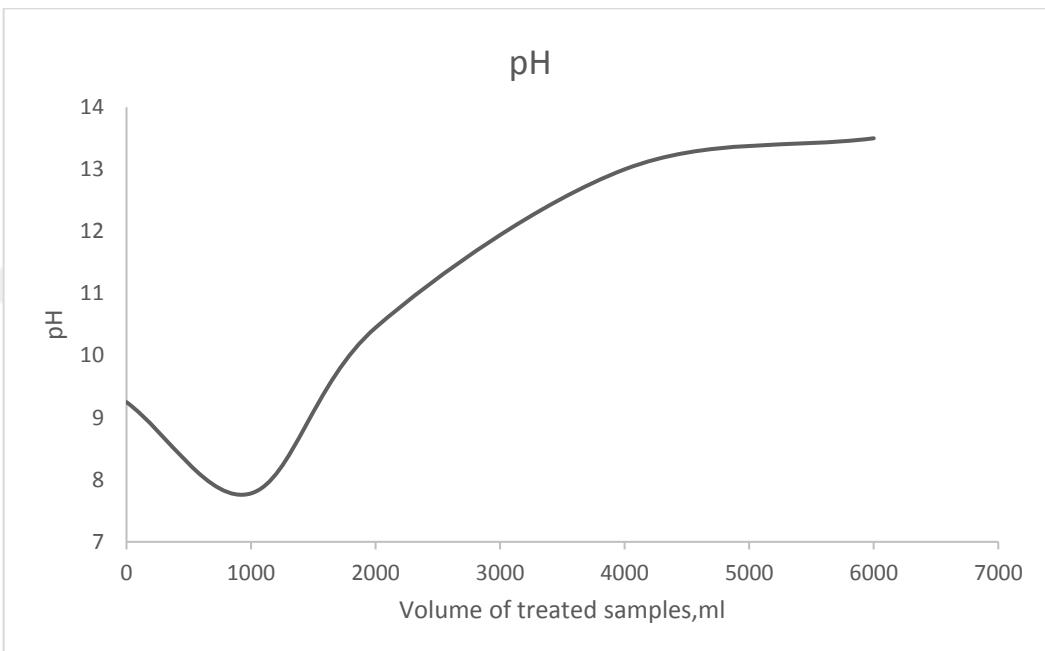


Figure 3.9: The pH before and after IE process.

3.2.2. COD Removal of Black azo dyes

COD was measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time. According to the results of COD removal from synthetic dyes after applying (IE) process has a good removal and the COD reduced to 200 mg/L. Figure 3.14 shows the COD values of RB5 before and after IE process.

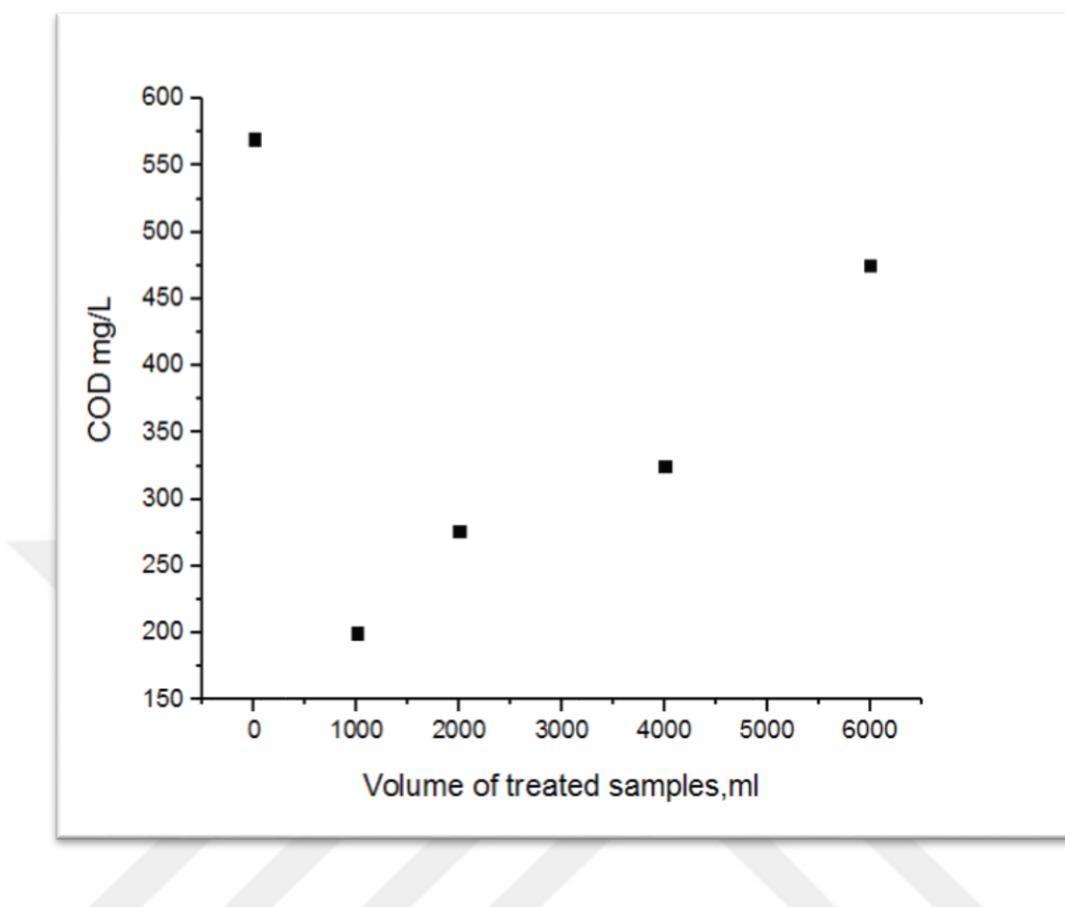


Figure 3.10: COD values of RB5 before and after IE.

3.2.3. TOC Removal of Black azo dyes.

TOC was conducted with Shimadzu TOC-VWP instrument with diluted samples if it is very concentrated. The effluent of synthetic azo dyes (RB5) are often accompanied high values of TOC due to the presence of several chemicals. Diverse methods are available for decolorizing textile wastewater, including Ion Exchange. Results showed the Batch process was very effective for TOC reduction. TOC levels were reduced after applying IE process to 11 mg/L. Figure 3.15 shows the TOC values of RB5 before and after applying IE.

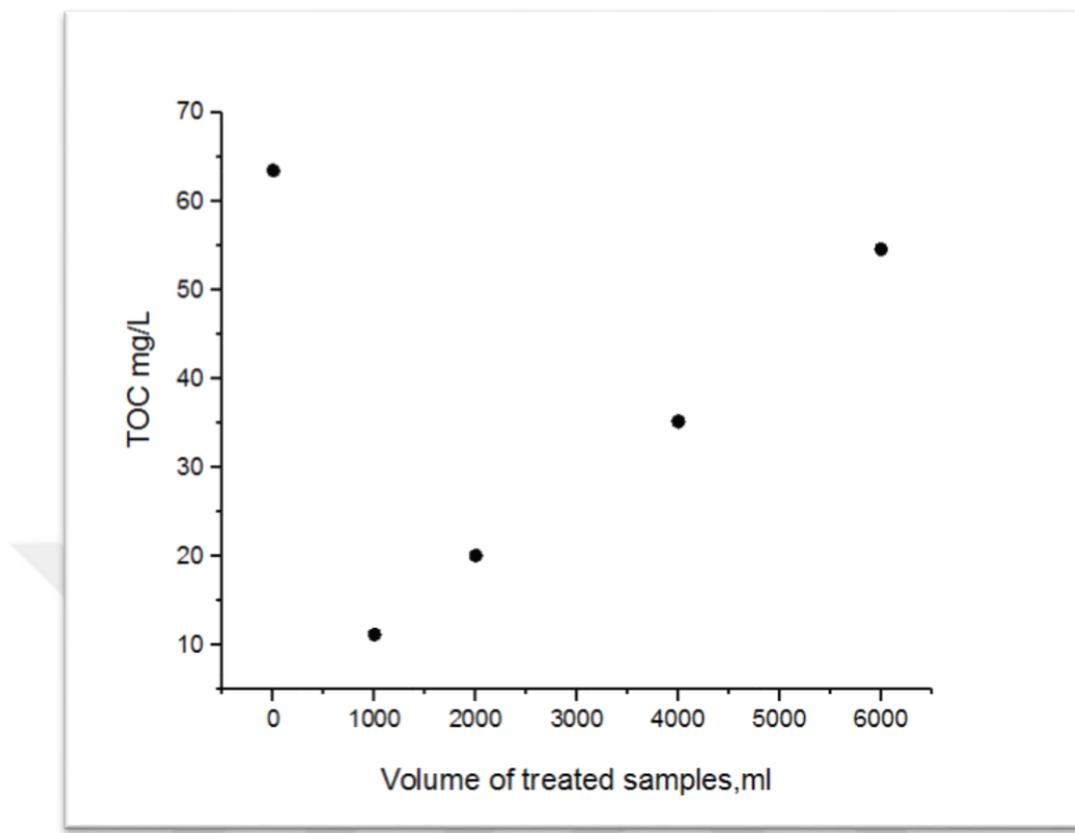


Figure 3.11: TOC values of RB5 before and after apply IE.

3.2.4. Detoxification of Synthetic dyes as a pretreatment method.

3.2.4.1. *Detoxification of Black azo(RB5) dyes by using Microtox.*

Microtox was established for toxic response and the (EC₅₀) was calculated. The 50% effective concentration (EC₅₀) values were determined for every standard substance using each assay as shown in (Figure 3.16).

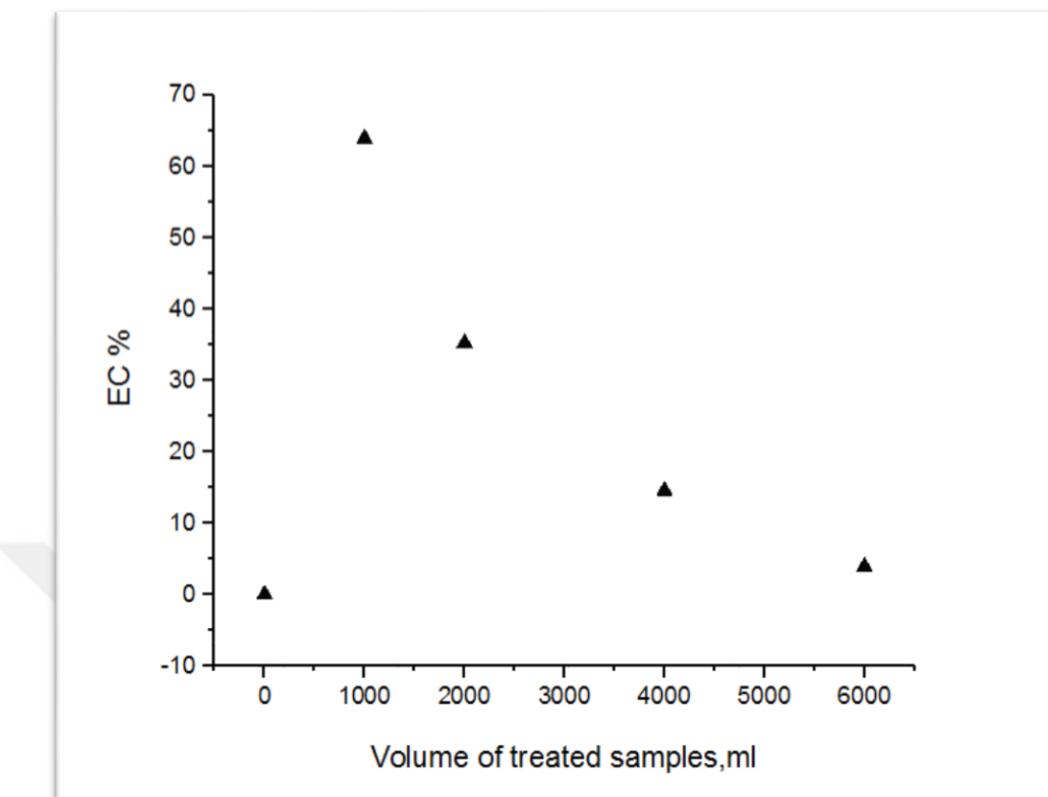


Figure 3.12: Acute toxicity before and after apply IE by using Microtox.

When the EC levels are high, this means that the RB5 is low in toxicity. In contrast, the water is highly toxic when the EC values are low. In this study the RB5 and the toxicity study before and after the application of IE we observed that the Synthetic dyes was low in toxicity.

3.3. DECOLORIZATION OF BIOLOGICAL TEXTILE WASTEWATER (BTTWW).

3.3.1. Decolorization of BTTWW after IE process.

Biologically treated textile wastewaters were subjected to color removal using an anion resin (OH^-). The color was reduced after applied IE process as shown in Figure (3.17). The results obtained after apply IE process shows a good performance of this process for decolorization from Biological textile wastewater (BTTWW).

Table 3.3: Characterization results of BTTWW.

Parameter	Range
pH	7.80-9.68
Conductivity(µs/cm)	6.78-7.80
Salinity (mg/L)	3.78-4.33
TDS (mg/L)	4.6-4.11
Color (pt, co)	150-1780

The performance of this process is a good efficiency for removal color from Biological textile wastewater and reduced the color value to 150 pt, co. The removal efficiency was achieved over 90 %. As shown in Figure (3.18) the color values were realized on the IE Process. For the absorbance measurements were given in Figure (3.19). According to these results, it is practical that at the effluent, it is expressively removed in the color of the biological textile wastewater (BTTWW). As we discussed earlier, removing of the color from textile wastewater samples from the plant after biological treatment yields good results and the resin can absorb the molecules from the surface.

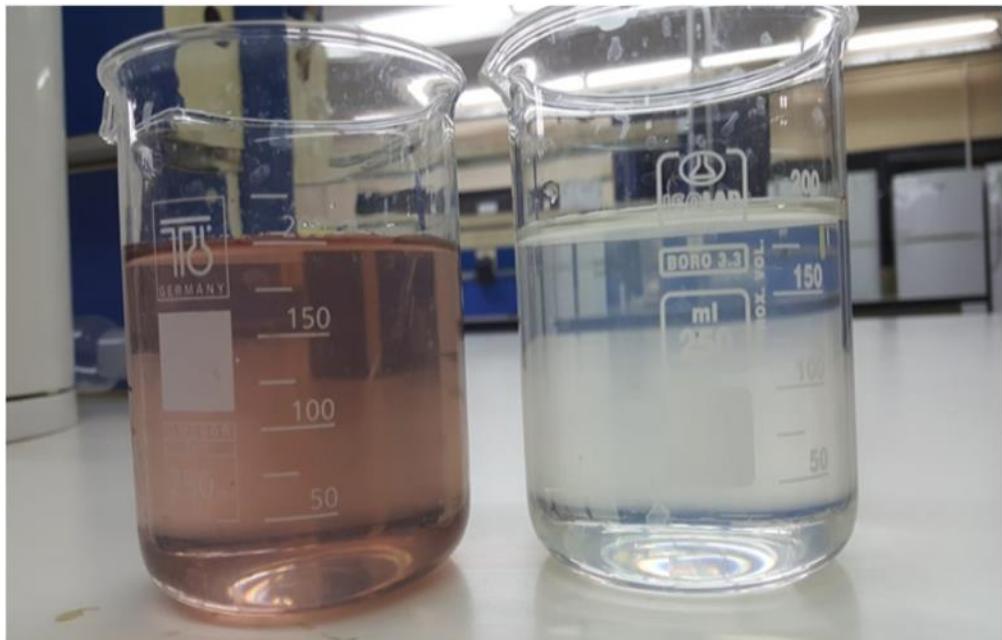


Figure 3.13: Decolorization of biological textile wastewater by IE process.

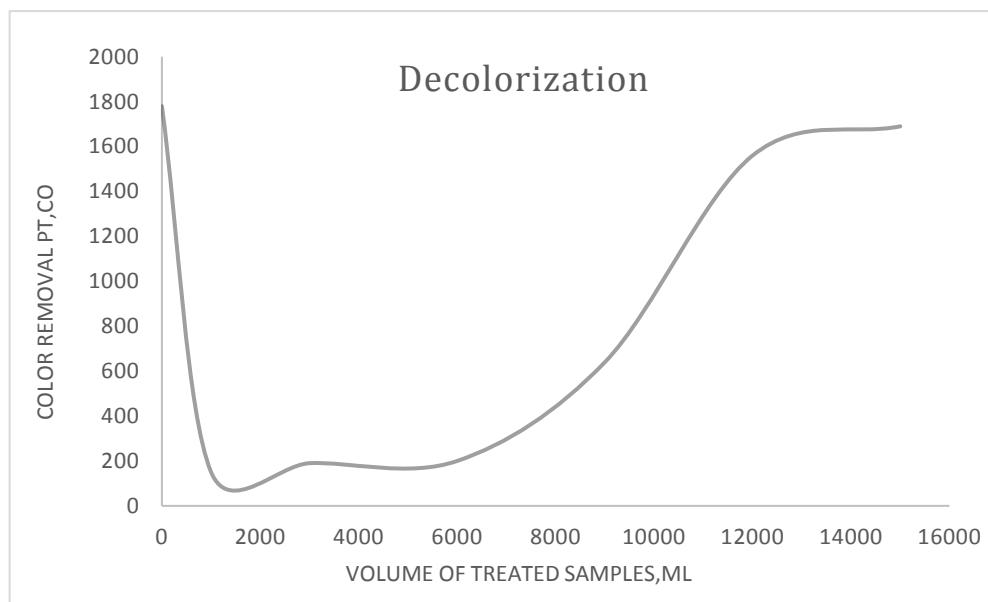


Figure 3.18: Color removal from BTTWW by using 25 ml from anion resin (OH^-) at pH 7.80

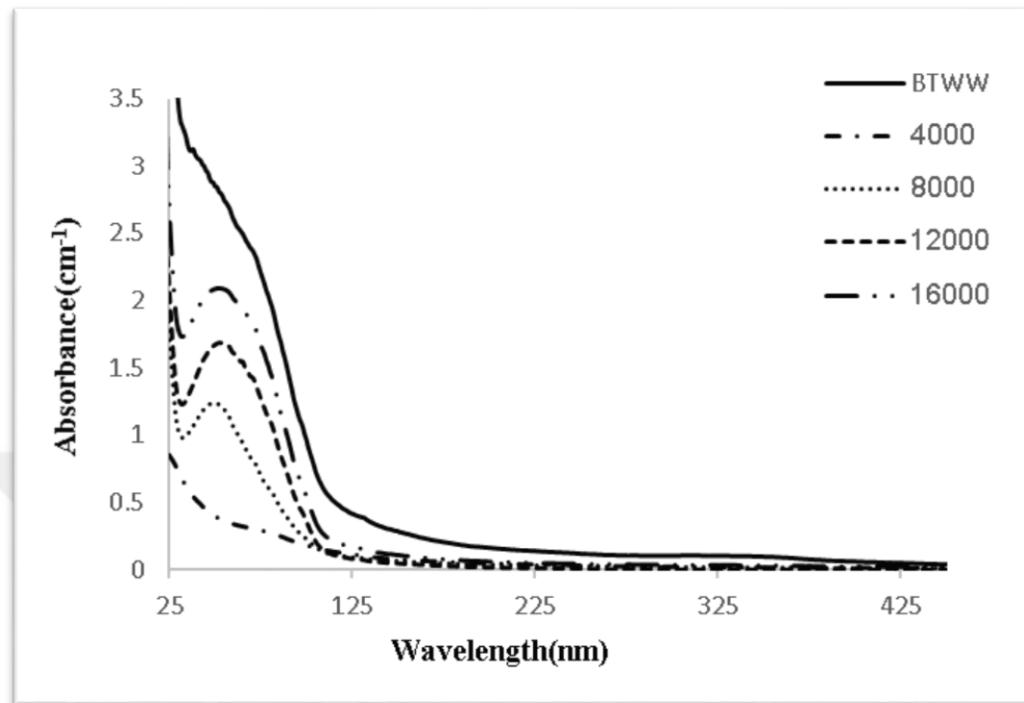


Figure 3.19: Absorbance of BTTWW before and after apply IE Process.

3.3.1.1. pH

pH values of biological textile wastewater were continuously monitored during IE system. At the end of the study, the pH value of the BTTWW was increased to 9.20. The anion resin exchange (OH^-) has a good performance for increasing the pH values because it gives anions to the biological textile wastewater after applying this process as a pretreatment method for decolorization of textile wastewater, and BTTWW has a good result after this process as shown in Figure (3.20).

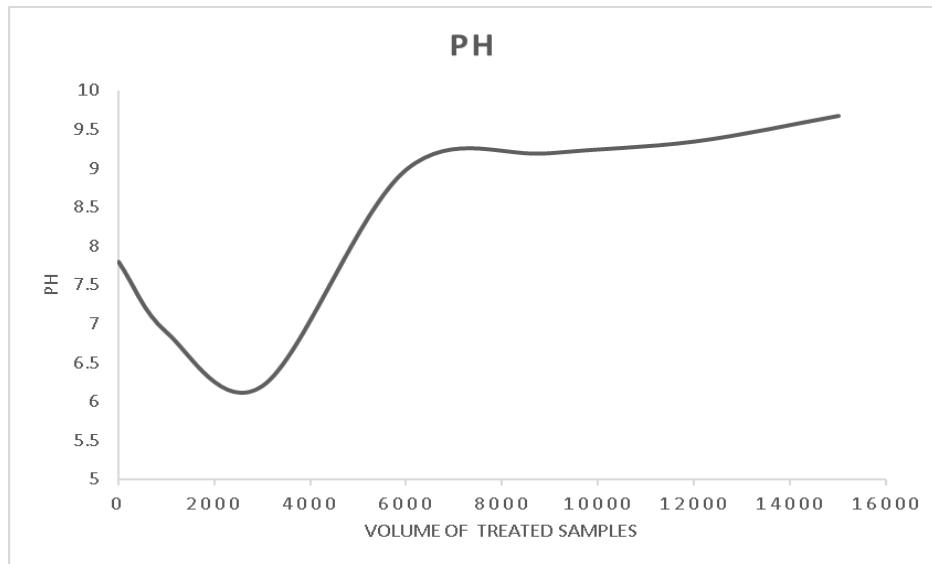


Figure 3.14: The pH values of BTTWW before and after IE process.

3.3.2. COD Removal of Biological treated textile wastewater.

COD assays is potassium dichromate ($K_2Cr_2O_7$) which is used in combination with sulphuric acid (H_2SO_4) for measuring the COD values before and after applying IE process and has a good performance for reduced COD values to 95 mg/l. Figure 3.21 shows the COD values of BTTWW before and after IE.

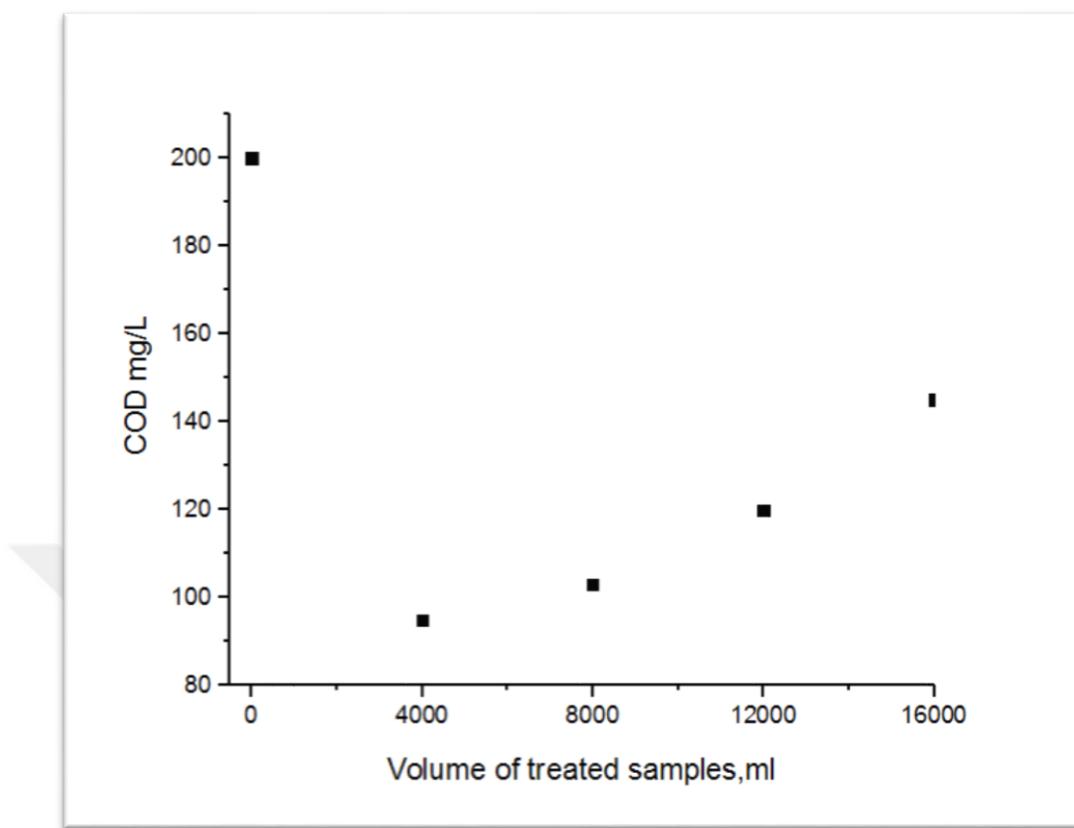


Figure 3.15: COD values of BTTWW before and after IE.

3.3.3. TOC Removal of BTTWW.

The Total organic carbon was conducted with Shimadzu TOC-VWP instrument with diluted samples if it is very concentrated. The effluent of Biological treated textile wastewater is often accompanied high values of TOC because of the presence of several chemicals. Results showed the Batch process was very effective for TOC reduction to BTTWW. TOC levels were reduced after applying IE process to 5.98 mg/L. Figure 3.22 shows the TOC values of BTTWW before and after applying IE process.

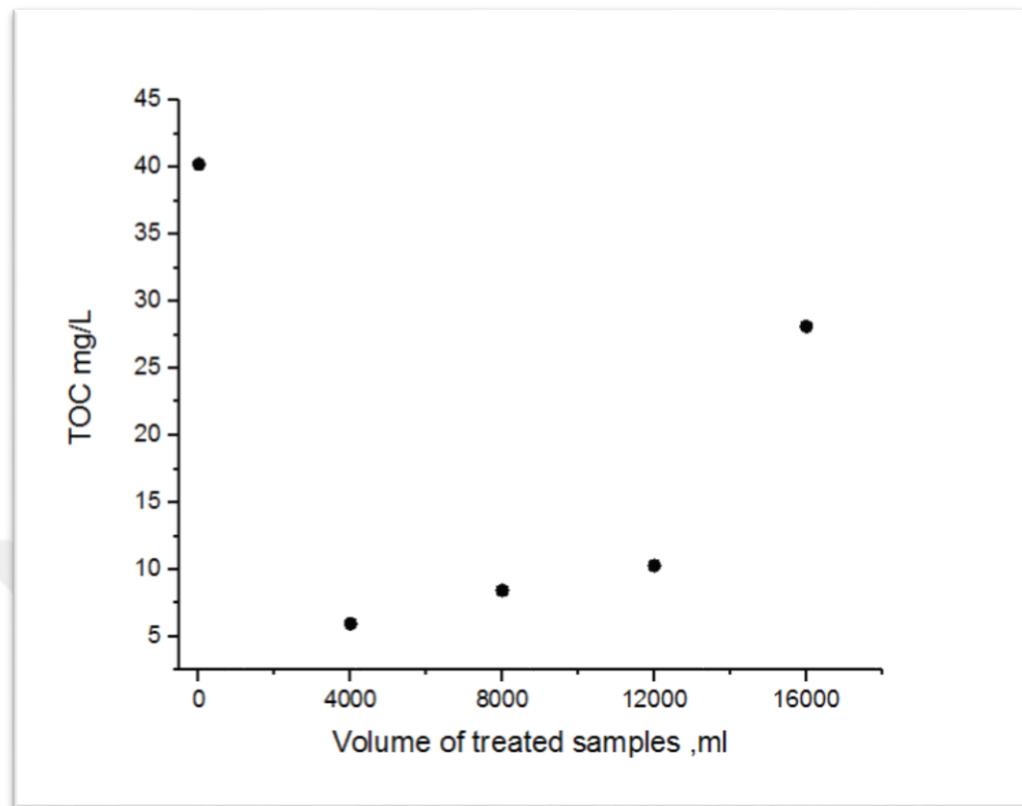


Figure 3.16: TOC values of BTTWW before and after IE.

3.3.4. Detoxification of BTTWW by using Microtox as a pretreatment method

If the EC levels are high, this means that the BTTWW is low in toxicity. In contrast, the water is highly toxic when the EC values are low. In this study the performance of IE process with BTTWW for detoxification .The results observed that the RTWW and Synthetic dyes were low in toxicity.However, the best performance of IE system for detoxification in BTTWW due to the EC was equals to 95 % after applying this process as shown in Figure (3.23) .

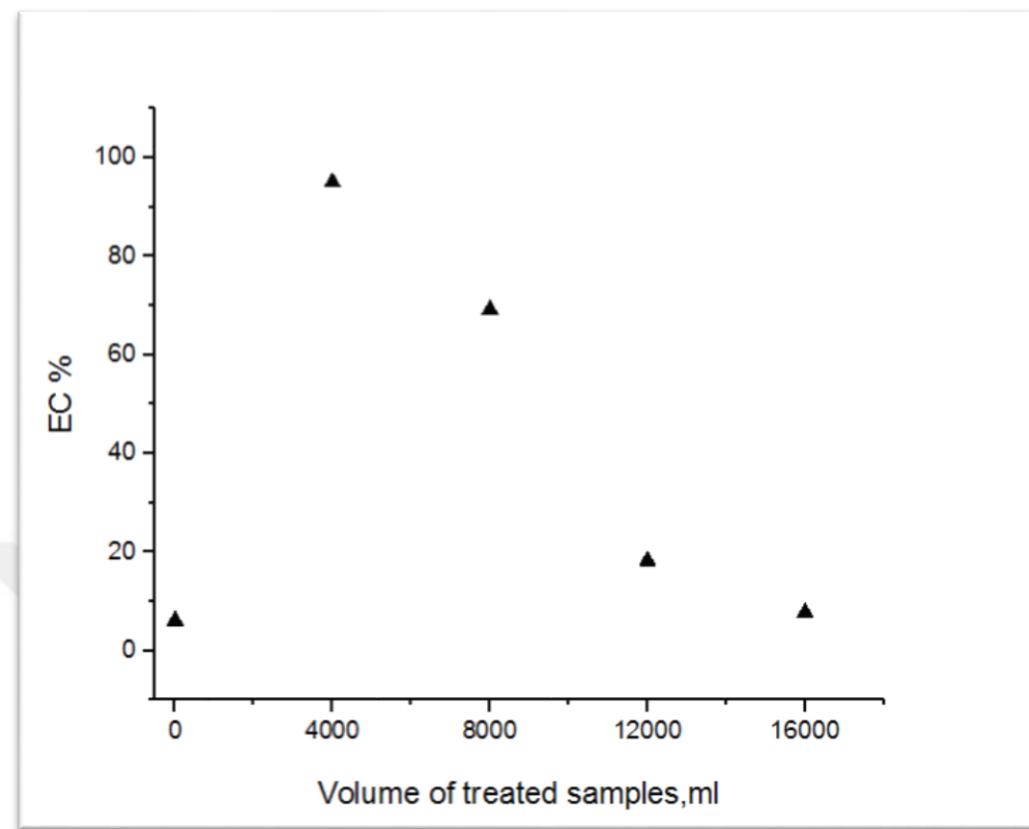


Figure 3.17: Detoxification of BTTWW before and after IE by using Microtox.

3.4. REGENERATION OF ANION RESIN (OH⁻).

Ion exchangers are processes that are widely used in many applications removal of color one of the most common and have a low operating cost due to regeneration reasons. The removal of color with ion exchangers has been a challenge for many years. However, anionic dyes react strongly with ionic modifiers. Regeneration of the ion exchangers with conventional anionic or basic solutions is therefore not possible. Regeneration by chlorination alone or color removal from waste is not possible. Chlorine reacts not only with paints but with other organics found in textile wastewaters.

3.4.1. Regeneration with Chlorine and <5% NaOH at 20 °C.

In order to regenerate the exhausted ion exchanger, in the case of conventional (OH⁻) resins, by added active chlorine Sodium hypochlorite with NaOH (<5%) at 20 °C (Figure 3.24).

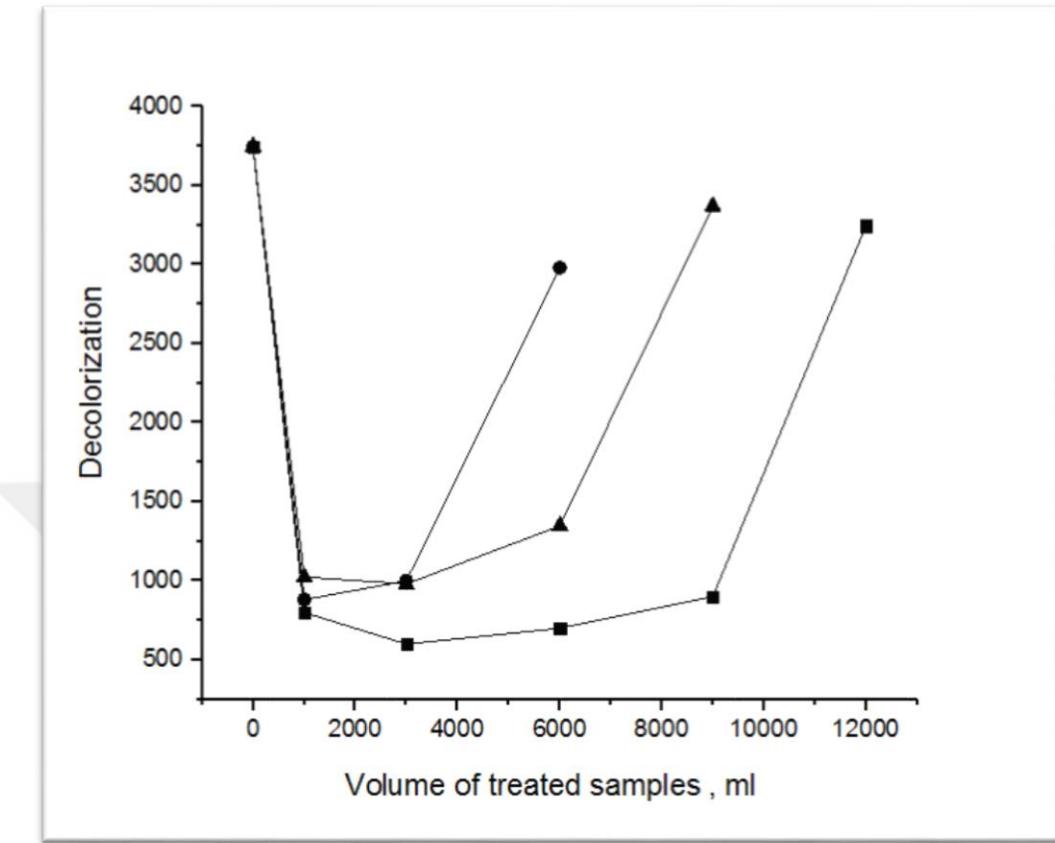


Figure 3.18: Apply Regeneration with Chlorine and NaOH at (20 $^{\circ}$ C) and (40 $^{\circ}$ C) .

As we can observed in Figure (3.24) the cold condition of regeneration was working but its not good as when increas the temperature in the range of 30-40 $^{\circ}$ C . The best performance of anion resin after applied Hydrothermal Chlorination Method for regeneration when increase the temperature in order to sped in regeneration of resin and to obtain good results

3.4.2. Regeneration with the same reagent (Chlorine and <5% NaOH at 40 $^{\circ}$ C).

In order to regenerate the exhausted ion exchanger, in the case of conventional (OH $^{-}$) resins, after more than 90% color removal from textile waste water, 40 $^{\circ}$ C active chlorine is added with (<5%) NaOH. The active chlorine compounds are oxidized, and the decomposition of the stain is followed by the ion exchange of the OH $^{-}$ ions present in the water to the ion-exchange surface of the ion exchanger, while at the same time the ion exchangers are prevented from being damaged by the active chlorine. Since the process can be regenerated and reused many times with Raw textile wastewater, the efficiency of removal the color is very high even when repeated regeneration several times as shown in Figure (3.25) .

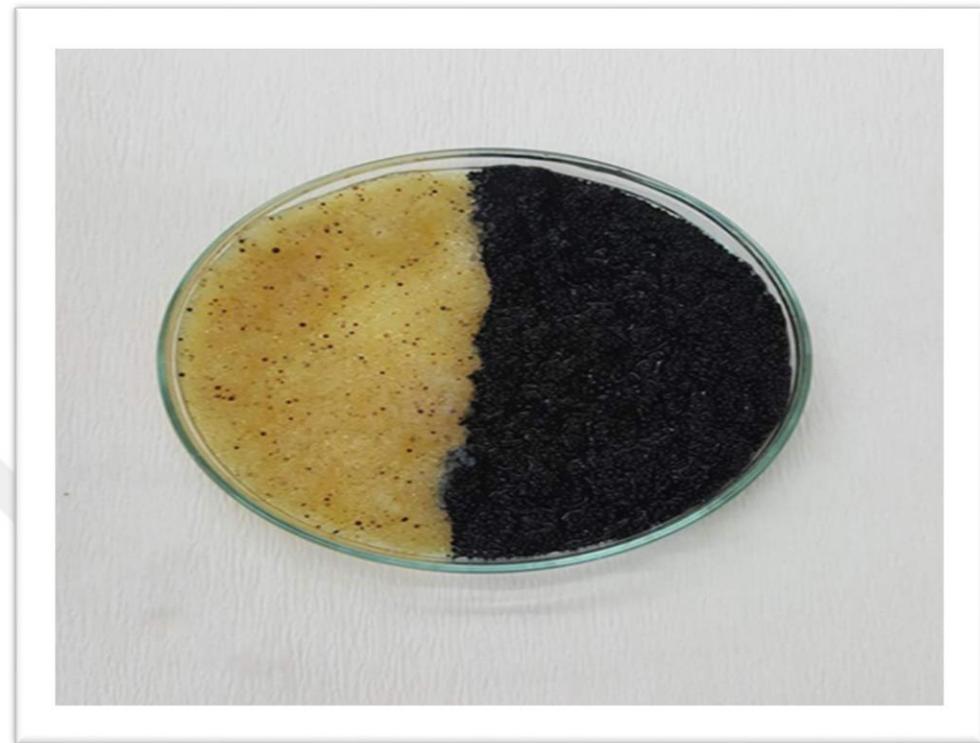


Figure 3.19: The anion resin (OH⁻) before and after Regeneration with Chlorine and <5% NaOH at 40 °C.

3.4.3. Decolorization of Raw textile wastewater after regeneration with the same reagent.

The color removal performance of the anion ion exchanger (25 ml) after 8 regenerations in untreated textile wastewater (RTWW) as shown in Figure (3.26). With the applied thermal chlorination regeneration, and use mixed solution of Chlorine and <5% NaOH at (40 °C). A total of 40.000 liters (40 m³) of textile wastewater with 25 ml of anionic resin was treated with the same efficiency as shown in Figure (3.27) .



Figure 3.20: The performance of the 25 ml of anion resin (OH^-) used after regeneration (8 regeneration) with Chlorine and $<5\%$ NaOH at $(40\text{ }^{\circ}\text{C})$.

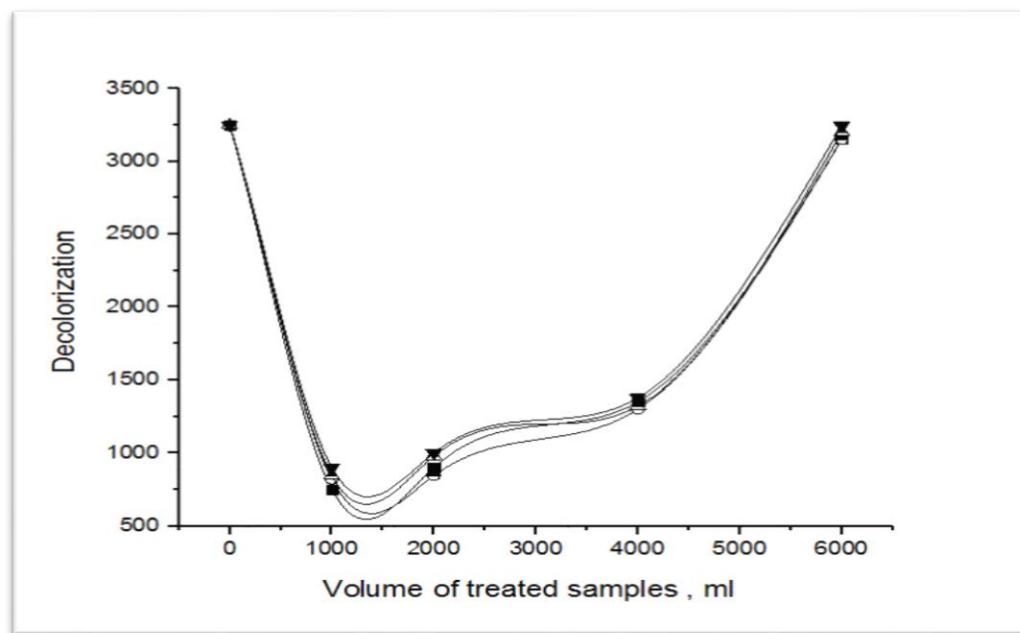


Figure 3.21: The color removal performance of the anion ion exchanger (25 ml) after 8 generations in untreated textile wastewater with chorine and $<5\%$ NaOH at $(40\text{ }^{\circ}\text{C})$.

Since the process can be regenerated and reused many times, the color removal operating costs are reduced by about 70 % according to the other color removal methods in practice .Because the installation cost of the system is low, it requires 90 % lower investment cost than other application. As shown in Figure (3.27) the color was high before applying this method and after thermal regeneration the anion resin can remove the color from textile wastewater.In addition the efficiency of removal was very good and we can repeated it several times . This method was achieved 8 times with the same reagent in order to investigate the good performance and at the same time to maintain the lower cost than other methods. Upon application of thermal regeneration by IE process, substantial increases for color removal values (Pt-Co) were achieved. In a similar manner, also in this study, the cost could be explained by the calculation of the cost of materials that used for thermal regeneration and compared with other methods. This method for regeneration found to be very efficient to meet the reuse standards.In addition, this method was lower in cost than other applications. Due to the cost of treatment regeneration could also be a wastewater reuse strategy in the textile industries.

3.4.4. COD Removal of Raw textile wastewater after apply regeneration.

COD was measured according to standard methods. The results of COD values of Raw textile wastewater after applying regeneration process of anion resin has a good reduction of COD levels even after repeated regeneration 8 times, the resin has the same efficiency in COD reduction from RTWW as shown in Figure (3.28).

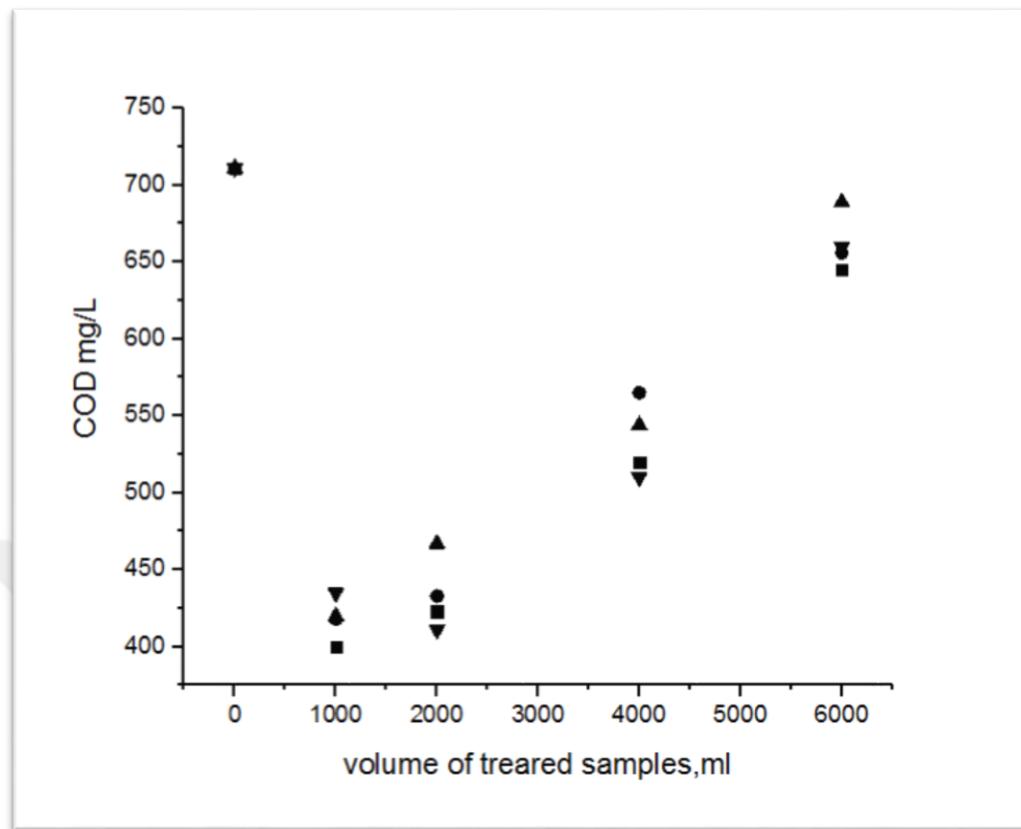


Figure 3.28 : The performance of depleted anion resin (25ml) with Raw textile wastewater after 8 regenerations in untreated textile wastewater with chorine and <5% NaOH at 40 °C for COD Removal.

3.4.5. TOC Removal of Raw textile wastewater after regeneration.

TOC was measured as a parameter to investigate the performance of resin before and after regeneration. The results of TOC values of Raw textile wastewater after applying regeneration process of anion resin has a good reduction of TOC levels even after repeated regeneration 8 times, the resin has the same efficiency in TOC reduction from RTWW as shown in Figure 3.29).

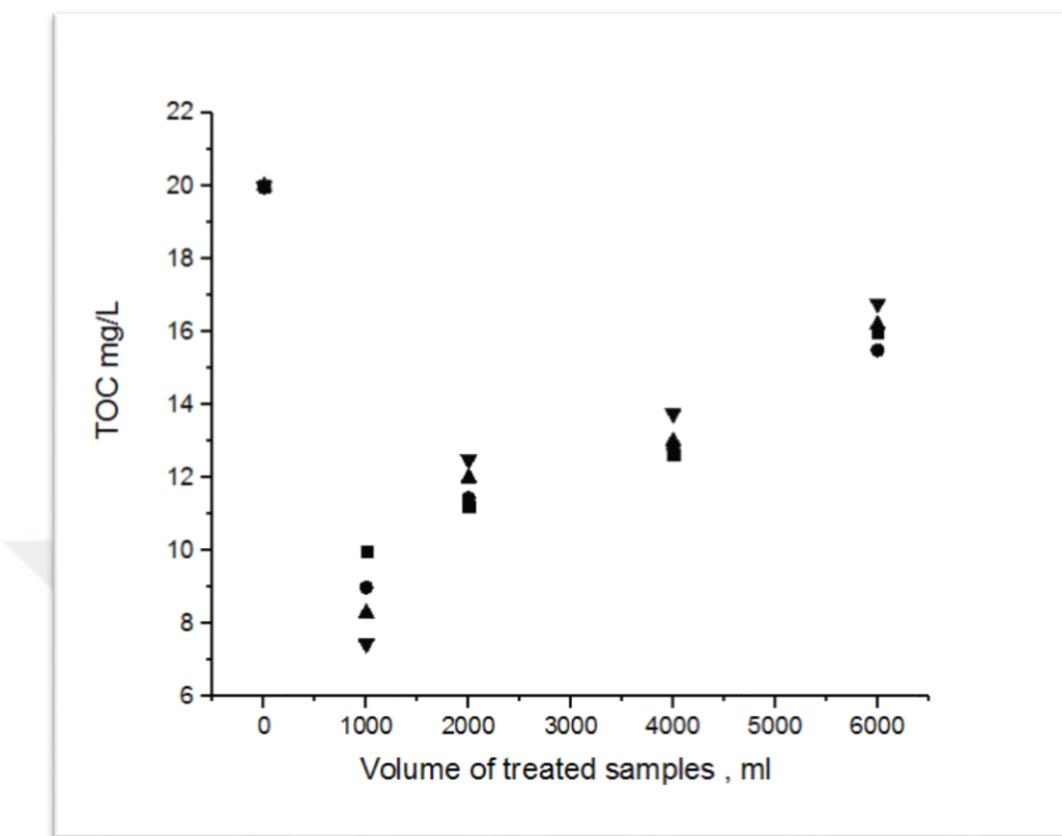


Figure 3.29: The performance of depleted anion resin (25ml) with Raw textile wastewater after 8 regenerations in untreated textile wastewater with chlorine and <5% NaOH at 40 °C for TOC removal.

3.4.6. Detoxification of Raw textile wastewater after regeneration.

These results revealed that RTWW induced complete toxic effect after 5 min exposure and 15 min showed the EC₅₀ value was 40.03 after regeneration was low toxic, while high toxic effect with low EC₅₀ equals to 6.18 $\mu\text{g L}^{-1}$ at initial Raw textile wastewater samples as shown in Figure (3.30).

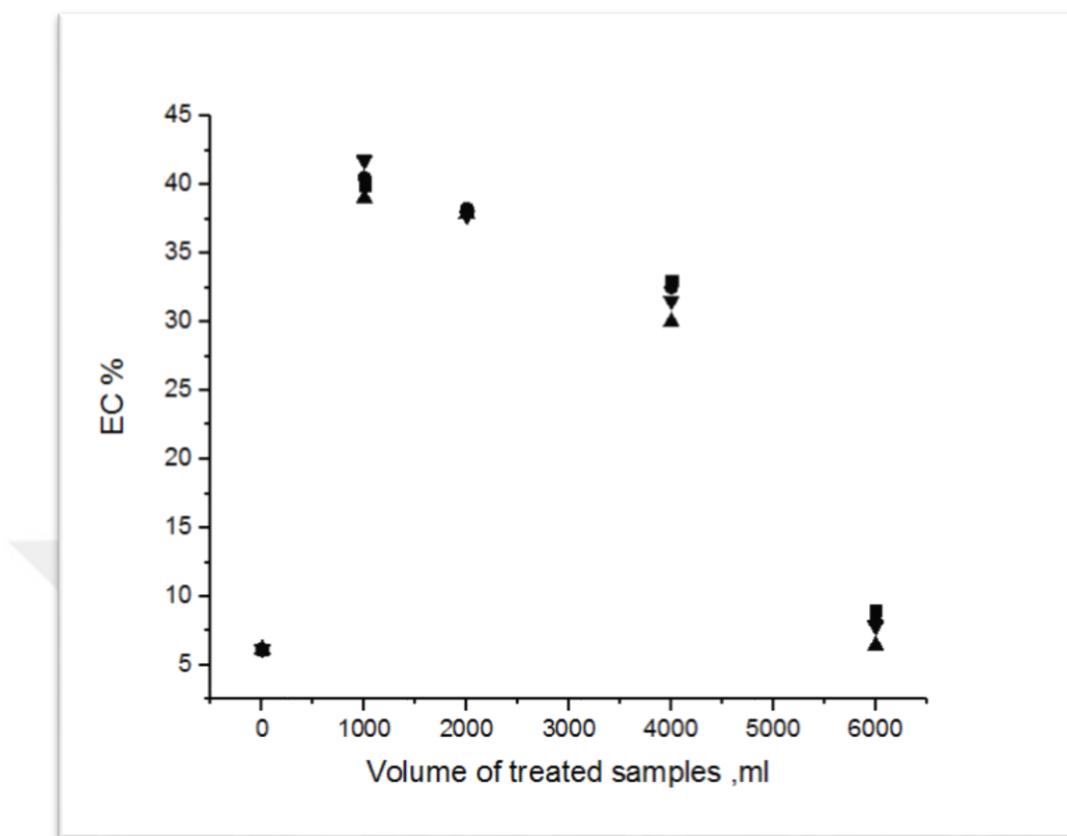


Figure 3.30: Detoxification of depleted anion resin (25ml) with Raw textile wastewater after 8 regenerations with chorine and <5% NaOH at 40 $^{\circ}\text{C}$.

The application of thermal regeneration of exhausted anion resin to enhanced to the treatment efficiency by IE process with RTWW by utilizing a mixed solution from chorine and <5% NaOH at (40 $^{\circ}\text{C}$). Although the anionic coatings are highly needed due to the irreversible blockage by covering the membrane surface in membrane wastewater removal units, the use of wastewater recycling systems in the textile sector is not widespread. This process will allow the membrane treatment systems to be used for textile wastewater, since the anionic dyeing that causes membrane blockages in the anionic structure is eliminated with a yield of over 98%. It is possible to provide effective and economical method.

4. DISCUSSION

The aim of this research was to investigate the performance of Ion-Exchange process (Batch process) to remove the color, COD, TOC and Toxicity from textile wastewater effluent from Gümüşsu Arıtma corporation located at Denizli, Turkey before and after treatment as a pretreatment method . It is known that IE process is very efficient method. Therefore, in this study Raw textile wastewater, Synthatic azo dyes and biological treated textile waste water were utilized as a benchmark for comparison.

Real textile wastewater (RTWW):

The decolorization of RTWW before and after applying IE process was shown in Figure (3.2).As seen the color was decreased from 3250 to 800 (pt, co) as shown in Figure (3.3). The pH values was increased to 7.75 due to the anion resin (OH^-) as shown in Figure (3.4). In a similar manner, (COD) was performed to investigate the performance of IE process. As shown in Figure (3.5).The COD values were decreased from 711 to 400 mg/L in the case of RTWW after utilizing this system. For (TOC) was also applied. Figure 3.6 depicts the (TOC) levels in to RTWW before and after applying IE process the value of TOC was 6.18 mg /L. In order to study validity of IE process to remove the toxic substances that causes mutagenic and carcinogenic effects from the textile wastewater samples the Daphnia magna was utilized as indicator for toxicity test to see the effect of samples on daphnids. In (RTWW) case there was not a big difference before and after Batch process. Therefore, acute toxicity was performed by using Microtox (Basic test). For (RTWW) the (EC%) was calculated by Microtox device as shown in Figure (3.7). The IE process had decreased the toxicity of RTWW since the EC was increased to 74 %. Therefore, high levels of EC % that means low toxicity, whereas low levels of EC % means high toxic.The performance of IE process was very good for decolorization and detoxification from RTWW.

Synthetic textile wastewater (Black azo dyes):

In a similar way, Synthatic azo dyes such as Black azo dyes (RB5) the most common dye in textile industry. The performance of IE process in the case of Black azo dyes was found to be 1000 (pt, co) after using Batch process as shown in Figure (3.9). The color was very high before applying this process but when applied anion exchange resin the removal of color was achieved

as shown in Figure (3.10). The pH values of Black azo dyes were continuously monitored during IE system (Batch process) and were increased up to 13.5 due to the (OH⁻) resin as shown in Figure (3.11). In this study we investigated the correlation between the absorbance at 450 nm and the different concentration of azo dyes as shown in Figure (3.13). The best performance was at 1 g from RB5 with 100 ml of distilled water was added slowly. For the COD measurement of RB5 was determined by the closed reflux method, after digestion of the samples in a COD digester over 2 hr at 150°C. As seen Figure (3.14). The COD values was reduced from 557 to 200 mg/L of Black azo dyes. Moreover, the (TOC) levels were also reduced from 63.45mg/L to 25mg/L as exhibited in Figure (3.15). For detoxification of synthetic azo dyes the acute toxicity was investigated by using Microtox before and after applying IE process. Basic test was applied by using IE process with RB5 samples in order to calculate the EC %. The EC % of Black azo dyes was 63% as described in Figure (3.16). Therefore, Black azo dyes was low in toxicity and also the IE process has a good results with decolorization and detoxification of synthetic azo dyes.

Biological treated textile wastewater (BTTWW):

The performance of IE process also was investigated for decolorization and detoxification from BTTWW were taken from Gümüşsu Aritma corporation located at Denizli, Turkey. The average of the color removal of BTTWW was 150 (pt, co) after applying IE system at pH 9.68 as shown in Figure (3.18). It was observed that over 90 % (pt, co) was removed after applying this system with BTTWW at pH 9.20. The absorbance was also measured by using spectrophotometer as depicted in Figure (3.19). The pH values of BTTWW were continuously monitored during IE system and were increased due to the (OH⁻) resin as shown in Figure (3.20). The good results at high values of Ph due to the anion resin and was very effective with decolorization of textile wastewater. In a similar manner, COD values was founded that over 80 % was removed after applying IE process with BTTWW as shown in Figure (3.21). TOC was also measured for BTTWW after applying IE process. The TOC value was diminished to 6.17 mg/L of as shown in Figure (3.22). The IE process had decreased the toxicity of BTTWW by calculated EC % by utilizing anion resin (OH⁻). Figure (3.23) depicts a high increasement of EC equals to 95% was observed for BTTWW samples, this means that IE process has a decent performance for detoxification of textile wastewater. The Optimum Decolorization and detoxification were achieved for BTTWW by using IE process as a pretreatment method. High amounts of treated

BTTWW samples were obtained after applying IE process using anion resin (OH⁻). The optimum operational condition determination for the removal of color, COD, TOC and the removal of toxicity were summarized in Table 4.1.

Table 4.1: The optimum operational condition determination for the removal of color, COD, TOC and the removal of toxicity of treated samples .

Parameter	Treated volume (ml) with 25 ml IE	Treated volume with 1 ml IE	Color Removal %	COD Removal %	TOC Removal %	Toxicity Removal %
RTWW	48.000	1.92	80%	Over 50%	50%	75%
Black azo dyes (RB5)	24.000	0.96	75%	65%	Over 50%	65%
BTTWW	64.000	2.56	90%	Over 80%	75%	90%

Regeneration of anion resin (OH⁻) :

The regeneration of exhausted (OH⁻) anion resin was utilized by using a mixed solution of sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) with a concentration(> 5%) at 20°C. As shown in Figure (3.25) the mentioned temperature was not sufficient for decolorization of textile wastewater. However, the efficiency of exhausted (OH⁻) anion resin was more effective when the temperature was increased to 40°C. The active chlorine compounds are oxidized, and the decomposition of the stain is followed by the ion exchange of the (OH⁻) ions present in the water to the ion-exchange surface of the ion exchanger, while at the same time the ion exchangers are prevented from being damaged by the active chlorine. The regeneration of exhausted anion (OH⁻) resin was repeated 8 times using the same mixed solution of NaOCl and NaOH (> 5%) and the same volume of wastewater at 40 ° C as shown in Figure (3.26). Almost the same color removal efficiencies were obtained as shown in Figure (3.27). With only selective color removal with ion resin, the regeneration solution was continuously used with only hypochlorite added, thus reducing the color removal operating costs in the textile sector by over 78%. It was found that the regeneration of anion resin (OH⁻) was not only effective for the decolorization of textile wastewater but also for both COD levels

was reduced to 400 mg/L as shown in Figure (3.28) and TOC values was reduced to 12 mg/L as shown in Figure (3.29). In addition, the regeneration of anion resin (OH^-) was successful for the detoxification. The EC values were calculated after 8 regeneration as shown in Figure (3.30).

5. CONCLUSION AND RECOMMENDATIONS

In this study, Ion-Exchange process was performed for decolorization and detoxification of textile wastewaters that a highly colored and containing high concentrations of COD, TOC and has a very high toxicity refer to containing a toxic substance and its mixture with dyes and other chemicals that are harmful to the environment after discharge this wastewater from textile industry.

- A systematic approach was followed for the determination of Color, COD, TOC and Toxicity concentrations of textile wastewaters from Gümüşsu Arıtma corporation in Denizli , Turkey. IE process has effectively decolorized and detoxified of textile wastewater samples such as RTWW, RB5 and BTTWW. Therefore, it should be considered that the best performance of this process and obtained a high volume of treated samples after biological treatment of textile wastewater.
- Color removal (80%),(75%) and (90%) was achieved by using IE process in the case of RTWW, RB5 and BTTWW, respectively. Moreover, batch process was very effective for COD , TOC and toxicity removal.
- The regeneration of exhausted anion resin (OH⁻) by using mixed solution of sodium hypochlorite(NaOCl) and sodium hydroxide <5% (NaOH) at 40°C was very efficiently even after repeating it 8 times using the same volume of resin with the same efficiency for decolorization and detoxification of textile waste water.
- The operating costs of Gümüşsu Arıtma corporation in Denizli , Turkey for decolorization from textile wastewater was 0.02 \$/m³. On the other hand, the unit cost of IE process for decolorization and detoxification from textile wastewater was 0.00013 \$/m³. Moreover, IE process has a validity up to 5 years. The operating costs of IE process for decolorization from textile wastewater are 154 times lower than the decolorization by using decolorant from Gümüşsu Arıtma corporation.

- Recycling systems can be applied to textile wastewater to provide effective and economical control of pollution in water environments. In this research, which investigates the reuse of textile wastewater obtained after application IE process, shows that it is possible to reuse the effluents after some simple and low-cost treatment processes, without having a negative impact on the product quality.

It is concluded that IE process, which is the cheapest method of treatment of textile wastewater, was used to remove color, COD, TOC and Toxicity. Batch process could be used in order to change the hardness and conductivity of the effluent as well as the removal of color and other parameters. IE process is widely available and therefore, the cost of the proposed effluent treatment method is low, very effective and ecofriendly.

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APPENDICES

**İSTANBUL ÜNİVERSİTESİ
BİLİMSEL ARAŞTIRMA PROJELERİ KOORDİNASYON BİRİMİ
VE TÜRK PATENT ENSTİTÜSÜ
BİLGİ VE DOKÜMANTASYON BİRİMİ**

BULUŞ BİLDİRİM FORMU

Buluşu Yapan/Yapanlar (Adı-Soyadı/Bölümü/Unvanı):

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Buluş Konusu Ürün/Yönteme İlişkin Projenin Adı, Kayıt Numarası, Başlangıç ve Bitiş Tarihi:

1. Projenin Adı:

Yüksek Lisans Tez Projesi: İyon Değiştirici Prosesi İle Tekstil Atık Sularından Renk ve Toksisite Giderimi “Decolorization and Detoxification of Textile Wastewater by Ion-Exchange Process”

Doktora Tez Projesi: Atıksuların Bipolar Membran Elektrodializ Prosesi ile Arıtılması ve Geri Kullanım Alternatiflerinin Değerlendirilmesi, “Wastewater Treatment by Membrane Electrodialysis Process and Evaluation of Reuse Alternatives”

2. Projenin Kayıt Numarası:-

3. Projenin Başlangıç Tarihi: 2014

4. Projenin Bitiş Tarihi: Devam Ediyor

Buluş Başlığı (Buluşu özetleyen bir başlık şeklinde yazılmalıdır. Örn. Poliolefin Üretim Yöntemi):

Atıksulardan Renk Giderimi için Hidrotermal Klorlama ile Anyonik Reçinelerin Rejenerasyonu Yöntemi

Önceki Teknik (Buluş konusunun ilgili olduğu teknik alanda var olan teknikler, benzer niteliğe sahip ürünler, varsa patentler ve diğer yayınlar):

1. Klasik iyon değiştirici sistemleri
2. Polimer Koagülasyonu
2. Fenton oksidasyonu,
3. Ozonlama ve diğer oksidasyon yöntemleri
4. Adsorpsiyon yöntemleri

Önceki teknikte saptanan teknik sorunlar:

1. Klasik iyon değiştirici prosesleri: İyon değiştiriciler sertlik gideriminde çok yaygın kullanılan ve rejenerasyon nedeni ile işletme maliyetleri çok düşük olan proseslerdir. İyon değiştiriciler ile renk giderimi yıllardır çalışılan bir husustur. Fakat anyonik boyar maddeler iyon değiştiriciler ile güçlü bağ yaparak reaksiyona girerler. Bu nedenle iyon değiştiricilerinin klasik anyonik/bazik çözeltiler ile (kostik veya NaCl çözeltileri ile) rejenerasyonu mümkün olmamaktadır.

Polimer koagülasyonu: gram seviyelerinde polimer kullanılması gerekmektedir. Yatırım maliyeti düşük olsa da işletme maliyeti yüksektir. Ortaya çıkan yüksek toksik çamur ayrıca bir problem olmaktadır. Sentetik polimerler kanserojen ve toksik kimyasal madde grupları içermektedir.

2. Ozonlama: Ozonlama sonrası çamur oluşmaması da prosesin enerji ihtiyacı yüksektir, ozonun hepsi suda kullanılamadığından kalan ozonun bertaraf edilmesi gerekmektedir. Dolayısı ile yatırım maliyeti yüksek olan ozon prosesinin işletme maliyetleri de yüksektir.

3. Fenton Prosesi: uzun yıllardır çalışılsa da düşük pH ($pH < 3.4$) gerektirmesinden dolayı alkali-bazik tekstil atık sularında kullanılması ekonomik olmamaktadır. Ayrıca aşırı asit ve baz

kullanılması ile atıksuyun iletkenliği daha da artmaktadır. Bundan dolayı uygulamaya geçilemeyen bir prosedür.

4. Adsorpsiyon: Aktif karbon adsorpsiyonu methodu (AKAM) tekstil atıksularında yüksek organik madde içeriğinden dolayı ekonomik olmamaktadır. AKAM prosesi tüm organikleri adsorbe eder, malzeme ömrü sınırlıdır ve rejenerasyonu yüksek sıcaklıklar gerektirdiğinden uygulanmamaktadır. Uygulansa bile belli bir rejenerasyon sonrası malzeme adsorpsiyon özelliğini kayıp etmektedir. Ortaya çıkan yüksek işletme maliyetlerinden dolayı atık su arıtımında kullanılması çok sınırlıdır ve tekstil atıksularında ekonomik açıdan uygulanabilir değildir.

5. Yalnız klorlama ile rejenerasyon veya atıksudan renk giderimi mümkün değildir. Klor sadece boyalarla değil tekstil atıksularında bulunan diğer organikler ile reaksiyona girerek toksik/kanserojen/biyolojik bozunurluğu çok düşük klorlu bileşikler oluştururlar.

Teknik sorunlara buluş ile getirilen çözümler (sonuca ulaşma şekli ayrıntılı bir biçimde açıklanmalıdır.):

1. Bu buluş çerçevesinde klasik Cl^- ve OH^- reçinelerinde tekstil atık sularından %98'in üzerinde renk giderimi sağlandıktan sonra tükenmiş iyon değiştiricinin rejenerasyonu için 30-40 °C aktif klor sırasıyla $\text{NaCl} (<\%5)$ ve $\text{NaOH} (<\%5)$ ile birlikte kullanılmıştır (Şekil 1). Aktif klor boyar maddelerin oksidasyonunu sağlarken boyar maddelerin parçalanması akabinde suda bulunan Cl^- veya OH^- iyonlarının tekrar iyon değiştirici yüzeyine iyon değişimi ile geçiş sağlanırken aynı zamanda iyon değiştiricilerinin aktif klordan dolayı zarar görmesi engellenmiştir.
2. Prosesin defalarca rejenerasyonu ve tekrar kullanımı mümkün olduğundan dolayı uygulamadaki diğer renk giderme metodlarına göre renk giderme işletme maliyetleri %70 civarında azaltılmıştır.
3. Sistemin kurulum maliyeti düşük olduğundan dolayı diğer uygulamadaki ozonlama prosesine göre %80 daha düşük bir yatırım maliyeti gerektirmektedir.
4. Polimer koagülasyonu ozonlama prosesine göre yatırım maliyeti düşük olsa da prosesin karıştırıcı, çamur toplama, çökeltme tankları, çamur pompa ve çamur yoğunlaştırıcı ekipmanlarından dolayı yer alanı ve ekipman maliyeti yüksektir. Geliştirilen bu metotta çamur oluşumu yoktur ve rejenerasyon solüsyonu eksik aktif klor kullanılarak defalarca

kullanılabilmektedir. Sistemin polimerler ile renk giderimine göre yatırım ve işletme maliyetleri sırasıyla %85 ve %78 daha düşüktür.

5. Pamuklu tekstil endüstrisinde anyonik boyalarının kullanımı %75'in üzerindedir. Dispers boyalar gibi diğer boyalar biyolojik arıtma sistemlerinde giderilirken çözünürlüğü yüksek anyonik boyaların biyolojik arıtmadada giderimi sadece çamur adsorpsiyonu kadar olabilmektedir. Geliştirilen bu metod ile sistem sadece belli başlı boyalar için değil biyolojik arıtma tesisinde giderilemeyen tüm anyonik boyalar için yüksek verimle çalışmaktadır.
6. Anyonik boyalar membran atıksu giderim ünitelerinde membran yüzeyini kaplayarak geri dönüşümsüz tıkanmalara neden olduğundan dolayı çok ihtiyaç olmasına rağmen atıksu geri dönüşüm sistemlerinin tekstil sektöründe kullanımı yaygınlaşmamıştır. Bu proses ile anyonik yapıdaki memebran tıkanmalarına sebep olan anyonik boyaların arıtımı %98 üzerinde bir verimle giderildiğinden dolayı membran arıtma sistemlerinin tekstil atıksuları için kullanılmasına olanak sağlayacaktır.

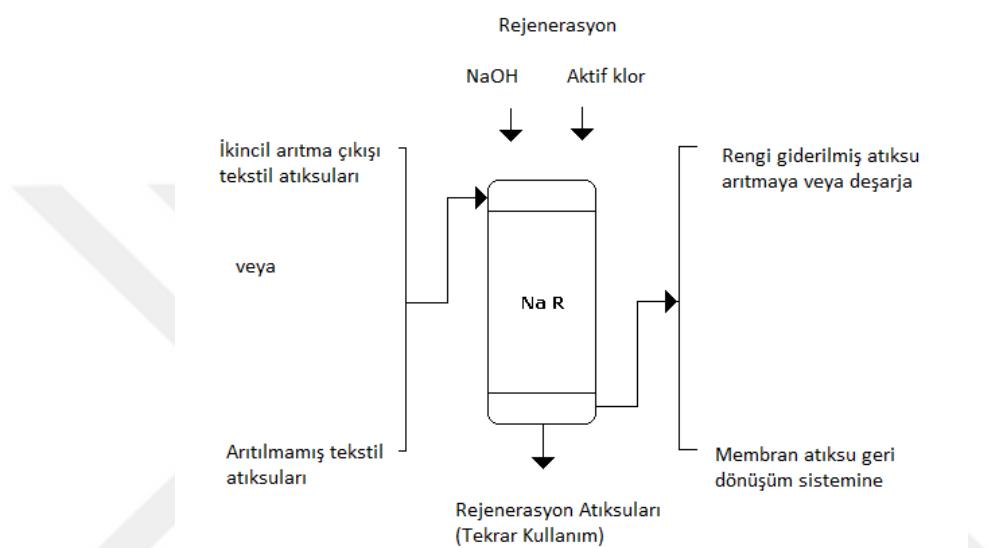
Sorunun çözümü ile elde edilen sonuçlar (ÖZET):

1. İyon reçinesi ile seçici olarak sadece renk giderimi yapılmış (Şekil 2-3.), rejenerasyon solüsyonu sadece hipoklorit eklenerken sürekli kullanılmış ve böylelikle Tekstil sektöründe renk giderme işletme maliyetleri %78'in üzerinde düşürülmüştür.
2. Mevcut uygulamalara göre (ozon ve polimer koagülasyonuna göre) %85 daha düşük bir yatırım maliyeti ile tekstil atıksularından renk giderimi yapılabilecektir.
3. Kanserojen boyaların maddelerin su alıcı ortamlarda etkin ve ekonomik kontrolü sağlanabilmektedir.
4. Boyaların maddeleri membranları tıkağından dolayı atıksu geri dönüşümü mümkün olmamaktadır. Elde edilen yüksek boyaların madde giderimi ile membran atıksu geri dönüşüm sistemleri tekstil atık suları için uygulanabilir olmaktadır.

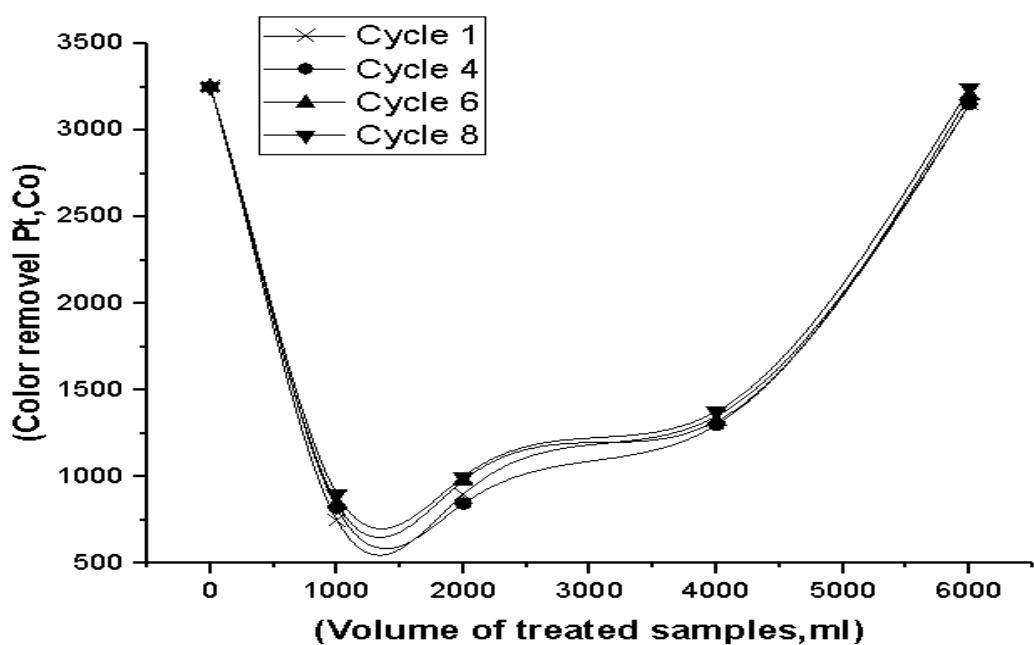
Teknik Resim ve Açıklamaya Yönelik Şemalar (Şekil ve şemada yer alan tüm parça ve alanlar numaralandırılarak adlandırılmalıdır.):

Üzerinde konsantrasyon halde tutulan anyonik boyalar ile tükenen OH^- ve Cl^- anyonik iyon reçinelerinin rejenerasyonu için:

1. Tükenmiş OH^- anyonik reçineler 30-40 $^{\circ}\text{C}$ de aktif klor/hipoklorit (NaHOCl) ve NaOH rejenerasyonu ($>5\%$) ile rejenere edilmiştir.
2. Tükenmiş Cl^- anyonik reçinesi ise 30-40 $^{\circ}\text{C}$ de aktif klor/hipoklorit (NaHOCl) ve NaCl ($<5\%$) ile rejenere edilmiş (Şekil 1) ve bu metotla 8 defa tüketilip rejenerasyon sonrası tekrar kullanılan iyon reçinelerinden aynı hacimde atıksu arıtlararak nerdeyse aynı renk giderim verimleri elde edilmiştir. (Şekil 2 ve 3)



Şekil 1. Geliştirilen sistemin tekstil sektöründe kullanımı



Şekil 2. Anyonik iyon değiştircisinin (25 ml) 8 jenerasyon sonrası arıtılmamış tekstil atıksuyundaki renk giderme performansı.

Uygulanan termal klorlama rejenerasyonu ile 25 ml anyonik reçine ile toplamda 40.000 Lt (40 m³) tekstil atıksuyu aynı verimle arıtılmıştır.



Atık su 1 4 6 8

Şekil 3. 8 Rejenerasyon (8 defa rejenerasyon) sonrası kullanılan iyon reçinesinin performansının görüntüsü.

■ Hizmet Buluşu: Söz konusu buluş üniversite öğretim elemanı veya diğer çalışanların üniversitedeki görevi sırasında ilgili faaliyeti yapması ile gerçekleştirilmiş veya buluşun ortaya çıkması sırasında üniversitenin faaliyeti ve deneyimlerinden faydalانılmıştır.

□ Serbest Buluş: Yukarıdaki durumdan farklı durumların olması halinde gerçekleşen buluşlardır.

BULUŞU YAPAN/YAPANLAR BU BULUŞ İLE İLGİLİ TEKNİK BİLGİ VE TİCARİ SİRLARINI ÜNİVERSİTE İÇİNDE VE/VEYA DIŞINDA ÜÇÜNCÜ KİŞİLER İLE PAYLAŞMAYACAKLARINI TAAHHÜT VE KABUL ETMEKTEDİR.

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2	Muhammed İberia AYDIN	% 15	Fikir Geliştirme deneyler	
3	Burak YÜZER	% 15	Fikir Geliştirme deneyler	
4	Amel Taher RABTI	% 20	Lab çalışmaları	
5	Üniversite	% 30	Alt yapı	

Araştırmacı ve yürütücülerin katkıları eşittir.

* Buluş birden fazla kişi tarafından yapılmış ise yapılan buluşa katkı paylarının belirtilmesi gerekmektedir. Buluşcular katkı payları konusunda aralarında anlaşamazlar ise yüzdeler “Fikri Haklar Kurulu” tarafından belirlenecektir.

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