İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

TREATABILITY OF DYE CARRIERS USED IN TEXTILE INDUSTRY

M.Sc. Thesis by

Burcu ÖZERKAN
(501011858)

Date of submission : 26 December 2004

Date of defence examination: 26 January 2005

Supervisor (Chairman): Prof. Dr. Fatoş GERMİRLİ BABUNA

Members of the Examining Committee: Prof. Dr. Seval SÖZEN (İ.T.Ü.)

Assoc. Prof. Dr. Oya OKAY (İ.T.Ü.)

JANUARY 2005

İSTANBUL TEKNİK ÜNİVERSİTESİ★ FEN BİLİMLERİ ENSTİTÜSÜ

TEKSTİL ENDÜSTRİSİNDE KULLANILAN BOYA TAŞIYICILARININ ARITILABİLİRLİĞİ

YÜKSEK LİSANS TEZİ

Çevre Müh. Burcu ÖZERKAN
(501011858)

TezinEnstitüyeVerildiğiTarih 26 Aralık 2004

Tezin Savunulduğu Tarih : 26 Ocak 2005

Tez Danışmanı: Prof. Dr. Fatoş GERMİRLİ BABUNA

Diğer Jüri Üyeleri: Prof. Dr. Seval SÖZEN (İ.T.Ü.)

Doç. Dr. Oya OKAY (İ.T.Ü.)

OCAK 2005

PREFACE

It is my pleasant duty to record my thanks to my valuable Professor Fatoş GERMİRLİ BABUNA for all her support and patience during the process and finalizing of my project.

I shall also express my gratitude to Associate Professor Gülen EREMEKTAR, Associate Professor İdil ARSLAN ALATON and Associate Professor Oya OKAY who helped in my ways in the preparation and production of my thesis.

I am also thankful to my supporters, my dear mother, Belkıs ÖZERKAN and my fiance Murat AYDIN for their continuous support.

And finally I am particularly indebted to my biggest supporter, my dear father Sabri ÖZERKAN with my deepest love and thanks.

January, 2005

Burcu ÖZERKAN
Environmental Engineer

CONTENTS **Page Number**

LIST OF TABLES vi
LIST OF FIGURES vii
ÖZET viii
SUMMARY ix

1. INTRODUCTION 1

1.1 Importance of The Study 1

1.2 Objective and Scope of The Study 1

2. LITERATURE SURVEY 3

2.1 Textile Industry 3

2.1.1 Wastewater Generation and Treatability 6
2.1.2 Dyeing Auxiliaries 11
2.1.2.1 Dye Carriers 13

2.2 Chemical Settling 15

2.2.1 Properties of Colloidal Solutions 16
2.2.1.1 Colloidal Stability 19
2.2.2 Properties of Coagulants Used in Coagulation 20
2.2.2.1 Aluminum Sulfate 20
2.2.2.2 Ferric Salts 21
2.2.2.3 Ferrous Salts 22
2.2.2.4 Lime 22
2.2.2.5 Sodium Bentonite 23
2.2.3 Coagulant Aids 23
2.2.3.1 Clays 23
2.2.3.2 Activated Silica 24
2.2.3.3 Polylectrolytes 24

3. MATERIALS AND METHODS 26

3.1 Material 26

3.1.1 Dye Carriers 26

3.2 Analytic Methods 26

3.2.1 Chemical Treatment Tests 27
3.2.1.1 Calculation of Sludge Disposal Costs 28
3.2.2 Activated Sludge Inhibition Tests 30
3.2.3 Toxicity Tests 34

4. EXPERIMENTAL RESULTS AND EVALUATION 36

4.1 Characterization of Wastewater 37

4.2 Chemical Treatability Experiments 38

4.2.1 Experimental Results Conducted with Sodium Bentonite 39
4.2.2 Experimental Results Conducted with Aluminum Sulfate 40
4.2.3 Experimental Results Conducted with Ferric Chloride 41
4.2.4 Experimental Results Conducted with Ferrous Sulfate 42
4.2.5 Calculation of Treatment Costs 44
4.2.5.1 Calculation of The Treatment Cost for Sodium Bentonite 45
4.2.5.2 Calculation of The Treatment Cost for Aluminum Sulfate 45
4.2.5.3 Calculation of The Treatment Cost for Ferric Chloride 47
4.2.5.4 Calculation of The Treatment Cost for Ferrous Sulfate 53
4.2.6 Cost Comparison of Treatment 61

4.3 Activated Sludge Inhibition Experiments 62

4.4 Toxicity Experiments 67

5. CONCLUSIONS AND RECOMMENDATION 71

REFRENCES 73

CURRICULUM VITAE 77

LIST OF TABLES

		Page No
Table 2.1.	Classification of Fibres Used in Textile Industry	**4**
Table 2.2.	Conventional Wastewater Characterization	**7**
Table 2.3.a.	Receiving Media Discharge Standards for Textile Wastewaters	**8**
Table 2.3.b.	Receiving Media Discharge Standards for Textile Wastewaters	**9**
Table 2.4.	Encountered Compounds in Dyeing Auxiliaries	**12**
Table 3.1.	Synthetic Medium	**30**
Table 3.2.	Concentrations of EC_{50} for 3,5-Dichlorophenol Reference Chemical at Different Aeration Times	**33**
Table 3.3.	Concentration of f/2 Medium Solutions	**34**
Table 4.1.	Physicochemical/toxicological Properties of The Dye Carrier Preparations Carrier I and Carrier II	**36**
Table 4.2.	Characterization of The Dye Carrier Formulations	**37**
Table 4.3.	The Results of Coagulation-Flocculation Experiments with The Application of Sodium Bentonite	**38**
Table 4.4.	The Results of Coagulation-Flocculation Experiments with The Application of Alum	**39**
Table 4.5.	The Results of Coagulation-Flocculation Experiments with The Application of Alum and Polyelectrolyte	**39**
Table 4.6.	The Results of Coagulation-Flocculation Experiments with The Application of Ferric Chloride	**40**
Table 4.7.	The Results of Coagulation-Flocculation Experiments with The Application of Ferric Chloride and Polyelectrolyte	**41**
Table 4.8.	The Results of Coagulation-Flocculation Experiments with The Application of Ferrous Sulfate	**42**
Table 4.9.	The Results of Coagulation-Flocculation Experiments with The Application of Ferrous Sulfate and Polyelectrolyte	**42**
Table 4.10.	Chemical Coagulant Prices	**43**
Table 4.11.	Cost of Chemicals for Coagulants and pH Adjustments Expended in Chemical Treatment	**58**
Table 4.12.	Cost of Sludge Disposal After Chemical Coagulation	**59**
Table 4.13.	Total Cost, Total Effluent COD and SVI parameters of Coagulation-Flocculation Experiments for Different Selected Coagulants Used in Chemical Treatment	**61**
Table 4.14.	Oxygen Uptake Rate and Percent Inhibition in OUR Obtained in Difference COD Values for Raw Carrier Formulations	**64**
Table 4.15.	Oxygen Uptake Rate and Percent Inhibition in OUR Obtained in Difference COD Values for Pretreated Carrier Formulations	**64**
Table 4.16.	EC_{50} Values Obtained for Raw and Pretreated Carrier Effluents	**65**
Table 4.17.	Percent Inhibition of *Phaeodactylum tricornutum* Values Obtained at Different Carrier Formulations Dilution	**67**
Table 4.18.	EC values of Carrier Solutions After 4 days Exposure to *P.tricornutum*	**69**

LIST OF FIGURES

		Page No
Figure 2.1:	General Diagram of Processes in The Textile Industry	**5**
Figure 2.2:	Representation of Helmholtz Electrical Double Layer	**17**
Figure 2.3:	Precipitation of Colloidal Particle by Charge Reduction	**18**
Figure 2.4:	Force Fields Between Colloids of Like Charge	**18**
Figure 2.5:	Charge System in a Colloidal Suspension.	**19**
Figure 3.1:	Laboratory Scale Jar Test Assembly For Coagulation Studies	**28**
Figure 3.2:	Percent Inhibition in Oxygen Uptake Rates Obtained for Aeration of Activated Sludge Test Reactors at 30. min. as a Function of Ln COD	**32**
Figure 3.3:	Percent Inhibition in Oxygen Uptake Rates Obtained for Aeration of Activated Sludge Test Reactors at 60. min. as a Function of Ln COD	**32**
Figure 3.4:	Percent Inhibition in Oxygen Uptake Rates Obtained for Aeration of Activated Sludge Test Reactors at 120. min. as a Function of Ln COD	**33**
Figure 4.1:	Activated Sludge Dissolved Oxygen Concentration for Raw Carrier 1 (a), Raw Carrier II (b), Chemically Pretreated Carrier 1 (c), Chemically Pretreated Carrier 2 (d) at Different Dilutions Versus Aeration Time Along with 30 Minutes	**63**
Figure 4.2:	Percent Inhibition in Oxygen Uptake Rates Obtained for Raw and Chemically Pretreated Carrier Formulation Effluents as a Function of Ln COD	**65**
Figure 4.3:	Percent Inhibition of *P.tricornutum* as a Function of Raw Carrier Formulation (a), Raw Carrier 2 Formulation (b), Pretreated Carrier 1 Formulation (c), Pretreated Carrier 2 Formulation (d) at Different Dilutions for 4 Days Counting	**69**

TEKSTİL ENDÜSTRİSİNDE KULLANILAN BOYA TAŞIYICILARININ ARITILABİLİRLİĞİ

ÖZET

Tekstil endüstrisinde boyama ve apreleme işlemlerinde biyositler, kırışıklık önleyiciler, deterjanlar, boya taşıyıcıları, ıslatıcılar vs. gibi çok sayıda yardımcı kimyasallar kulanılmaktadır. Bunların arasından boya taşıyıcıları, sentetik elyafın boyanmasında sıklıkla uygulanmaktadır. Boya taşıyıcıları, suyu sevmeyen özellikte dağıtıcı boyaların düşük sıcaklık koşullarında ($\leq$ 100 °C) kumaşa emilimini ve yayılımını attırmaktadır. Yünlü elyaf yüksek sıcaklıklarda boyanmaya dayanmadığından, boya taşıyıcıları yün ve polyester karışımı kumaşların boyanma aşamasında önemlidirler. Boya taşıyıcılarının çoğu insanlar, diğer memeliler ve su ortamında yaşayan organizmalar için zehirlidir. Bunlar düşük seviyede biyolojik ayrışabilirlik özelliğie sahiptirler. Bu nedenle boya taşıyıcılarının biyolojik arıtma (tekstil endüstrisi atıksularına uygulanan en yaygın arıtma metodu) üzerindeki davranışlarının belirlenmesi önem kazanmaktadır.

Bu araştırmanın amacı, tekstil endüstrisinde kullanılan boya taşıyıcılarının ortama verdikleri kirlilik düzeylerinin belirlenmesi ve bu maddelerin arıtılabilirliklerinin incelenmesidir. Boya taşıyıcılarının ilave edildiği boya banyolarından elde edilen atıksular üzerinde kimyasal oksidasyon uygulanması önceden yürütülmüş çalışmalarda belirtilmiştir. Fakat istenilen arıtma verimi elde edilememiştir. Bu çalışmada iki farklı yapıdaki boya taşıyıcı formulasyonları (Carrier 1 & Carrier 2) farklı koagülantlar kullanılarak laboratuvar ölçekli koagülasyon-flokülasyon deneylerine tabi tutulmuşlardır. Optimum koagulant dozajları ile birlikte optimum pH değerleri saptanmıştır. Ham boya taşıyıcı formulasyonları ve koagülasyon flokülasyon uygulanan önarıtılmış boya taşıyıcı formulasyonları üzerinde *Phaeodactylum tricornutum* (deniz algi) kullanılarak zehirlilik test edilmiştir. ISO Standardı Su Kalitesi - Aktif Çamur Oksijen Tüketim Engelleme Deneyi belirtilen boya taşıyıcı numuneler üzerinde uygulanmıştır. Bu engelleme deneyinin amacı, önarıtmanın biyolojik arıtılabilirlik üzerindeki etkilerinin gösterilmesidir.

Arıtabilirlik çalışmalarıyla ilgili sonuçlar, Carrier solusyonları için demir sülfatlı kimyasal çöktürmenin önarıtma için uygun bir metod olduğunu göstermiştir. pH 9'da 750 mg/L ve 550 mg/L demir sülfat dosajının uygulanması, sırasıyla Carrier 1 ve Carrier 2 formulasyonları için optimum arıtmayı vermiştir. Önarıtılmış Carrier 1 atıksuyunun aktif çamur mikroorganizmalarının aktivitesi üzerinde yavaşlatıcı etkisini engelleme deneyleri göstermiştir. Diğer taraftan kimyasal olarak önarıtılmış Carrier 2 atıksuyunun yavaşlatıcı etkisi ham Carrier 2 formulasyonundan daha az olarak gözlemlenmiştir. Zehirlilik testi sonuçlarına göre, *Phaeodactylum tricornutum* türü için ham Carrier atıksuları önarıtılmış Carrier atıksularından daha zehirlidir.

TREATABILITY OF DYE CARRIERS USED IN TEXTILE INDUSTRY

SUMMARY

A lot of auxiliaries such as biocides, crease-proofing agents, surfactants, dye accelerants (carriers), wetting agents etc. are used in dyeing and finishing operations of textile industry. Among them dye carriers are frequently applied in batch dyeing of synthetic fibers. Dye carriers promote the absorption and diffusion of hydrophobic disperse dyestuffs under low-temperature ($\leq 100\ ^{o}C$) conditions. They are important in dyeing blend fibers of wool and polyester, as wool can not withstand dyeing under high temperatures. Most of the dye carriers are toxic to humans, other mammals and aquatic organisms. They have a poorly biodegradable nature. Therefore the determination of the reactions of dye carriers on the biological treatment processes (the most common treatment method applicable to textile wastewaters) is important.

The objective of this research is, to determine the pollutant levels of dye carriers used in textile industry and to evaluate their treatabilities. Previously conducted studies stated that, the chemical oxidation was applied to wastewaters obtained from textile processing dye baths, where dye carriers were added. However, required removal efficiencies have not been obtained. In this study, two different dye carrier preparations (Carrier 1 & Carrier 2) are subjected to lab scale coagulation-flocculation experiments by the use of different coagulants. Optimum coagulant dosages together with the optimum pH values are assessed. Toxicity is tested using *Phaeodactylum tricornutum* (marine microalgae) on both raw dye carrier effluents and dye carrier effluents chemically pretreated with the application of coagulation-flocculation. ISO Standard Water Quality- Test for The Inhibition of Oxygen Consumption by Activated Sludge is applied on the mentioned dye carrier samples. The aim of this inhibition assay is to visualize the effects of pretreatment on biological treatability.

The results associated with treatability studies for Carrier solutions showed that chemical precipitation with ferrous sulfate is a suitable method for preliminary treatment. The application of 750 mg/L and 550 mg/L ferrous sulfate dosage at pH 9, yielded the optimum treatment for Carrier 1 and Carrier 2 formulations respectively. Inhibition assays indicated that pretreated Carrier 1 effluent has an inhibition effect on activated sludge microorganisms' activity. On the other hand, the inhibition effect of chemically pretreated Carrier 2 effluent is observed to be less than raw Carrier 2 formulation. According to toxicity test results, raw Carrier effluents are more toxic than pretreated Carrier effluents to *Phaeodactylum tricornutum* species.

CHAPTER 1 INTRODUCTION

1.1 Importance of The Study

The natural resources which have been used by humans since thousands of years are in danger in last decades because of accelerated population growth due to the developments in science and technology and rapid increase in industrialization. Industrial pollution which is a result of the rapid industrialization has negative effect on the ecological stability. It is possible to at least slow down this trend by enforcing discharge standards.

Nowadays, from the environmental pollution point of view the big share comes from industries. Textile industry is an important sector in our Turkish economy and takes approximately 20 % of our industrial production. Auxiliaries such as dyestuffs, anti-foaming agents, salts, dispersants etc. used in finishing operations are essential components for textile industry. From the point of biological treatability and toxicity, how the dye carriers additives used in textile industry react after an application of preliminary treatment, has to be identified.

1.2 Objective and Scope of The Study

The aim of this study is to determine the treatability and toxicity of textile dye carriers. Dye carrier formulations are important for dyeing blend fibers of wool and polyester, as wool can not withstand dyeing under high temperatures.

The scope of this study focuses on the wastewater originated from process baths which the mentioned chemicals were added. The bath contents are chemically treated by sodium bentonite, alum, ferric chloride and ferrous sulfate. The results are analysed for Chemical Oxygen Demand (COD) removal efficiencies, Sludge Volume Index (SVI) values and treatment costs. Treatability results are evaluated under the view of acute toxicity tests and Oxygen Demand Inhibition by Activated Sludge assays on raw and pretreated wastewaters in optimum conditions.

As defined above according to the aim of the study a brief information is given about the textile industry and the specifications of dye carriers used in textile industry. The effect of the dye carriers on the ecosystem and the effect of chemical treatment on biological treatability and toxicity are presented in section 2.

In section 3; the followed experimental methods are presented.

In section 4; the data obtained from the performed experiments are given and evaluated.

In section 5; the results are summarized and interpreted.

CHAPTER 2 LITERATURE SURVEY

2.1 Textile Industry

Textile industry is defined as manufacturing the yarn from natural or synthetic fibers, afterwards by weaving or knitting of these fibers to produce the cloth and finally finishing the products by applying procedures such as bleaching, dyeing, mercerizing etc.(Morais *et al.,* 1999).

Textile industry both in Turkey and in the world is an important sector from the economical and the strategical point of view. There is no doubt that, characterization and the treatability of wastewaters originating from textile industry and/or determination of the treatment systems for these wastewaters is a matter of great importance for Turkish industry.

The textile industry uses different raw materials, employs different techniques, applies different chemicals, involves different operations and processes (Germirli Babuna et al., 1999). The first step of textile production is the production of raw fibre. Natural origin fibres and chemical (man-made) fibres are two general categories used in textile industry that is shown in Table 2.1.

Textile industry consists of different sub-sectors, forming a sequence, beginning with the production of raw materials (man-made fibres) and proceeding to semi processed ones such as yarn, woven and knitted fabrics with their finishing processes and ending with carpets, home textiles, clothing and industrial use textiles name as final products.

Table 2.1 Classification of Fibres Used in Textile Industry (EC, 2001)

Natural Origin Fibres	Animal origin	Raw wool Silk fibre Hair	
	Vegetable origin	Raw cotton fibre Flax Jute	
	Mineral origin	Asbestos (not used in the textile industry)	
Chemical (man-made) Fibres	Natural polymer fibres	Viscose, cupro, lyocell Acetate Triacetate	
	Synthetic polymer fibres	Inorganic polymer	Glass for fibre glass Metal for metal fibre
		Organic polymer	Polyester (PES) Polyamide (PA) Acrylic (PAC) Polypropylene (PP) Elastene (EL)

The main finishing process line in the textile industry consists of pretreatment, dyeing, printing, finishing and coating, including washing and drying. The basic processes in the textile industry are schematically represented in Figure 2.1.

Pretreatment processes should ensure the removal of foreign materials from the fibres. Pretreatment techniques depend on the kind and the form of the fibre to be treated.

Various dyes are applied to the textile material for coloring in dyeing processes. Textile dyeing involves the application of basic chemicals such as alkali, salts, reducing and oxidising agents, etc. Auxiliaries assist dyeing processes in the dye formulation and are commonly added at a later stage to the dye liquor (EC, 2001). Detailed information about dyeing auxiliaries presented in the following part of this chapter.

Printing, like dyeing, is a process for applying color to a fabric. Print colour is applied only to defined areas so, this involves different techniques with respect to dyeing. Textile plants usually employ cotton and synthetic fibres and include an integrated printing and dyeing operations, applying a wide variety of organic dyes (Villegas Navarro et al., 2000).

Finishing may involve mechanical/physical and chemical treatments that often takes place after coloring the material. The finishing agents are required to give the textile material the desired properties.

Washing and rinsing are two most common operations in the textile industry. Washing is normally carried out in hot water (40 – 100 °C) in the presence of a wetting agent and detergent. Water characteristics, choice of detergents, temperature, pH and rinsing stage are important factors in washing.

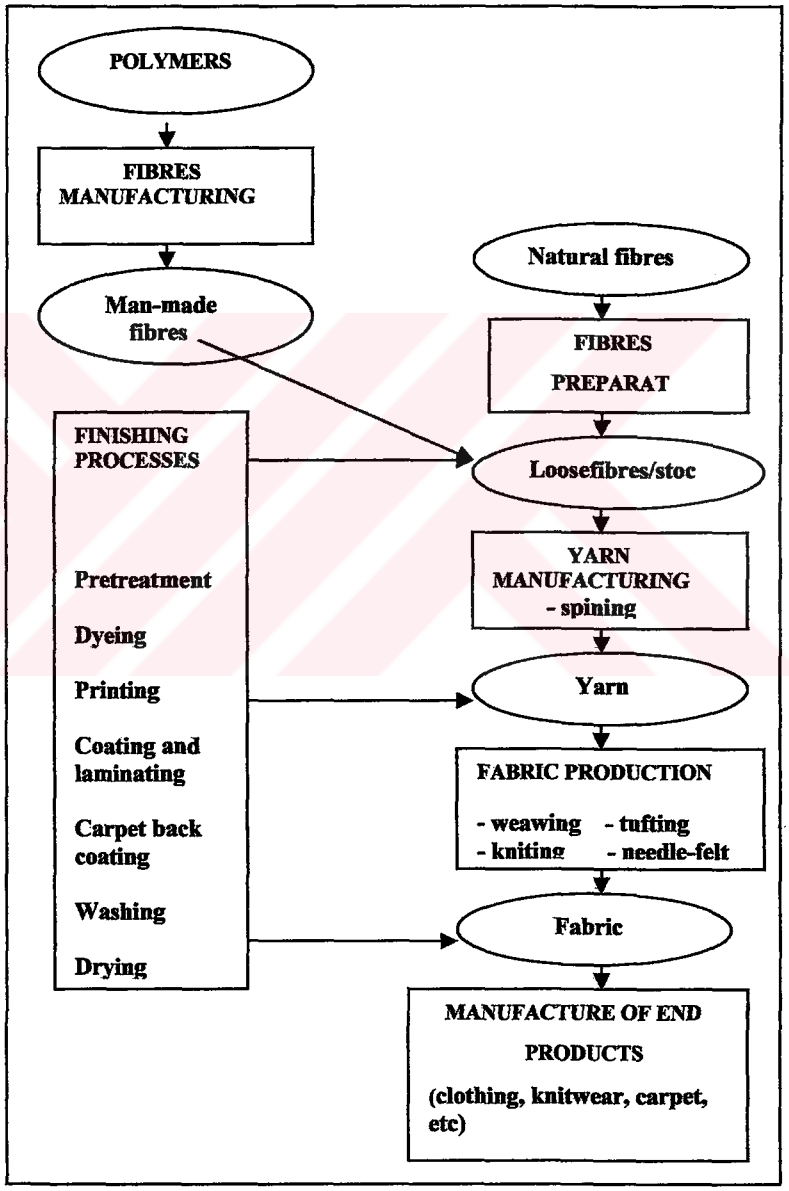


Figure 2.1 General Diagram of Processes in The Textile Industry (EC, 2001)

2.1.1 Wastewater Generation and Treatability

Wastewaters originating from textile industry contain various pollutants including a high content of organic matter and color problem depending on forms of dyes, surface active materials and textile additives used in process (Grau, 1991). A large portion of the wastewater generated by the textile industry originates from dyeing operations. In general, the dyeing wastewater is known to contain strong color, refractory COD load, salinity, high temperature and highly fluctuating pH.

Textile industry is one of the other industries which consumes an important amount of water. During the typical dyeing operation, for each tone of dyed material 1000 litres of water is consumed (Kumar et al., 2001). In the survey involves textile finishing effluents characterization, the unit water consumption and organic load are highly variable in a range of 20-231 m^3ton^{-1} fabric and 14-236 kg $COD.ton^{-1}$ fabric, respectively are determined by Orhon et al. (2003).

In dyeing procedure the wastewater's primary source is dyeing bath and washing water. The quality and quantity of wastewater which originates from a textile factory, might vary daily even hourly depending on the type and the color of used dyes, the type of the clothes and the concentration of the additive agents. The strong dye is an important component of textile wastewater. The primary source of the color of textile wastewater is the dyes (Gülkaya, 2001). The dye content of wastewater is effected on a large scale by the characteristics of that wastewater especially by pH, color, suspended solid (SS) and COD concentration.

Orhon et al. (2003) investigated the wastewaters originating from textile finishing operations in terms of their characterization, treatability and reuse alternatives. 24 different cases covering a wide range of processes from dyeing, printing, desizing, kiering, bleaching to brightening applied to cotton woven fabric, silk woven fabric, wool woven fabric, knit fabric etc. by the use of desizing enzymes, optical brightener, pigment, basic dyes etc. are evaluated. Evaluation of the data outlined in Table 2.2 presents that the COD values vary in a wide range between 365 and 49170 mg/L. The Suspended Solid (SS) values in the Table differ between 10–3500 mg/L and depending on the nature of applied processes and used dyes, the pH values of effluents vary from acidic to alkaline character.

Table 2.2 Conventional Wastewater Characterization (Orhon et al., 2003)

Type of Wastewater	Total COD mgl^{-1}	SS mgl^{-1}	TKN mgl^{-1}	NH_4-N mgl^{-1}	Total P mgl^{-1}	pH
Cotton denim fabric*	1910	10400	31	9.4	18.5	8.0
Cotton denim fabric*	1940	11200	32	1.0	35	8.9
Cotton denim fabric*	2400	9700	35	5.6	34	9.3
Cotton knit fabric	2300	135	14	ND	4.5	10.1
Cotton knit fabric	955	105	ND	ND	ND	9.6
Cotton knit fabric	1980	170	25	21	27	10.2
Cotton knit fabric	1180	100	14	ND	13	10.3
Cotton knit fabric	4738	70	45	ND	ND	ND
Cotton knit fabric	2100	700	62	ND	13.6	10.5
Cotton knit fabric	672	48	ND	ND	ND	ND
Cotton knit fabric	1470	490	110	0.5	4	10.9
Cotton knit fabric	828	65	22	ND	10	ND
Cotton /PES knit fabric	2400	370	20	0.2	7	10.2
Cotton /PES knit fabric	2070	85	34	ND	29	ND
PES knit fabric	1985	213	27	1.7	9	5.8
Wool/PES knit fabric	1445	<10	73	50	ND	7
Viscose rayon knit fabric	728	29	16	ND	32	ND
Silk**+Cotton***woven fabric	1070	105	110	62	2	8.2
Cotton knit fabric	785	125	30	20	ND	7.4
Cotton knit fabric	49170	9500	1765	368	ND	8.5
Wool woven fabric	650	30	ND	ND	ND	5.7
Wool yarn	1080	3500	ND	ND	ND	4.1
Wool yarn	365	1450	ND	ND	ND	6.2
Acrylic fiber and yarn	1900	90	72	ND	4.2	4.5
*Organized Industrial District**	932	225	54	ND	7.9	8.2
Domestic Sewage	410	210	43	32	7.2	7.4

*previously dyed jeans **80 % of the production; ***20 % of the production ND: not determined

Wastewaters generated in textile industrial processes, contain organic compounds which are not easily amenable to chemical or biological treatment. This can be attributed to the chemical composition and flow rates, as well as to the particular compounds used (industrial dyes, auxiliaries found in dye bath), many of which are hardly biodegradable. From the point of controlling the industrial pollution, it is quite important to apply a suitable treatment before discharging of the wastewaters which have high color, COD, SS and metal concentrations for the textile industry.

Main environmental issues arising from the activities in the textile industry are the medium-to-low refractory COD load, color, salinity, AOX and SO_4^{-2} (EPA, 1995). Receiving Media Discharge Standards for textile industry wastewaters are determined for different seven type of product processes by the Water Pollution Control Regulations. The standards applied for wastewaters originating from textile industry are given in Table 2.3.a and 2.3.b.

Table 2.3.a Receiving Media Discharge Standards for Textile Wastewaters (TÇM, 1999)

	Knit textile processing		Carpet textile processing		Synthetic textile processing	
Parameter	Composed Sample (2h.)	Composed Sample (4h.)	Composed Sample (2h.)	Composed Sample (4h.)	Composed Sample (2h.)	Composed Sample (4h.)
BOD_5 (mg/l)	50	40	120	100	100	80
COD (mg/l)	300	200	300	200	400	300
SS (mg/l)	-	-	160	120	-	-
NH_4-N (mg/l)	5	-	5	-	-	-
Chloride (mg/l)	0.3	-	0.3	-	-	-
Chrome (mg/l)	-	1	-	-	-	-
Sulfide (mg/l)	2	-	0.1	-	0.1	-
Sulfite (mg/l)	0.1	-	1	-	-	-
Phenol (mg/l)	11	0.5	1	0.5	1	0.5
Zinc (mg/l)	-	-	-	-	12	10
Grease and oil (mg/l)	10	-	10	-	-	-
Fish bioassay (ZSF)	4	3	4	3	3	2
pH	6-9	6-9	6-9	6-9	6-9	6-9

Table 2.3.b Receiving Media Discharge Standards for Textile Wastewaters (TÇM, 1999)

	Fibre production processing		Woven textile processing		Cotton textile processing		Wool washing processing	
Parameter	Composed Sample (2h.)	Composed Sample (4h.)	Composed Sample (2h.)	Composed Sample (4h.)	Composed Sample (2h.)	Composed Sample (4h.)	Composed Sample (2h.)	Composed Sample (4h.)
BOD_5 (mg/l)	80	60	90	70	90	60	200	100
COD (mg/l)	350	240	400	300	250	200	400	300
SS (mg/l)	-	-	140	100	160	120	400	300
NH_4-N (mg/l)	5	-	5	-	5	-	5	-
Chloride (mg/l)	0.3	-	0.3	-	0.3	-	0.3	-
Chrome (mg/l)	2	1	2	1	2	1	2	1
Sulfide (mg/l)	0.1	-	0.1	-	0.1	-	0.1	-
Sulfite (mg/l)	1	-	1	-	1	-	1	-
Phenol (mg/l)	-	-	1	0.5	-	-	-	-
Grease and oil (mg/l)	10	-	-	-	10	-	200	100
Fish bioassay (ZSF)	4	3	4	3	4	3	4	3
pH	6-9	6-9	6-9	6-9	6-9	6-9	6-9	6-9

Many different types of physical, chemical and biological treatment methods can be applied on textile wastewaters because dyed wastewater effluents show very changeable characteristics (Mahdavi et al., 2001). The balancing and precipitation procedures for dyed wastewaters which originates from textile industry are used as pretreatment purpose. On the other hand, since the direct precipitation procedure could not provide enough treatment efficiency, chemical treatment have to be performed with coagulant addition.

Biological treatment is the most commonly used technology applied in textile industry. The applied biological treatment systems are activated sludge system, aerated lagoons, trickling filters etc. Long aerated activated sludge systems are more successful towards toxic effects and shock loadings. However, because of high concentration of solids and heavy metals in textile wastewaters, before biological treatment, the physico-chemical pretreatment is necessary (Şengül, 1986).

Partial chemical oxidation with H_2O_2 is experimentally tested on the wastewaters originating from acrylic fibre and yarn dyeing plants and prescribed as effective pretreatment, reducing the total COD from 199 mg/L to around 700 mg/L (Germirli Babuna et al., 1999).

Özbelge et al. (2001) have investigated the removal of phenolic compounds from rubber- textile wastewaters by physico-chemical process by using four different types of coagulants ($Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $FeSO_4$, $FeCl_3$) with or without lime addition, in jar-test experiments. The optimum treatment conditions in the applied physico-chemical method are obtained by using 50 % $FeCl_3$ solution and lime at different dosages.

Çelik (2004) studied the treatment efficiency of coagulation with alum and ferric chloride as a physico-chemical treatment of Samur Carpet Dyeing Factory's wastewater. According to jar test results, alum addition is more effective on COD removal efficiency with 86 percent .

Chemical treatment, as a pretreatment application before biological treatment is also an alternative in the treatment scheme, when insoluble disperse dyes are used and removal of toxicity is necessary (Tünay, 1996). Conventional chemical treatment consist of electrolyte and polyelectrolyte addition in order to cause coagulation of the dyes and other colloidal solids, followed by precipitation. In the process, a partial

decolorisation is usually observed and the COD is reduced due to suspended solids removal. Destruction of the wastewater's color by means of coagulation/flocculation techniques using ferrous sulfate and/or lime have been carried out on textile wastewaters. Destruction of color and COD reached its maximum value (85 - 95 % and 70 %, respectively) when lime and ferrous sulfate were applied at a concentration of 800 and 1000 mg/L respectively, however it was not advantageous since it led to the production of high amounts of precipitated sludge (Georgio et al., 2002).

Selçuk (2005) also found that approximately 50 - 60 % color, 60 % COD and 70 - 80 % toxicity were removed at 1000 mg/L and 1500 mg/L ferrous and aluminum sulfate respectively. However, the required doses for optimum toxicity reduction are not economical due to the chemical sludge production. Ozonation was relatively effective in reducing color absorbances and toxic effects of textile effluents.

The other treatment methods which have been applied to textile wastewaters containing heavy metals, are chemical oxidation, neutralization and filtration. Chemical oxidation is applied as the last step of treatment. In general ozone and chlorine are used as oxidants. These chemicals have additional advantages such as providing water disinfection (Metcalf and Eddy, 1984). The use of ozone in wastewater treatment is responsible for decolorization and a partial oxidation while at the same time COD reduction of the industrial dyes. Tzitzi et al., (1994) who investigated the pretreatment of textile industry wastewaters with ozone determined that much better results were obtained using ozonation after the coagulation-precipitation stage. The explanation about chemical precipitation as a chemical treatment process is given in the part of 2.2.

2.1.2 Dyeing Auxiliaries

Textile plants usually employ cotton and synthetic fibers and include an integrated printing and dyeing operation, applying a wide variety of organic dyes (Weltrowski et al., 1996; Achwal, 1997). Purged water is used in textile finishing factories but often this is not enough and auxiliary formulations need to be added to the dyeing baths. Auxiliaries are commonly used as essential components in dyeing processes. Some of them are biodegradable, while others have poor biodegradability. They are thrifty soluble in water and are therefore largely eliminated by adsorption on the

activated sludge in wastewater treatment plants (EC, 2001). Soluble substances in water are frequently encountered in dyeing auxiliaries. Compounds that belong to this category are listed in Table 2.4.

Table 2.4 Encountered Compounds in Dyeing Auxiliaries (EC, 2001)

	Additional remarks
- Condensation products of beta-naphthalene sulphonic acids and formaldehyde	Modified condensation products of naphthalene sulphonic acid with formaldehyde are reported to have about 70 % bioeliminability
- Lignin sulphonates	
- Acrylic acid-maleic acid co-polymers	Elimination rate depends on the content of Ca^{++} ions in the wastewater
- o-phenylphenol derivatives - Methylnaphthalene derivatives	Also toxic for aquatic species
- Cyanamide-ammonia salt condensation products	
- Polyvinylpyrrolidones	
- Quaternary ammonium compounds	Also toxic for aquatic species
- Ethoxylated fatty amines	
- Alklyphenol ethoxylates	Metabolites of alkylphenol ethoxylates are reported to influence the reproduction of aquatic specie by disrupting the endocrine system
- Chlorinated aromatic compounds such as trichlorobenzenes or dichlorotolune (carriers)	Also characterised by high acute toxicity
- Biphenyl derivatives (carriers)	Also characterised by high acute toxicity

The ones most commonly used to assist the dyeing process are presented based on their function in the process as follows:

a. De-aerating and penetrating agents: The function of the de-aerating agents is expelling the air from the textile contained in the dye bath. The use of penetrating agents is associated with the dyeing of yarns, where they enhance transport of the dye into the yarn assembly. Commonly used commercial products are mainly readily bio-eliminable compounds such as alcohol polyglycol ethers and esters.

b. Dispersing agents: Dispersing agents allow the application of dye's colorants in the form of aqueous dispersions. Additional amounts of dispersants are usually added in the subsequent steps of the dyeing process to maintain the

stability of the dispersion throughout the dyeing process. Vat, disperse and sulphur dyes have a high content of dispersing agents in their formulation.

c. Levelling agents: Levelling agents are the most important class of dyeing auxiliaries which are used to improve the uniform distribution of the dye in the fibre. Two main groups of these agents can be identified as products which have an affinity for the dye and which have an affinity for the fibre.

d. Acid donors: The shift of pH occurs as the acid is released by hydrolysis during heating or as one of the acid/base components is transferred to another phase such as the fibre or air, e.g. ammonia release to air with ammonium sulphate. Acid donors represent products designed to create shifts in dye bath pH. They are widely used for wool and/or polyamide fibres to control the absorption of anionic dye onto the fibre.

e. Antifoaming agents: These products are designed to suppress foam formation. Antifoaming agents do not negatively influence the quality of dyeing. Silicone derivatives are the major group that belongs to this type of agents.

Another dyeing auxiliary seperated from the above-mentioned agents is dye carriers. They are important for dyeing blended fibres of wool and polyester.

2.1.2.1 Dye Carriers

Carriers are used in batch dyeing of synthetic fibres (particularly polyester fibres) to promote the adsorption and diffusion of disperse dyes into the fibre under low-temperature (< 100 °C) conditions withstand dyeing under high temperature. Exhaust dyeing of single polyester and polyester blends can be carried out either in autoclaves at high temperature (HT - dyeing at 130 °C, which is usually applied for pure PES and wool-free PES blends) or at normal dyeing temperatures (95 °C – 100 °C, which is applied for PES/wool blends) also wool can withstand dyeing under high temperature conditions (above 100 °C) with the help of so-called carriers. Typical carrier formulations contain 60 - 80 % of active substances and 10 - 30 % of emulsifier and sometimes a small percentage of solvent (EC, 2001).

Typical active substances for dyeing accelerants include:

- halogenated benzenes (1, 2 dichlorobenzene; 1, 2, 4 - trichlorobenzene; dichlorotoluene)
- aromatic hydrocarbons such as alpha - and beta - methylnaphthalene, diphenyl, trimethylbenzene, etc.
- phenols such as o - phenylphenol, benzylphenol, etc.
- carboxylic acid and their esters such as methyl, butyl and benzyl benzoate, methylsalicylate, phthalic acid, dimethylphthalate, dibutylphthalate and diethylhexylphthalate
- alkyl phthalimidies such as N - butylphthalimide.

Carriers include a wide group of organic compounds, many of them steam volatile, poorly biodegradable and toxic to humans and aquatic life. Aslan Alaton et al. (2004) investigated the treatability and acute toxicity of two commercially important textile dye carriers, which are both known as toxic and refractory. Results implied that ozonation pretreatment of carrier effluent did not improve biocompatibility.

Hydrophobic - type carriers exhaust at about 75 – 90 % are absorbed by the textile and only the emulsifiers and the hydrophilic - type carriers such as phenols and benzoates derivatives are found in the wastewater. The carriers that remain on the fibre after dyeing and washing, are partially volatilised during dyeing and fixing operations and can give rise to air emissions. Traces can still be found on the finished product, thus representing a potential problem for the consumer. Not only do water and air become contaminated by the emissions, but it is increasingly suspected that consumer health problems can be caused by remobilisation of halogenated carriers (e.g. 1, 2, 4 - trichlorobenzene) in the treated textiles (EC, 2001).

Dyeing at high temperature also requires higher energy consumption. The balance between the different effects involved (the effects of the hazardous carriers on the environment and the effects of higher energy consumption) is, however, still largely in favour of the application of this technique. Due to the sensitivity of the wool substrate to high temperatures, it is still necesssary to use carriers when dyeing polyester blends and, in particular, polyester/wool blends. In these cases, hazardous carriers can be replaced by chlorine-free substances with improved toxicological environmental characteristics. New carriers are based on:

- benzylbenzoate
- and N - alkylphthalimide

PES/wool blends may be dyed with benzylbenzoate and N - alkylphthalimide based carriers. Because of their low volatility, odour nuisance is negligible but they are less effective than conventional carriers (EC, 2001).

2.2 Chemical Settling

Treatment of textile wastewater by precipitation/flocculation in order to reduce organic load and especially color has been performed for more than 100 years. Many chemical treatment processes have been used extensively to treat textile wastewaters. Most of the chemical studies, such as chemical precipitation (Tünay et al., 1996), adsorption by activated carbon (Al-Degs et al., 2000) and some natural absorbents (Morais et al., 1999), photocatalytic oxidation (Arslan et al., 1999; So et al., 2002), ozonation (Liokou et al., 1997; Lin and Lai, 2000) and Fenton's oxidation (Arslan and Balcıoğlu, 2001; Kang et al., 2002) focused on color removal.

Chemical settlement is a chemical treatment method which provides the precipitation of solid substances whether dissolved or suspended in water by changing their physical state and this is releaved from coagulation, flocculation and settling steps.

Chemical coagulation is the process of forming flocculant particles in a liquid by the addition of a chemical coagulant; also the removal of colloidal or finely divided suspended matter from the liquid by the floc, and the agglomeration of the flocculated matter. The aim of the coagulation/flocculation process is to remove realcitrant organic compounds from the leachate (Silva et al., 2004). Flocculation consists in the mechanical entrapment of agglomerated particles by adsorption onto the floc formed with the coagulant chemicals. After coagulation to destabilize the particles and flocculation to generate large particles, the materials can subsequently be separated from the wastewater by sedimentation.

Chemical precipitiation is commonly used for removing heavy metals such as Cu, Zn, Cr, Hg and SS, phosphorus, hardness, etc. in wastewaters (Stephenson and Blavkburn, 1998; Tünay, 1996; Pontius, 1990).

Orhon et al. (2003) examined the effect of chemical treatment on biological treatability and applied chemical precipitation with sodium bentonite and ozonation experiments to the effluents of two cotton knit fabric processing cases. The results of physicochemical treatability indicated that, the optimum COD and color removals of 47 % and 69 % respectively, were obtained with sodium bentonite.

2.2.1 Properties of Colloidal Solutions

The big amounts of different pollutants in water which the dimensions vary between 1-100 nm are named as collodial substances. Some of these pollutants can be removed from water by simple precipitation. The pollutants which do not precipitate spontaneously because of their small dimensions can be removed from the wastewater only by forcing the substances to come together to have bigger dimensions (Weber and Walter, 1972).

Colloids are the grains which has small dimensions but larger surface areas. In liquid medium they move in a electrical fields. Surface of colloids load magnitude and their bulkiness depend on the ion content and pH value of liquid phase.

A colloidal solution is a two phase system and it may be of several combinations in terms of physical states. Colloidal solutions which have a liquid dispersion medium are known as sols, and they may be divided into two groups: One is lyophobic (liquid-resisting) and the other is lyophilic (liquid-accepting). Lyophobic sols are unstable comparison with lyophilic sols. In the lyophobic sols, small amounts of appropriate electrolytes may be able to cause agglomeration or coagulation of the dispersed particles.

Coagulation is brought about by the adsorption of opposite ions and then by the reduction of electric charges on the particles. About a colloidal solution, an "electrical double layer" of electric charges of opposite signs exists at the intersurface of the liquid and solid. In modern way of interpretation, this double layer is made up of a layer of charges firmly attached to the solid, and a layer of mobile yet loose charges extending to the solution that is seen in Figure 2.2 (Howe, 1967).

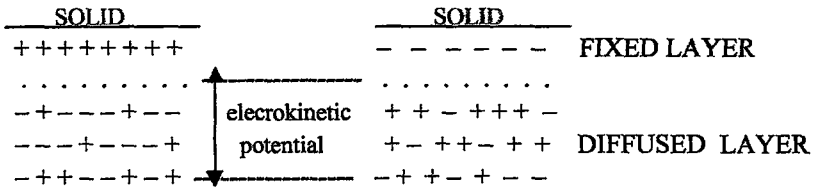


Figure 2.2 Representation of Helmholtz Electrical Double Layer

The net charge of the loose or "diffuse" layer is equal to that of the layer firmly attached to the solid except of opposite signs. The electric charges of the fixed layer may be positive in one case yet negative in another. On account of the distribution of electric charges extending from the boundary of the fixed layer to the solution, there is an "electrokinetic (zeta) potential". It is belived that the existance of electrical double layers surrounding all colloidal particles constitutes the stability of colloidal solution through the prevention of the agglomeration of particles. If one ion is adsorbed to the particle having opposite charge, the electrokinetic potential is decreased as the charge is reduced. Agglomeration, adhesion and subsequently coagulation will take place when mutual repulsion is reduced as the electrokinetic potential is decreased as given in Figure 2.3 (Howe, 1967).

Optimum coagulation will take place when the electrokinetic potential is zero. This is so-called "isoelectric" point. The electrokinetic potential may be reduced by two possibilities; namely, (1) decreasing the distance between the two oppositely charged layers or (2) increasing the charge on the "diffuse" layer thus decreasing the net charge on the particle.

When two colloids come in close proximity there are two forces acting on them. The electrostatic potential created by the ions surrounding each colloid reacts to resist the particles, thus preventing contact.

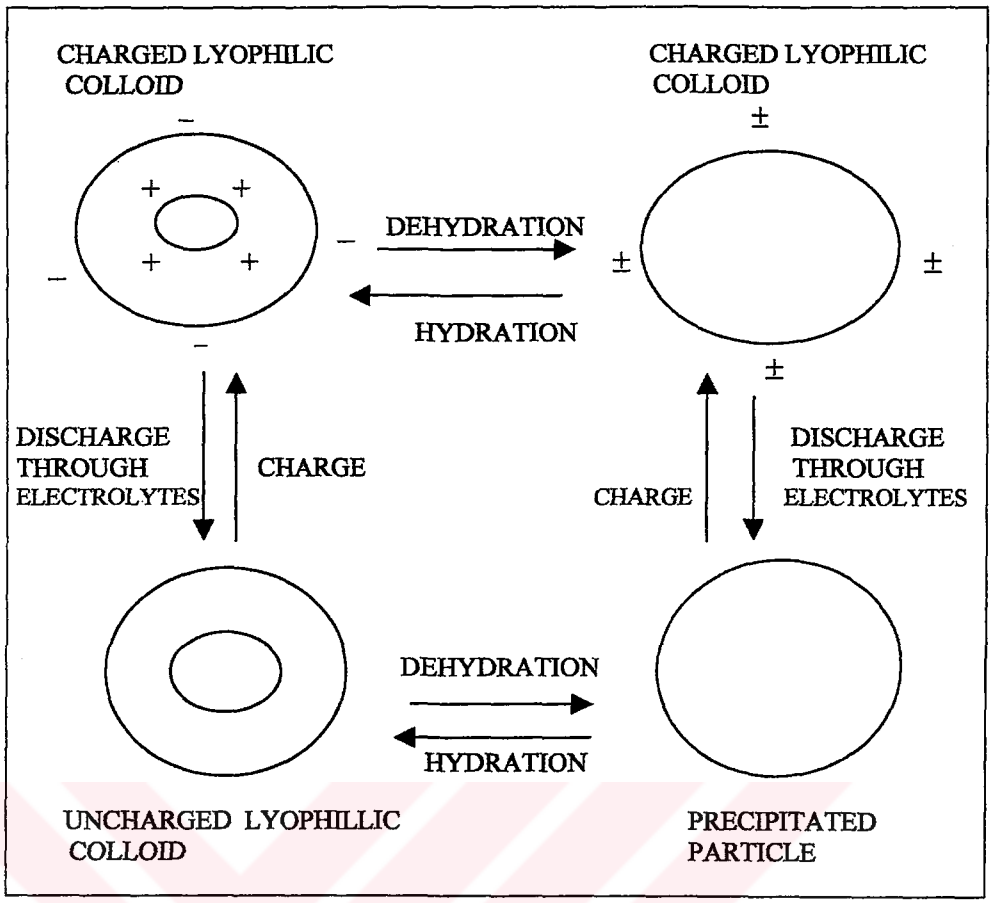


Figure 2.3 Precipitation of Colloidal Particle by Charge Reduction.

The second force, an attraction force called the van der Waals force, supports contact. This force decreases more rapidly than the electrostatic potential, but is a stronger force at close distance. The sum of two forces as they relate to one colloid in close proximity to another is illustrated in Figure 2.4.

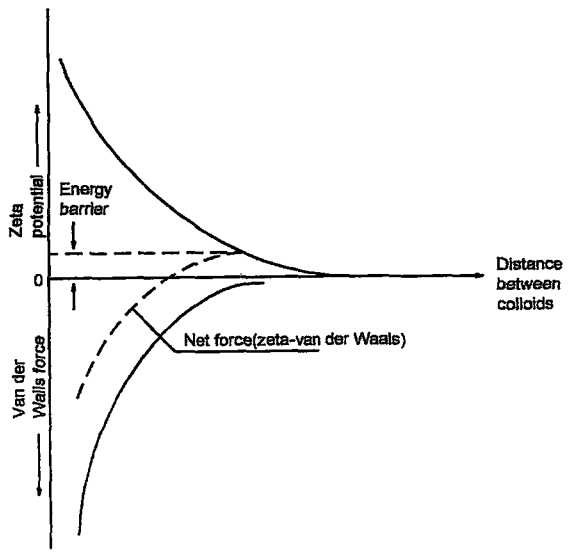


Figure 2.4 Force Fields Between Colloids of Like Charge (Peavy, et al., 1985).

As noted in the figure, the net force is repulsive at greater distances and becomes attractive only after passing through a maximum net repulsive force, called energy barrier, at some distance between colloids. Once the force becomes attractive, contact between the particles takes place. Mechanical agitation of the water may impart enough momentum to larger particles to move them across the energy barrier (Peavy, et al., 1985).

2.2.1.1 Colloidal Stability

Colloidal suspensions that do not agglomerate naturally are called stable. The most important factor contributing to the stability of colloidal suspensions is the excessively large surface-to-volume ratio resulting from their very small size. In many instances, some colloidal solutions possess the ability to resist a change of net charge in te colloidal particles by other ions. This phenomenon is known as the stability of colloidal solution. Ions contained in the water near the colloid will be affected by the charged surface. A negatively charged colloid with a possible configuration of ions around it is shown in Figure 2.5.

In order to remove colloids from water, the necessity is spoiling their stability. Elimination of electrical loads on the coloidal substances is named as destability of colloid solution. In chemical precipitation; different kinds of coagulants may spoil the colloids stability. Consequently, it will require more ions of opposite charge to break down the stability in order to produce coagulation.

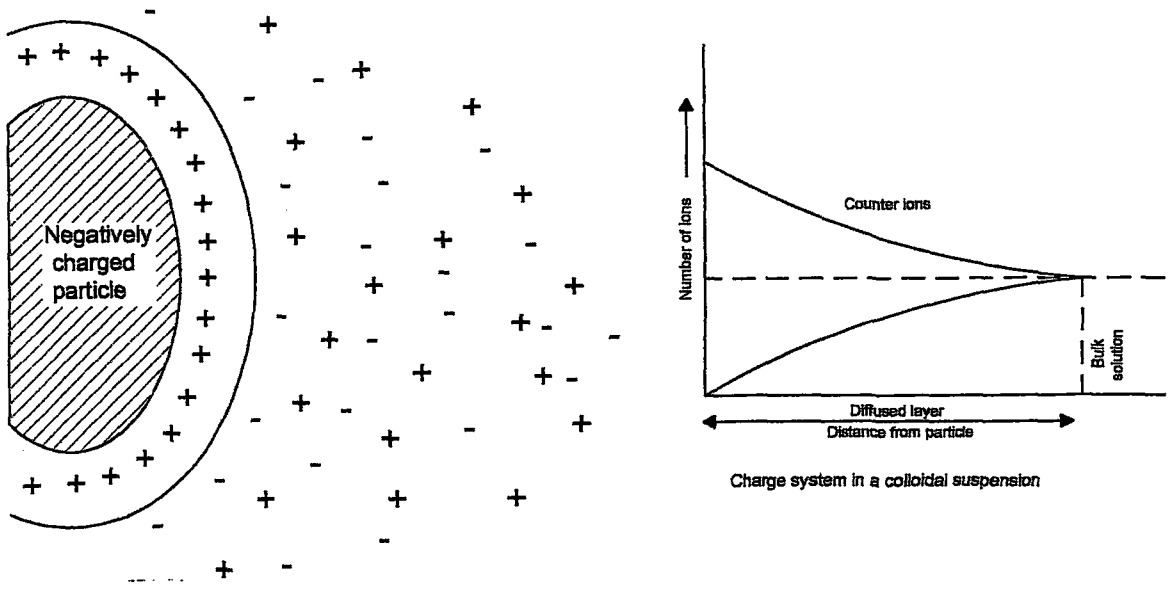


Figure 2.5 Charge System in a Colloidal Suspension (Peavy, et al., 1985).

Active carbon adsorption was applied on the colloidal systems which have pollutioners such as DDT, chlorobenzene in their content and afirmative results were taken (Nemerow and Agardy, 1997).

2.2.2 Properties of Coagulants Used in Coagulation

Flocculation agents are specifically selected in order to maximize COD and color removal, and to minimize sludge formation. In water treatment plants, chemical coagulation is usually accomplished by the addition of trivalent metallic salts such as $Al_2(SO_4)_3$ (aluminum sulfate), $FeCl_3$ (ferric chloride) or ferrous salts. Selection and optimum dosages of coagulants are determined experimentally by the jar tests. Commonly used coagulants in water purification are mentioned here.

2.2.2.1 Aluminum Sulfate

Aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) also commonly known as alumina sulfate, is the most widely used coagulant. It is available in acid to basic forms, containing from about 14.5 to 17.5 per cent Al_2O_3 (the theoritical content of Al_2O_3 in pure $Al_2(SO_4)_3.18H_2O$ is 15.3 per cent). The most important point is that both hydrogen (H^+) and hydroxyl ions (OH^-) are involved ; therefore, the pH is important like:

$$Al(OH)_3 + 3\,H^+ \longleftrightarrow Al^{+3} + 3\,H_2 \qquad (2.1)$$

$$Al(OH)_3 + OH^- \longleftrightarrow Al(OH)_4 \qquad (2.2)$$

At acidic condition,

$$Al(OH)_3 \longrightarrow Al^{+3} + 3\,(OH)^- \qquad (2.3)$$

The floc produced by alum is believed to be a hydrous oxide although some scientists considered it as a complex basic salt. However, aluminum sulfate is amphoteric. Its hydroxide will dissolve at high pH, probably also due to peptization (re-dispersion of precipitating colloidal substance) (Howe, 1967).

The reaction of $Al_2(SO_4)_3$ with water to form $Al(OH)_3$ is reversible and occur like (Casey, 1997):

$$Al_2(SO_4)_3.18H_2O + 3\,Ca(HCO_3)_2 \longrightarrow 2\,Al(OH)_3 + 3\,CaSO_4 + 6\,CO_2 + 18\,H_2O \qquad (2.4)$$

Simply,

$$Al^{+3} + 3\ HCO_3^- \longrightarrow Al(OH)_3 + 3\ CO_2 \qquad (2.5)$$

can be written.

The pH range for an optimum floc formation and precipitation occurs at pH of 5.5 to 6.8 when Na_2CO_3 is added and 5.7 when $Ca(OH)_2$ is added. Generally, cations extend the zone to the alkaline side and anions extend the zone to the acid side.

In addition to alum, sodium aluminate ($NaAlO_2$), aluminum chlorohydrate ($Al2Cl(OH)_5$, potassium alum $8Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ and ammonia alum $(Al_2(SO_4)_3 \cdot (NH_4)_2 \cdot 24H_2O$ are also used as coagulants. Sodium aluminate has a wider pH range of flocculation (5.0 – 8.5) over alum, pH is not reduced appreciably. It supplies three times as much as available alumina as alum however, it is an expensive chemical.

2.2.2.2 Ferric Salts

The ferric salts used as a coagulating agent are ferric chloride ($FeCl_3$) and ferric sulfate ($Fe_2(SO_4)_3$). The pH range for optimum floc formation by ferric salts is 3 to 11. The ferric floc is thought to be a hydrous oxide ($Fe_2O_3 \cdot H_2O$ or $Fe_2O_3 \cdot XH_2O$).

Iron salts, particularly ferric chloride, react similarly to the aluminum reactions. The most suitable coagulant in chemical treatment for dye industrial wastewaters is ferric chloride (Nandy et al., 2002).

Both ferric salts will react with bicarbonates, carbonates, and hydroxides. The end products are ferric hydroxide and new salts of sulfate or chloride and carbon dioxide when bicarbonates and carbonates are involved.

$$Fe^{+3} + 3\ HCO_3^- \longrightarrow Fe(OH)_3 + 3\ CO_2 \qquad (2.6)$$

The advantages of using ferric salts as coagulants are: the flocs produced have optimum size and appreciable resistance to breaking-up; the wide pH range of application; low cost; and the flocs formed are easy to settle and to be filtered.

2.2.2.3 Ferrous Salts

The ferrous salts that have been used as coagulants are ferrous sulfate or copperas ($FeSO_4 . 7H_2O$) and chlorinated copperas ($FeSO_4 . 7H_2O + ½ Cl_2$). Ferrous sulfate is available in crystal or granules, "sugar sulfate", and is readily soluble in water (Nordell, 1962). Sulfates are easier to remove from water than chlorides. Moreover, the use of sulfate avoids the introduction of chlorides in the wastewater and in the sludge to be incinerated.

When it reacts with the alkaline in water, ferrous hydroxide $Fe(OH)_2$ is formed. The oxidation is accomplished by adding base or lime.

$$FeSO_4 . 7H_2O + Ca(HCO_3)_2 \longrightarrow Fe(HCO_3)_2 + CaSO_4 + 18\ H_2O \qquad (2.7)$$

Adding lime,

$$Fe(HCO_3)_2 + 2\ Ca(OH)_2 \longrightarrow Fe(OH)_2 + 2\ CaCO_3 + 2\ H_2O \qquad (2.8)$$

After this reaction, Fe^{+2} turns to Fe^{+3}

$$4\ Fe(OH)_2 + O_2 + 2\ H_2O \longrightarrow 4\ Fe(OH)_3 \qquad (2.9)$$

The oxidation is generally complete at pH of above 8. Each 1 part of $FeSO_4 .7H_2O$ added requires 0.03 part of oxygen for oxidation to complete (Howe, 1967).

2.2.2.4 Lime

Lime reacts with bicarbonate or orthophosphorus compounds to form the insoluble precipitates of calcium carbonate or hydroxyapatite as shown in the following equations:

$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2\ H_2O \qquad (2.10)$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow CaCO_3 + 2\ H_2O \qquad (2.11)$$

$$5\ Ca^{+2} + 4\ OH^- + 3\ HPO_4^{-2} \longrightarrow Ca\ OH(PO_4)_3 \downarrow + 3\ H_2O \qquad (2.12)$$

The lime dosage to achieve a given phosphate or turbidity removal is more a function of wastewater alkalinity than concentration. Calcium carbonate is the most desired coagulant because of its low cost.

2.2.2.5 Sodium Bentonite

Clays whose base mineral is montmorillonite named as Bentonite have been successfully used as coagulant. In general, they formulated like $Al_2(Si_4O_{10}(H_2O)_2)n$ H_2O. The most important specification of bentonites are variable cation content, particule dimensions and high adsorbtion abilities. The crystal structure of bentonites consists of two dimensional (Al-O-OH) oxtahedral structure which was present between two dimensional silisium oxygen (SiO) tetrahedra layer and two layers of Si-O. There is a strong ionic band between silica and alumina layers and weeker Van der Waal forces between alternate unit layers. Si and Al ions whichby in a regular structure can be replaced by other ions (Gökşen, 2003).

When the bentonite crystal was placed in a diluted solution Van derWaals bonds between unique cells are seperated from each other. Their water adsorbtion can be reached to 5-6 times of their weight because of their bigger surface areas. These characteristics prove that, the bentonites are very well coagulants (Güngör, 1992).

2.2.3 Coagulant Aids

Coagulation aids form large floc particles that settle down through the solution and absorb the particles of coagulated turbidity. These chemicals act as "binders " or "bridges" in that they mechanically entrap or stick floc particles together. The most widely used coagulants aid may be briefly classified as (1) clays (2) activated silica and (3) polyelectrolytes.

2.2.3.1 Clays

Certain clays are widely used as coagulant aids in the removal of color from high color waters. High color waters, the floc, formed by coagulation, consists largely of organic matter and is too light to settle readily and that addition of a clay, "weights" the floc so that it settles much more rapidly (Peavy, et al., 1985).

It has been found in practice that small dosages of clay, when used in conjuction with aluminum or iron coagulants, did result in the formation of a good and rapidly settling floc; effected a better removal of the color, other organic matter and suspensoids; and broadened the pH range required for coagulation (Nordell, 1961).

2.2.3.2 Activated Silica

Activated silica is an effective coagulant aid for the removal of turbidity, color, organic matter and other suspendois. Many processes have been reported in connection with the application of silicates in water purification and wastewaters treatment. However, the silicates must be activated with an acid or base in order to produce colloidal flocs and they are frequently used with aluminum salts. The activation of silicates may be illustrated in the following reactions (Howe, 1967):

$$3\,H^{+} + Na_2SiO_3 \longrightarrow H_3SiO_3^{+} + 2\,Na^{-} \qquad (2.13)$$

$$OH^{-} + H_3\,SiO_3^{+} \longleftrightarrow H_4\,SiO_4^{+} \longleftrightarrow SiO(OH)_3^{-} + H^{+} \qquad (2.14)$$

Higly acid Favored Highly alkaline

and

$$2\,H_4\,SiO_4^{+} \longrightarrow SiO(OH)_3\,.\,SiO(OH)_3 + H_2O \qquad (2.15)$$

The advantages claimed for the use of activated silica are : rapid formation of flocs, tough floc, quick settling, reduction of alum dosage, good turbidity and color removal, and better coagulation at lower temperature. On the other hand, activated silicate is not favorable for coagulation: at high temperature, with iron salts, and at high pH.

2.2.3.3 Polyelectrolytes

The term polyelectrolytes has been applied to certain complex synthetic and natural organic products which may be used as coagulant aids with an aluminum or iron coagulant or, in certain applications, as coagulants. Also, these materials may be further classified as being cationic, anionic or non-ionic polyelectrolytes.

Cationic polyelectrolytes and some nonionic water soluble gums are effective flocculants for solid suspensions over wide ranges of pH and electrolyte concentration. Anionic polyelectrolytes are effective flocculants for clays having negative (-) charges only when the polymer also contains nonionic polar group – hydroxyl or amide, and/or the anion is carboxyl COO^{-} (Howe, 1967).

The improvement in floc formation, settling and clarification which may be effected by the right dosage of the proper polyelectrolyte are often startling. As to what is the right dosage and what is the proper electrolyte, this may readily be determined, in each case, by means of Jar Test.

In addition to above, there are several other factors that may affect coagulation of particles appreciably. pH is an important factor that affects the rate and the necessary concentration of electrolytes for coagulation. It has been observed that an increase in temperature would decrease the time for coagulation. Viscosity, conductivity and alkalinity are other factors affecting coagulation. Also, an increase in flocculation time with proper agitation will tend to reduce the amount of coagulant to a minimum.

The effective and economical practice of coagulation process must be based on the know-how of the mechanism of coagulation, the factors affecting coagulation, and the properties of coagulants used. Experiments, therefore, must be conducted to evaluate the best conditions for effective coagulation and thus the most suitable coagulants. The required dosage of coagulants is determined by their efficiencies which in turn are governed by their chemical and physical characteristics, concentrations, effects of other salts present, pH, alkalinities, viscosity, time and speed of mixing, and temperature. Laboratory studies by means of "jar tests" are the simpliest way to evaluate the best results of coagulation.

CHAPTER 3 MATERIAL AND METHODS

3.1 Material

3.1.1 Dye Carriers

In this study, two different carrier formulations namely Carrier I and Carrier II being frequently applied to dye polyester–elastane blends are subjected to chemical treatment because of their high organic content. The textile carrier formulations are obtained from a textile dyeing and finishing factory located in Istanbul (Pisa Tekstil). Dye carriers are subjected to lab–scale coagulation-flocculation experiments by the use of different coagulants. Optimum coagulant dosages together with optimum pH values is assessed by discussing COD removal efficiencies, sludge volume index (SVI) values and treatment costs.

Test for the inhibition of Oxygen Consumption by Activated Sludge is determined on the mentioned wastewaters to visualize the effect of pretreatment on biological treatability. Toxicity is also be tested using *Phaeodactylum tricornutum* on both raw and pretreated textile carriers with coagulation-flocculation.

3.2 Analytical Methods

All analytical measurements except the determination of the COD parameter are performed in accordance with Standard Methods (1998). COD measurements are accomplished with the ISO 6060 method (1986). For the BOD_5 tests conducted with alkali–iodide azide Winkler Method as described in Standard Methods (APHA-AWWA-WPCF, 1998) is used. For the inhibition assays, acclimated activated sludge that is previously fed with synthetic municipal wastewater (SWW) is used as the seed source. AP 40 fibre glass filter is used for SS measurements. For measurement of turbidity Hach Model 2100A, for rapid and low mixing Fhipps and Bird trademark Jar Test equipment (RPM) have been used. For metal analyses the atomic absorption equipment ATI-Unicam 929 has been used

3.2.1 Chemical Treatment Tests

In this investigation, the following procedure is used in coagulation-flocculation experiments:

_ Dosing $Al_2(SO_4)_3$, $FeCl_3$ and $FeSO_4$ at different dosages on 250 ml sample

_ Adjusting pH to desired degree by using $Ca(OH)_2$

_ Applying rapid mixing (5 minutes at 134 rpm)

_ Applying slow mixing (5 minutes at 54 rpm)

_ Adding %1 of 1 ml anionic polyelectrolyte at the end of the fifth minutes of low mixing (if necessary)

_ Applying flocculation (30 minutes)

_ Separating top of the phase

_ Measuring Sludge Volume Index (SVI) parameter at the under of the phase

_ On the top of the phase;

- Measuring pH
- Measuring Total Chemical Oxygen Demand (COD)
- Measuring turbidity

Experiments run with sodium bentonite ($Al_2(Si_4O_{10}(H_2O)_2)n\ H_2O$);

_ Dosing sodium bentonite at different dosages on 250 ml sample

_ Adjusting pH to desired degree by using $Ca(OH)_2$

_ Applying rapid mixing (3 minutes at 134 rpm)

_ Applying flocculation (3 minutes)

_ Applying rapid mixing (3 minutes at 134 rpm)

_ Applying flocculation (3 minutes)

_ Applying rapid mixing (3 minutes at 134 rpm)

_ Applying flocculation (30 minutes)

_ Separating top of the phase

_ Measuring SVI parameter at the under of the phase

_ On the top of the phase;

- Measuring pH
- Measuring Total Chemical Oxygen Demand
- Measuring turbidity

_ At the end of the chemical treatability tests, the optimum dosages and pH's are determined for each coagulant by evaluating the effluent total COD, SVI values and involved treatment costs.

The jar test is performed by using a series of glass containers. These glass containers have uniform size and shape and at least 600 ml capacity. The diagram of a jar is shown in Figure 3.1.

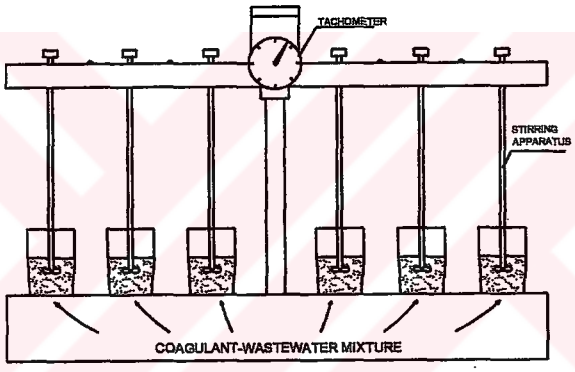


Figure 3.1 Laboratory Scale Jar Test Assembly For Coagulation Studies.

3.2.1.1 Calculation of Sludge Disposal Costs

It is thought that dewaterizing of formed sludge by using sludge drying beds is the most economical method. Besides, it is assumed that, dewatered sludge by using sludge drying beds is disposed. Daily sludge volume and dried sludge weights are experimentally determined and used for the cost of discharging sludge. The dimensions of sludge drying beds and thickness of sludge cake which was formed on the surface of drying bed at the end of the drying time is calculated for the selected dosages of different coagulants. Using thickness of sludge cake and area of sludge drying bed the volume of the sludge which have to be discharged is determined. Costs of sludge transport are calculated by considering the dried sludge volume.

The method is used to determine the dimensions of sludge drying bed and the thickness of sludge cake on the surface of the drying bed is given below (EPA, 1987)

Dry time for once spread at drying beds is;

$$t_d = \frac{(y_0)(1 - S_0 / S_f)(1 - D)}{(k_e)(E_v)} \quad (3.1)$$

At the end of the dry time thickness of the sludge cake formed on the surface of drying bed is;

$$y_f = y_0 \cdot \frac{S_0}{S_f} \quad (3.2)$$

calculated with this equation. Here,

t_d : drying time for one spread, (month)
y_0 : initial highness of sludge, (cm)
S_0 : percentage of initial solid substance
S_f : percentage of final solid substance
D : Ratio of water loss by drainage
E_v : average evaporation from free water surface, (cm/month)
k_e : the ratio of evaporation from sludge to evaporation from free water surface
y_f : thickness of sludge cake formed on the surface of the bed
as expressed.

Ratio of water loss by drainage (D) can be 75 % or more than this value at the out of well conditioned sludge and also k_e can be accepted as 0.6 (EPA, 1987). Value of E_v depends on geographical and meteorological characteristics of the region. For the calculation of initial solids percentage; unit sludge volume, weight of formed sludge and specific weight of sludge are used. Weight of dried solid substance which was experimentally obtained is divided by sludge weight to find percentage of initial solids (S_0). In Turkey, the limit value of solids substance presented in formed sludge is defined as 35 % by the Solid Waste Regulations. At the end of the chemical precipitation specific weight of formed sludge changes between 1.005– 1.05 g/L in addition, value of y_0 is advised to be between 15 – 30 cm (Metcalf &Eddy, 1984;

Vesilind, 1980). According to İSKİ data annual average evaporation from the free water surface is 1100 mm/year for İstanbul (Gökşen, 2003).

3.2.2 Activated Sludge Inhibition Tests

Activated sludge inhibition tests are conducted in accordance with a test procedure described in ISO 8192. The distilled water which have been used during analysis, have not any substances that could be impeded the growth of microorganisms. All experiments are run at a constant temperature of 20 ± 2 ^{0}C in a clean atmosphere. The quantity of used biomass have been chosen at a level to reduce dissolved oxygen concentration from 9 mg/L to 1 mg/L under the blank control. The samples are diluted with appropriate amounts of SWW (COD_{SWW} = 400 – 800 mg dm^{-3}) to obtain a series of different Carrier COD fractions thereby keeping a constant total COD in the (Carrier + SWW) effluent mixture. The heterotrophic mass used in the activated sludge inhibition test is fed with a diluted synthetic municipal wastewater. Synthetic medium stock solution is given in Table 3.1.

Table 3.1 Synthetic Medium (OECD synthetic sewage water diluted 1:1000) (ISO-8192, 1999)

Components	**Amounts**
Peptone	16 g
Meat extract	11 g
Urea	3.0 g
Sodium chloride (NaCl)	0.7 g
Dehydrate calcium chloride ($CaCl_2.2H_2O$)	0.4 g
Heptahydrate magnesium sulfate ($MgSO_4.7H_2O$)	0.2 g
Monohydrogen potassium phosphate (K_2HPO_4)	2.8 g
Distilled water	1000 mL

Raw and pretreated samples are diluted with at least four different SWW. SWW as well as raw and pre-treated carrier effluent samples are aerated for 30 min in test beakers containing proper amounts of activated sludge acclimated previously to SWW. The F/M (Food-to-Microorganisms) ratio is set between 0.16 - 0.22 mg COD mg $MLVSS^{-1}$ day^{-1} (MLVSS = 2000 – 4000 mg dm^{-3}). The decrease in dissolved oxygen concentration (in mg dm^{-3}) in the blank synthetic wastewater (SWW) as well

as in different dilutions of raw and pre-treated carriers effluent samples is monitored for 2 - 4 min using a WTW Oxi Digi 2000 model oxygen meter. Oxygen uptake rates (OUR) (in mg dm^{-3} h^{-1}) in the blank (SWW) and diluted Carrier effluent samples are calculated based on the linear part of decreasing dissolved oxygen concentration curves as a function of the aeration time. Percent inhibition of OUR, i.e. I_{OUR}, for every tested sample dilution, is calculated using the following equation;

$$I_{OUR}(\%) = [(R_B - R_T) \times 100] / R_B \quad (3.3)$$

R_B, is the oxygen uptake rate in the blank sample (mg/L.h),

R_T, is the oxygen uptake rate in the sample effluent mixture (mg/L.h)

The I_{OUR} values are thereafter plotted against ln COD's (natural logarithm of the CODs at different Carrier effluent dilutions) of Carrier formulations effluent. The COD content of raw and pre-treated carrier formulation effluent resulting in in 50 % decrease in OUR (i.e.EC_{50} values; in mg dm^{-3}) is calculated by interpolation of the lnCOD versus percent I_{OUR} plots obtained for different carrier effluent samples .

The heterotrophic sludge sensitivity is checked by means of a reference test chemical (3,5–dichlorophenol). Its EC_{50} value (5-30 mg dm^{-3}) is reconfirmed by applying the ISO 8192 test procedure. According to this procedure; 3600 mg/L activated sludge is added into the solution which was diluted with SWW in 250 ml total volume and contains 3,5–dichlorophenol at different dilutions (0. 10, 20, 30, 40 and 50 mg/L). The concentration values that causes 50 % inhibition are calculated at t = 30., 60. and 120. minutes of activated sludge oxygen uptake rate, and these are shown in Figures 3.2, 3.3 and 3.4. Also they are summarized at Table 3.2 (Gürses, 2005).

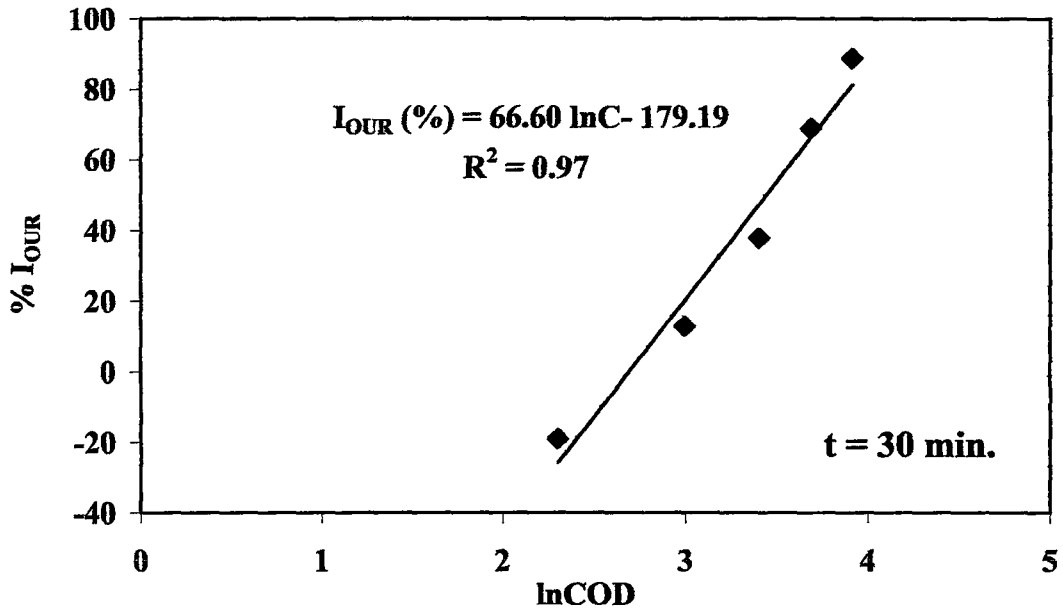


Figure 3.2 Percent Inhibition in Oxygen Uptake Rates (I_{OUR} values) Obtained for Aeration of Activated Sludge Test Reactors at 30. min. as a Function of Ln COD (MLVSS = 3600 mg/L)

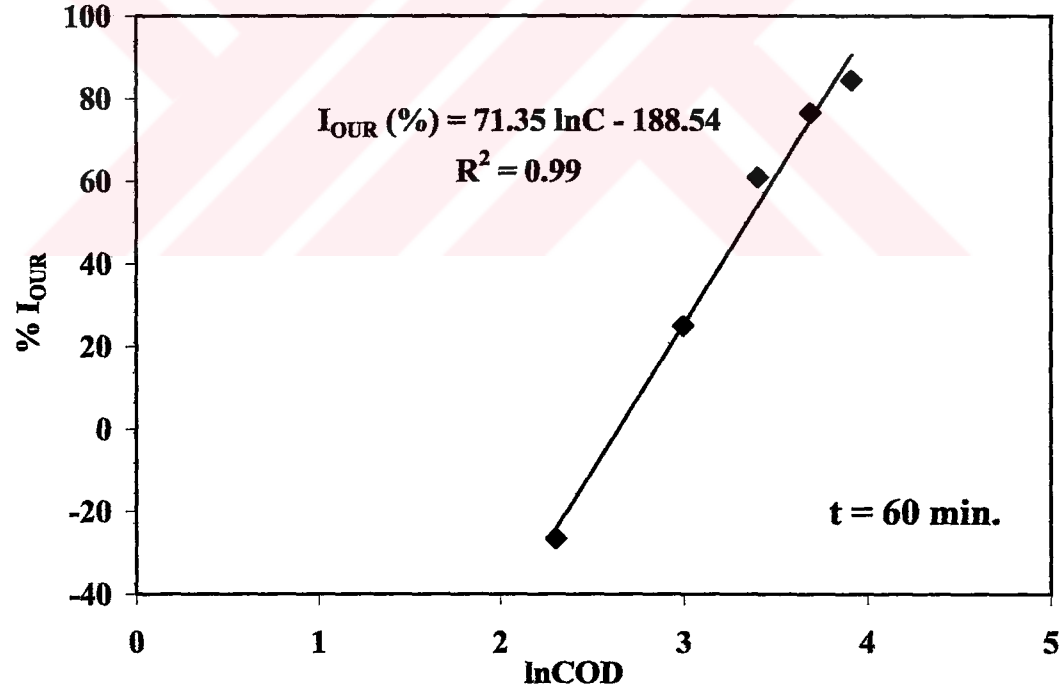


Figure 3.3 Percent Inhibition in Oxygen Uptake Rates (I_{OUR} values) Obtained for Aeration of Activated Sludge Test Reactors at 60. min. as a Function of Ln COD (MLVSS = 3600 mg/L)

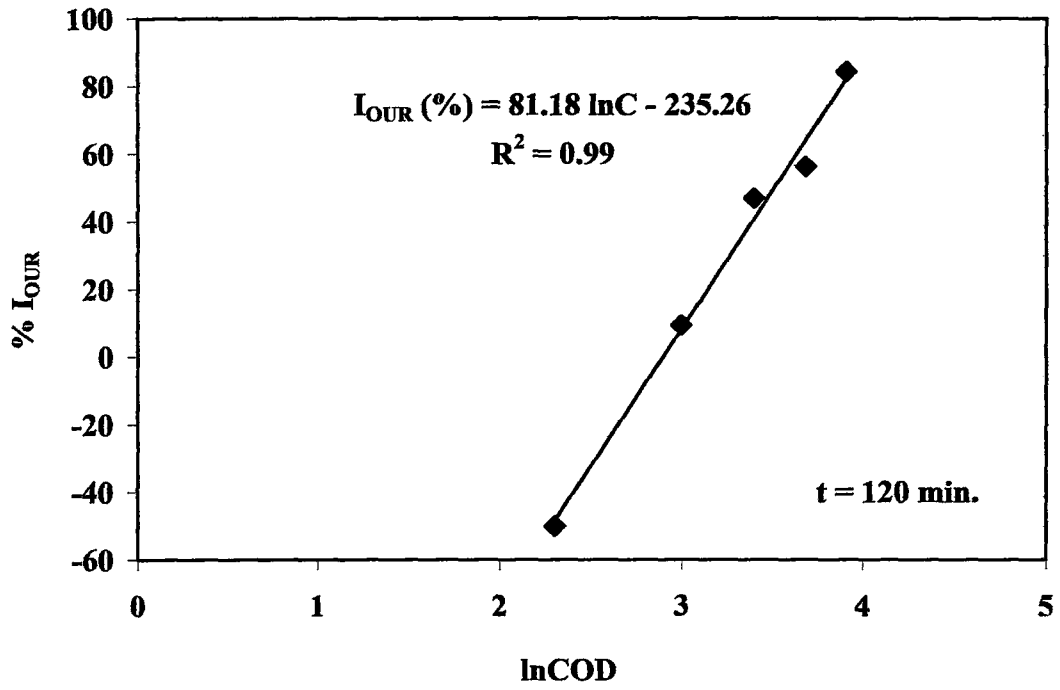


Figure 3.4 Percent Inhibition in Oxygen Uptake Rates (I_{OUR} values) Obtained for Aeration of Activated Sludge Test Reactors at 120. min. as a Function of Ln COD (MLVSS = 3600 mg/L)

Table 3.2 Concentrations of EC_{50} for 3,5-Dichlorophenol Reference Chemical at Different Aeration Times

Aeration time (min.)	**EC_{50} (mg/L)**
30	31
60	28
120	34

According to Table 3.2, the obtained average EC_{50} values at 30., 60. and 120. minutes is 31 mg/L. For reference material (3,5 dichlorophenol) EC_{50} values of the reaction times of t =30, 60, and 120 minutes are almost the same. Therefore it is determined that 30 minutes of aeration time for the activated sludge inhibition test that is performed with Carrier formulation wastewaters is enough.

3.2.3 Toxicity Tests

Batch algal bioassays are conducted in accordance with a test procedure described in US EPA 600/9-78-08. The test depends on determination of the chronical toxicity of wastewaters on indicator species of *Phaeodactylum tricornutum* (marine algae) (Okay et al., 2004). Batch algal bioassays are applied to raw and pretreated Carrier formulations. The assays are performed in a temperature controlled room (T = 20 ± 1 °C) continuously illuminated by cool-white fluorescent lamps (3500-4000 lux) Species are cultured in f/2 medium tabulated in Table 3.3.

In toxicity tests, the test materials are prepared at several dilutions. Filtered seawater and NaCl solution (13 NaCl g/L) are used to prepare raw and pretreated Carrier dilutions respectively. The raw Carrier formulations of which the toxicities will be determined are filtered through 0.45 μm Millipore filter paper. At the end of the preparations, pHs of the samples are adjusted to 7.00.

Table 3.3 Concentration of f/2 Medium Solutions (Guillard, 1972)

Sample No	Components	Concentration (g/L)
1	$NaNO_3$	75
2	$NaH_2PO_4.H_2O$	5
3	$Na_2SiO_3.5H_2O$	12.9
4	$CuSO_4.5H_2O$	0.005
	$ZnSO_4.7H_2O$	0.011
	$CoCl_2.6H_2O$	0.005
	$MnCl_2.4H_2O$	0.090
5	$FeCl_3.6H_2O$	0.909

All the substances mentioned in the Table 3.3 are weighted one by one, dissolved in distilled water and completed to 1 liter of volume.

The one below procedure is followed in toxicity tests;

- Adding 13 gr NaCl to a liter of pretreated Carrier effluents and dissolved completely. Raw Carrier effluents are dissolved in filtered (Millipore 0.45 μm) seawater.

- The dilution of pretreated Carrier effluents (% 2, %5, %10, %20, %40, %75) are prepared with 13 gr NaCl /L in 250 ml Erlenmeyer flasks.
- In 250 ml Erlenmeyer flasks, different dilutions of raw Carrier formulations (%1, % 2, %5, %10) are prepared with filtered seawater.
- f/2 medium solutions (1ml / 1L) are added to the Erlenmeyer flasks .
- The control sample is prepared by adding 500 ml dilution of f/2 medium and addition of *Phaeodactylum tricornutum* (10000 cells/ml) in a 250 ml Erlenmeyer flasks by completing with the NaCl diluted solution or with filtered seawater for pretreated and raw carrier formulations respectively.
- The algal species of *Phaeodactylum tricornutum* (4 days cultures) is added to raw and pretreated sample's flasks as the final volume to be 10000 cells / ml.
- The growth of algae is followed by counting cells daily (Coulter Counter Beckman Model Z 2) for 7 days.

The results are expressed as the graph of percent inhibition of *Phaeodactylum tricornutum* as a function of raw and pretreated Carrier effluents at different dilutions.

CHAPTER 4 EXPERIMENTAL RESULTS AND EVALUATION

4.1 Characterization of Wastewater

In the present study two extremely recalcitrant dye carriers, namely Carrier I and Carrier II are subjected to chemical treatment. These two commercially important textile dye carriers are obtained from a textile factory. Wastewaters generated in textile industrial processes, contain organic compounds which are not easily amenable to chemical or biological treatment (Tzitzi M, et al., 1994). Carrier formulations have high COD values due to particular compounds in their structure. The physicochemical/toxicological properties and characterization of the dye Carriers preparations are given in Table 4.1 and Table 4.2 respectively.

Table 4.1 Physicochemical/toxicological Properties of The Dye Carrier Preparations Carrier I and Carrier II (Arslan Alaton I, et al., 2004)

Property	**Information or Value**	
	Carrier I	**Carrier II**
Form, colour	Liquid, light yellow	Liquid, yellowish
Chemical characterization	Mixture of aromatic carbohydrates with one anionic & one non-ionic surfactant	Non chloride solvent with anionic & ionic surfactants
Active Ingredients	Isobutanol (1.6 % w/w) & tetrapropylene benzene sulfonate – Ca salt (3.6 % w/w)	Butyl benzoate (67 % w/w) & TEA dodecylbenzene suphonate(17 % w/w)
Boiling point	160 °C	ND*
Vapor pressure & density	1.38 hPa and 0.92 g ml^{-3} at 20 °C	ND*
Fish toxicity (test species: guppy)	1 - 10 mg l^{-1} LC_0	ND*
Bacterial toxicity	100 – 1000 mg l^{-1} EC_{50}	ND*

ND* : Not determined.

Table 4.2 Characterization of The Dye Carrier Formulations

Parameter	Carrier I	Carrier II
BOD_5 (mg/L)	0.4	1.6
COD (mg/L)	5000	4800
pH	6	6

In general wastewaters originating from the textile factory is known to contain strong colour, high organic load and COD concentrations (EPA, 1995). COD values belong to Carrier I is measured as 5000 mg/L and Carrier II is measured as 4800 mg/L which are very high when compared to discharge standards given in Table 2.3.a. and Table 2.3.b.

Biological treatability experiments can not be directly performed to Carrier solutions as they are not biodegradable at all. Therefore coagulation-flocculation experiments are carried out on Carrier 1 and 2 preparations as pretreatment step aiming to ease the biological treatment and determination of appropriate conditions for chemical treatability studies are decided.

4.2 Chemical Treatability Experiments

Coagulation-flocculation experiments are applied to the textile carrier formulations. In the lab-scale chemical tretability studies four different coagulants; namely sodium bentonite, alum, ferric chloride and ferrous sulfate are used. In this respect, the effect of chemical treatment on raw solutions (Carrier 1 and Carrier 2) is monitored for each coagulant at various pH values and chemical dosages. Optimum pH values and dosages for each coagulant are experimentally determined on the basis of COD removal percentages, SVI values and treatment costs.

For all experimental studies, the carriers are added to distilled water to give a final concentration of 2,5 g/L in aqueous solution because Carriers have been added to dye bath like that in textile factory. COD and SVI measurements are repeated twice. In experiments, adding coagulant before lime yielded better results in terms of the treatment efficiency and the settling behaviour of the formed flocs.

Table 4.2 Characterization of The Dye Carrier Formulations

Parameter	Carrier I	Carrier II
BOD_5 (mg/L)	0.4	1.6
COD (mg/L)	5000	4800
pH	6	6

In general wastewaters originating from the textile factory is known to contain strong colour, high organic load and COD concentrations (EPA, 1995). COD values belong to Carrier I is measured as 5000 mg/L and Carrier II is measured as 4800 mg/L which are very high when compared to discharge standards given in Table 2.3.a. and Table 2.3.b.

Biological treatability experiments can not be directly performed to Carrier solutions as they are not biodegradable at all. Therefore coagulation-flocculation experiments are carried out on Carrier 1 and 2 preparations as pretreatment step aiming to ease the biological treatment and determination of appropriate conditions for chemical treatability studies are decided.

4.2 Chemical Treatability Experiments

Coagulation-flocculation experiments are applied to the textile carrier formulations. In the lab-scale chemical tretability studies four different coagulants; namely sodium bentonite, alum, ferric chloride and ferrous sulfate are used. In this respect, the effect of chemical treatment on raw solutions (Carrier 1 and Carrier 2) is monitored for each coagulant at various pH values and chemical dosages. Optimum pH values and dosages for each coagulant are experimentally determined on the basis of COD removal percentages, SVI values and treatment costs.

For all experimental studies, the carriers are added to distilled water to give a final concentration of 2,5 g/L in aqueous solution because Carriers have been added to dye bath like that in textile factory. COD and SVI measurements are repeated twice. In experiments, adding coagulant before lime yielded better results in terms of the treatment efficiency and the settling behaviour of the formed flocs.

The treatability experiments with lime are conducted on pH 9 and 11. The results indicated inadequate flocculation and settling for both dye Carrier formulations.

All coagulation/flocculation experiments performed on Carrier preparations are applied at lower coagulant dosages than shown in the below tables. However, there is no precipitation is obtained from these experiments therefore their results are not given in the following tables.

4.2.1 Experimental Results Conducted with Sodium Bentonite

The treatability experiments with sodium bentonite are carried out at pH value of 9 and 11. However the results obtained from dosing different dosages of bentonite indicate inadequate COD removal efficiencies for both Carrier 1 and Carrier 2 formulations as given in Table 4.3, it is concluded that precipitation with sodium bentonite is not a suitable method for preliminary treatment of Carrier 1 and 2 preparations.

Table 4.3 The Results of Coagulation-Flocculation Experiments with The Application of Sodium Bentonite ($Al_2(Si_4O_{10}(H_2O)_2)nH_2O$)

	Dosage (mg/L)	Effluent COD (mg/L)	COD Removal (%)	SVI (ml/gr)	Turbidity (NTU)
Carrier 1					
pH 9	500	3744	28	3	>1000
	750	3408	35	4	>1000
	1000	3312	36	7	>1000
	2000	3072	41	11	>1000
pH 11	500	3171	39	11	>1000
	750	2864	45	10	>1000
	1000	2688	48	4	>1000
Carrier 2					
pH 9	500	4368	9	20	>1000
	600	4282	5	12	>1000
	650	4459	7	11	>1000
	800	4373	9	16	>1000
	1000	4085	15	24	>1000
	2000	4243	12	23	>1000
pH 11	600	4162	13	21	>1000
	650	4128	14	6	>1000
	700	4301	10	9	>1000
	1500	4400	8	10	>1000
	2000	3595	25	5	>1000
	2500	3624	25	6	>1000
	4000	3216	33	52	>1000

4.2.2 Experimental Results Conducted with Aluminum Sulfate

Experimental studies carried out on Carrier 1 and 2 solutions with aluminum sulfate are performed at pH value of 6 that is the original pH of the Carrier solutions. For Carrier 1 formulation, the application of alum did not give satisfactory results due to the high SVI value. The limit SVI value is 120 ml/gr. As seen in Table 4.4, 850 mg/L alum addition to Carrier 2 formulation is found to be adequate to reach the required COD removal efficiency (82 %) and SVI value (32 ml/gr).

Table 4.4 The Results of Coagulation-Flocculation Experiments with The Application of Alum ($Al_2(SO_4)_3$)

Carrier 1					
	Dosage (mg/L)	**Effluent COD (mg/L)**	**COD Removal (%)**	**SVI (ml/gr)**	**Turbidity (NTU)**
pH 6	500	749	86	179	200
	750	586	89	164	160
	1000	357	91	127	29
	1250	299	94	198	31
Carrier 2					
pH 6	***850***	***845***	***82***	***32***	***125***
	1000	768	84	22	67

The results associated with chemical treatability by the use of alum and polyelectrolyte are shown in Table 4.5.

Table 4.5 The Results of Coagulation-Flocculation Experiments with The Application of Alum and Polyelectrolyte

Carrier 1					
	Dosage (mg/L)	**Effluent COD (mg/L)**	**COD Removal (%)**	**SVI (ml/gr)**	**Turbidity (NTU)**
pH 6	500	461	91	>150	ND
	750	691	87	153	ND
	1000	163	97	226	ND
Carrier 2					
pH 6	850	2098	56	37	ND

ND : Not determined.

For Carrier 1 formulation, SVI values are higher than the limit value of 120 ml/gr similar to experiments conducted without polyelectrolyte. COD removal efficiency (56 %) for Carrier 2 formulation is not as high as the values obtained from the

application without polyelectrolyte addition. Therefore it is not considered among the optimum data points.

4.2.3 Experimental Results Conducted with Ferric Chloride

Experimental studies carried out on Carrier 1 and 2 solutions with ferric chloride are performed at pH's of 9 and 11. According to results, as given in Table 4.6, applying different ferric chloride doses showed good COD removal efficiencies but improper SVI values for Carrier 1 formulation at pH 9. Only the run performed with 1250 mg/L ferric chloride at a pH of 9 is observed to generate a good sludge. Another selected dosage is determined as 650 mg/L at pH 11 for Carrier 1 effluent. For Carrier 2 effluent, all the mentioned ferric chloride dosages at pH's of 9 and 11 satisfy the required results in terms of COD removal efficiencies and sludge characteristics. The selected dosage is determined as 650 mg/L at a pH of 9 for Carrier 2 formulation.

Table 4.6 The Results of Coagulation-Flocculation Experiments with The Application of Ferric Chloride ($FeCl_3$)

Carrier 1					
	Dosage (mg/L)	**Effluent COD (mg/L)**	**COD Removal (%)**	**SVI (ml/gr)**	**Turbidity (NTU)**
pH 9	500	418	92	300	62
	600	257	95	180	24
	750	255	95	150	20
	1000	284	95	136	30
	1250	**240**	**95**	**92**	**13**
pH 11	600	410	92	132	110
	650	**365**	**93**	**100**	**64**
	750	268	95	69	40
	1000	ND	ND	50	25
Carrier 2					
pH 9	**650**	**641**	**87**	**29**	**44**
	700	628	87	29	37
pH 11	650	707	85	24	43
	700	636	87	23	15

ND : Not determined.

The results associated with chemical treatability by the use of ferric chloride and polyelectrolyte are shown in Table 4.7.

Table 4.7 The Results of Coagulation-Flocculation Experiments with The Application of $FeCl_3$ and Polyelectrolyte

Carrier 1					
	Dosage (mg/L)	**Effluent COD (mg/L)**	**COD Removal (%)**	**SVI (ml/gr)**	**Turbidity (NTU)**
pH 9	500	312	94	171	42
	600	301	94	178	41
	650	227	96	172	22
	750	269	95	149	25
pH 11	500	ND	ND	167	55
	750	216	96	96	14
Carrier 2					
pH 9	600	883	82	16	340
	650	854	82	25	320
	700	495	90	28	10
pH 11	600	701	85	28	120
	650	604	87	18	10
	700	553	88	42	23

ND : Not determined.

Similar to that of the experiments conducted without polyelectrolyte, for Carrier 1 formulation SVI values are higher than the limit value of 120 ml/gr, except at the dosage of 750 mg/l at pH value of 11. For Carrier 2 preparation, the experimental studies conducted on pH 9 and 11 with ferric chloride dosages gave satisfactory results. However, it is not considered as the optimum data point because polyelectrolyte addition to solutions make treatment cost more expensive.

4.2.4 Experimental Results Conducted with Ferrous Sulfate

Experimental studies carried out on Carrier 1 and 2 solutions with ferrous sulfate are performed at pH value of 9 and 11. For Carrier 1 formulation, experiments showed good COD removal efficiencies but improper SVI values. As seen in Table 4.8, measured SVI values are higher than 120 ml/gr, except at the ferrous sulfate dosage of 750 mg/L and 850 mg/L at pH 9. The results of experimental study conducted on pH 11, did not show required sludge characteristics. The application of all ferrous sulfate dosages at pH of 9 and 11 are determined to be adequate results in terms of COD removal efficiencies and SVI values for Carrier 2 formulation.

The selected dosage is determined as 550 mg/L at a pH of 9 and 750 mg/L at a pH of 11 for Carrier 1 and 2 formulation respectively. The results associated with chemical treatability by the use of ferrous sulfate and polyelectrolyte are shown in Table 4.9.

Table 4.8 The Results of Coagulation-Flocculation Experiments with TheApplication of Ferrous Sulfate ($FeSO_4$)

Carrier 1					
	Dosage (mg/L)	**Effluent COD (mg/L)**	**COD Removal (%)**	**SVI (ml/gr)**	**Turbidity (NTU)**
pH 9	400	365	93	736	128
	500	232	96	195	110
	600	294	94	193	45
	750	**380**	**93**	**91**	**60**
	850	275	95	50	28
	1000	384	93	104	33
pH 11	500	223	96	183	65
	600	271	95	171	40
	750	389	93	176	17
	1000	914	82	134	17
Carrier 2					
pH 9	500	2010	58	37	ND
	550	**800**	**83**	**85**	**50**
	600	708	85	47	46
	650	699	85	43	21
	700	584	88	75	15
	800	701	85	61	17
pH 11	550	1322	73	48	535
	600	682	86	52	13
	650	758	84	53	34
	700	595	88	47	ND

ND : Not determined.

Table 4.9 The Results of Coagulation-Flocculation Experiments with The Application of Ferrous Sulfate ($FeSO_4$) and Polyelectrolyte

Carrier 1					
	Dosage (mg/L)	**Effluent COD (mg/L)**	**COD Removal (%)**	**SVI (ml/gr)**	**Turbidity (NTU)**
pH 9	500	250	95	174	ND
	750	230	96	161	ND
	1000	720	86	145	ND
pH 11	500	240	95	307	32
	750	259	95	202	10
	1000	730	86	>125	ND
Carrier 2					
pH 9	400	2179	54	9	500
	500	1216	75	18	495
	600	736	85	45	225
	700	787	84	39	20
pH 11	500	1856	61	27	700
	600	595	88	47	ND

Similar to that of the experiments conducted without polyelectrolyte, for Carrier 1 formulation all SVI values are higher than the limit value of 120 ml/gr. The experimental studies conducted with ferrous sulfate and polyelectrolyte addition could not give required effect on COD removal efficiencies for Carrier 2 formulations. Therefore, it is not considered as the optimum data point.

Chemical precipitation experiments carried out on Carrier 1 and 2 formulations with sodium bentonite, aluminum sulfate, ferric chloride and ferrous sulfate are presented above. At the end of the experiments, selected different coagulant dosages for both Carrier solutions are determined by evaluating the COD removal efficiencies, SVI values and also amount of applied doses. From the selected dosages, the optimum ones are chosen according to their treatment cost value. Information about how to calculate the treatment cost for every selected different coagulant dosages are given in the following sub-sections.

4.2.5 Calculation of Treatment Costs

Treatment costs are one of the most important factors for choosing the optimum chemical coagulant dosages in chemical treament. The following costs are given on a unit wastewater flow rate of 50 m^3. In this study, textile dye carrier preparations are subjected to lab-scale coagulation-flocculation experiments. Treatment costs are calculated for every selected coagulant by using the unit of chemical coagulant prices as given in Table 4.10. The total cost consist of cost of chemicals for coagulation, cost of pH adjustments and cost of sludge disposal.

Table 4.10 Chemical Coagulant Prices

Chemical Coagulant	Unit Price ($/kg)
Aluminum Sulphate [$Al_2(SO_4)_3.18H_2O$]	0,27
Calcium Hydroxide [$Ca(OH)_2$]	0,06
Iron II Sulphate [$FeSO_4.7H_2O$]	0,066
Iron III Chloride [$FeCl_3$]	0,175
Sulfuric Acid [H_2SO_4]	0,03
Sodium Hydroxide [NaOH]	0,02
Sodium Bentonite [$Al_2(Si_4O_{10}(H_2O)_2)nH_2O$)]	0,15
Anionic Parestil 2350 Polyelectrolyte	3

4.2.5.1 Calculation of The Treatment Cost for Sodium Bentonite

Experimental studies carried out on Carrier 1 and 2 preparations with sodium bentonite are performed at pH 9 and 11. According to results, application of different bentonite dosing did not have any effect on COD removal efficiency at all, therefore bentonite is not considered among the optimum data points. For this reason treatment cost calculation for sodium bentonite is not performed.

4.2.5.2 Calculation of The Treatment Cost for Aluminum Sulfate

In studies, SVI parameter is found to be higher than the limit value of 120 ml/gr for Carrier 1 solution therefore any alum dosage can not be selected. For Carrier 2 solution 850 mg/L alum dosage at a pH value of 6 is selected with appropriate SVI value and COD removal efficiency. Cost of daily alum consumption for selected dosage is calculated below.

In order to achieve desired pH value for Carrier 2 solution, 1,35 N $Ca(OH)_2$ is used and taken into account in coagulation-flocculation experiments. To prepare 1 N $Ca(OH)_2$, 74 grams of $Ca(OH)_2$ is dissolved in 1 liter of distilled water. To prepare 1,35 N $Ca(OH)_2$, 100 grams of $Ca(OH)_2$ is dissolved in 1 liter of distilled water. 1 liter of 1,35 N $Ca(OH)_2$ price is 0,006 $. Cost of chemicals for coagulants and pH adjustments are calculated for the process which has a daily wastewater flow rate of 50 m^3.

In experiments used unit price for alum is 0.27 $/kg. Cost of chemical treatment for Carrier 2 with the application of 850 mg/L alum dosage at a pH of 6 is calculated as:

Daily alum consumption = 850 mg/L × 50,000 L = 42,5 kg

Daily alum cost = 42,5 kg/day × 0,27 $/kg = 11,475 $/day

It is determined from the experiments that in order to bring pH of Carrier 2 preparation to 6, 230 liters of 1,35 N $Ca(OH)_2$ chemical should be used. It is known that 1 liter of 1,35 N $Ca(OH)_2$ price is 0,006 $. In this case the daily $Ca(OH)_2$ cost is:

230 L/day × 0,006 $/L = 1,38 $/day

There is no polyelectrolyte consumption in these set dosages therefore cost of polyelectrolyte is not calculated. Experiments concerning alum applications are

performed at pH 6 hence pH values need not be readjusted before entering biological treatment.

Cost of sludge disposal is calculated below.

At the end of the chemical precipitation experiments with the application of 850 mg/L alum dosage at a pH of 6, 220 ml sludge is formed for a liter of wastewater. Suspended solids weight of sludge is 7 gr. For this situation, daily sludge volume and suspended solids weight of sludge are calculated as :

V_{sludge} = 0,220 L sludge/L ww × 50,000 L ww/day = 11000 L sludge/day

M_{sludg} = 0,007 kg sludge /L ww × 50,000 L ww/day = 350 kg sludge /day

Specific weight of sludge is given between 1,005 - 1,05 kg/L in the literature (Metcalf & Eddy, 1984; Vesilind,1980). When the specific weight of sludge accepted as 1,04 kg/L, the percentage of suspended solids in sludge (S_o) can be calculated as:

S_o = 350 kg / (11000 L × 1,04 kg/L) = 0,031

After dewaterizing the sludge, final solid substance is accepted as 35 % limit value. Water ratio that is lost by drainage (D) and k_e are accepted as 0.6. Sludge drying time (t_d) and height of dried sludge on the bed (y_f) are calculated by using the equations (3.1) and (3.2) respectively. The initial height of sludge (first application depth) (y_0) is taken as 30 cm and annual average evaporation from the free water surface (E_v) is accepted as 9,1 cm/month.

As a result of application of 850 mg/L alum at pH 6, drying time (t_d) of sludge is :

t_d = [30 cm × (1-0,031/0,35) × (1-0,6)] / [(0,6× 9,1cm/month)]

t_d = 2,003 month = 60 day

Height of dry sludge (y_f) on the bed is:

y_f = 30 cm × (0,031 / 0,35) = 2,657 cm

Sludge drying bed volume is calculated by using sludge dry time and daily flow rate of sludge. Area of sludge drying bed is calculated by using the initial height of spreaded sludge (y_0).

V_{bed} = 11000L sludge /day × 60 day = 660000 L = 660 m^3

$A_{bed} = V_{bed} / y_0$

$A_{bed} = 660\ m^3 / 0{,}3\ m = 2200\ m^2$

Dried sludge volume need to be transported is found by using sludge drying bed area and dried sludge height.

$V_{dry\ sludge} = A_{bed} \times y_f/100$

$V_{dry\ sludge} = 2200\ m^2 \times 2{,}657\ cm / 100\ cm/m = 58{,}454\ m^3$ dry sludge

If 2 m^3 of sludge was carried by tractor and cost of each convance was 20 $, cost of sludge transportation could be calculated as follows;

Cost of sludge transportation = 20 $ × 58,454 m^3 / 2 m^3 = 584,54 $

Cost of daily sludge disposal = 584,54 $ / 60 day = 9,742 $/day

Total daily cost is found by the addition of cost of daily alum, cost of daily lime and cost of daily sludge disposal. Cost of unit wastewater treatment is found by using 50 m^3 flow rate of wastewater per a day.

Total daily cost = 11,475 $/day + 1,38 $/day + 9,742 $/day = 22,597 $/day

Unit wastewater treatment cost = 22,597 $/day / 50 m^3/day = 0,452 $/ m^3 ww.

Cost of chemicals and cost of sludge disposal associated with chemical treatability by the use of aluminum sulfate are shown in Table 4.11 and Table 4.12 respectively.

4.2.5.3 Calculation of The Treatment Cost for Ferric Chloride

In studies, for Carrier 1 solution 1250 mg/L and 650 mg/L ferrous sulfate dosages at pH values of 9 and 11 respectively, are selected according to their required SVI values. For Carrier 2, 650 mg/L ferrous sulfate dosage at pH 9 is found as required result in terms of COD removal efficiency and SVI value. Cost of daily ferric chloride consumption for selected dosages are calculated below.

In order to achieve desired pH value for Carrier formulations, 1,35 N $Ca(OH)_2$ and 0,1 N H_2SO_4 are used and taken into account. To prepare 1 N $Ca(OH)_2$, 74 grams of $Ca(OH)_2$ is dissolved in 1 liter of distilled water. To prepare 1,35 N $Ca(OH)_2$, 100 grams of $Ca(OH)_2$ is dissolved in 1 liter of distilled water. To prepare 0,1 N H_2SO_4, 2,8 ml of 36 N H_2SO_4 is added to 1 liter of distilled water. It is known that 1 kg $Ca(OH)_2$'s price is 0,06 $ and 1 liter of 0,1 N H_2SO_4's price is 0,03 $ therefore the prices for 1 liter of 1,35 N $Ca(OH)_2$ and 1 liter of 0,1 N H_2SO_4 are 0,006 $ and

$0{,}84\times10^{-4}$ $ respectively. Cost of chemicals for coagulants and pH adjustments are calculated for the process which has a daily wastewater flow rate of 50 m^3.

In experiments used unit price for ferric chloride is 0.175 $/kg. Cost of chemical treatment for Carrier 1 solution with the application of 1250 mg/L ferric chloride dosage at a pH of 9 and 650 mg/L ferric chloride dosage at a pH of 11 are calculated. In addition, for Carrier 2 solution, with the application of 650 mg/L ferric chloride dosage at a pH of 9 is calculated below.

Carrier 1 :

Daily ferric chloride consumption = 1250 mg/L × 50,000 L = 62,5 kg

= 650 mg/L × 50,000 L = 32,5 kg

Daily ferric chloride cost = 62,5 kg/day × 0,175 $/kg = 10,938 $/day

= 32,5 kg/day × 0,175 $/kg = 5,688 $/day

It is determined from the experiments that in order to bring pH of 1250 mg/L ferric chloride dosage to 9 and pH of 650 mg/L dosage to 11, 460 and 270 liters of 1,35 N $Ca(OH)_2$ chemical respectively, should be used. In this case daily $Ca(OH)_2$ cost is :

460 L/day × 0.006 $/L = 2,76 $/day (for 1250 mg/L dosage)

270 L/day × 0.006 $/L = 1,62 $/day (for 650 mg/L dosage)

There is no polyelectrolyte consumption in these set dosages therefore cost of polyelectrolyte is not calculated.

In case of precipitation for carrier formulations at pH 9 and pH 11, pH should be readjusted before the entrance of the biological treatment. In order to adjust desired pH value of pretreated Carrier 1 formulations, 200 litres and 160 liters of 0,1 N H_2SO_4 for 1250 mg/L ferric chloride dosage at a pH value of 9 and 650 mg/L dosage at pH 11 are used respectively. In this case daily H_2SO_4 cost is:

200 L/day × 0,000084 $/lt = 0,017 $/day (for 1250 mg/L dosage)

160 L/day × 0,000084 $/lt = 0,013 $/day (for 650 mg/L dosage)

Cost of sludge disposal is calculated below.

At the end of the chemical precipitation experiments with the application of 1250 mg/L at pH 9 and 650 mg/L ferric chloride dosage at a pH of 11, 292 ml and 284 ml

sludges are formed respectively, for a liter of wastewater. Suspended solids weight of sludge is 3,2 gr for 1250 mg/L ferric chloride dosage and 2,8 gr for 750 mg/L ferric chloride dosage. For this situation, daily sludge volume and suspended solids weight of sludge are calculated as;

V_{sludge} = 0,292 L sludge/L ww × 50,000 L ww/day = 14600 L sludge/day

(for 1250 mg/L dosage)

V_{sludge} = 0,284 L sludge/L ww × 50,000 L ww/day = 14200 L sludge/day

(for 650 mg/L dosage)

M_{sludge} = 0,0032 kg sludge /L ww × 50,000 L ww/day = 160 kg sludge /day

(for 1250 mg/L dosage)

M_{sludge} = 0,0028 kg sludge /L ww × 50,000 L ww/day = 140 kg sludge /day

(for 650 mg/L dosage)

Specific weight of sludge is given between 1,005 - 1,05 kg/L in the literature (Metcalf & Eddy, 1984; Vesilind,1980). When the specific weight of sludge accepted as 1,04 kg/L, the percentage of suspended solids in sludge (S_o) can be calculated as :

S_o = 160 kg / (14600 L × 1,04 kg/L) = 0,011 (for 1250 mg/L dosage)

S_o = 140 kg / (14200 L × 1,04 kg/L) = 0,009 (for 650 mg/L dosage)

After dewaterizing the sludge, final solid substance is accepted as 35 % limit value. Water ratio that is lost by drainage (D) and k_e are accepted as 0.6. Sludge drying time (t_d) and height of dried sludge on the bed (y_f) are calculated by using the equations (3.1) and (3.2) respectively. The initial height of sludge (first application depth) (y_0) is taken as 30 cm and annual average evaporation from the free water surface (E_v) is accepted as 9,1 cm/month.

As a result of application of 1250 mg/L ferric chloride at pH 9 and application of 650 mg/L ferric chloride at pH 11, drying time (t_d) of sludge is :

t_d = [30 cm × (1-0,011 /0,35) × (1-0,6)] / [(0,6× 9,1cm/month)]

t_d = 2,129 month = 64 day (for 1250 mg/L dosage)

t_d = [30 cm × (1-0,009/0,35) × (1-0,6)] / [(0,6× 9,1cm/month)]

t_d = 2,141 month = 64 day (for 650 mg/L dosage)

Height of dry sludge (y_f) on the bed is:

$y_f = 30\ cm \times (0{,}011 / 0{,}35) = 0{,}943\ cm$ (for 1250 mg/L dosage)

$y_f = 30\ cm \times (0{,}009 / 0{,}35) = 0{,}771\ cm$ (for 650 mg/L dosage)

Sludge drying bed volume is calculated by using sludge dry time and daily flow rate of sludge. Area of sludge drying bed is calculated by using the initial height of spreaded sludge.

$V_{bed} = 14600L$ sludge /day $\times 64$ day $= 934400\ L = 934{,}4\ m^3$ (for 1250 mg/L dosage)
$V_{bed} = 14200L$ sludge /day $\times 64$ day $= 908800\ L = 908{,}8\ m^3$ (for 650 mg/L dosage)

$A_{bed} = V_{bed} / y_0$

$A_{bed} = 934{,}4\ m^3 / 0{,}3\ m = 3114{,}666\ m^2$ (for 1250 mg/L dosage)

$A_{bed} = 908{,}8\ m^3 / 0{,}3\ m = 3029{,}333\ m^2$ (for 650 mg/L dosage)

Dried sludge volume need to be transported is found by using sludge drying bed area and dried sludge height.

$V_{dry\ sludge} = A_{bed} \times y_f / 100$

$V_{dry\ sludge} = 3114{,}666\ m^2 \times 0{,}943\ cm / 100 cm/m = 28{,}032\ m^3$ dry sludge

(for 1250 mg/L dosage)

$V_{dry\ sludge} = 3029\ m^2 \times 0{,}771\ cm / 100 cm/m = 24{,}232\ m^3$ dry sludge

(for 650 mg/L dosage)

If $2\ m^3$ of sludge was carried by tractor and cost of each convance was 20 $, cost of sludge transportation could be calculated as follows;

Cost of sludge transportation = $20\$ \times 28{,}032\ m^3 / 2\ m^3 = 280{,}32\$$

(for 1250 mg/L dosage)

Cost of sludge transportation = $20\$ \times 24{,}232\ m^3 / 2\ m^3 = 242{,}32\$$

(for 650 mg/L dosage)

Cost of daily sludge disposal = 280,32 $ / 64 day = 4,38 $/day at 1250 mg/L dosage

= 242,32 $ / 64 day = 3,786 $/day at 650 mg/L dosage

Total daily cost is found by the addition of cost of daily ferric chloride, cost of daily lime and cost of daily sludge disposal. Cost of unit wastewater treatment is found by using 50 m^3 flow rate of wastewater per a day.

Total daily cost = 10,938 $/day + 2,76 $/day + 0,017 $/day + 4,38 $/day

= 18,095 $/day (for 1250 mg/L dosage)

Total daily cost = 5,688 $/day + 1,62 $/day + 0,013 $/day + 3,786 $/day

= 11,107 $/day (for 650 mg/L dosage)

Unit wastewater treatment cost = 18,095 $/day / 50 m^3/day = 0,362 $/ m^3 ww.

(for 1250 mg/L dosage)

Unit wastewater treatment cost = 11,107 $/day / 50 m^3/day = 0,222 $/ m^3 ww.

(for 650 mg/L dosage)

Carrier 2 :

Daily ferrous chloride consumption = 650 mg/L × 50,000 L = 32,5 kg

Daily ferrous chloride cost = 32,5 kg/day × 0,175 $/kg = 5,688 $/day

It is determined from the experiments that in order to bring pH of 650 mg/L ferric chloride dosage to 9, 260 liters of 1,35 N $Ca(OH)_2$ chemical should be used. In this case daily $Ca(OH)_2$ cost is :

260 L/day × 0.006 $/day = 1.56 $/day

There is no polyelectrolyte consumption in these set dosages so polyelectrolyte cost is not calculated.

In case of precipitation for carrier 2 formulation at pH 9, pH should be readjusted before the entrance of the biological treatment. In order to adjust desired pH value of pretreated Carrier 2 formulation, 200 litres of 0,1 N H_2SO_4 for 650 mg/L ferric chloride dosage at a pH value of 9 is used. In this case daily H_2SO_4 cost is:

200 L/day × 0,000084 $/L = 0,017 $/day

Cost of sludge disposal is calculated below.

At the end of the chemical precipitation experiments with the application of 650 mg/L alum dosage at a pH of 9, 232 ml sludge is formed for a liter of wastewater.

Suspended solids weight of sludge is 8 gr. For this situation, daily sludge volume and suspended solids weight of sludge are calculated as;

V_{sludge} = 0,232 L sludge/L ww × 50,000 L ww/day = 11600 L sludge/day

M_{sludge} = 0,008 kg sludge /L ww × 50,000 L ww/day = 400 kg sludge /day

Specific weight of sludge is given between 1,005 - 1,05 kg/L in the literature (Metcalf & Eddy, 1984; Vesilind,1980). When the specific weight of sludge accepted as 1,04 kg/L, the percentage of suspended solids in sludge (S_o) can be calculated as:

S_o = 400 kg / (11600 L × 1,04 kg/L) = 0,033

After dewaterizing the sludge, final solid substance is accepted as 35 % limit value. Water ratio that is lost by drainage (D) and k_e are accepted as 0.6. Sludge drying time (t_d) and height of dried sludge on the bed (y_f) are calculated by using the equations (3.1) and (3.2) respectively. The initial height of sludge (first application depth) (y_0) is taken as 30 cm and annual average evaporation from the free water surface (E_v) is accepted as 9,1 cm/month.

As a result of application of 650 mg/L ferric chloride at pH 9, drying time (t_d) of sludge is :

t_d = [30 cm × (1-0,033/0,35) × (1-0,6)] / [(0,6× 9,1 cm/month)]

t_d = 1,991month = 60 day

Height of dry sludge (y_f) on the bed is:

y_f = 30 cm × (0,988 / 0,35) = 2,829 cm

Sludge drying bed volume is calculated by using sludge dry time and daily flow rate of sludge. Area of sludge drying bed is calculated by using the initial height of spreaded sludge.

V_{bed} = 11600L sludge /day × 60 day = 696000 L = 696 m^3

$A_{bed} = V_{bed} / y_0$

A_{bed} = 696 m^3 / 0,3 m = 2320 m^2

Dried sludge volume need to be transported is found by using sludge drying bed area and dried sludge height.

$V_{dry\ sludge} = A_{bed} \times y_f / 100$

$V_{dry\ sludge}$ = 2320 m^2 × 2,829 cm / 100cm/m = 65,633 m^3 dry sludge

If 2 m^3 of sludge was carried by tractor and cost of each convance was 20 $, cost of sludge transportation could be calculated as follows;

Cost of sludge transportation = 20$ × 65,633 m^3 / 2 m^3 = 656,33 $

Cost of daily sludge disposal = 656,33 $ / 60 day = 10,939 $/day

Total daily cost is found by the addition of cost of daily ferric chloride, cost of daily lime and cost of daily sludge disposal. Cost of unit wastewater treatment is found by using 50 m^3 flow rate of wastewater per a day.

Total daily cost = 5,689 $/day + 1,56 $/day + 0,0168 $/day +10,939 $/day

= 18,203 $/day

Unit wastewater treatment cost = 18,203 $/day / 50 m^3/ day = 0,364 $/$m^3$ ww.

Cost of chemicals and cost of sludge disposal associated with chemical treatability by the use of ferric chloride are shown in Table 4.11 and Table 4.12 respectively.

4.2.5.4 Calculation of The Treatment Cost for Ferrous Sulfate

In studies, experiments conducted at the pH of 9 with a ferrous sulfate dosage of 750 mg/L for Carrier 1 and at the same pH with the dosage of 550 mg/L for Carrier 2 formulations gave pleasing results in terms of required COD removal efficiency and SVI values. Cost of daily ferrous sulfate consumption for selected dosages are calculated below.

In order to achieve desired pH value for Carrier formulations, 1,35 N $Ca(OH)_2$ and 0,1 N H_2SO_4 are used and taken into account. To prepare 1 N $Ca(OH)_2$, 74 grams of $Ca(OH)_2$ is dissolved in 1 liter of distilled water. To prepare 1,35 N $Ca(OH)_2$, 100 grams of $Ca(OH)_2$ is dissolved in 1 liter of distilled water. To prepare 0,1 N H_2SO_4, 2,8 ml of 36 N H_2SO_4 is added to 1 liter of distilled water. It is known that 1 kg $Ca(OH)_2$'s price is 0,06 $ and 1 liter of 0,1 N H_2SO_4 's price is 0,03 $ therefore the prices for 1 liter of 1,35 N $Ca(OH)_2$ and 1 liter of 0,1 N H_2SO_4 are 0,006 $ and $0{,}84\times10^{-4}$ $ respectively. Cost of chemicals for coagulants and pH adjustments are calculated for the process which has a daily wastewater flow rate of 50 m^3.

In studies used unit price for ferrous sulfate is 0.066 $/kg. Cost of chemical treatment for Carrier 1 solution with the application of 750 mg/L ferrous sulfate dosage at a pH

of 9 and for Carrier 2 solution with the application of 550 mg/L ferrous sulfate dosage at a pH of 9 are calculated below.

Carrier 1 :

Daily ferrous sulfate consumption = 750 mg/L × 50,000 L = 37,5 kg

Daily ferrous sulfate cost = 37,5 kg/day × 0,066 $/kg = 2,475 $/day

It is determined from the experiments that in order to bring pH of 750 mg/L ferrous sulfate dosage to 9, 150 liters of 1,35 N $Ca(OH)_2$ chemical should be used. In this case daily $Ca(OH)_2$ cost is :

150 L/day × 0.006 $/L = 0,9 $/day

There is no polyelectrolyte consumption in these set dosages therefore cost of polyelectrolyte is not calculated.

In case of precipitation for Carrier 1 formulation at pH 9, pH should be readjusted before the entrance of the biological treatment. In order to adjust desired pH value of pretreated Carrier 1 formulation, 50 litres of 0,1 N H_2SO_4 for 750 mg/L ferrous sulfate dosage at a pH value of 9 is used. In this case daily H_2SO_4 cost is:

50 L/day × 0,000084 $/lt = 0,004 $/day

Cost of sludge disposal is calculated below.

At the end of the chemical precipitation experiments with the application of 750 mg/L ferrous sulfate dosage at a pH of 9, 284 ml sludge is formed for a liter of wastewater. Suspended solids weight of sludge is 3 gr. For this situation, daily sludge volume and suspended solids weight of sludge are calculated as;

V_{sludge} = 0,284 L sludge/L ww × 50,000 L ww/day = 14200 L sludge/day

M_{sludge}= 0,003 kg sludge /L ww × 50,000 L ww/day = 150 kg sludge /day

Specific weight of sludge is given between 1,005 - 1,05 kg/L in the literature (Metcalf & Eddy, 1984; Vesilind,1980). When the specific weight of sludge accepted as 1,04 kg/L, the percentage of suspended solids in sludge (S_o) can be calculated as:

S_o = 150 kg / (14200 L × 1,04 kg/L) = 0,010

After dewaterizing the sludge, final solid substance is accepted as 35 % limit value. Water ratio that is lost by drainage (D) and k_e are accepted as 0.6. Sludge drying time

(t_d) and height of dried sludge on the bed (y_f) are calculated by using the equations (3.1) and (3.2) respectively. The initial height of sludge (first application depth) (y_0) is taken as 30 cm and annual average evaporation from the free water surface (E_v) is accepted as 9,1 cm/month.

As a result of application of 750 mg/L ferrous sulfate at pH 9, drying time (t_d) of sludge is :

t_d = [30 cm × (1-0,010/0,35) × (1-0,6)] / [(0,6× 9,1cm/month)]

t_d = 2,135 month = 64 day

Height of dry sludge (y_f) on the bed is:

y_f = 30 cm × (0,010 / 0,35) = 0,857 cm

Sludge drying bed volume is calculated by using sludge dry time and daily flow rate of sludge. Area of sludge drying bed is calculated by using the initial height of the spreaded sludge.

V_{bed} = 14200L sludge /day × 64 day = 908000 L = 908,8 m^3

$A_{bed} = V_{bed} / y_0$

A_{bed} = 908,8 m^3 / 0,3 m = 3029,333 m^2

Dried sludge volume need to be transported is found by using sludge drying bed area and dried sludge height.

$V_{dry\ sludge} = A_{bed} \times y_f/100$

$V_{dry\ sludge}$ = 3029,333 m^2 × 0,857 cm / 100cm/m = 25,961 m^3 dry sludge

If 2 m^3 of sludge was carried by tractor and cost of each convance was 20 $, cost of sludge transportation could be calculated as follows;

Cost of sludge transportation = 20 $ × 25,961 m^3 / 2 m^3 = 259,61 $

Cost of daily sludge disposal = 259,61 $ / 64 day = 4,056 $/day

Total daily cost is found by the addition of cost of daily ferrous sulfate, cost of daily lime and cost of daily sludge disposal. Cost of unit wastewater treatment is found by using 50 m^3 flow rate of wastewater per a day.

Total daily cost = 2,475 $/day + 0,9 $/day + 0,004 $/day + 4,056 $/day

= 7,435 $/day

Unit wastewater treatment cost = 7,435 $/day / 50 m^3/ day = 0,149 $/m^3$ ww.

Carrier 2:

Daily ferrous sulfate consumption = 550 mg/L × 50,000 L = 27,5 kg

Daily ferrous sulfate cost = 27,5 kg/day × 0,066 $/kg = 1,815 $/day

It is determined from the experiments that in order to bring pH of 550 mg/L ferrous sulfate dosage to 9, 120 liters of 1,35 N $Ca(OH)_2$ chemical should be used. In this case daily $Ca(OH)_2$ cost is :

120 L/day × 0.006 $/L = 0,72 $/day

There is no polyelectrolyte consumption in these set dosages therefore cost of polyelectrolyte is not calculated.

In case of precipitation for carrier 2 formulation at pH 9, pH should be readjusted before the entrance of the biological treatment. In order to adjust desired pH value of pretreated Carrier 2 formulation, 160 litres of 0,1 N H_2SO_4 for 550 mg/L ferrous sulfate dosage at a pH value of 9 is used. In this case daily H_2SO_4 cost is:

160 L/day × 0,000084 $/lt = 0,013 $/day

Cost of sludge disposal is calculated below.

At the end of the chemical precipitation experiments with the application of 550 mg/L ferrous sulfate dosage at a pH of 9, 280 ml sludge is formed for a liter of wastewater. Suspended solids weight of sludge is 3,3 gr. For this situation, daily sludge volume and suspended solids weight of sludge are calculated as;

V_{sludge} = 0,280 L sludge/L ww × 50,000 L ww/day = 14000 L sludge/day

M_{sludge} = 0,0033 kg sludge /L ww × 50,000 L ww/day = 165 kg sludge /day

Specific weight of sludge is given between 1,005 - 1,05 kg/L in the literature (Metcalf & Eddy, 1984; Vesilind,1980). When the specific weight of sludge accepted as 1,04 kg/L, the percentage of suspended solids in sludge (S_o) can be calculated as:

S_o = 165 kg / (14000 L × 1,04 kg/L) = 0,011

After dewaterizing the sludge, final solid substance is accepted as 35 % limit value. Water ratio that is lost by drainage (D) and k_e are accepted as 0.6. Sludge drying time (t_d) and height of dried sludge on the bed (y_f) are calculated by using the equations (3.1) and (3.2) respectively. The initial height of sludge (first application depth) (y_0) is taken as 30 cm and annual average evaporation from the free water surface (E_v) is accepted as 9,1 cm/month.

As a result of application of 550 mg/L ferrous sulfate at pH 9, drying time (t_d) of sludge is :

t_d = [30 cm × (1-0,011/0,35) × (1-0,6)] / [(0,6× 9,1cm/month)]

t_d = 2,129 month = 64 day

Height of dry sludge (y_f) on the bed is:

y_f = 30 cm × (0,011/ 0,35) = 0,943 cm

Sludge drying bed volume is calculated by using sludge dry time and daily flow rate of sludge. Area of sludge drying bed is calculated by using the initial height of spreaded sludge.

V_{bed} = 14000L sludge /day × 64 day = 896000 L = 896 m^3

$A_{bed} = V_{bed} / y_o$

A_{bed} = 896 m^3 / 0,3 m = 2986,666 m^2

Dried sludge volume need to be transported is found by using sludge drying bed area and dried sludge height.

$V_{dry\ sludge} = A_{bed} \times y_f/100$

$V_{dry\ sludge}$ = 2986,666 m^2 × 0,943 cm / 100cm/m = 28,164 m^3 dry sludge

If 2 m^3 of sludge was carried by tractor and cost of each convance was 20 $, cost of sludge transportation could be calculated as;

Cost of sludge transportation = 20 $ × 28,164 m^3 / 2 m^3 = 281,64 $

Cost of daily sludge disposal = 281,64 $ / 64 day = 4,4 $/day

Total daily cost is found by the addition of cost of daily ferrous sulfate, cost of daily lime and cost of daily sludge disposal. Cost of unit wastewater treatment is found by using 50 m^3 flow rate of wastewater per a day.

Total daily cost = 1,815 $/day + 0,72 $/day + 0,013 $/day + 4,4 $/day

= 6,948 $/day

Unit wastewater treatment cost = 6,948 $/day / 50 m^3/ day = 0,139 $/$m^3$ ww.

Cost of chemicals and cost of sludge disposal associated with chemical treatability by the use of ferrous sulfate dosages are shown in Table 4.10 and Table 4.11 respectively.

Table 4.11 Cost of Chemicals for Coagulants and pH Adjustments Expended in Chemical Treatment

pH	Chemical Substance	Dosage (mg/L)	Costs of Coagulants and pH Adjustingt Chemicals						Cost of pH Adjustment Before Biological Treatment			Total Cost of Chemicals	
			kg/day	Unit Cost ($/kg)	Cost of Coagulant ($/day)	Cost of 1,35 N $Ca(OH)_2$ (L/day)	Cost of Unit ($/L)	Cost of 1,35N $Ca(OH)_2$ ($/day)	Cost of 0,1 N H_2SO_4 (L/day)	Unit Cost ($/L)	Cost of 0,1N H_2SO_4 ($/day)	$/day	$/$m^3$ wastewater
Carrier 1													
9	$FeCl_3$	1250	62,5	0,175	10,938	460	0,006	2,76	200	0,000084	0,017	13,715	0,274
11	$FeCl_3$	650	32,5	0,175	5,688	270	0,006	1,62	160	0,000084	0,013	7,321	0,146
9	$FeSO_4$	750	37,5	0,066	2,475	150	0,006	0,9	50	0,000084	0,004	3,379	0,068
Carrier 2													
6	$Al_2(SO_4)_3$	850	42,5	0,27	11,475	230	0,006	1,38	-	-	-	12,855	0,257
9	$FeCl_3$	650	32,5	0,175	5,688	260	0,006	1,56	200	0,000084	0,017	7,264	0,145
9	$FeSO_4$	550	27,5	0,066	1,815	120	0,006	0,72	160	0,000084	0,013	2,548	0,051

Table 4.12 Cost of Sludge Disposal After Chemical Coagulation

pH	Chemical Substance	Dosage (mg/L)	Amount of Sludge (L/day)	Mass of Sludge (kg/day)	Specific Weight of Sludge (ton/m^3)	SS value of Sludge (%)	Target value of SS (%)	Drainage Ratio	Average Evaporation from Free Water Surface (cm/month)	Evaporation Ratio from Sludge Surface (%)	Drying Time (day)	Volume of Required Drying Bed (L)	Area of Drying Bed (m^2)	Height of Dried Sludge on Bed (m)	Total Volume of Dried Sludge (m^3)	Cost of Sludge Transportation	
																($/day)	($/$m^3$)
Carrier 1																	
9	$FeCl_3$	1250	14600	160	1,04	0,011	0,35	0,6	9,1	0,6	64	934400	5840	0,009	28,032	4,38	0,088
11	$FeCl_3$	650	14200	140	1,04	0,009	0,35	0,6	9,1	0,6	64	908800	3029,333	0,008	24,232	3,786	0,076
9	$FeSO_4$	750	14200	150	1,04	0,010	0,35	0,6	9,1	0,6	64	908800	3029,333	0,009	25,961	4,056	0,081
Carrier 2																	
6	$Al_2(SO_4)_3$	850	11000	350	1,04	0,031	0,35	0,6	9,1	0,6	60	660000	2200	0,027	58,454	9,742	0,195
9	$FeCl_3$	650	11600	400	1,04	0,033	0,35	0,6	9,1	0,6	60	696000	2320	0,028	65,633	10,939	0,219
9	$FeSO_4$	550	14000	165	1,04	0,011	0,35	0,6	9,1	0,6	64	896000	2986,666	0,009	28,164	4,4	0,088

4.2.6 Cost Comparison of Treatment

At chemical precipitation experiments with the application of sodium bentonite, optimum dosages can not be determined due to the fact that Carrier 1 and Carrier 2 solutions did not show adequate COD removal efficiencies. Therefore chemical treatment cost for sodium bentonite is not considered.

The results of experimental studies performed on Carrier formulations with aluminum sulfate show that the optimum dosage is selected only for Carrier 2 preparation due to high SVI values of Carrier 1 effluent. However, this selected dosage for Carrier 2 preparation, which is 850 mg/L alum dosage, results in a treatment cost of 0,452 $/m^3$ is considered as the most expensive alternative. On the other hand, SVI value (32 ml/gr) and COD removal efficiency (82 %) of Carrier 2 formulation are adequate.

Chemical treatment experiments carried out on Carrier 1 preparation with 1250 mg/L ferric chloride dosage at pH 9 results in 95 % COD removal efficiency. In this dosage, SVI parameter is observed as 92 ml/gr and treatment cost is calculated as 0,362 $/m^3$. For 650 mg/L ferric chloride dosage at pH 11, 93 % COD removal efficiency, 100 ml/gr SVI value and 0,222 $/m^3$ treatment cost are obtained. The coagulation of Carrier 2 effluent with 650 mg/L dosage of ferric chloride at pH of 9 results in 29 ml/gr of SVI and 87 % COD removal efficiency with the treatment cost of 0,452 $/m^3$.

According to results obtained from the chemical treatability studies, application of 750 mg/L ferrous sulfate dosage to Carrier 1 preparation at pH 9 in a treatment cost of 0,149 $/m^3$ is considered as the least costly alternative. Besides, in this dosage SVI parameter is observed as 91 ml/gr and COD removal efficiency is measured as 93 %. For Carrier 2 preparation, it is also seen that 550 mg/lt ferrous sulfate dosage at pH 9 results in the most suitable cost alternative when compared to treatment costs of other coagulants. COD removal efficiency for Carrier 2 effluent is 83 % and it's SVI value is 85 ml/gr which is lower than the limit value of 120 ml/gr. Therefore, costs of coagulation flocculation applied with ferrous sulfate represent the optimum alternatives for both Carrier formulations.

According to cost of sludge disposal calculations it is observed that, when sludge formation increases the investment cost also increases but operational cost decreases.

The results associated with the chemical treatability studies by the use of ferrous sulfate showed that at a pH of 9 with the application of 750 mg/L dosage for Carrier 1 preparation and the application of 550 mg/L dosage for Carrier 2 preparation are determined as the optimum dosages.

Table 4.13 summarizes the total cost, total COD and SVI parameters of coagulation-flocculation experiments for selected coagulants.

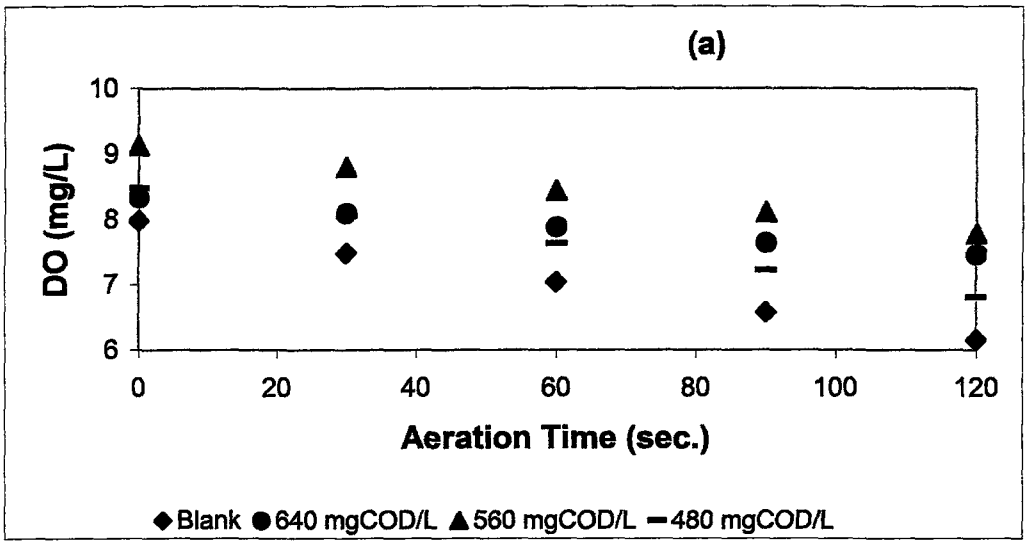
Table 4.13 Total Cost, Total Effluent COD and SVI parameters of Coagulation-Flocculation Experiments for Different Selected Coagulants Used in Chemical Treatment

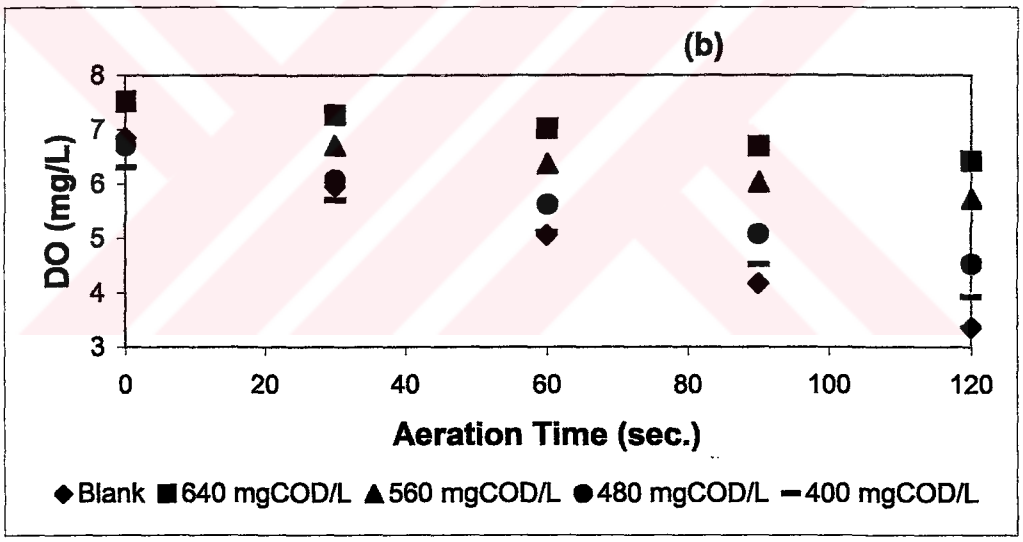
Carrier 1						
pH	**Chemical Substance**	**Dosage (mg/lt)**	**Total Effluent COD (mg/lt)**	**COD Removal (%)**	**SVI (ml/gr)**	**Total *Cost of* Treatment ($/m^3)**
9	$FeCl_3$	1250	240	95	92	0,362
11	$FeCl_3$	650	365	93	100	0,222
9	**$FeSO_4$**	**750**	**380**	**93**	**91**	**0,149**
Carrier 2						
6	$Al_2(SO_4)_3$	850	845	82	32	0,452
9	$FeCl_3$	650	641	87	29	0,364
9	**$FeSO_4$**	**550**	**800**	**83**	**85**	**0,139**

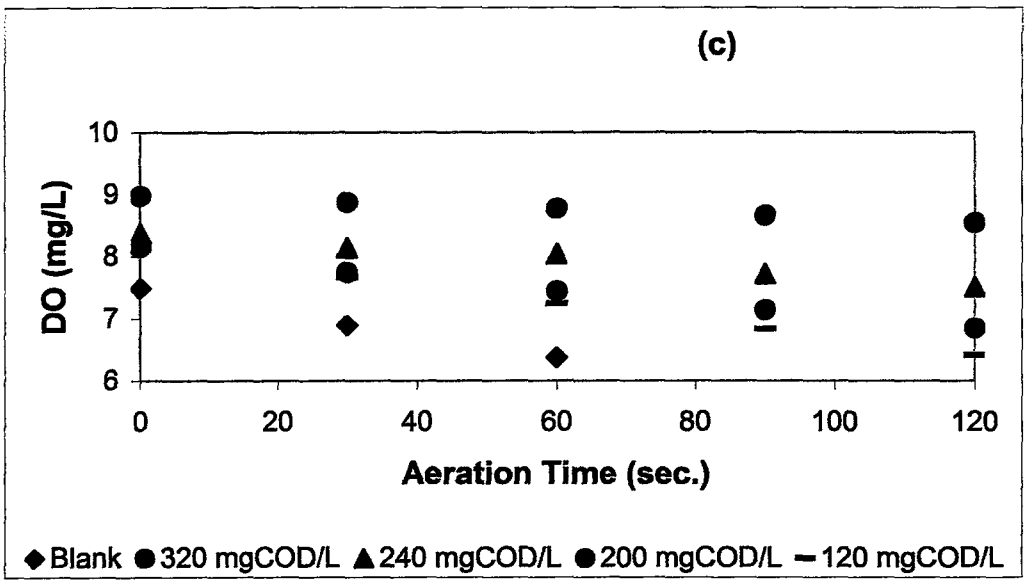
4.3 Activated Sludge Inhibition Experiments

The activated sludge inhibition test is applied on raw Carrier effluents and the optimum points of pretreated Carrier effluents which are determined after cost analyses of coagulation-flocculation experiments. "EC 50" values (in mg dm^{-3} COD of Carrier formulations effluents) are determined individually for toxicity comparison. The COD content of raw Carrier effluents and treated Carrier effluents, which are chemically pretreated with the application of coagulation-flocculation, resulting in 50 % decrease in OUR (in mg dm^{-3}) is calculated by interpolation of the lnCOD versus percent I_{OUR} plots obtained for different Carrier effluent samples. The heterotrophic mass used in the activated sludge inhibition test is fed with a synthetic medium municipal wastewater (SWW). Carrier formulation effluents were diluted with SWW. SWW as well as raw and pretreated Carrier effluent samples are aerated for 30 min. in test beakers containing proper amounts of activated sludge being previously acclimated to SWW. The F/M (Food-to-Microorganisms) ratio is set between 0.12 - 0.22 mg COD mg $MLVSS^{-1}$ day^{-1} (MLVSS = 2000 – 4000 mg dm^{-3}).

Oxygen consumption rates for Carrier formulations at different dilutions versus aeration time is given in Figure 4.1.







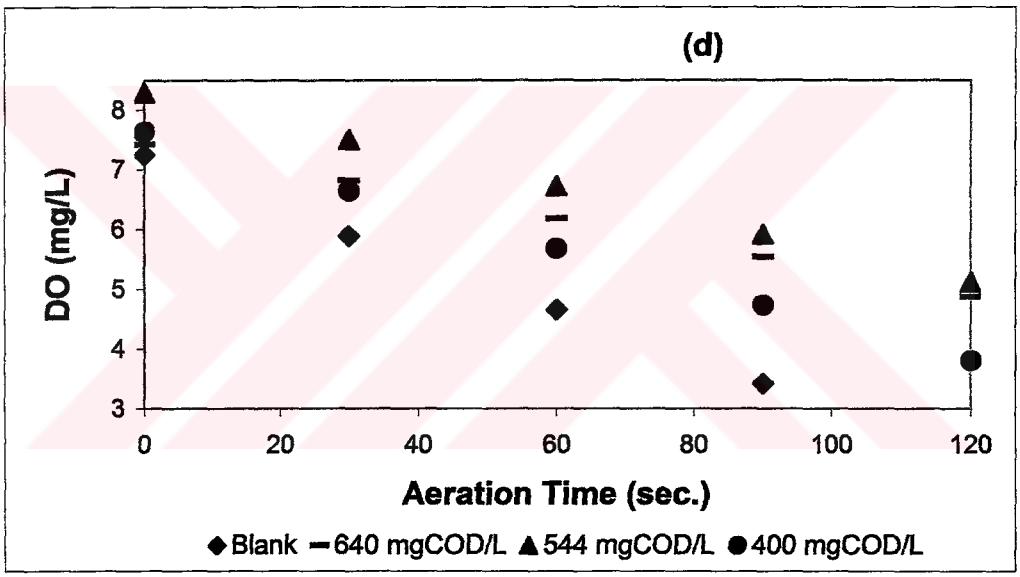
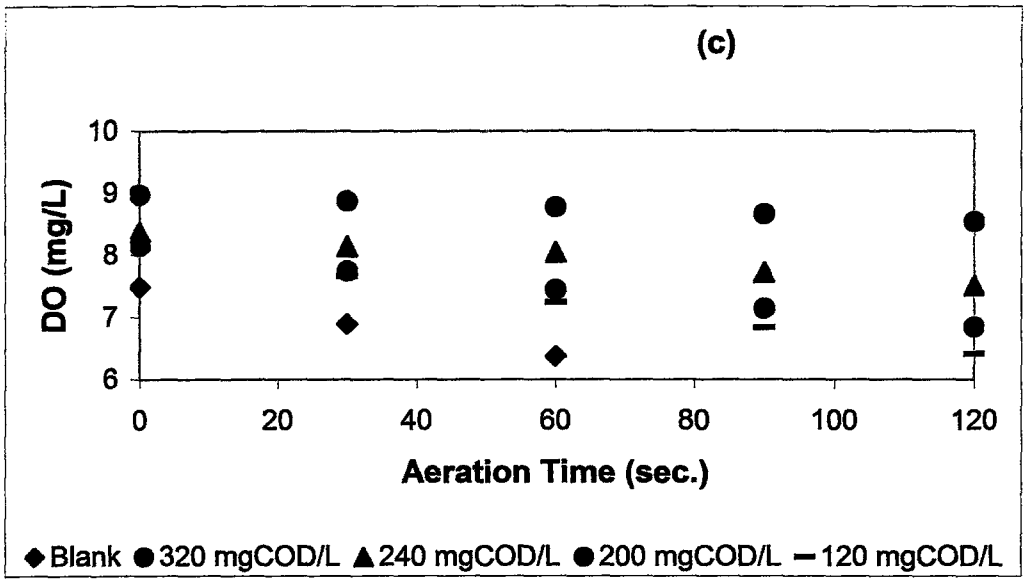


Figure 4.1. Activated Sludge Dissolved Oxygen Concentration for Raw Carrier I (a), Raw Carrier II (b), Chemically Pretreated Carrier 1 (c), Chemically Pretreated Carrier 2 (d) at Different Dilutions Versus Aeration Time Along With 30 Minutes. Pretreatment : At pH 9, the coagulation-flocculation application of 750 mg/L and 550 mg/L ferrous sulfate dosage for Carrier 1 and Carrier 2 preparation respectively. Experimental conditions : F/M = 0.16 mg COD mg $MLVSS^{-1}$ day^{-1} (for raw and pretreated Carrier I), F/M = 0.22 mg COD mg $MLVSS^{-1}$ day^{-1} (for raw and pretreated Carrier II), MLVSS = 2000 – 4000 mg dm^{-3}

Oxygen uptake rates (OUR) (expressed in mg dm^{-3} h^{-1}) in the blank (SWW) and diluted Carrier effluent samples are calculated based on the linear part of decreasing dissolved oxygen concentration curves as a function of the aeration (i.e. biological treatment) time. Percent inhibition of OUR, i.e. I_{OUR}, for every tested sample dilution, is calculated using the (3.3) equation given in Chapter 3. OUR and percent



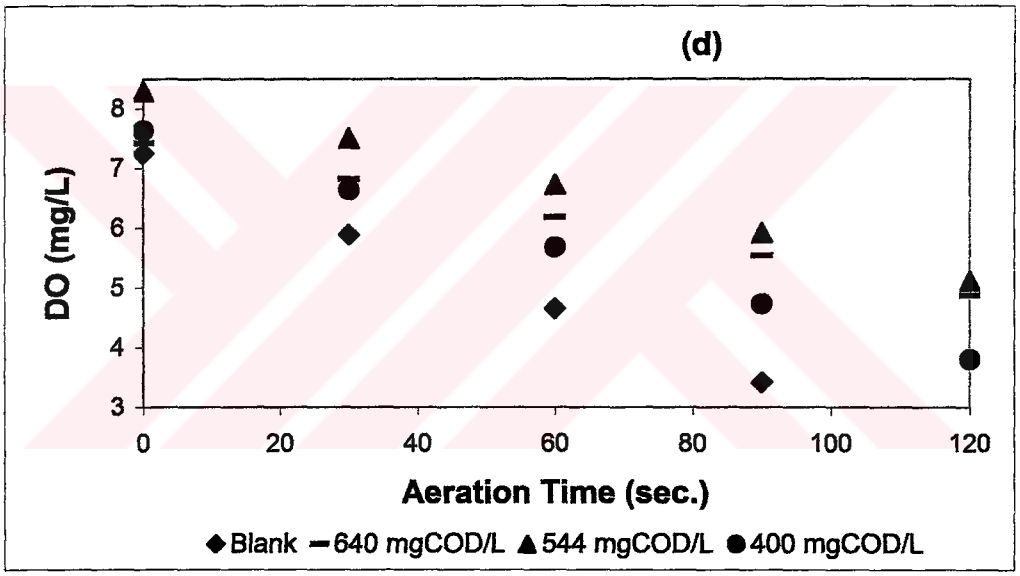


Figure 4.1. Activated Sludge Dissolved Oxygen Concentration for Raw Carrier I (a), Raw Carrier II (b), Chemically Pretreated Carrier 1 (c), Chemically Pretreated Carrier 2 (d) at Different Dilutions Versus Aeration Time Along With 30 Minutes. Pretreatment : At pH 9, the coagulation-flocculation application of 750 mg/L and 550 mg/L ferrous sulfate dosage for Carrier 1 and Carrier 2 preparation respectively. Experimental conditions : F/M = 0.16 mg COD mg $MLVSS^{-1}$ day^{-1} (for raw and pretreated Carrier I), F/M = 0.22 mg COD mg $MLVSS^{-1}$ day^{-1} (for raw and pretreated Carrier II), MLVSS = 2000 – 4000 mg dm^{-3}

Oxygen uptake rates (OUR) (expressed in mg dm^{-3} h^{-1}) in the blank (SWW) and diluted Carrier effluent samples are calculated based on the linear part of decreasing dissolved oxygen concentration curves as a function of the aeration (i.e. biological treatment) time. Percent inhibition of OUR, i.e. I_{OUR}, for every tested sample dilution, is calculated using the (3.3) equation given in Chapter 3. OUR and percent

inhibition in OUR (I_{OUR}) obtained in difference COD Values for raw and pretreated Carrier formulations are tabulated in Table 4.14 and 4.15.

Table 4.14 Oxygen Uptake Rate (OUR) and Percent Inhibition in OUR (I_{OUR}) Obtained in Difference COD Values for Raw Carrier Formulations

Carrier I-raw			
Dilution (%)	COD (mg/L)	OUR (mg/L.h)	I_{OUR} (%)
Blank	600	54.72	-
80 %	480	26.28	52
70 %	420	40.68	26
60%	360	50.04	9
Carrier II-raw			
Blank	800	105.12	-
80 %	640	33.48	68
70 %	560	51.48	51
60%	480	64.08	39
50%	400	71.28	32

Table 4.15 Oxygen Uptake Rate (OUR) and Percent Inhibition in OUR (I_{OUR}) Obtained in Difference COD Values for Pretreated Carrier Formulations

Carrier I-pretreated			
Dilution (%)	COD (mg/L)	OUR (mg/L.h)	I_{OUR} (%)
Blank	400	65.16	-
80 %	320	12.96	80
60 %	240	25.56	61
50 %	200	38.52	41
30 %	120	50.76	22
Carrier II-pretreated			
Blank	800	150.12	-
80 %	640	76.68	49
68 %	544	95.4	37
50%	400	114.84	24

The COD content of raw and pretreated Carrier formulation effluents resulting in 50 % decrease in OUR (i.e EC_{50} values; in mg dm^{-3}) is calculated by interpolation of the ln COD versus percent I_{OUR} plots obtained for different Carrier effluent samples are shown in Figure 4.2.

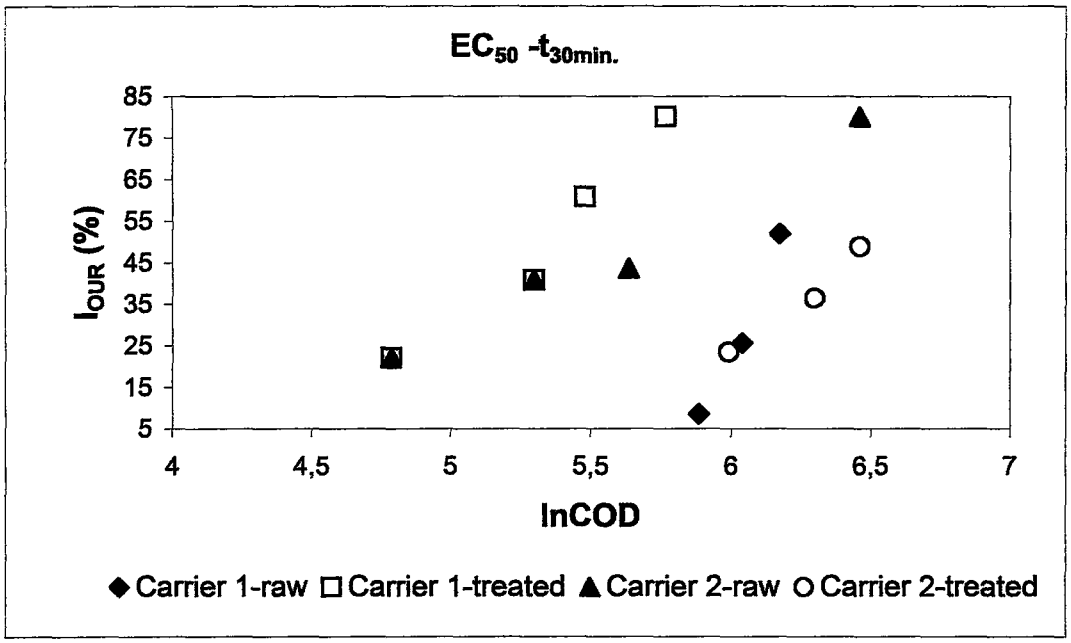


Figure 4.2 Percent Inhibition in Oxygen Uptake Rates (I_{OUR} values) Obtained for Raw and Chemically Pretreated Carrier Formulation Effluents as a Function of LnCOD. Pretreatment : At pH 9, the coagulation-flocculation application of 750 mg/L and 550 mg/L ferrous sulfate dosage for Carrier 1 and Carrier 2 preparation respectively. Experimental conditions : F/M = 0.16 mg COD mg $MLVSS^{-1}$ day^{-1} (for raw and pretreated Carrier I), F/M = 0.22 mg COD mg $MLVSS^{-1}$ day^{-1} (for raw and pretreated Carrier II), MLVSS = 2000 – 4000 mg dm^{-3}

To see the differences of inhibition effect of pretreated Carrier formulations on activated sludge microorganisms, coagulation-flocculation experiments is also performed in different way as applying the slow mixing for 2 hours. EC_{50} values obtained for raw and pretreated Carrier effluents are summarizing in Table 4.16.

Table 4.16 EC_{50} Values Obtained for Raw and Pretreated Carrier Effluents

Carrier effluent type	EC_{50} (mg dm^{-3} COD)
Carrier 1 - raw	481
Carrier 1 - pretreated-mixed for 15 min.	204
Carrier 1 - pretreated mixed for 2h.	320
Carrier 2 - raw	529
Carrier 2 - pretreated mixed for 15 min.	673
Carrier 2 - pretreated-mixed for 2 h.	570

According to experimental findings, the order of increasing toxicity for Carrier 2 effluent is as follows; Carrier 2 – pretreated mixed for 15 min.< Carrier 2 - pretreated-mixed for 2 h..< Carrier 2 – raw. Similar to that findings, the order of

increasing toxicity for Carrier 1 effluent is as follows; Carrier 1 – raw < Carrier 1 - pretreated-mixed for 2 h.< Carrier 1 – pretreated-mixed for 15 min.

Application of coagulation-flocculation experiments in different way (applying slow mixing for 2 hours) did not influence the results of Carrier effluents' inhibition effect because evident differences can not be obtained.

In conclusion, the inhibition effect of chemically pretreated Carrier 2 formulation, namely ecocarrier, is observed to be less than raw Carrier 2 formulation. Therefore it can be concluded that coagulation-flocculation is an appropriate pre-treatment alternative for Carrier 2 preparations. On the other hand, inhibition tests showed that pretreated Carrier 1 effluents exerted more inhibitiory effect on activated sludge microorganisms.

Perez et al. (2002), Hislop (1999) stated that some metal complexes may occur during coagulation. Previous studies have shown that sulfate, dyes and metal complexes may result in toxic effect (Navarro et al., 1999; Wang et al., 2002). Thus, toxic effect of Carrier 1 formulation during coagulation may be attributable to any or conjugated toxic effect of metal complex formations.

4.4 Toxicity Experiments

The toxicity test is applied on raw Carrier formulations and the optimum points of pretreated Carrier formulations which are determined after cost analyses of chemical treatment. The aim of the toxicity experiments is to determine the toxic effects of textile dye Carrier effluents on the marine microalga, *Phaeodactylum tricornutum* (*P.tricornutum*) by using laboratory-scale toxicity tests. In bioassays, Carrier formulations are prepared at different dilutions before adding the test cultures (10000 cells/ml). The growth of indicator algal species of *P.tricornutum*, which were incubated in diluted water, is monitored 7 days with counting the cells.

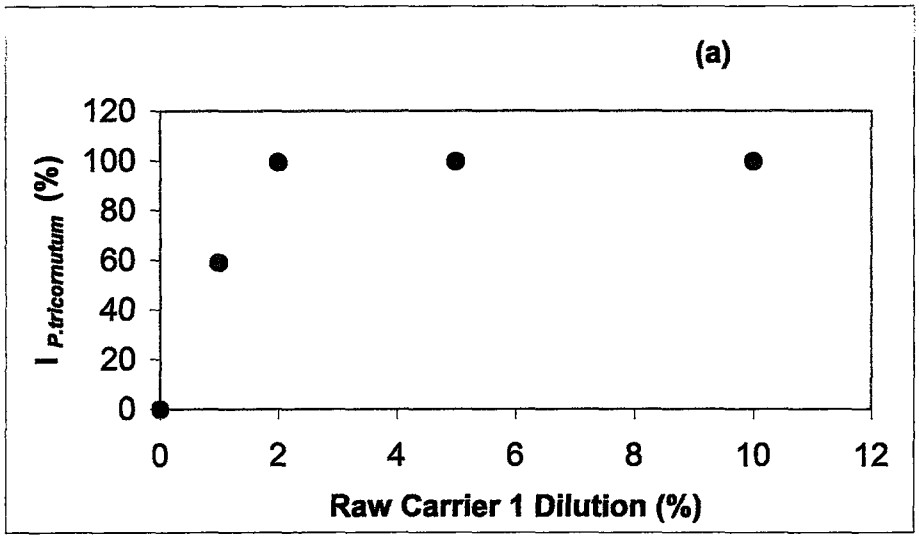
The percent inhibition values of *P.tricornutum* ($I_{P.tricornutum}$) which are obtained for different dilutions of raw Carrier effluents and treated Carrier effluents, which are pretreated with the application of coagulation-flocculation, are detected after 4 days of counting and results are summarized in Table 4.17.

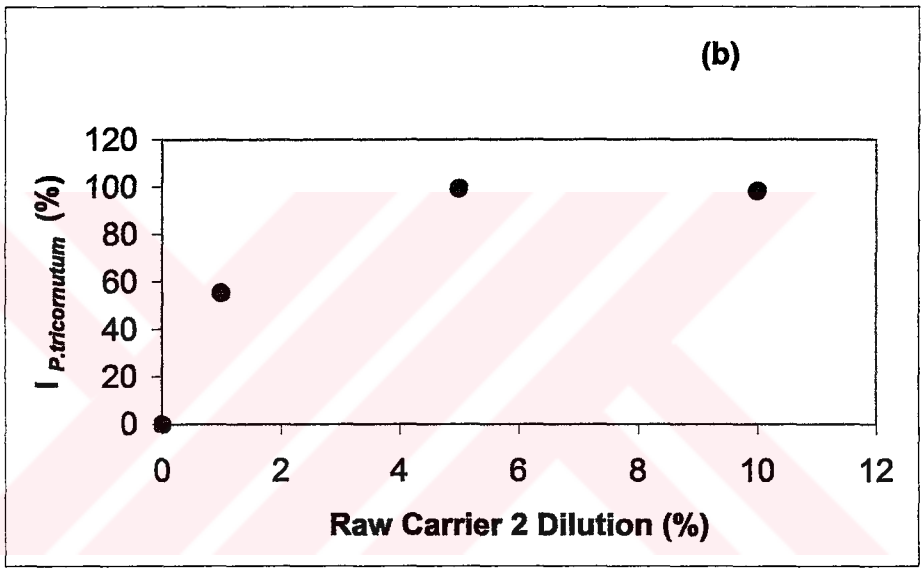
Table 4.17 Percent Inhibition of *Phaeodactylum tricornutum* Values Obtained at Different Carrier Formulations Dilutions

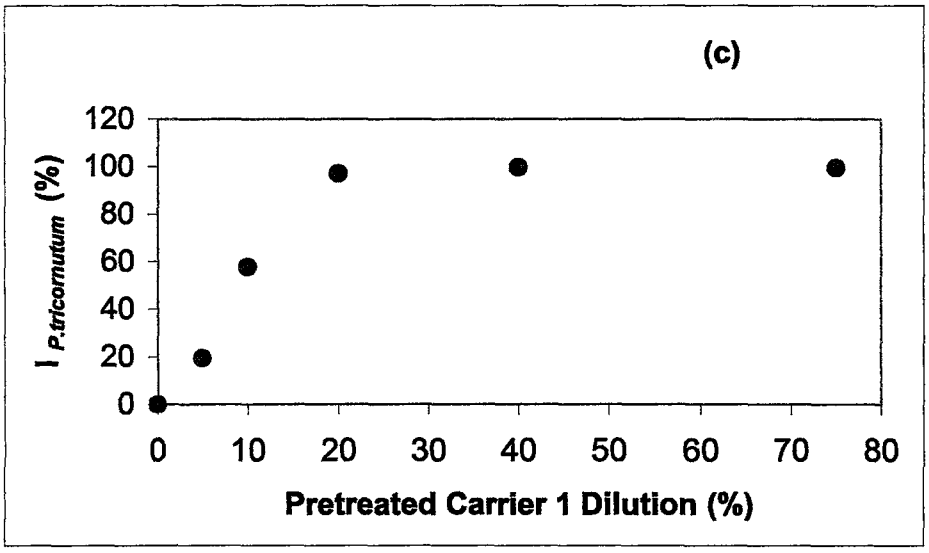
Sample	Sample Dilution (%)	I $_{P.tricornutum}$ (%)
Raw Carrier 1	1	59.0
	2	99.5
	5	99.7
	10	99.7
Raw Carrier 2	1	55.5
	5	99.4
	10	98.3
Pretreated Carrier 1	5	19.5
	10	57.8
	20	97.2
	40	99.8
	75	99.6
Pretreated Carrier 2	2	28.7
	5	60.0
	10	73.0
	20	98.8
	40	98.4

The obtained values from the Table 4.17 show that, increasing the addition of Carrier effluents cause an increase in the inhibition of algal activity. On the other hand, the dilution rates of raw Carrier preparations (1 %, 2 %, 5 %, 10 %) are lower than the raw Carrier preparations (2 %, 5 %, 10 %, 20 %, 40 %, 75 %). Because the raw Carrier preparations have more toxic effect on *P.tricornutum* than pretreated Carrier preparations. For instance, percent inhibition of marine microalga is found as 100 in raw Carrier formulation at a dilution of 10 (%). However, *Phaeodactylum tricornutum* species are inhibited as approximately 100 % in pretreated Carrier formulation at a dilution of 40 (%).

According to these results, chemically pretreated Carrier formulations with the application of coagulation/flocculation, are found less toxic than raw Carrier formulations which are not subjected to the chemical treatment. Figure 4.3 shows the percent inhibition of *P.tricornutum* versus Carrier preparations at different dilutions.


(a)
120
100
80
60
40
20
0
I P.tricornutum (%)
0
2
4
6
8
10
12
Raw Carrier 1 Dilution (%)


(b)
120
100
80
60
40
20
0
I P.tricornutum (%)
0
2
4
6
8
10
12
Raw Carrier 2 Dilution (%)


(c)
120
100
80
60
40
20
0
I P.tricornutum (%)
0
10
20
30
40
50
60
70
80
Pretreated Carrier 1 Dilution (%)

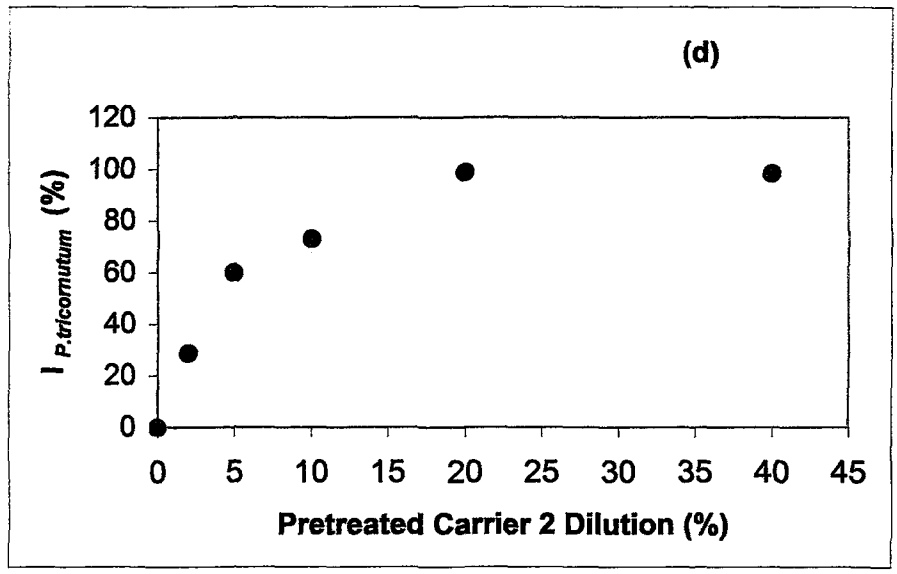


Figure 4.3 Percent Inhibition of *P.tricornutum* as a Function of Raw Carrier 1 Formulation (a), Raw Carrier 2 Formulation (b), Pretreated Carrier 1 Formulation (c), Pretreated Carrier 2 Formulation (d) at Different Dilutions for 4 Days Counting. Pretreatment : At pH 9, the coagulation-flocculation application of 750 mg/L and 550 mg/L ferrous sulfate dosage for Carrier 1 and Carrier 2 preparation respectively

The dilutions of raw and pretreated Carrier effluents resulting in 20, 50 and 80 percents of *P.tricornutum* (i.e. EC_{20}, EC_{50}, EC_{80}) are obtained from the 4 days exposure graphs and given in Table 4.18.

Table 4.18 EC values of Carrier Solutions After 4 days Exposure to *P. tricornutum*

Test Substance	EC_{20}	EC_{50}	EC_{80}
Carrier 1-raw	0.40	0.75	1.5
Carrier-2-raw	0.40	0.80	3.25
Carrier 1-pretreated	5	9	16
Carrier 2-pretreated	2	4	13

On the basis of EC values obtained for Carrier formulations, it is observed that if raw and chemically pretreated Carrier effluents are evaluated separately, similar results are obtained. Besides, when the raw Carrier effluents are compared with the pretreated ones, it is seen from the Table 4.18 that, Carrier 1 effluent is found less toxic (chemically treated well) than Carrier 2 effluent. For instance, EC_{50} value of raw Carrier 1 and 2 preparations is found as 0.8. After the application of chemical

treatment to Carrier solutions, EC_{50} value is increased to 4 for pretreated Carrier 2; and 9 for pretreated Carrier 1, which is approximately 2.5 times.

In conclusion, the coagulation/flocculation process contributed to decrease the toxicity of Carrier formulations, as determined in the bioassays on *P. tricornutum*. On the contrary, it is not effective in reducing the toxicity for Carrier 1 effluent performed on the inhibition test on activated sludge microorganisms. However, the different responses of the tested organisms may make an adequate interpretation of the results difficult since toxicity results depend on the characteristics of the effluent, which change with the coagulant content of treatment.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATION

In the present study the chemical treatability of two extremely recalcitrant textile dye carriers, namely Carrier I and Carrier II are investigated. Dye carriers are subjected to lab–scale coagulation-flocculation experiments by use of different coagulants; namely sodium bentonite, alum, ferric chloride and ferrous sulfate. Optimum coagulant dosages together with optimum pH values are assessed based on the obtained COD removal efficiencies, sludge volume indexes and treatment costs.

Experimental studies carried out on both carrier effluents with bentonite at pH of 9 and 11 indicate inadequate COD removal efficiency therefore it is concluded that precipitation with sodium bentonite is not a suitable method for preliminary treatment. The results associated with chemical treatability by the use of ferrous sulfate showed that for Carrier 1 formulation, the application of 750 mg/L dosage at a pH of 9 yielded the optimum treatment. On the other hand for Carrier 2 formulation, the application of 550 mg/L ferrous sulfate dosage at a pH of 9 is observed to give the optimal result.

The activated sludge inhibition test is applied and EC 50 values are determined for raw and chemically pretreated carrier effluents individually. According to results, activated sludge inhibition occurred when Carrier 1 effluent was subjected to pretreatment. The results for Carrier 2 formulation associated with inhibition tests indicated that chemically pretreated Carrier 2 effluent inhibited the activity of microorganisms less than raw Carrier 2 effluent.

The studies are performed to determine the toxic effects of raw and pretreated carrier formulations on the marine microalga, *Phaeodactylum tricornutum* using laboratory-based toxicity bioassays. Chemically pretreated Carrier 1 and 2 effluents by the coagulation/flocculation process are detected to beless toxic than raw Carrier 1 and 2 effluents towards *Phaeodactylum tricornutum.*

It is concluded that, for Carrier 2 effluent, chemical treatment with the application of coagulation/flocculation is an effective method in terms of activated sludge inhibition test and marine algae toxicity bioassay. However, for Carrier 1 effluent, activated sludge inhibition tests indicated that the application of coagulation/flocculation increases the inhibition effect of activated sludge microorganisms' activity.

Chemical treatment with coagulation / flocculation protocoles as pretreatment, is recommended to certain textile dyeing auxiliaries which are not easily amenable to biological treatment. It should be noted that experimental treatability tests should be performed in order to find out what sort of pretreatment procedure is suitable for different kinds of textile auxiliaries.

REFERENCES

Achwal, W. B., (1997). Problems During Analysis of Textiles as Per Eco-standards and the Consumer Articles Ordinance. Part II, *Colourage*, **44**, 31-32..

Akça, l., Sevimli, M. F., Alp, K., 1998. Boya Sanayi Arıtma Tesisi Çamurlarının Karakterizasyonu ve Uzaklaştırılması, *İTÜ 6. Endüstriyel Kirlenme Kontrolü Sempozyumu,* İstanbul, 3 – 5 Haziran, s.s.183-190.

Al-Degs, Y., Khraisheh, M. A. M., Allen, S. J. and Ahmad, M. N., (200). Effect of Carbon Surface Chemistry on the Removal of Reactive Dyes From Textile Effluent, *Water Res.* **34**, 927-935.

APHA, AWWA, and WEF, 1995. Standard Methods for the Examination of Water and Wastewater, 18 th ed., Washington DC, USA.

Arslan-Alaton, I., Eremektar, G., Germirli Babuna, F.G., Selçuk, H. and Orhon, D., (2004). Chemial Pre-treatment of Textile Dye Carriers With Ozone: Effects on Acute Toxicity and Activated Sludge Inhibition, *Fresenius Environmental Bulletin,* **13**, 1040-1044

Arslan, I. and Balcıoğlu, A., (2001). Degredation of Remazol Black B Dye and Its Simulated Dyebath Wastewater by Advanced Oxidation Processes in Heterogenous and Homogenous Media, *Color technol.* **117**, 38-42.

Casey, T. J., (1997). Unit Treatment Processes in Water and Wastewater Engineering, *Elsevier Science,* Amsterdam.

Çelik, E., 2004. Tekstil Atıksuyunun Fizikokimyasal Yöntemlerle Arıtımı, *9. Endüstriyel Kirlenme Kontrolü Sempozyumu,* İstanbul, 02– 04 -Mayıs, 547-553.

EPA, 1995. Best Management Practices for Pollution Prevention in The Textile Industry, *US Environment Protection Agency*

EPA, 1987. Design Manual, Dewatering Municipal Wastewater Sludges, *US Environment Protection Agency, EPA-625/1-87-014.*

European Community, (EC, 2001). Integrated Pollution Prevention and Control (IPPC) Refence Document on Best Available Techniques (BAT) for The Textile Industry, Brussels.

Germirli Babuna, F., Soyhan B., Eremektar G. and Orhon D., (1999). Evaluation of Treatability for Two Textile Mill Effluents, *Wat. Sci. Tech.* **40**, 145-152.

Georgiou, D., Aivazidis, A., Hatiras, J. and Gimouhopoulos, K., (2003). Treatment Of Cotton Textile Wstewater Using Lime and Ferrous Sulfate, *Water Research,* **37**, 2248-2250.

Gökşen, S., (2003). Boya Endüstrisi Atıksularının Arıtılabilirliği, *Yüksek Lisans tezi,* İTÜ. Fen Bilimleri Enstitüsü, İstanbul.

Grau, P., (1991). Textile Industry Wastewater Treatment, *Water Sci.Technol.* **24**, 97-103.

Guillard, R.R.L., (1972). Culture of phytoplankton for feeding marine invertebrates. In *Culture of Marine Invertebrate Animals* ; Smith, W.L.; Chanley, M.H., Eds.; Plenum Press: New York, p.p. 29-60.

Güngör, N., (1992). Radyoaktif Atık Yönetiminde Bentonit, *İTÜ Dergisi, **50**,4.*

Gürses, F., (2004). Antibiyotik Formulasyon Atıksuların Fenton-Benzeri ve Foto-Fenton-Benzeri İleri Oksidasyon Prosesleri ile Arıtılabilirliğinin İncelenmesi, *Yüksek Lisans tezi,* İTÜ. Fen Bilimleri Enstitüsü, İstanbul.

Hislop K. A. and Bolton J. R., (1999). The Photochemical Generation of Hydroxyl Radicals in The UV-vis/Ferrioxalate/H_2O_2system, *Environ Sci. Technol.* **33**, 3119-3126.

Howe Robert H. L., (1967). Applied Chemistry for Water Purification and Wastes Treatment, *Çağlayan Scientific Publisher,* İstanbul, p.p. 127-144.

ISO, 1986. Water Quality-Detrmination of the Chemical Oxygen Demand, Ref. No: ISO 6060.

ISO, 1999. Oxygen Demand Inhibition Effect by Activated Sludge, Ref No: ISO 8192.

Kang, S.-F., Liao, C.-H and Chen, M.-C., (2002). Pre-Oxidation and Coagulation of Textile Wastewater by The Fenton Process, *Chemosphere,* **46**, 923-928.

Kumar, M. D., Selvi, K., Begum A., Vanathi T. and Yamuna, R.T., (2001). Waste'coir pith- a Potential Biomass for The Treatment of Dyeing Wastewaters, *Biomass and Bioenergy,* **21**(6), 477-483.

Lin, S. H. and Lai, C. L., (2000). Kinetic Characteristic of Textile Wastewater Ozonation in Fluidized and Fixed Activated Carbon Belts, *Water Res.* **34**, 763-772.

Liokou, S., Pavlou, S. and Lyberat, G., (1997). Pretreatment of Azo Dyes Using Ozone, *Water Sci. Technol.* **36**, 155-163.

Mahdavi, A., Donelly, T. and Anderson, G. K., (2001). Color Removal From a

Simulated Dye Wastewater Using a Two Phase Anaerobic Packed Bed Reactor, *Water Research,* **35**,(2), 425-432.

Metcalf and Eddy, (1984). Wastewater Engineering Treatment, Disposal, Reuse, *Metcalf and Eddy In.,* New Delhi.

Metes A., Koprivanac N. and Glasnovic A., (2000). Flocculation as a Treatment Method for Printing Ink Wastewater, *Water Environmental Research Science,* **72**, 680-688.

Morais, L. C., Freitas, O. M., Gonçalves, E. P., Vasconcelos, L. T. and Beça, C. G. G., (1999). Reactive Dyes Removal From Wastewaters by Adsorption on Eucalyptus Bark: Variables That Define The process, *Water Res.* **33**, 979-989.

Nandy T., Vyas R. D., Shastry S. and Kaul S. N., (2002). Optimization of Coagulants for Pretreatment of Printing Ink Wastewater, *Environmental Engineering Science,* **19**, 1-7.

Nemerow, N. L., Agardy, F. J., (1997). Strategies of Industrial and Hazardous Waste Management, *Environmental Engineering Series, Van Nostrand Reinhold Publishes*, New York.

Nordell E., (1961). Water Treatment for Industrial and Other Uses, *2nd Edition Reinhold Publishing Corporation,* New York, p.p. 348-360.

Okay O.S., Tüfekçi V. and Donkin P., (2002). Acute and Chronic Toxicity of Pyrene to The Unicellular Marine Alga *Phaeodactylum tricornutum, Bull. Environmental Contamination and Toxicology, 68*, 600-605.

Okay O. S., Karacık B., Tüfekçi V. and Tolun L.G., (2004). Kompleks Atıksuların Deniz Ekosistemine Etkilerinin Biyodeney ve Biyogösterge Teknikleri ile Belirlenmesi, 9. *Endüstriyel Kirlenme Sempozyumu,* İstanbul, 02-04 Mayıs, s.s. 501-508.

Orhon D., Kabdaşh I., Germirli Babuna F., Sözen S., Dulkadiroglu H., Dogruel S., Karahan O. and Insel G., (2003). Wastewater Reuse for The Minimization of Fresh Water Demand in Coastal Areas Selected Cases From the Textile Finishing Industry, *J.Env.Sc.* 8

Özbelge T. A, Özbelge Ö. H. and Başkaya S. Z., (2002). Removal of Phenolic Compounds from Rubber-Textile Wastewaters by Physico-chemical Methods, *Chemical Engineering and Processing,* 41, 719-730.

Peavy, H. S., Rowe, D. R. and Tchobanoglous, G., (1985). Environmental Engineeering, *MC-Graw-Hill Book Company,* Singapore. s.s. 131-140.

Perez, M., Torrades, F., Domenech, X. and Peral J., (2002). Fenton and Photo-Fenton Oxidation of Textile Effluents, *Wate Res.* **36**, 2703-2710.

Pontius, F. W., (1990). Water Quality and Treatment, *Mc Graw Hill,* New York.

Selçuk H., (2005). Decolorization and Detoxification of Textile Wastewater by Ozonation and Coagulation Processes, *Dyes and Pigments,* **64**, 217-222.

Silva, A. C., Dezotti, M. and Sant Anna Jr., (2004). Treatment and Detoxification of a Sanitary Landfill Leachate, *Chemosphere*, **55**, 207-214.

So, C. M., Cheng, M.Y., Yu, J. C. and Wang, P.K., (2002). Degradation of Azo Dye Procin Red MX-5B by Photocatlytic Oxidaiton, *Chemosphere* , **46**, 905-912.

Stephenson, R. L. and Blavkburn J. B., (1998). The Handbook of Industrial Wastewate Systems, *Jr Lewis Publishers,* Washington.

Şengül, F., (1986). Endüstriyel Atıksuların Arıtılması, *Dokuz Eylül Yayınları,* İzmir.

Tünay O., Kabdaşh I., Orhon D. and Eremektar G., (1996). Color Removal From Textile Wastewater, *Water Sci. Technol.* **34**, 9-16.

Tünay, O., (1996). Çevre Mühendisliğinde Kimyasal Prosesler, *İTÜ İnşaat Fakültesi Matbaası,* İstanbul.

Türkiye Çevre Vakfı (TÇV), 1999. Türk Çevre Mevzuatı, *Önder Matbaa Yayın No: 134,* s.s. 812-814.

Tzitzi, M., Vayenas, D. V. and Lyberatos G., (1994). Pretreatment of Textile Industry Wastewaters With Ozone, *Wat. Sci. Tech.* **29**, 151-160.

USEPA, (1971). Algal Assay Procedures: Bottle Test, Corvallis, *EPA 600/9-78-018,*Oregon.

Vesilind P. A., 1980. Treatment and Disposal of Wastewater Sludges, *Ann Arbor Science Publishers Inc.,* Michigan.

Villegas-Navarro, A., Romero Gonzalez, M. C., Rosas Lopez, E., Dominguez Aguilar, R. and Sachetin Marçal, W., (1999). Evaluation of Daphnia Magna as An Indicator of Toxicity and Treatment Efficacy of Textile Wastewaters, *Environment International,* **5**, 619-624.

Wang, C., Yediler, A., Lienert, D., Wang, Z. and Kettrup A., (2002). Toxicity Evaluation of Reactive Dyestuffs, Auxiliaries and Selected Effluents in Textile Finishing Industry to Luminescent Bacteria Vibrio fischeri, *Chemosphere*,**46**, 619-624.

Weber , J. R., and Walter, J., 1972. Physicochemical Processes for Water Quality , Control, *Wiley Inc.,* New York.

Weltrowski, M., Partry J. and Bourget, M., (1996). Rective Filter for Textile Dyes Adsorption, *Adv. Chitin. Sci.* **1**, 462-469.

CURRRICULUM VITAE

Burcu Özerkan was born in Ankara 1978. She graduated from Bilfen Private High School in 1996. She received her B. Sc. degree in Environmental Engineering from Sakarya University in 2001. She started studying for her master's degree in 2002 in Environmental Biotechnology Programme of İstanbul Technical University.