İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

# EFFECT OF BIOLOGICAL TREATMENT ON PSD-BASED COD, TOC AND COLOR PROFILES IN TEXTILE WASTEWATERS

**M.Sc. THESIS**

**Atalay ALTUN**

**Department of Environmental Engineering**

**Environmental Biotechnology Programme**

**Thesis Advisor: Assoc. Prof. Dr. Serdar Doğruel**

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

# TEKSTİL ENDÜSTRİSİ ATIKSULARINDA DANECİK BOYUT DAĞILIMI TEMELLİ KOİ, TOK VE RENK PROFİLLERİ ÜZERİNE BİYOLOJİK ARITMANIN ETKİSİ

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***to my beloved mother and father,***

## FOREWORD

I would like to express my sincere appreciation to my thesis advisor, Assoc. Prof. Dr. Serdar Doğruel, whose expertise, understanding, generous guidance and support made it possible for me to work on a topic that was of great interest to me. It was a pleasure working with him. My appreciation also goes to Assoc. Prof. Dr. Güçlü İnsel, for his help and precious advices.

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May 2016 Atalay ALTUN

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**SYMBOLS**

| | |
|---|---|
| $\mathbf{C_T}$ | : Total COD Concentration [MCOD/L$^3$] |
| $\mathbf{C_S}$ | : Total Biodegradable COD Concentration [MCOD/L$^3$] |
| $\mathbf{C_I}$ | : Total Inert COD Concentration [MCOD/L$^3$] |
| $\mathbf{S_T}$ | : Total Dissolved COD Concentration [MCOD/L$^3$] |
| $\mathbf{S_S}$ | : Readily Biodegradable COD Concentration [MCOD/L$^3$] |
| $\mathbf{S_I}$ | : Soluble Inert COD Concentration [MCOD/L$^3$] |
| $\mathbf{S_P}$ | : Soluble Inert Microbial Products [MCOD/L$^3$] |
| $\mathbf{X_T}$ | : Total Particulate COD Concentration [MCOD/L$^3$] |
| $\mathbf{X_S}$ | : Slowly Hydrolyzable COD Concentration [MCOD/L$^3$] |
| $\mathbf{X_I}$ | : Particulate Inert COD Concentration [MCOD/L$^3$] |
| $\mathbf{X_P}$ | : Particulate Inert Microbial Products [MCOD/L$^3$] |
| **OUR** | : Oxygen Utilization Rate [M/L$^3$.T] |

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## EFFECT OF BIOLOGICAL TREATMENT ON PSD-BASED COD, TOC AND COLOR PROFILES IN TEXTILE WASTEWATERS

### SUMMARY

As the industrialization has rapidly increased, the production of wastes accelerates and threatens the environment as well as the existence of many living forms. In raw wastewaters, organics forms a typical and significant fractionation of the pollution. There are processes such as activated sludge systems in treatment plants to reduce organic pollutants to meet the disposal regulations. This study offers particle size measurement by sequential filtration/ultrafiltration as an alternative method for wastewater characterization in order to determine appropriate treatment technology. Moreover, the correlation between particle size distribution (PSD) and chemical oxygen demand (COD) fractionation provides an insight into biological treatability.

In this study, wastewater samples were obtained as two sets from the influent and effluent streams of wastewater treatment plant located in an organized industrial district, Bursa, Turkey. The influent wastewater sample was characterized by a COD level of around 711 mg/L, with 185 mg/L of TOC and 1034 Pt-Co of color. Apart from the characterization experiments, COD fractionation was determined. Particle size distribution method was used for COD, TOC and color profiles. Especially, PSD-based COD fractionation by sequential filtration/ultrafiltration serves as fingerprints for industrial wastewater. PSD-based COD fractionation profiles identify that the bulk of the COD both for influent and effluent flow is in the soluble form (< 2nm). Moreover, treatment efficiencies were determined by comparing the profiles of the influent and effluents. The study shows that biological treatment is effective, especially in soluble part.

The TOC experiments were used as a tool for wastewater characterization. The results show that COD and TOC profiles exhibit similar trends with regard to the particle size distribution. The studies on color profiles in wastewater reveals that the biological treatment process is not very effective on removing color from the wastewater.

PSD-based fractionation also complemented the results of respirometric analyses and provided supporting information for the interpretation of biodegradation characteristics.

# TEKSTİL ENDÜSTRİSİ ATIKSULARINDA DANECİK BOYUT DAĞILIMI TEMELLİ KOİ, TOK VE RENK PROFİLLERİ ÜZERİNE BİYOLOJİK ARITMANIN ETKİSİ

## ÖZET


Çevre; insanların ve diğer canlıların yaşamları boyunca ilişkilerini sürdürdükleri ve karşılıklı olarak etkileşim içinde bulundukları fiziki, biyolojik, sosyal, ekonomik ve kültürel ortamdır. İnsanlık tarihinin en başından beri, çevre, insanların hayatında önemli bir rol oynamaktadır. Çevrenin sunduğu kaynakların doğru bir şekilde kullanılamaması, doğanın dengesini olumsuz bir şekilde etkilemektedir. Dahası, günümüzde endüstriyelleşme oranı yükseldikçe, atık üretimi de o oranda artmakta, çevre ve bütün canlı formları için tehdit oluşturmaktadır. Özellikle tekstil endüstrisi, tüm endüstriler arasında önemli bir yere sahiptir. Atıksularda organik kirleticiler, tüm kirleticilerin önemli bir kısmını oluşturmaktadır. Atıksu arıtma tesislerinde, aktif çamur gibi prosesler kullanılıp, atıksuların organik kirleticilerden arındırılması ve deşarj standartlarının sağlanması amaçlanmaktadır. Bu çalışmada fıltrasyon/ultrafiltrasyon ile partikül boyut dağılımı analizi, atıksular için doğru arıtma yöntemi belirlenebilmesi amacıyla atıksu karakterizasyonu için alternatif bir yöntem olarak önerilmektedir. Ayrıca, partikül boyut dağılımı (PBD) ile kimyasal oksijen ihiyacı (KOİ), biyolojik arıtılabilirlik açısından ilişkilendirilmektedir.

Bu çalışmada, atıksu örnekleri Bursa'da bulunan arıtma tesisinin giriş ve çıkışından Nisan ve Mayıs aylarında, belirli zaman aralıklarında alınmıştır. Örneklerin alındığı arıtma tesisi, organize sanayi bölgesinde yer almaktadır. Organize sanayi bölgesinin büyük bir çoğunluğu tekstil sektöründen olmakla beraber; plastik ve kimya, elektrik-elektronik, mobilya, otomotiv ve inşaat gibi başka sektörlerden de firmalar bulunmaktadır. Tesislerden gelen atıksular aynı arıtma tesisinde arıtılmaktadır. Yapılan atıksu karakterizasyon deneylerinde, giriş akımı için KOİ 711 mg/l, TOK 185 mg/l ve renk Platinyum Kobalt (Pt-Co) cinsinden 1034 olarak belirlenmiştir. Çıkış akımı için ise, KOİ 106 mg/l, TOK 54 mg/l ve renk Platinyum Kobalt (Pt-Co) cinsinden 677 olarak belirlenmiştir. Atıksu karakterizasyonu ile birlikte kimyasal

oksijen ihtiyacı fraksiyonu belirlenmiştir. Partikül boyut dağılımı, KOİ, TOK ve renk profillerini çizebilmek için kullanılmıştır. Özellikle, filtrasyon/ultrafiltrasyon kullanılarak belirlenen KOİ fraksiyonu, endüstriyel atıksu için bir kimlik görevi görmektedir.

Filtrasyon/ultrafiltrasyon ile yapılan partikül boyut dağılımı analizlerinin sonuçlarına göre; giriş ve çıkış için kimyasal oksilen ihtiyacının büyük bir kısmı çözünebilir kısımda yer almaktadir (< 2nm). Ayrıca, biyolojik arıtma verimleri, giriş ve çıkış KOİ değerleri karşılaştırılarak saptanmıştır. Çalışmaya göre, biyolojik arıtma özellikle çözünebilir kısımda olmak üzere, toplamda %85 oranında bir arıtma verimi ile atıksuyun genelinde etkili olmaktadır.

TOK deneyleri atıksu karakterizasyonu için bir araç olarak kullanılmıştır. Giriş akımı için TOK 185 mg/l, çıkış akımı için 54 mg/l olarak saptanmıştır. Deney sonuçlarına göre; KOİ ve TOK partikül boyut dağılımı açısından benzer trendler göstermiştir. Toplam organik karbonun büyük bir kısmı çözünebilir kısımda yer almaktadır (< 2nm). Dahası, biyolojik arıtım toplam organik karbonu büyük ölçüde gidermektedir.

Renk konusundaki çalışmalarda, atıksudaki rengin büyük bir kısmının çözünebilir kısımda yer aldığı gözlemlenmiştir. Dahası, biyolojik arıtımın atıksudaki renk konusunda %30 gibi bir verimlilik sağladığı belirlenmiştir. Giriş akımı için renk 1034 Pt-Co, çıkış akımı için 677 Pt-Co olarak saptanmıştır. Atıksuda bulunan muhtemel zor çözünen boya türleri dolayısıyla, biyolojik arıtımın atıksudaki rengi yeterince gideremediği sonucuna varılmaktadır.

Respirometrik analiz deneyleri, atıksudaki KOİ fraksiyonunu belirlemek için kullanılmıştır. Çalışmada, toplam KOİ'nin büyük bir çoğunluğunun çözünebilir formda olduğu saptanmıştır. Ayrıca hızlı hidroliz olabilen KOİ, bütün KOİ fraksiyonları arasında en büyük paya sahip olan fraksiyondur. Ham atıksu için, $S_H$, toplam KOİ'nin %70'ini, biyolojik olarak ayrışabilen KOİ'nin %86'sını oluşturmaktadır. Ham atıksu için, inert KOİ oranları da saptanmıştır. İnert part, 45mg/l çözünmüş inert kısımla birlikte toplamda 135 mg/l olarak belirlenmiştir. Bu oran toplam KOİ'nin %19'unu oluşturmaktadır.

Partikül boyut dağılımı temelli KOİ fraksiyonu, respirometrik analiz sonuçlarını tamamlayıcı niteliktedir. Ayrıca, biyodegredasyon karakterizasyonu tahminleri için de destekleyici bilgiler içermektedir. Partikül boyut dağılımı analizi ve respirometrik analizin beraber kullanılması, halihazırda uygulanan arıtma yöntemlerinin potansiyellerinin ve sınırlarının belirlenmesinde oldukça önemli bir yöntem olarak görülmektedir. Böylece, her atıksu için ona uygun arıtma yöntemleri kullanılarak, en yüksek verimde arıtım yapmaya olanak sağlanmış olmaktadır.

# 1. INTRODUCTION

## 1.1. General

The environment is the sum of total of all surroundings of a living organism, including natural forces and other living things, which provide conditions for development and growth. It depends on all physical, biological, chemical factors, which constitutes the environment. In substance, the relationship between the humankind and the environment is mutual. The environment plays a significant role in human's life, that it serves as a living space and provides resources that are consumed by humans. Moreover, it makes all the waste assimilated, which is produced by humans. However, it is undeniable that the environment has a limited capacity to perform these roles.

Since the beginning of mankind, the humans live in the natural world and use all the resources providing by the nature to live and to maintain their presence. The environment is used as a shelter and it provides the basic needs such as food and water. As the human population has increased, their activities such as industrialization and urbanization have rapidly grown that in turn accelerate the production of wastes that threatens the environment as well as the existence of many living forms. Humans have been continuously disturbing the balance of nature and removing its essential components, therefore, in the future, there will be potential health risk that puts all living forms in danger. All the resources such as water, air and soil have been contaminated by the additives, which are called "pollutants".

Pollution is the introduction of contaminants into an environment, of whatever predetermined or agreed upon proportions or frame of reference; these contaminants cause instability, disorder, harm, or discomfort to the physical systems or living organisms therein. Albeit, there are different kinds of pollution such as soil pollution and air pollution, the pollution of water has a vital concern to mankind.

Water is a crucial substance in the environment, which covers about 70% of Earth's surface by forming the oceans, lakes and rivers as well as the groundwater. Water has a vital role in all living systems, which allows life exists. However, developing countries and population growth have caused to rise in the demand for water. As the demand for water increases, it will be difficult to supply high-quality water resources, thus, all countries will face the famine in the near future.

The quality of water generally depends on the relationship between physical, biological and chemical reactions. Water bodies such as lakes and rivers are subject to a dynamic state of change due to their geologic age and geochemical characteristics. Since, this dynamic balance has been changed by the human activity, it resulted in pollution in aquatic system causing fish killing, offensive taste and odor. The one of the most important reason that causes this problem is the environmental impacts of textile industries. During the production, thousands of different chemicals to get the textile end product are used. As a result, untreated effluents coming from the industries containing a substantial organic and suspended load cause water pollution.

In sum, applying the proper treatment method for textile industry wastewaters is crucial. The characterization of wastewater should be comprehensively determined and the methods such as particle size distribution (PSD) and COD fractionation should be used together.

## 1.2 Aim and Scope of the Thesis

The aim of this study is to explore the correlation between physical segregation and biodegradability of the organic constituents. For this purpose, the wastewater samples were obtained as two sets from the influent and effluent streams of wastewater treatment plant located in an organized industrial district, Bursa, Turkey. The samples taken from the influent and effluent biological treatment streams were subjected to conventional wastewater characterization, sequential filtration/ultrafiltration experiments for COD, TOC and color profiles, and respirometric analyzes. Comparative evaluation of the COD, TOC and color profiles of the textile wastewater before and after biological treatment was applied to better interpret the effect of biological treatment on the investigated pollutant parameters. Respirometric tests based on Oxygen Uptake Rate (OUR) profiles were carried out on the unfiltered and filtered (450, 100kDa, 1 kDa)  influent samples to determine the biodegradability related COD fractions.

# 2. LITERATURE REVIEW

## 2.1. Overview of Textile Industry

The industry means the manufacturing or technically productive enterprises in a particular field, country, region, or economy viewed collectively, or one of these individually. A single industry is often named after its principal product such as textile industry.

The textile industry is one of the longest and most complex manufacturing industrial chains, covering the entire production cycle from raw materials to semi-processed products (yarns, woven and knitted fabrics with their finishing process), to final products (carpets, home textiles, clothing and industrial use textiles) (Lotito, 2012). The textile industries generally use fibres. The vegetable fibres such as cotton, animal fibres such as wool, and a wide range of synthetic materials such as nylon and polyester are used to produce final products. It exhibits a typical variation in scale, ranging from large-scale mechanized to small-scale traditional units (UNIDO, 2012).

The first step in the production of a textile product is the manufacture of fibres or, in the case of natural fibres, the manipulation of these fibres into useful fibres. Afterward, the fibres are turned into yarn by spinning or texturing. Preparation, dyeing and finishing can be done on yarn or on the textile product obtained through knitting, weaving, and non-woven techniques. The last step is the fabrication of a finished product (Hendrickx and Boardman, 1995).

## 2.2. Textile Industry in Turkey

Turkey is a leading country with a share of 3.7% in world trade of textile and garment and it is among the most competitive countries including China, India and South Korea, in terms of labor force, raw material and marketing. Moreover, Turkey has the 2$^{nd}$ rank in the textile and garment export to European Union countries, 7$^{th}$ rank in cotton production, 4$^{th}$ rank in cotton consumption, 5$^{th}$ rank in fibre yarn production, and 4$^{th}$ rank in open-end yarn production in the world rankings (UNIDO, 2012). It is estimated that approximately 2,000,000 people, 450,000 of which in textile and 1,500,000 in garment industry are employed in Turkey.

Some parts in Turkey have specific sectors of textile industry. According to UNIDO, (2012), it is examined that yarn production generally is in Istanbul, Kahramanmaraş, Adıyaman and Gaziantep, while Denizli is the province that has the biggest part of producing towel, bathrobe and home textile. In addition, yarn manufacturing in Uşak, textile finishing in Çorlu, cotton weaving and finishing in Adana have become prominent as Istanbul stand out in garment manufacturing. Yarn production capacity of Turkey is 3,500,000 tons in total with 2,300,000 tons of short-fibre, 400,000 tons of long-fibre, 800,000 tons of filament yarn production. Total installed capacity is estimated as 1,350,000 tons for weaving and 2,250,000 tons for knitting. A production capacity of 400,000 tons for non-woven, rug and technical textile is also available.

One of the most important environmental problems is that the amount of wastewater discharged and the chemical loads it carries. As indicated by Turkish Statistical Institute, textile and garment industry is in charge of 15% of industrial water consumption (191.5 million $m^3$), which makes it 2nd largest industrial water consumer inside of the entire Turkish manufacturing sector. Water pollution due to textile industry has turned into a noteworthy issue in Turkey. Another critical ecological issue connected with the textile industry is high energy utilization and related $CO_2$ discharges. In Turkey, the textile industry has been accounted for the 3$^{rd}$ most energy intensive sector.

### 2.3. General Processes of Textile Industry

As it is indicated by Patel and Vashi, (2015) and Walters et al., (2005), there are general processes in textile industry given below:

#### 2.3.1. Fibre preparation

Natural fibres always need to be cleaned before the production. This case is the most intensive one since the fibres containing 20-40% impurities in the form wool grease, dyed perspiration and a loading of pesticides. In order to remove these impurities, large amounts of hot water, containing non-ionic detergents and inorganic salts are used.

During the production of synthetic fibres, a number of reactive species and a wide range of chemicals are used.

**Figure 2.1 :** Fibre preparation.

### 2.3.2. Spinning

Spinning process contains various mechanical processes such as comb, align and spin them in order to produce a yarn. Chemical auxiliaries are used to provide lubrication, allowing high speed processing.

**Figure 2.2 :** Spinning.

Since it has realized that mineral oils such as poly aromatic hydrocarbons (PAHs) cause pollution, they have been substituted for synthetic oils and ester oils. During the applying of oils, emulsifiers such as alcohol ethoxylates and alkyl phenol ethoxylates are required. Synthetic oils have no impurities as much as mineral oils, and also ester oils are biodegradable.

### 2.3.3. Weaving

Weaving interweaves two or more opposite yarn systems. On a weaver weft yarn is woven between taught, parallel warp yarns. The warp yarns are under tension and are subjected to stress during weaving as the weft yarn is inserted between them at great speed.

**Figure 2.3 :** Weaving.

So as to decrease harm caused by the numerous contacts, the shed must persevere through chemical preparation. As a result, the size types have a priority. The size structures a film rendering yarn more slippery and stronger. Hence it reduces friction, the number of free fibre ends that might interfere with the weaving process and the number of warp yarn breakages.

In this process, the sizing agents such as auxiliaries are widely used, especially for cotton. Viscosity regulators, antihistatic agents, wetting agents, defoaming agents and preservatives are the additional agents for the size preparations of cotton. The other sizes for fibres do not contain auxiliaries as much as cotton and mostly they contain a preservative.

### 2.3.4. Singeing

Singeing is performed with yarns and fabrics. Basically, the material is exposed to a gas flame in order to get rid of protruding. The protruding fibres may cause non-uniform dye uptake. The advantage of this process is that there are no chemical agents needed. However, dust and volatile organic compounds (VOCs) are still a problem.

**Figure 2.4 :** Singeing.

### 2.3.5. Desizing

During this process, the size removal is carried out before dyeing. The way of this process relies on the type of size applied. Water-soluble size might just be washed out, as water insoluble size requires chemical or enzymatic degradation. As a result, a large load gets into wastewater streams.

### 2.3.6. Scouring

The natural fibres contain impurities such as waxes, pectins and proteins and they needed to be removed. Thus, hot sodium hydroxide, a surfactant and an agent must be used. Besides, organic solvents or detergents may be used in order to scour the wool.

**Figure 2.5 :** Scouring.

### 2.3.7. Bleaching

By this process, the fabric is exposed to bleach liquor. Generally, the hydrogen peroxide is used to treat the fabric. Besides, there are other chemicals used such as sodium chloride, formic acid, sulfuric acid and caustic soda to get rid of natural coloring material. The process starts with washing the fabric with water. Then, by using dilute acid and sodium bisulfate, last traces of chlorine are removed. In the final step, the fabric must be soaped, then washed and finally treated with optical whitening agent. As a result, this process causes pollution, which is 10-20% of the total pollution.

**Figure 2.6 :** Bleaching.

### 2.3.8. Mercerising

This process is used specifically for the cotton. This process improves tensile strength, lustre and ability to take up dyes. During the process, sodium hydroxide solution baths are used. After the use of solution, it may be reused or NaOH is recovered and used during other various processes.

**Figure 2.7 :** Mercerising.

### 2.3.9. Dyeing

Dyeing is one of the most important parts of the textile industry in terms of the environment. Because, this unit contributes 15-20% of the total pollution load. During the process, the different types of dyes and auxiliary chemicals are used. There is a wide range of dyes such as disperse dyes, basic dyes, acid dyes, vat dyes, reactive dyes, sulfur dyes, direct dyes, azoic dyes, developed dyes, fluorescent dyes, mordant dyes and oxidation-based dyes.

**Figure 2.8 :** Dyeing.

### 2.3.10. Printing

In contrast to dying process, printing allows a range of different colors to be used. Generally, the process needs between 5 and 10 pastes to create a single pattern. In order to get color, either pigments or dyes are used.

**Figure 2.9 :** Printing.

Pigment printing is gaining popularity in textile industry. Since, the pigment has no regular proclivity for the fabric, there must be binding system such as acrylates to attach the pigment to the fabric.

There is another printing system called plastisol used for t-shirts. The color is connected in a glue of PVC and plasticizer, forming a recognizably tactile layer. Bis phthalate (DEHP), benzyl butyl phthalate (BBP), diisononyl phthalate (DINP), and dihexyl phthalate (DHP) is the most used plasticizers for printing. These plasticizers are very toxic and puts environment in danger. Moreover, PVC is another problem for environment and human's health. Nowadays, PVC free printing is used. Unfortunately, the printing process contributes to COD loading and creates pollution.

### 2.3.11. Finishing

Finishing process is the final process. The fabric is washed in order to remove the unfixed dyes. After that, it must be treated by using starches to finish the fabric. This process creates significant pollution. As the process is done, the wastewater starts to be strongly colored; moreover, it contains fixing agent such as soap and minerals.

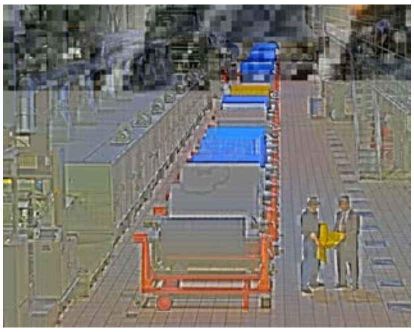


**Figure 2.10 :** Finishing.

### 2.4. Effect of Applied Processes on the Characteristics of Textile Wastewater

The textile industry contributes significantly to the pollution in environment by converting natural or hand-made fibres into fabrics and products. Environmental problems generally start by utilizing pesticides in order to cultivate natural fibres or the discharges during the production of synthetic fibres. After that, a number of processes are implemented in order to process the fibres and to produce textile end product by using thousands of different chemicals. As a result, the water pollution arises due to the discharge of effluents. The wastewater coming from washing operations contains an organic and suspended pollution load. Effluents arising from processes are generally alkaline, strong smelling and coloured by chemicals. Among the products applied during the process, the most elevated environmental load emerges from dyes, salts, detergents and organic acids. The most of the chemicals coming from effluent are significantly toxic and can lower the dissolved oxygen.

As it is indicated in UNIDO, (2012) and Walters et al., 2005, the textile industry contains a number of processes. Each process utilizes different kinds of chemicals causing different impacts on the environment.

#### 2.4.1. Fibre production

In this process, there are two types of fibres, which are natural and synthetic. The environmental problems arising from synthetic fibres, such as polyester and polyacryl are the use of energy and the toxic compounds. On the other hand, natural fibre, such as cotton, needs large amounts of pesticides and artificial fertilizers to grow.

### 2.4.2. Spinning

The spinning of fibres creates dust and other particles dispersing into the air causing respiratory problems. Moreover, since the aqueous preparations must be protected from degradation, preservatives such as bactericides should be added. As a result, these preservatives will end up in effluent.

### 2.4.3. Washing/Scouring

During this process, a number of agents, such as detergents, alkalis, soaps, anti-static compounds, foamers and complex agents are used. As a result, the effluent containing these agents cause pollution and discomfort to the receiving environment.

### 2.4.4. Weaving/Knitting

The weaving and knitting process is one of the most important parts of the textile industry. During this process, the excessive amount noise and dust cause negative working conditions for workers.

### 2.4.5. Bleaching

The best-known bleaching agents are hydrogen peroxide, sodium chlorite and sodium hypochlorite. Moreover, auxiliary chemicals such as surfactants and optical brighteners are also used. The negative consequences of bleaching are the use of energy and the chemicals. The most significant chemical that has a negative effect on the environment is chlorine.

### 2.4.6. Mercerising

Mercerising is a process where NAOH and a lot of water are used in. The residual NAOH coming from this process gets into the stream causing environmental problems.

### 2.4.7. Dyeing/Printing

Dyeing and Printing is the most important process in terms of environment. This process not only generates a lot of waste, but also it consumes a lot of energy. Moreover, there is a wide range of chemicals and auxiliary materials using through the process. The effluent may be hot, alkaline, odorous and highly coloured causing treatment problems.

### 2.4.8. Finishing

During last process, variety of finishing chemicals is utilized to accomplish some special characteristics such as water and flame resistance. Some compounds such as bromated diphenylethers has heavy metals inside causing disposal problems. This compound is hard to treat by using conventional biological treatment. Moreover, biocides such as polychlorinated phenols (PCP) and metallic salts are highly toxic for the environment.

As previously stated, the water used during the processes depends on the mill, processes and the materials produced. Each process uses a large amount of water, which will eventually become wastewater. Pretreatment, dyeing, printing and finishing stages are the most significant parts in terms of pollution. In particular, desizing is the process that has a largest part in pollution. Due to discharge of the sizes during desizing process, cause a significant pollution. Moreover, in scouring, dirt, oil, and waxes coming from natural fibres also discarded into wastewater. Dyeing process also forms 15-20% of the COD load of a mill. The wastewater coming from dyeing process is highly salt and colored.

## 2.5. Characteristics of Textile Wastewater

The term "wastewater characteristics" refers to the organic and inorganic materials, total nitrogen, total phosphorus and so on (Melcer et al., 2004). In textile industries, there is significant amount of wastewater coming from each process. Due to the type of process, fabric and chemicals used, the volume and composition of wastewater may differ from one process to another. Despite the fact that the composition of wastewater may be different even for the same process, there are general values given for a better understanding of pollution. The characteristics of the typical textile wastewater are given in Table 2.1 (Ghaly, 2014). A composite wastewater from an integrated textile plant consists of the following materials: starches, dextrin, gums, glucose, waxes, pectin, alcohol, fatty acids, acetic acid, soap, detergents, sodium hydroxide, carbonates, sulfides, sulfites, chlorides, dyes, pigments, carboxymethyl cellulose, gelatin, peroxides, silicones, fluorocarbons, and resins (Walters et al., 2005).

**Table 2.1 :** Characteristics of typical untreated textile wastewater (Ghaly, 2014).

| Parameter | Range |
|---|---|
| pH | 6-10 |
| Temperature (°C) | 35-45 |
| Total dissolved solids (mg/L) | 8,000-12,000 |
| BOD (mg/L) | 80-6,000 |
| COD (mg/L) | 150-12,000 |
| Total suspended solids (mg/L) | 15-8,000 |
| Total Dissolved Solids (mg/L) | 2,900-3,100 |
| Chlorine (mg/L) | 1,000-6,000 |
| Free chlorine (mg/L) | <10 |
| Sodium (mg/L) | 70% |
| Trace elements (mg/L) | |
| Fe | <10 |
| Zn | <10 |
| Cu | <10 |
| As | <10 |
| Ni | <10 |
| B | <10 |
| F | <10 |
| Mn | <10 |
| V | <10 |
| Hg | <10 |
| $PO_4$ | <10 |
| Cn | <10 |
| Oil & grease (mg/L) | 10-30 |
| TNK (mg/L) | 10-30 |
| $NO_3$-N (mg/L) | <5 |
| Free ammonia (mg/L) | <10 |
| $SO_4$ (mg/L) | 600-1000 |
| Silica (mg/L) | <15 |
| Total Kjeldahl Nitrogen (mg/L) | 70-80 |
| Color (Pt-Co) | 50-2,500 |

Since the wastewater characteristics have very significant impact on system performance, it should be known in terms of providing predictions of system behavior (Melcer, et al., 2004). As the wastewaters coming from the textile industry contains organics, color, metals and chemicals, they threaten the environment and put all living forms in danger. The characteristics of the wastewater associated with textile manufacturing operations are given in Table 2.2 (Patel and Vashi, 2015).

**Table 2.2 :** The characteristics of the wastewater associated with each textile processes (Patel and Vashi, 2015).

| Process | Effluent Composition | Nature |
|---|---|---|
| Sizing | Starch, waxes, wetting agents carboxymethyl cellulose (CMC) Polyvinyl alcohol (PVA) | High in BOD, High COD |
| Desizing | Starch, CMC, PVA, fats wax, pectin | High BOD, COD, SS, DS |
| Bleaching | Sodium hypochlorite,NaOH acids, surfactant, Cl2, H2O2 sodium phosphate, cotton fiber | High alkalinity, high SS |
| Mercerizing | Sodium hydroxide, cotton wax | High pH, low BOD, high DS |
| Dyeing | Dyestuffs urea, reducing agents oxidizing agents, acetic acid detergents, wetting agents | Strong colored, high COD High DS, low SS, low heavy metals |
| Printing | Pastes, urea, starches, gums oils, binders, acids, thickeners cross-linkers, reducing agents alkali | High colored, high BOD, high COD oily appearance,slightly alkaline high suspended solid |

The rules of disposal of effluents have been imposed by the environmental agencies all around the world in order to protect the environment from pollution caused by the textile industry. These agencies defined certain limits (Ghaly, 2014). Some of the regulations defined by several countries are given in Table 2.3 (Sonibare and Yusuff, 2004).

**Table 2.3 :** Discharge limits of various countries (Sonibare and Yusuff, 2004).

| Parameter | CCME | China | BIS | Hong Kong | FEPA | Mexico | Thailand | Philippines | Indonesia | Bangladesh | SL |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 6.5-8.5 | 6-9 | 5.5-9 | 6-10 | 6-9 | 6-8.5 | 5-9 | 6-9 | 6-9 | 6.5-9 | 6-8.5 |
| Temperature (°C) | 30 | - | 50 | 43 | 40 | - | - | 40 | - | 40-45 | 40 |
| Colour (Pt-Co) | 100 | 80 | None | 1(Lovibond) | 7(Lovibond) | - | - | 100-200 | - | - | 30 |
| TDS mg/L | 2000 | - | 2100 | - | 2000 | - | 2000-5000 | 1200 | - | 2100 | 2100 |
| TSS mg/L | 40 | 150 | 100 | 800 | 30 | - | 30-150 | 90 | 60 | 100 | 500 |
| Sulphide µg/L | 200 | 1000 | 2000 | 1000 | 200 | - | - | - | - | 1000 | 2000 |
| Free Chlorine µg/L | 1000 | - | 1000 | - | 1000 | - | - | 1000 | - | - | - |
| COD mg/L | 80 | 200 | 250 | 2000 | 80 | < 125 | 120-400 | 200-300 | 250 | 200 | 600 |
| $BOD_5$ mg/L | 50 | 60 | 30 | 800 | 50 | < 30 | 20-60 | 30-200 | 85 | 150 | 200 |
| Oil & Grease mg/L | - | - | 10 | 20 | 10 | - | 300 | 5-15 | 5 | 10 | 30 |
| Dissolved Oxygen µg/L | 6000 | - | - | ≥ 4000 | - | - | - | 1000-2000 | - | 4500-8000 | - |
| Nitrate µg/L | 13000 | - | 10000 | - | 20000 | 10000 | - | - | - | 10000 | 45000 |
| Ammonia µg/L | 0.1 | - | - | 500 | 0.2 | - | - | - | - | 5000 | 60 |
| Phosphate µg/L | <4000 | 1000 | 5000 | 5000 | 5000 | - | - | - | 2000 | - | 2000 |
| Calcium µg/L | - | - | - | - | 200000 | - | - | 200000 | - | - | 240000 |
| Magnesium µg/L | 200000 | - | - | - | 200000 | - | - | - | - | - | 150000 |
| Chromium µg/L | 1 | - | 100 | 100 | <100 | 50 | 500 | 50-500 | 500 | 2000 | 50 |
| Aluminium µg/L | 5 | - | - | - | <1000 | 5000 | - | - | - | - | - |
| Copper µg/L | <1000 | 1000 | 3000 | 1000 | <1000 | 1000 | 1000 | 1000 | 2000 | 500 | 3000 |
| Manganese µg/L | 5 | 2000 | 2000 | 500 | 5.0 | 200 | 5000 | 1000-5000 | - | 5000 | 500 |
| Iron µg/L | 300 | - | 3000 | 1500 | 20000 | 1000 | - | 1000-20000 | 5000 | 2000 | 1000 |
| Zinc µg/L | 30 | 5000 | 5000 | 600 | <10000 | 10000 | - | 5000-10000 | 5000 | 5000 | 10000 |
| Mercury µg/L | 0.026 | - | 0.01 | 1 | 0.05 | - | 5 | 5 | - | 10 | 1 |

CCME - Canadian Council of Ministers of the Environment
BIS - Bureau of Indian Standards
FEPA - Federal Environmental Protection Agency (United States)
SL - Sri Lanka

There are rules of disposal of effluents for Turkey defined by SKKY. The regulations for textile industry are given in Table 2.4 (SKKY). Since the treatment plant is located in organized industrial district, the regulations for organized industrial district given in Table 2.5 should be taken into consideration.

**Table 2.4 :** Discharge limits of textile wastewater (SKKY).

| Parameter | Value |
|---|---|
| COD (mg/l) | 300 |
| TSS (mg/l) | 200 |
| pH | 6-9 |
| Color (Pt-CO) | 260 |

**Table 2.5 :** Discharge limits of organized industrial district (SKKY).

| Parameter | Value |
|---|---|
| COD (mg/l) | 300 |
| TSS (mg/l) | 100 |
| TP (mg/l) | 1 |
| Grease | 10 |
| Pb (mg/l) | 1 |
| TKN (mg/l) | 15 |
| $SO_4$ (mg/l) | 1500 |
| pH | 6-9 |
| Color (Pt-Co) | 260 |

### 2.6. Treatment of Textile Wastewater

Since the textile industry wastewater contains high level of COD and other substances, the treatment methods become significant. Due to wide variety of inorganic and synthetic organic pollutants such as solvents, dyes, detergents, oils, metallic wastes and suspended solids, the treatment of textile industry becomes difficult. There are traditional methods which are formed by the pyhical, chemical and biological methods.

There are 3 treatment methods given below (Ghaly et al., 2014):

#### 2.6.1. Primary treatment

This treatment contains processes that reduces the floating and suspended solids in wastewater by mechanical means. In primary treatment processes, sedimentation tanks and fine screens are generally used. First of all, the effluent is screened for coarse suspended solids. After that, the effluent flows to sedimentation tank in order to reduce suspended particles by gravity. According to Das (2000), sedimentation is not effective, because it does not remove colloidal particles. Thus, it is a better way to replace it with coagulation.

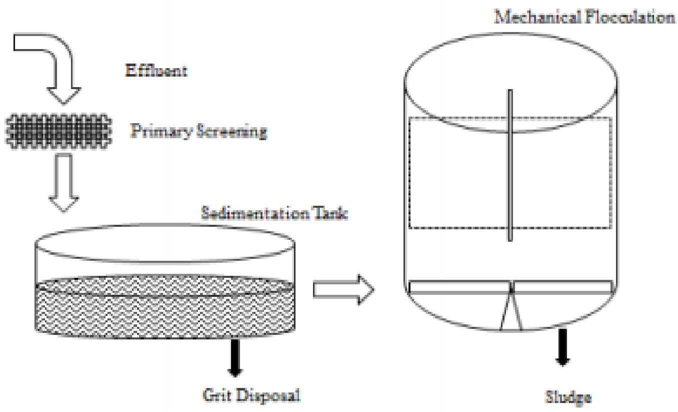



**Figure 2.11 :** Primary treatment (Ghaly et al., 2014).

The other process is mechanical flocculation involving slow mixing of the effluent gathering the small particles together to form bigger particles. After that, the settled particles removed as sludge. The disadvantage of this process is that the formation of flocs is difficult to control.

### 2.6.2. Secondary treatment

The main purpose of this treatment method is to reduce the COD and other contents such as phenol and oil, also to control its color. This type of treatment needs microorganisms under aerobic conditions. Aerated lagoons, trickling filter and activated sludge systems are among the aerobic system used in the secondary treatment (Das, 2000).

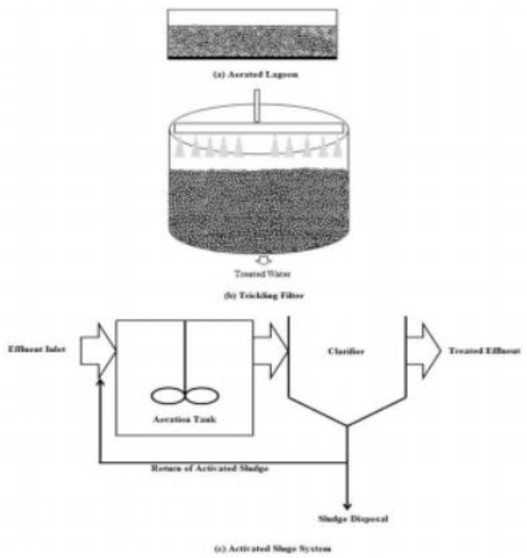



**Figure 2.12 :** Secondary treatment (Ghaly et al., 2014).

### 2.6.3. Tertiary treatment

Electrodialysis, reverse osmosis and ion exchange are the technologies known as tertiary treatments. Reverse osmosis is the well-known method which remove total dissolved solid contents with a high efficiency of 90%. Moreover, Ion exchange technique is also commonly used as tertiary treatment.

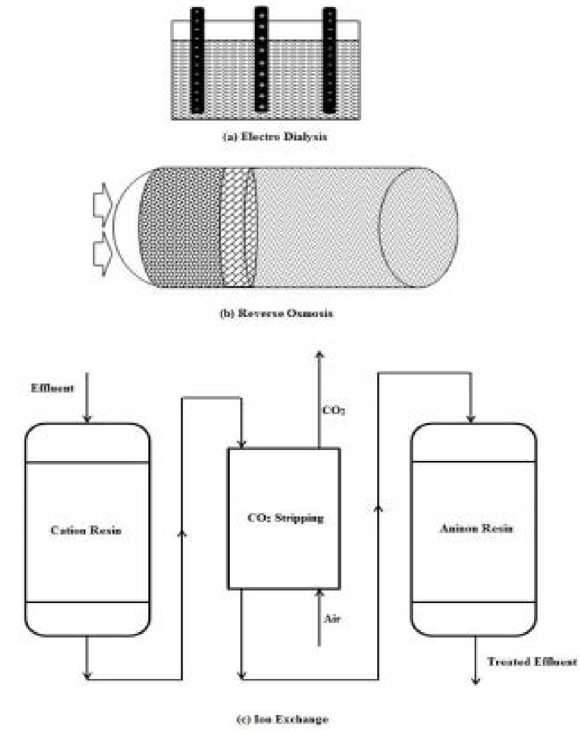



**Figure 2.13 :** Tertiary treatment (Ghaly et al., 2014).

# 3. BIODEGRADATION OF ORGANIC MATTER IN WASTEWATERS

## 3.1. COD Fractionation

The identification of wastewater characteristics relating to the organic part is crucial in terms of the standpoint of process kinetics and prediction of effluent quality (Orhon and Çokgör, 1997). Most of certain industrial wastewaters have organic compounds with a great variety of individual chemicals. Since determining the presence and quantity of organic substrates are useful, collective analytical parameters such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are used for describing the performance of a wastewater treatment facility and the quality of its effluent. However, the BOD test is not very suitable for the characterization of wastewaters, since it does not determine all organic compounds in wastewaters. Therefore, COD is more useful parameter than BOD as it enables one to make appropriate correlations among substrate, biomass and dissolved oxygen in terms of the description of the activated sludge process.

Since wastewater comprises a complex mixture of organic and inorganic material, it is important that the organic materials should be divided into groups due to their behaviors in the activated sludge process. The primary division is identified with whether the material is biodegradable or unbiodegradable. For biodegradable part, the organic part is divided into readily biodegradable and slowly biodegradable portions. The readily biodegradable substrate consists of relatively small molecules, which can be easily transported into the cell without any further reaction. The slowly biodegradable fraction is larger and more complex, thus, they needs an extracellular breakdown for utilization. Since, the slowly biodegradable fraction covers a wide range of particle size distribution from soluble to particulate, this part further divided into rapidly hydrolysable fraction and slowly hydrolysable fraction. The unbiodegradable (inert) fraction represents material that does not react or reacts so slowly that any loses in the treatment plant are negligible. The soluble part passes directly through the system without affecting the biochemical reactions, whereas the particulate part is entrapped in the sludge and removed with the excess sludge (Melcer et al., 2003).

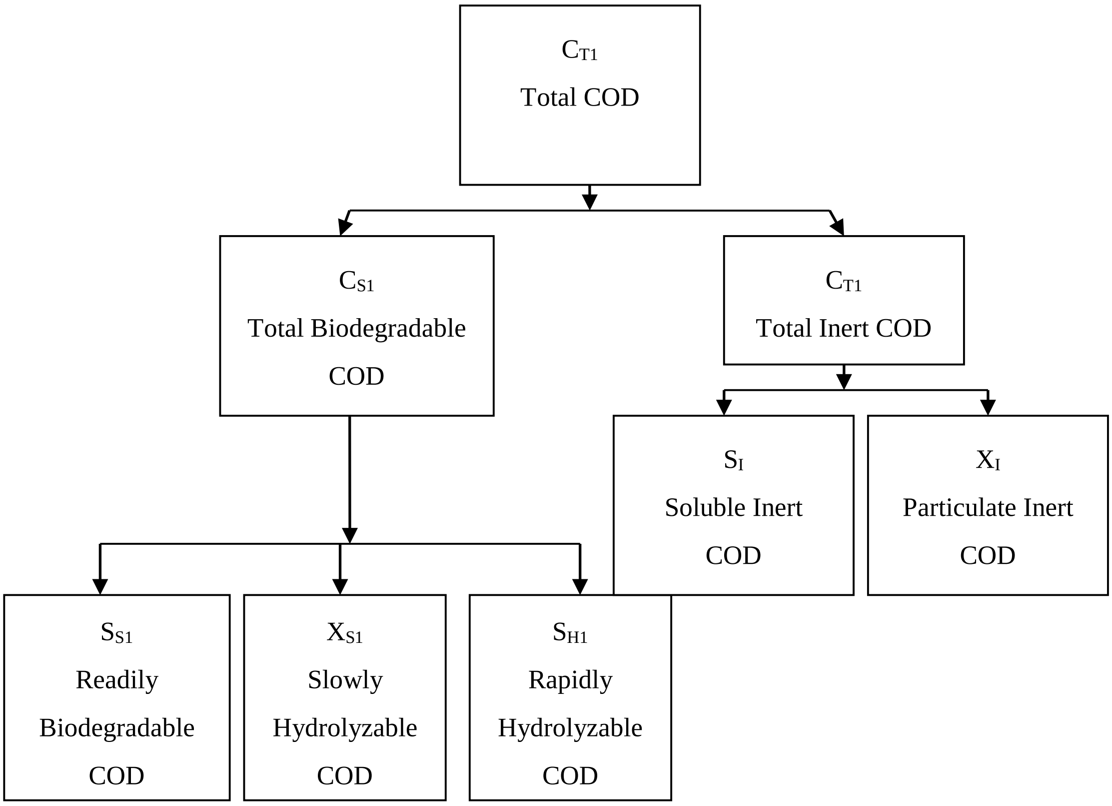



**Figure 3.1 :** COD fractionations in wastewaters

Biodegradability may have a relationship with particle size and physical state in solution, demonstrating that the observed difference in biokinetic responses of activated sludge microflora to soluble and particulate organics has been speculated to be due to the difference in the particle sizes of these constituents (Wentzel MC *et al*., 1999, Dulekgurgen *et al*., 2005).

Batch experiments done with Oxygen Utilization Rate (OUR) measurement is used for the determination of organic matter (Kristen *et al*., 1982).

### 3.1.1.Readily biodegradable organic matter

Readily biodegradable organic matter consists of material that can be directly absorbed by the organism and metabolized inside the cells for energy and synthesis. The readily biodegradable fraction is composed of soluble compounds such as volatile fatty acids, simple carbohydrates, alcohols and amino acids. Volatile fatty acids make up the important part of this component.

The determination of readily biodegradable organic matter rely on respirometric measurements conducted under aerobic or anoxic conditions, using continuous or batch reactors. The aerobic batch test is a method, which basically depends on observation of the oxygen uptake rate (OUR) showing the amount of oxygen utilization per unit time, per unit reactor volume, due to microbial activities (Orhon and Çokgör, 1997). This method is the most practical since it has the least requirement in terms of analytical/laboratory facilities.

### 3.1.2.Rapidly hydrolyzable organic matter

The rapidly hydrolyzable fraction is made up of complex organic material that requires extracellular breakdown prior to utilization by the organism. This fraction may account for 15-25% of total COD in raw wastewaters. Moreover, the rapidly hydrolyzable organic matter consists of dissolved and colloidal solids.

The rapidly hyrolyzable organic matter is hydrolysed under aerobic conditions. Hydrolysis process can be finished in a few hours, but some changes in this fraction may occur during wastewater transport in sewers.

Rapidly hydrolyzable organic matter can be determined by using the continuous tests with the help of Oxygen Utilization Rate (OUR) (Solfrank and Gujer, 1991).

### 3.1.3.Slowly hydrolyzable organic matter

In wastewaters, the majority of organic materials are present in a form, which is not suitable for internal cell metabolism. Since these substances are characterized by high molecular weight and complex molecules, they requires extracellular breakdown to be metabolized by the organisms.

Slowly hydrolyzable fraction mostly consists of particulate form. Moreover, most of the biodegradable organic matter is composed of this fraction (Henze *et al.*, 1987). According to Activated Sludge Model No: 1, slowly hydrolyzable organic matter constitutes 40-60 % of the total COD in raw wastewaters.

As the utilization of slowly hydrolyzable organic matter is challenging, hydrolysis is the rate limiting step for this fraction under aerobic or anoxic conditions. Since, the hydrolysis rates are not stable, it is a better way to separate these components into groups. Albeit, the reason of these changing rates could not be determined yet, the researches show that the hydrolysis rates depend on the conditions. For instance, under aerobic and anoxic conditions, hydrolysis is slower than the anaerobic conditions (Henze and Mladenovski, 1991).

According to activated sludge model Ekama *et al*., 1986, the slowly biodegradable organic matter can be determined by using Oxygen Utilization Rate (OUR) experiments.

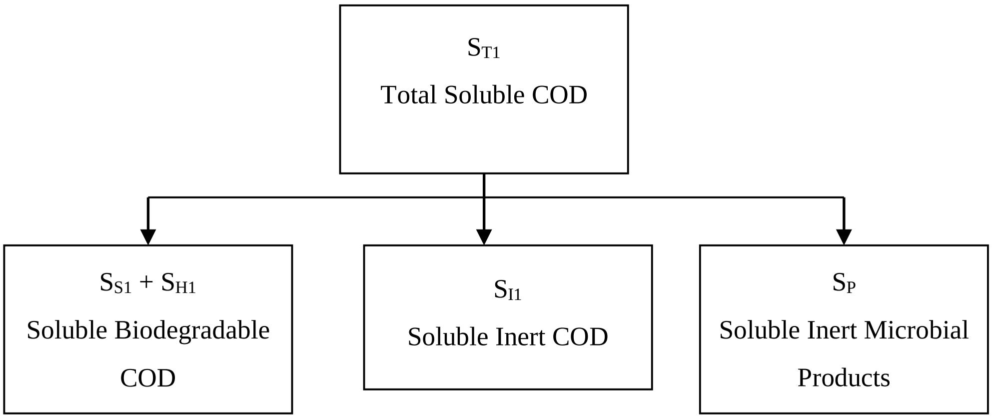



**Figure 3.2 :** Soluble COD components.

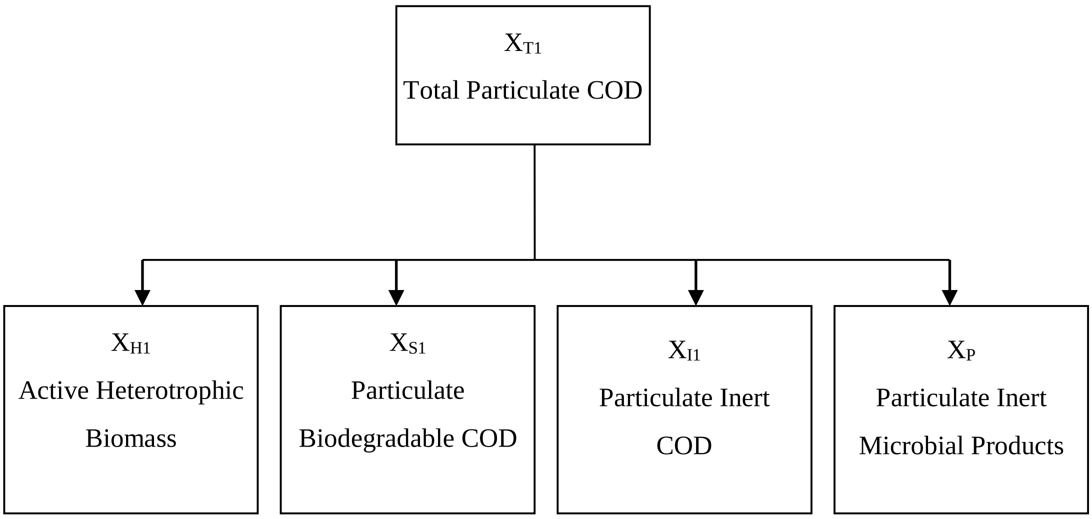



**Figure 3.3 :** Particulate COD components.

### 3.1.4. Soluble unbiodegradable (inert) organic matter

The soluble unbiodegradable fraction in influent wastewater is soluble organic material unaffected by biological action in the system. The magnitude of this component is crucial in terms of activated sludge system behavior; particularly with respect to effluent COD quality, volatile solids production and oxygen demand. The soluble unbiodegradable COD leaves the system without affecting the biochemical reactions (Melcer et al., 2003). Soluble organic matter components in the effluent flow are given in the Figure 3.2.

$$S_{IT}=S_{I1}+S_P \tag{3.1}$$

Since the soluble residual microbial product fraction ($S_P$) is a microbial end-products excreted from the cells, the effluent component is bigger than influent component.

The formation of inerts during the decay of the cell and hydrolysis must be included in terms of good modeling. This approach is used in ASM 1 (Henze *et al.*, 1987, Solfrank and Gujer, 1991).

### 3.1.5. Particulate unbiodegradable (inert) organic matter

Particulate unbiodegradable COD is entrapped inside the sludge biomass and accumulates in the system, then only removed with the sludge in the treatment process. At steady state, the mass of $X_I$ entering the system in the influent will be balanced by the mass leaving via the sludge wastage stream and in the effluent (Melcer et al., 2003). The size of this component is important in terms of volatile solids production and oxygen demand. Figure 3.3 shows the particulate COD components in the effluent flow.

There are two kinds of particulate inert components: the particulate inert fraction in raw wastewater and the particulate inert fraction produced during the activated sludge metabolism with the suspended organics. Particulate and soluble inert organic matter components can be determined with the experiments (Kappeler and Gujer, 1992).

## 3.2. Respirometry (OUR Test)

The basic understanding and interpretation of complex biochemical reactions taking place in the activated sludge process has been strengthened with the recognition of dissolved oxygen as a significant model component ant its incorporation into mechanistic models. Since, it is known that dissolved oxygen (DO) and nitrate are the final electron acceptors, there is an electron balance between biodegradable COD, biomass and electron acceptor by dissolved oxygen (Orhon et. al., 2009).

Respirometry is an experiment that measures biological oxygen consumption rate under certain experimental conditions. Since, the oxygen utilization occurs during the process due to biomass growth and substrate removal, respirometry is a useful method in terms of identifying the treatment efficiency and modeling (Spanjers et. al., 1998). This method provides the informations given below:

- indicating the composition of the wastewater

- giving a direct indication of the specific activity of certain fractions

- generating quantitative information on how the biomass interacts with wastewater components and how purification performs

The oxygen utilization rate (OUR) is the rate that shows the change in the dissolved oxygen concentration during the biochemical transformations in activated sludge process. OUR is very useful tool in terms of the determination of biodegradable COD fractions and other stoichiometric model coefficients (Orhon et. al., 2009).

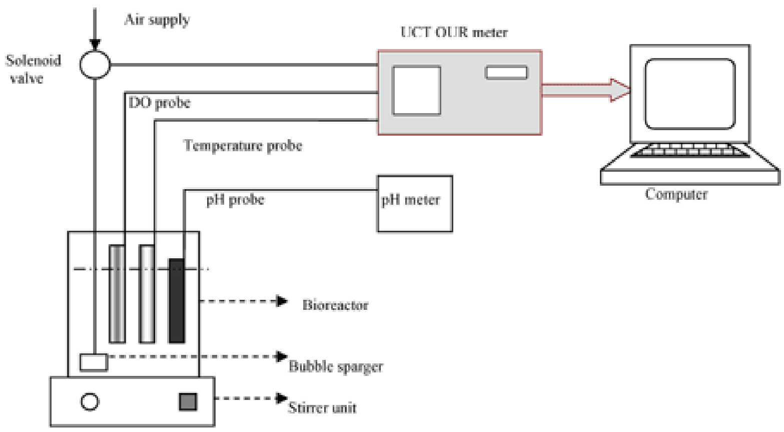



**Figure 3.4 :** Respirometry.

The respirometric experiments carried out by using dissolved oxygen electrodes. The well-known respirometric experiment is the lab-scale respirometer set-up. During the experiment, the activated sludge system composed of biomass fed with wastewater in an aerated reactor vessel is sampled continuously. The sampling method is that the samples are transferred into closed vessel where the OUR measurement occurs by using oxygen electrodes. The depletion of dissolved oxygen is monitored in certain period of time. The schematic example of OUR profile (F/M:0.2) is given in figure 3.5 (Orhon et. al., 2009).

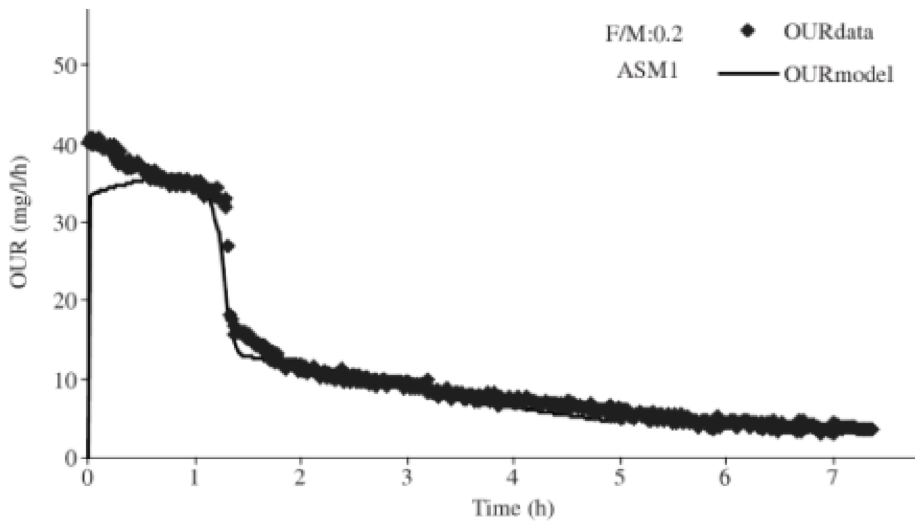



**Figure 3.5 :** The schematic example of OUR profile (Orhon et. al., 2009).

COD fractionation of the textile wastewaters in the literature is given in Table 3.1. According to studies, total COD mostly consists of soluble form. Moreover, $S_H$ is the most significant one among all fractions.

**Table 3.1 :** COD fractionation in the literature.

| Literature | $C_{T1}$ (mg/l) | $C_{S1}$ (mg/l) | $S_{H1}$ (mg/l) | $S_{S1}$ (mg/l) | $X_{S1}$ (mg/l) | $X_{I1}$ (mg/l) | $S_{I1}$ (mg/l) |
|---|---|---|---|---|---|---|---|
| Yildiz et al., 2007* | 775 | 465 | 417 | 25 | 230 | 50 | 55 |
| Dogruel, 2000** | 955 | 675 | 245 | 110 | ND | ND | 320 |
| Ubay Cokgor et al., 2000*** | 860 | 515 | 355 | 144 | 229 | 117 | 17 |

* Acrylic fiber carpet; ** Cotton knit fabric; *** Predominantly textile

# 4. CHARACTERIZATION OF PARTICLES ACCORDING TO THEIR SIZE DISTRIBUTIONS IN WASTEWATER

## 4.1. Particle Size Distribution

In general, textile industry effluent is a wastewater with complex characteristics. It contains high level of organic pollutants characterized with chemical oxygen demand (COD) concentrations. Since the conventional characterization alone cannot give accurate information, more comprehensive information becomes of significance. Thus, PSD-based COD fractionation has been found and used by the researchers for a better insight into wastewater characterization. This process is used for municipal, industrial waste streams and also for domestic and textile wastewaters, with a suggestion of providing a more in-depth comprehension in terms of COD fractions and their biodegradability characteristics in relation to particle size categories (Doğruel et al., 2006).

Size distribution for pollutants is crucial for the comprehension of wastewater characteristics in terms of the estimation of appropriate treatment technologies and expected removal performances. The size range of settleable pollutants in wastewater is generally above $10^5$nm, which practically defines the performance of plain settling. Furthermore, filters with pore sizes of 450 and 1600 nm help investigate the size of particles that can be removed by means of chemical settling. Particles in wastewaters have conveniently been grouped into operational size categories, namely dissolved ($<$1nm), colloidal (1–$10^3$ nm), supracolloidal ($10^3$–$10^5$ nm) and settleable ($>10^5$ nm). Lately, ultrafiltration, among other methods, is successfully used to identify and differentiate wastewater pollutants within much narrower ranges (Engström and Gytel, 2000; Sophonsiri and Morgenroth, 2004; Doğruel et al., 2006).

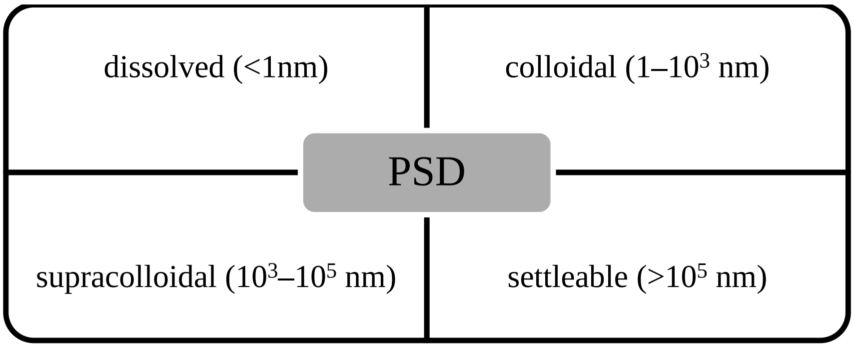



**Figure 4.1 :** Particle size distribution.

As PSD serves as the fingerprint for wastewaters, textile wastewater and domestic sewage are different from each other in terms of particle size distribution. For domestic sewage, the bulk of the COD is seen at the size ranges above 450 nm, and only a relatively small portion is at the soluble range. For the textile wastewater, COD fractionation is more complex. Yet, significant COD fractions are also present in a number of other size intervals, due to different specific chemicals used in the process (Dulekgurgen *et al*., 2006).

In time, several technics, mostly depending on respirometry, have so far been proposed for the quantitative characterization of the COD fractions for biodegradability. However, most of these procedures take a lot of time and generally require acclimated biomass (Ekama et al., 1986; Orhon et al., 1998, 1999; Çokgör et al., 1998; Carvalho et al., 2001). Moreover, physical separation methods alone cannot recognize the biodegradable and non-biodegradable portions. Thus, in order to optimize the COD fractionation, it would be more useful to practice both methods together. Combining particle size distribution and OUR experiments by using filtration/ultrafiltration and respirometric methods develop a better insight into the interpretation of COD and biodegradability. Furthermore, this method would also give useful information for optimization of treatment techniques by showing which size fraction is more important within the overall organic content and how the biodegradation characteristics of COD fractions differ in terms of treatment requirements (Doğruel et al., 2006).

## 4.2. Ultrafiltration

Filtration is a separation process of components from a fluid stream based on size differences. Membrane is the key for filtration. It acts as a selective barrier in order to achieve separation.

**Table 4.1 :** The characteristics of the membrane processes (Cheryan, 1986).

| Process | Driving Force | Retentate | Permeate |
|---|---|---|---|
| Osmosis | Chemical Potential | Solutes, Water | Water |
| Dialysis | Concentration Difference | Large molecules<br>Water | Small molecules<br>Water |
| Microfiltration | Pressure | Suspended particles<br>Water | Dissolved solutes<br>Water |
| Ultrafiltration | Pressure | Large molecules<br>Water | Small molecules<br>Water |
| Nanofiltration | Pressure | Small molecules<br>Divalent Salts, Water | Monovalent ions<br>Undissociated acids, Water |
| Reverse Osmosis | Pressure | All solutes, Water | Water |
| Pervaporation | Pressure | Nonvolatile molecules<br>Water | Volatile small molecules<br>Water |

According to Cheryan (1986), the well-known separation processes are microfiltration (MF), ultrafiltration (UL), nanofiltration (NF) and reverse osmosis (RO). A wide range of particle and molecular sizes is covered by this applications. As seen in Table 4.1 (Cheryan, 1986), the characteristics of membrane processes are different from each other. For instance, osmosis is a semipermeable membrane and only water permates through it. The driving force for osmosis is chemical potential.

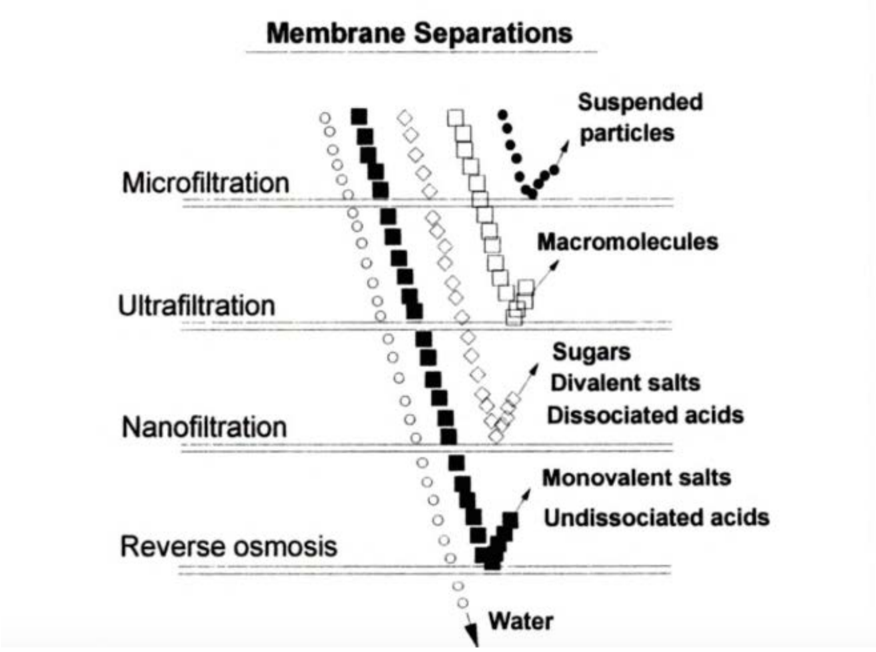



**Figure 4.2 :** Membrane separations (Cheryan, 1986).

Microfiltration, ultrafiltration, nanofiltration and reverse osmosis are driven by hydraulic pressure. As shown in Figure 4.2 (Cheryan, 1986), the membrane characteristics are different for each process. Microfiltration retains suspended particles in the range between 0.10 µm and 5 µm, while reverse osmosis is designed to retain all components and only water permeates. The detailed information is given in Figure 4.3.

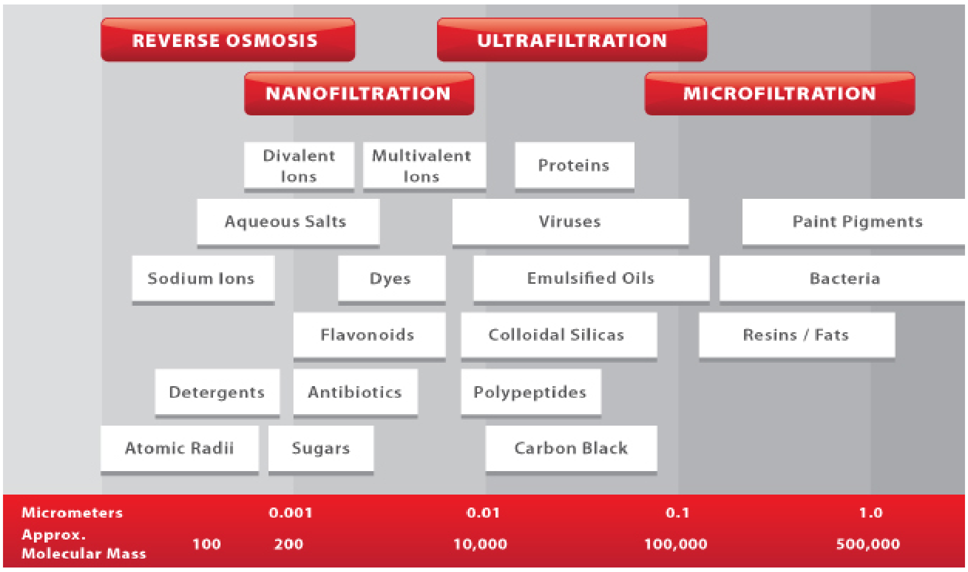



**Figure 4.3 :** Membrane separations.

Ultrafiltration (UF) is defined as a low-pressure membrane filtration process. This process works in the range between 0.005 µm and 0.1 µm, and retains macromolecules such as viruses, albumin, pepsin and glucose. Albeit, membranes are classified due to the size of the components, UF membranes are classified by their molecular weights. This terminology is known as "molecular weight cut-off".

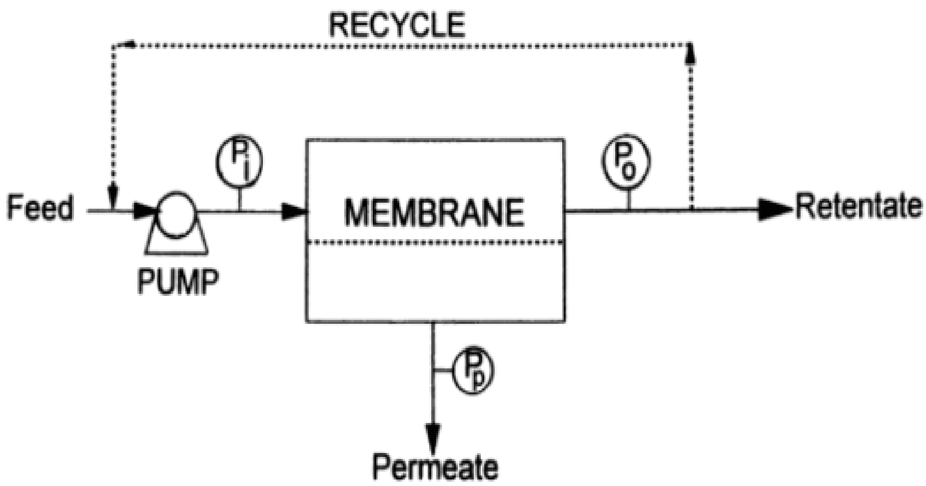



**Figure 4.4 :** Ultrafiltration (Cheryan, 1986).

In its simplest form, as seen in Figure 4.4 (Cheryan, 1986), the pressure forces small particles to permeate through the membrane, while the larger particles are retained. The working methods for ultrafiltration are dead-end filtration, cross-flow filtration and hybrid-flow filtration.

Dulekgurgen et al. (2006) studied PSD-based COD fractionation in textile wastewater. According to Figure 4.5, the bulk (around 36%) of the COD in textile wastewater consists of soluble organic matter (<2 nm) and only about 19% is particulate (>1600 nm).

Dulekgurgen et al. (2007) studied PSD-based COD fractionation in textile wastewater. According to Figure 4.6, the bulk (around 37%) of the COD in textile wastewater consists of soluble organic matter (<2 nm) and about 25% is between 450 and 1600 nm. The particulate part is 16%.

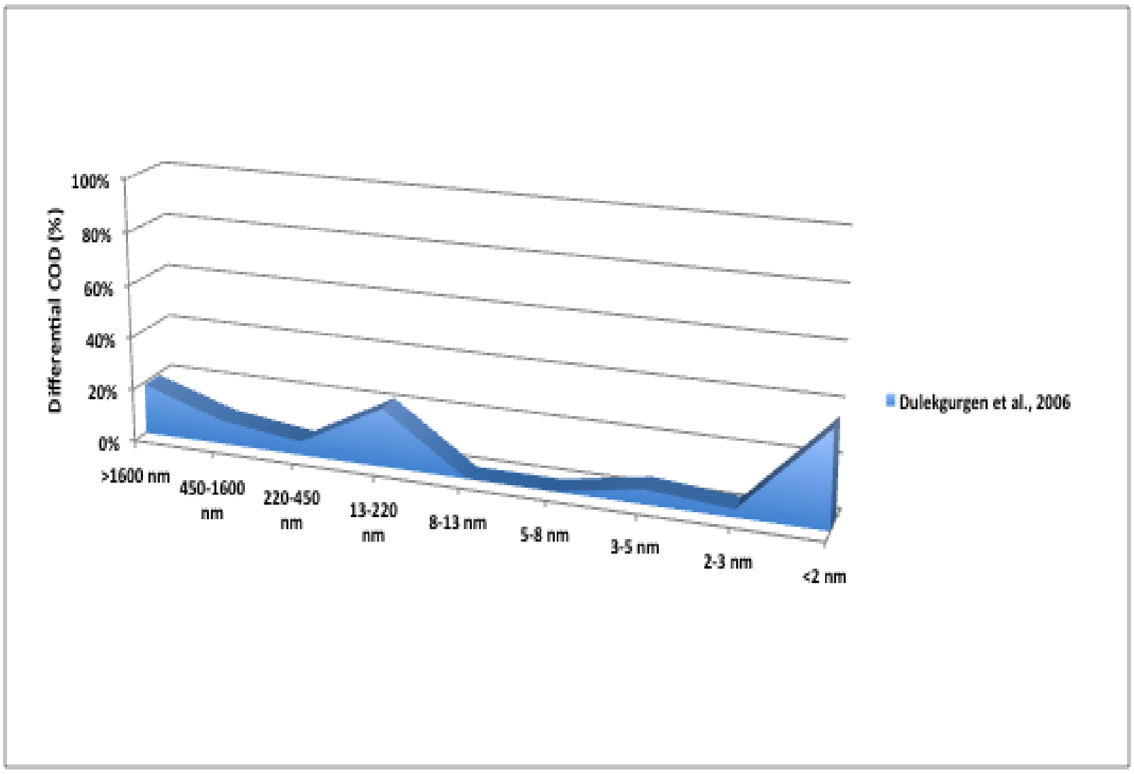



**Figure 4.5 :** Particle size distribution (Dulekgurgen et al., 2006).

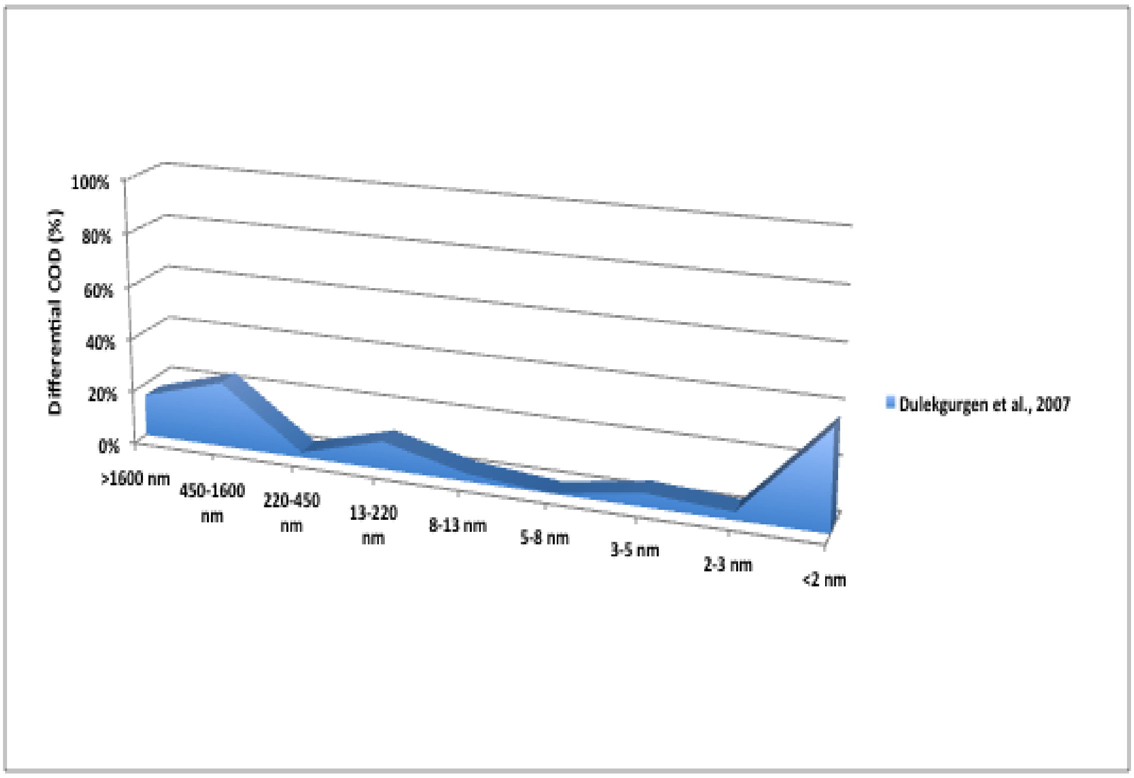



**Figure 4.6 :** Particle size distribution (Dulekgurgen et al., 2007).

# 5. MATERIALS AND METHODS

## 5.1. Experimental Schedule

- Gathering the early studies from literature about textile wastewater
- Determining the textile wastewater treatment plant
- Determining the sample intake point
- Arranging the experimental schedule
- Taking samples from influent and effluent per month during April and May
- Conventional Characterization
- Sequential filtration/ultrafiltration
- COD experiments of influent and effluent for selected size intervals
- Respirometric (OUR) Experiments
- Color Experiments
- TOC Experiments
- Correlation of the COD fractionation and Particle Size Distribution with the results obtained

## 5.2. Study Area

Wastewater samples were obtained from investigated wastewater treatment plant located in organized industrial district, Bursa, Turkey. The treatment facility has come into service in April 2007 with 70,000 cubicmeters/day. In treatment plant, there are biological treatment facilities treating industrial and domestic wastewater originating from the businesses in organized industrial district. The organized industrial district mostly consists of textile industry. There are another sectors such as plastic, carpet and home furniture producing wastewater. The process scheme of the wastewater treatment plant is given in Figure 5.1.

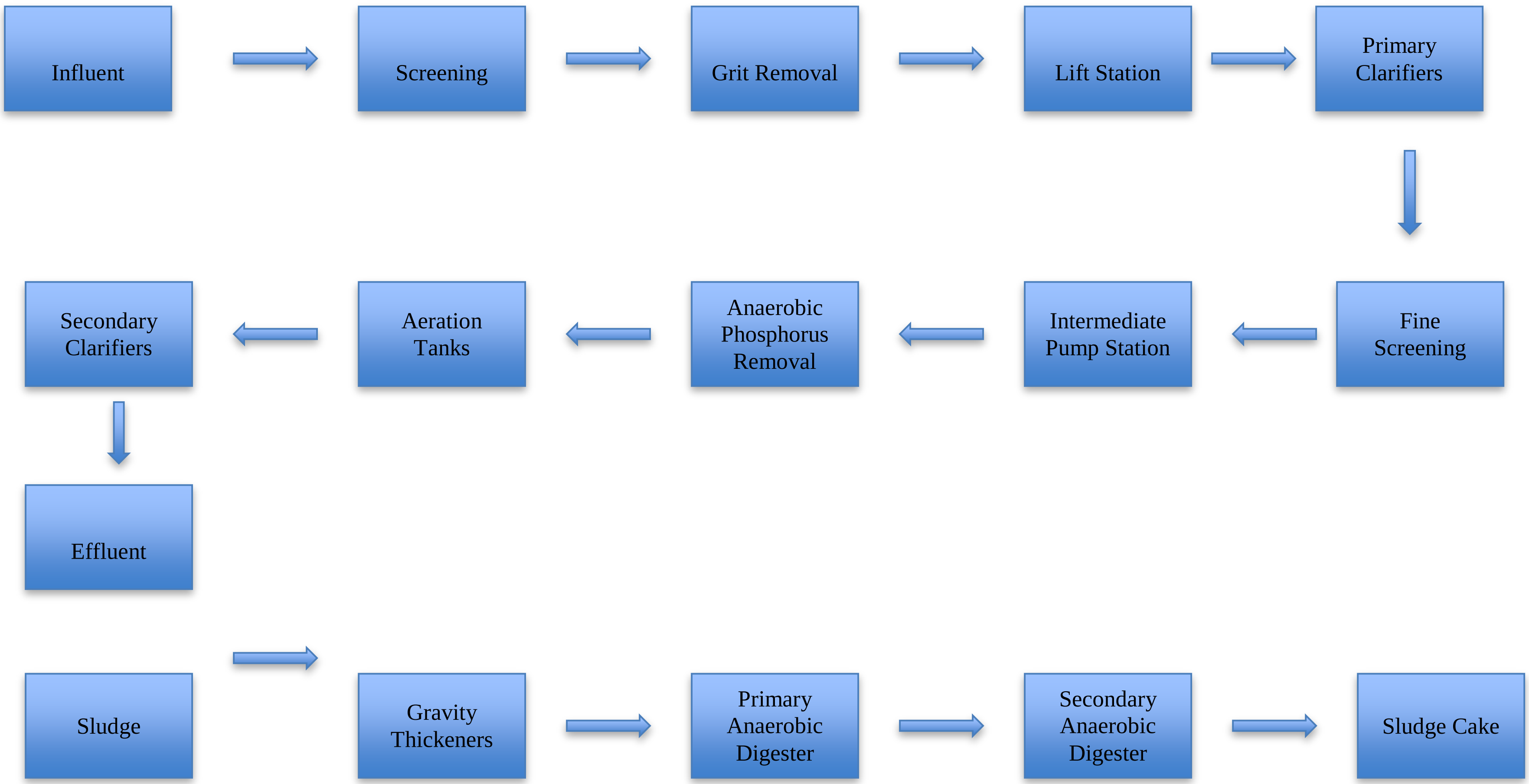



**Figure 5.1 :** The process scheme of the investigated wastewater treatment plant.

Since the treatment plant has extended aeration, biological nitrogen and phosphorus are removed. The facility works biologically, but it also has a chemical treatment systems in order to remove unexpected wastewater coming from the businesses. Wastewater characterization of investigated treatment plant is given in Table 5.1 and Table 5.2.

**Table 5.1 :** The influent wastewater characterization of investigated treatment plant

| Influent | April | May |
|---|---|---|
| Total COD (mg/L) | 1008 | 880 |
| TSS (mg/L) | 234 | 245 |
| $NH_3$-N (mg/L) | 34 | 24 |
| TN | 50 | 37 |
| TP (mg/L) | 5 | 8 |
| Color $\lambda$ = 436 nm | 21 | 18 |
| $\lambda$ = 525 nm | 24 | 20 |
| $\lambda$ = 620 nm | 20 | 16 |
| Pt-Co Unit | 907 | 809 |
| pH | 9.0 | 9.0 |
| BOD | 277 | 234 |
| Alkalinity | 772 | 675 |
| Grease | 85 | 77 |

**Table 5.2 :** The effluent wastewater characterization of investigated treatment plant

| Effluent | April | May |
|---|---|---|
| Total COD (mg/L) | 83 | 78 |
| $NH_3$-N (mg/L) | 0.1 | 0.1 |
| Total phosphorous (mg/L) | 2 | 3 |
| Color $\lambda$ = 436 nm | 14 | 14 |
| $\lambda$ = 525 nm | 16 | 15 |
| $\lambda$ = 620 nm | 12 | 9 |
| pH | 8 | 8 |
| BOD | 2 | 1 |
| TN | 7 | 6 |

Experiments were conducted on the samples taken as two sets from the influent and effluent streams of the wastewater treatment plant.

### 5.3. Conventional Characterization

The experiments for the conventional characterization were conducted in duplicates as defined in the Standard Methods (APHA *et al.*, 2005). COD experiments were performed also in duplicates in accordance with Standard ISO 6060 (International Organization for Standardization, 1986). The measurement of suspended solids (SS) and volatile suspended solids (VSS) were performed with Millipore AP40 glass fiber filters with an effective pore size of approximately 1200~1600 nm. The spectrophotometric color experiments were conducted in accordance with the German Legislation (Anhang 38, 1993 updated online in 2004). Optical density values obtained for all size ranges were recorded at three different wavelengths of 436, 525 and 620 nm.

### 5.4. Sequential Filtration/Ultrafiltration

All filtration/ultrafiltration experiments were performed under positive pressure (0.6-1.2 atm; N2 as the inert gas), in a continuously stirred cell with a volumetric capacity of 400 mL (Amicon, Model 8400). A final volume of 100 mL permeate was determined to be sufficient in order to run COD experiments in duplicates and to measure color values. Samples were filtered continuously through conventional filters with pore sizes of 1200–1600 nm (Millipore AP40, glass fiber), 450nm (Durapore$^{S}$ HV, polyvinylidene fluoride [PVDF]), and 220 nm (Durapore$^{S}$ GV, PVDF) (Millipore Corp., Bedford, MA 01730). Selected differential gas pressure was 0.7 atm and maximum temperature limit was +85 ˚C for the Durapore disposable filters. The pressure was hold about 0.35 atm during the filtration experiments conducted with disposable filters. During the ultrafiltration experiments, permeates from 220 nm membrane filter were filtered through ultrafiltration membranes with nominal molecular weight cut-off (MWCO) values of 100, 30, 10, 3, and 1 kDa (PL series, Millipore, MA). Maximum temperature limit and the pH range recommended for all ultrafiltration membranes are +50 ˚C and 3.0-13.0, relatively. Recommended maximum working pressure is 0.7 atm for the 100 kDa membrane, and 3.7 atm for the others. All experiments were performed at room temperature and at a pH range of 7.2–8.8. The pressure for the 100 kDa ultrafiltration membrane discs was 0.6 atm, and for the others was 1.2 atm. These pressures are recommended by the manufacturer. Fig. 3.2 is the schematic presentation of the sequential filtration/ultrafiltration procedure.

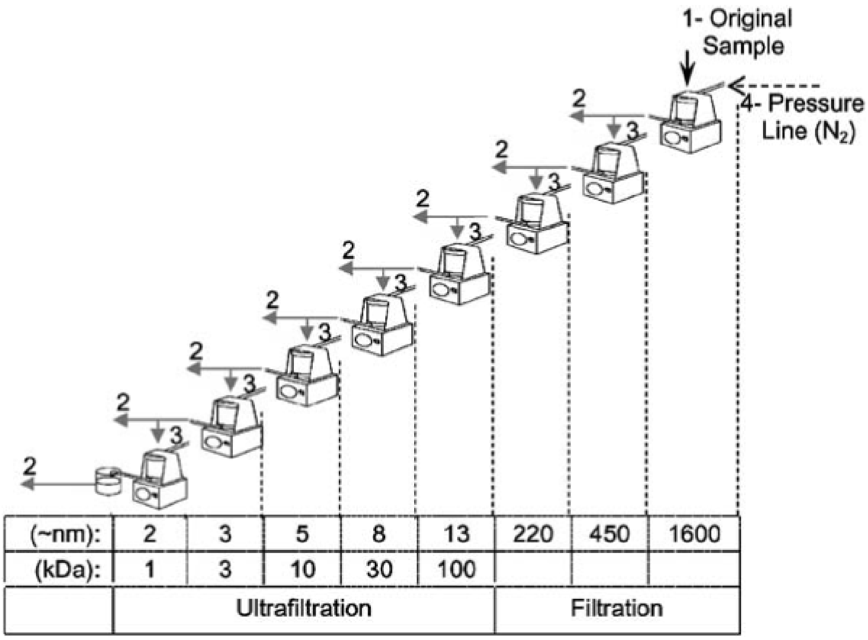



**Figure 5.2 :** The schematic presentation of the sequential filtration/ultrafiltration.

As it is seen in Figure 5.2, there are numbers representing the parts of the experiment. Number one represents the non-settled, non-filtered but mixed original sample, as number two represents aliquot of the filtrate from the previous step for COD experiments. Number three represents aliquot of the filtrate from the previous step which will be used for the next filtration/ultrafiltration steps and number four represents $N_2$ gas line providing positive pressure.

As filtration/ultrafiltration was used as an analytical tool in this study, the experiment was conducted as batches of 10–120 minutes, depending on the selected filter size. As mentioned before, the filtrate volumes were quite small (adjusted to obtain a final volume of 100 mL permeate after filtering through the last membrane disc) to allow for the analytical COD experiments and color analyzes and for continuing with the following filtration/ultrafiltration steps. All cleaning (consecutive washes with dI water, 70% ethanol, and finally two times with dI water, under the selected working pressure, as well as rinsing the entire system with dI water after washing with 70%

ethanol), testing (with dI water), and conditioning procedures, recommended by the manufacturer, were conducted before and after filtering the samples, to confirm that no implication of fouling or other effects were observed through the flow-rate profiles.

### 5.5. Oxygen Utilization Rate (OUR) Analyses

A series of experiments were executed in terms of determining soluble COD ($S_T$) fractions of the influent of the textile wastewater treatment plant. The soluble readily biodegradable COD, $S_S$, was determined in accordance with the respirometric technique defined by Ekama *et al.* (1986).

OUR analyses were conducted with Manotherm RA 1000 respirometry device. RA 1000 respirometry device involves a 5 liters plexi-glaxan main reactor and a cell where OUR is measured.

There are important subjects that should be controlled:

- Aeration and mixing conditions must be adequate in the main reactor
- Effluent oxygen value must be bigger than 2 mg/l
- No air bubble in the respiration cell
- Circulation pump is working on the respiration cell
- Control of pH and temperature

The respirometer was operated continuously with a closed reaction/measurement volume of 750 ml. Biomass, taken from the aeration tank of the corresponding treatment plant and fed with raw textile wastewater in a fill-and-draw reactor, was used in the respirometric analysis. Experiments were conducted with textile wastewater samples which are raw, filtered through 450 nm, 100 kDa and 1 kDa at a different food/ microorganism (F/M) ratio for each one. Activated sludge has been aerated for a few minutes before the wastewater addition to prevent the sudden fall in the oxygen concentration. To prevent the absence of the nitrogen and phosphorus during the experiment, 10 ml Solution A and Solution B were added for 1000 mg/l COD (O'Connor, J.T., 1972).

The OUR profile obtained from the respirometric experiment conducted with textile wastewater samples which are raw, filtered through 450 nm, 100 kDa and 1 kDa.

The OUR curve starts with the endogenous respiration level of the acclimated biomass, rapidly increases to a plateau associated with the selected F/M ratio and the amount of $S_S$ present in the wastewater sample, and declines as dictated by the hydrolysis and subsequent utilization of $S_H$. After reduction of all available substrate, the OUR profile reaches a second threshold level associated with endogenous respiration. The only soluble fraction at this phase is $S_I$, which cannot be degraded further since these fraction consists of inerts. The area defined by the OUR curve above the endogenous respiration level gives the total amount of dissolved oxygen consumed, $DO_T$. Based on process stoichiometry, $DO_T$ can be directly used to yield the amount of available substrate without additional information on other parameters. The area under the OUR curve might further be fractionated to identify $DO_{SS}$ defining the amount of oxygen used for the utilization of the readily biodegradable COD fraction, $S_S$, which might be calculated using the following mass balance equation, provided that the heterotrophic yield coefficient, $Y_H$ for the wastewater is known (Ekama et al., 1986; Çokgör et al., 1998):

$$S_S = \frac{\Delta O_{SS}}{1 - Y_H} \tag{5.1}$$

The remaining portion of the oxygen consumed, $DO_{SH}$, corresponds to the rapidly hydrolysable COD fraction of the wastewater, $S_H$:

$$S_H = \frac{\Delta O_{SH}}{1 - Y_H} \tag{5.2}$$

The soluble inert COD fraction, $S_I$ might be calculated by using the following mass balance for total soluble COD, $S_T$ (Orhon and Okutman, 2003):

$$S_T = S_S + S_H + S_I \tag{5.3}$$

**Table 5.3 :** The parameters for OUR analyses.

| | COD | Wastewater (ml) | Biomass (ml) | $V_T$ (ml) | TSS (mg/l) | VSS (mg/l) | F/M |
|---|---|---|---|---|---|---|---|
| **Raw WW** | 711 | 1000 | 1250 | 2250 | 5960 | 4480 | 0,13 |
| **0,45 nm** | 585 | 645 | 1400 | 2045 | 4680 | 4080 | 0,07 |
| **100 kDa** | 472 | 600 | 1400 | 2000 | 5460 | 3980 | 0,05 |
| **1 kDa** | 367 | 600 | 1400 | 2000 | 4600 | 3500 | 0,13 |

# 6. RESULTS

## 6.1. Conventional Characterization

### 6.1.1. Sample I

**Influent**

The results of the conventional characterization for sample I taken from the influent stream are summarized in Table.6.1.

According to wastewater characterization experiments, the COD of the raw wastewater is 711 mg/l and suspended solids concentration is 205 mg/l, as TKN and TP of the wastewater are 58 mg/l and 3 mg/l, respectively. Total COD, VSS, TKN and TP of the wastewater are in the medium concentration and the pH is 9.1.

**Table 6.1 :** Conventional characterization – influent stream (Sample I).

| Parameter | | Value |
|---|---|---|
| Total COD (mg/L) | | 711 |
| Soluble COD[a] (mg/L) | | 585 |
| TOC (mg/L) | | 185 |
| DOC[a] (mg/L) | | 152 |
| TSS (mg/L) | | 205 |
| TKN (mg/L) | | 58 |
| $NH_3$-N (mg/L) | | 27 |
| Total phosphorous (mg/L) | | 3 |
| Color (OD) | $\lambda$ = 436 nm | 0.307 |
| | $\lambda$ = 525 nm | 0.242 |
| | $\lambda$ = 620 nm | 0.143 |
| | Pt-Co Unit | 1034 |
| pH | | 9.1 |

[a] Soluble organic carbon fractions; filtered through 450 nm membrane.

**Effluent**

The results of the conventional characterization for sample I taken from the effluent stream are summarized in Table.6.2.

According to wastewater characterization, the COD of the raw wastewater is 106 mg/l, TOC and TP of the wastewater are 54 mg/l and 2 mg/l, respectively. Total COD, TOC and TP of the wastewater is in the medium concentration and the pH is 8.1.

**Table 6.2 :** Conventional characterization – effluent stream (Sample I).

| Parameter | | Value |
|---|---|---|
| Total COD (mg/L) | | 106 |
| Soluble COD[a] (mg/L) | | 88 |
| TOC (mg/L) | | 54 |
| DOC[a] (mg/L) | | 46 |
| $NH_3$-N (mg/L) | | 0.1 |
| Total phosphorous (mg/L) | | 2 |
| $PO_4$-P (mg/L) | | 0.3 |
| Color (OD) | $\lambda$ = 436 nm | 0.186 |
| | $\lambda$ = 525 nm | 0.182 |
| | $\lambda$ = 620 nm | 0.117 |
| | Pt-Co Unit | 677 |
| pH | | 8.1 |

[a] Soluble organic carbon fractions; filtered through 450 nm membrane.

### 6.1.2. Sample II

The results of the conventional characterization for sample II taken from the influent are summarized in Table.6.3.

According to wastewater characterization, the COD of the raw wastewater is 673 mg/l, suspended solids concentration is 325 mg/l, as TKN and TP of the wastewater are 48 mg/l and 5 mg/l, respectively. Total COD, VSS, TKN and TP of the wastewater is in the medium concentration and the pH is 8.9.

**Table 6.3 :** Conventional characterization – influent stream (Sample II).

| Parameter | | Value |
|---|---|---|
| Total COD (mg/L) | | 673 |
| Soluble COD[a] (mg/L) | | 555 |
| TOC (mg/L) | | 175 |
| DOC[a] (mg/L) | | 144 |
| TSS (mg/L) | | 325 |
| TKN (mg/L) | | 48 |
| $NH_3$-N (mg/L) | | 19 |
| Total phosphorous (mg/L) | | 5 |
| Color | λ = 436 nm | 0.369 |
| | λ = 525 nm | 0.244 |
| | λ = 620 nm | 0.157 |
| | Pt-Co Unit | 1232 |
| pH | | 8.9 |

[a] Soluble organic carbon fractions; filtered through 450 nm membrane.

### 6.1.3. Comparison with the previous studies

Comparative evaluation of the values presented in Table 6.4 shows that the samples evaluated in this study are quite representative, since their conventional characteristics are reasonably close to the average characteristics given in the previous studies.

**Table 6.4:** Conventional characterization of textile industries in literature.

*ND: Not Defined

| Literature | Total COD (mg/l) | Soluble COD (mg/l) | TSS (mg/l) | TKN (mg/l) | NH4-N (mg/l) | Total P (mg/l) | pH (mg/l) |
|---|---|---|---|---|---|---|---|
| Orhon et al., 1996 | 1070 | 620 | 105 | 110 | 62 | 2 | 8.2 |
| Orhon et al., 1999 | 932 | 580 | 225 | 54 | ND | 7.9 | 8.2 |
| Dulekgurgen et al., 2006 | 1340 | 965 | 115 | 25 | ND | 5 | 8.8 |

### 6.2. Sequential Filtration/Ultrafiltration for PSD-Based COD Fractionation

The results obtained for the PSD-based COD fractionation are reviewed in tables. In these tables, the cumulative values for a given filter size represent the COD below the selected filter. The differential COD, between the two consecutive filter sizes, reflects the difference of the two corresponding COD values. No quiescent settling was applied before starting the filtration experiments so that the first values given in the table correspond to the total COD content (sum of settleable, supracolloidal, colloidal, and soluble portions) of the samples.

#### 6.2.1. Sample I

**Influent**

**Table 6.5 :** Cumulative and differential COD values after PSD – influent stream (Sample I).

| Separation Technique | Particle size (nm) | Cumulative COD (mg/L) | Size Category (nm) | Differential COD (mg/L) |
|---|---|---|---|---|
| *Total* | | 711 | | |
| *Filtration* | | | | |
| AP40 filter | 1600 | 593 | > 1600 | 118 |
| HV filter | 450 | 585 | 450–1600 | 8 |
| GV filter | 220 | 579 | 220–450 | 6 |
| *Ultrafiltration* | | | | |
| 100 kDa | 13 | 472 | 13–220 | 107 |
| 30 kDa | 8 | 450 | 8–13 | 22 |
| 10 kDa | 5 | 448 | 5–8 | 2 |
| 3 kDa | 3 | 413 | 3–5 | 35 |
| 1 kDa | 2 | 367 | 2–3 | 46 |
| | | | < 2 | 367 |

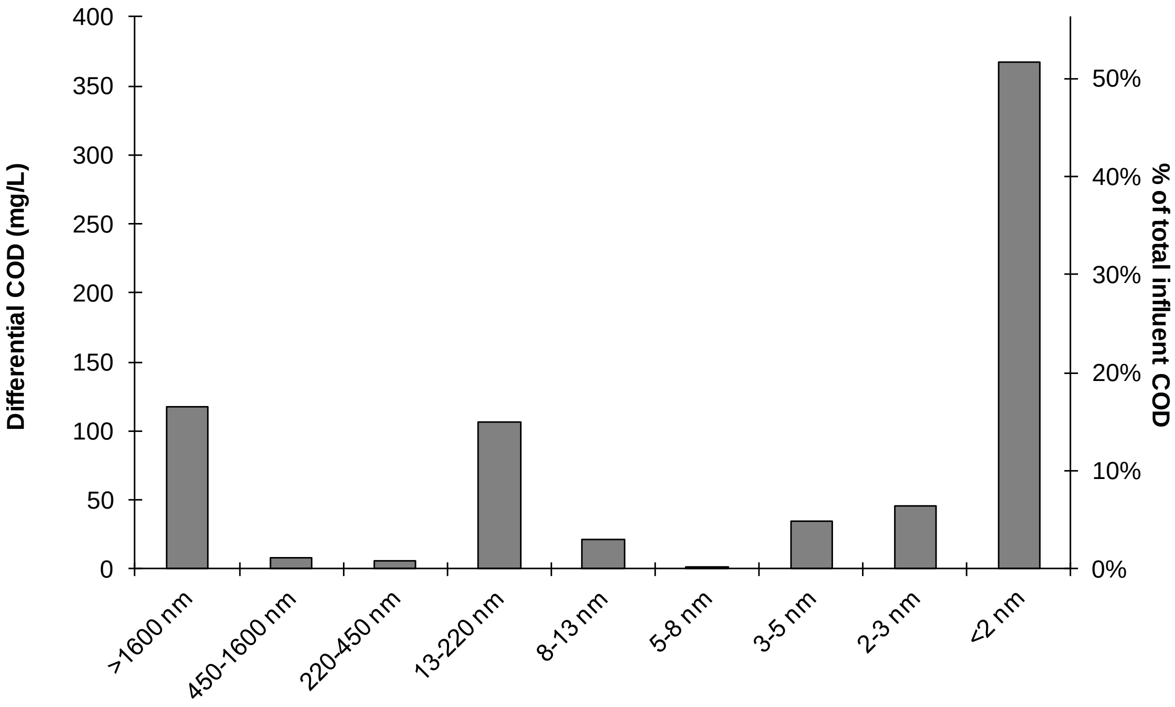



**Figure 6.1 :** PSD analysis and percent COD distribution – influent stream(Sample I).

Results for the sequential filtration/ultrafiltration studies for Sample 1 presented in Table 6.5 and Figure 6.1. According to Table 6.5 and Figure 6.1, the bulk (around 50%) of the COD for influent stream is in the soluble form. The particulate part is 17% and 15% of the total COD is in 13-220 nm. The rest of the COD is seen to be distributed among other intervals and is negligible.

**Effluent**

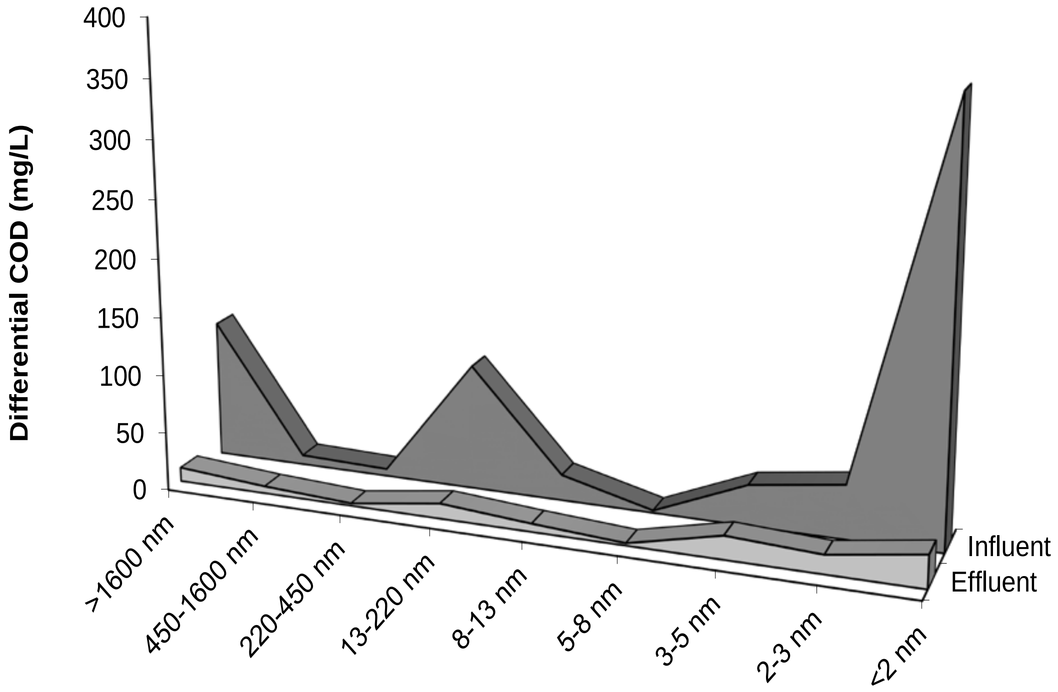
**Table 6.6 :** Cumulative and differential COD values after PSD – effluent stream (Sample I).

| Separation Technique | Particle size (nm) | Cumulative COD (mg/L) | Size Category (nm) | Differential COD (mg/L) |
|---|---|---|---|---|
| *Total* | | 106 | | |
| *Filtration* | | | | |
| AP40 filter | 1600 | 94 | > 1600 | 12 |
| HV filter | 450 | 88 | 450–1600 | 6 |
| GV filter | 220 | 86 | 220–450 | 2 |
| *Ultrafiltration* | | | | |
| 100 kDa | 13 | 73 | 13–220 | 13 |
| 30 kDa | 8 | 66 | 8–13 | 7 |
| 10 kDa | 5 | 64 | 5–8 | 2 |
| 3 kDa | 3 | 44 | 3–5 | 20 |
| 1 kDa | 2 | 28 | 2–3 | 16 |
| | | | < 2 | 28 |

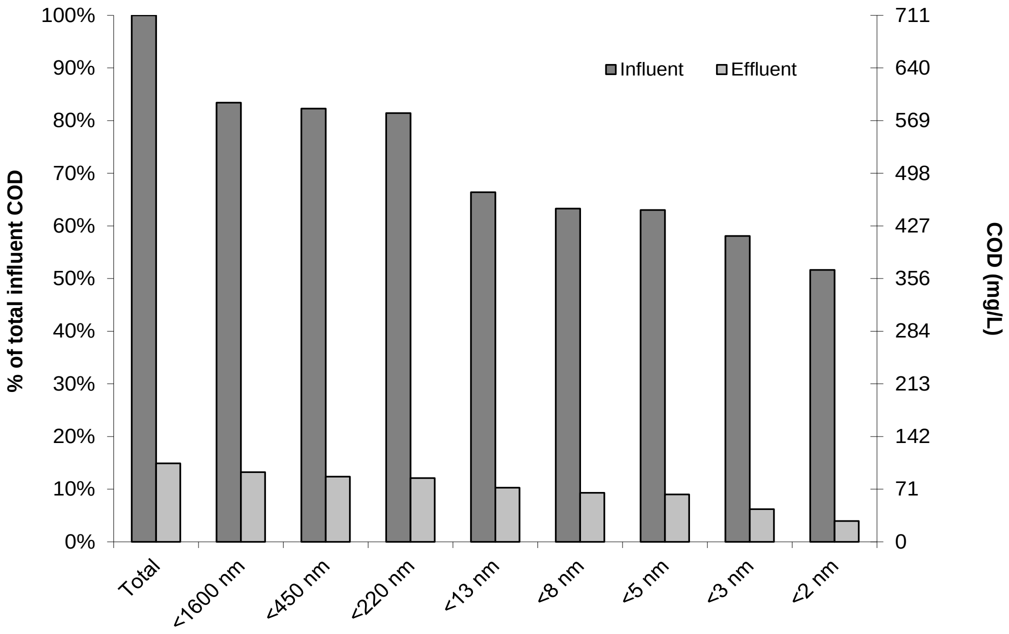
Results for the sequential filtration/ultrafiltration studies for the effluent of Sample 1 presented in Table 6.6. According to Table 6.6, the bulk (23.5%) of the COD for effluent stream is in the soluble form. The particulate part is 11% and 12% of the total COD is in 13-220 nm. The rest of the COD is seen to be distributed among other intervals and is negligible.

**Before and after biological treatment**

Comparative presentation of the COD profiles of the textile wastewater before and after biological treatment is reviewed in Fig. 6.2, which highlights the significant difference between the influent and effluent samples. The figures show that biological treatment effectively removed the soluble COD, present as one of the significant fractions in the influent. Results given in Table 6.7 indicate that 50% of the total effluent COD (28 mg/L, remaining after biological treatment) is in the soluble range (< 2nm). For the particulate and the colloidal parts, which are the other significant parts of the wastewater, the considerable decrease observed at the effluent.




(a)




(b)

**Figure 6.2 :** PSD-based COD fractionation of textile industry wastewater before and after biological treatment (a): distribution of COD fractions; (b): impact of biological treatment.

**Table 6.7 :** Cumulative and differential COD values of the textile industry wastewater before and after biological treatment.

| Separation Technique | Particle size (nm) | Cumulative COD (mg/L) | | Size Category (nm) | Differential COD (mg/L) | |
|---|---|---|---|---|---|---|
| | | Sample | | | Sample | |
| | | Biol. Treatment Influent | Biol. Treatment Effluent | | Biol. Treatment Influent | Biol. Treatment Effluent |
| *Total* | | 711 | 106 | | | |
| *Filtration* | | | | | | |
| AP40 filter | 1200~1600 | 593 | 94 | > 1600 | 118 | 12 |
| HV filter | 450 | 585 | 88 | 450-1600 | 8 | 6 |
| GV filter | 220 | 579 | 86 | 220-450 | 6 | 2 |
| *Ultrafiltration* | | | | | | |
| 100 kDa | 13 | 472 | 73 | 13-220 | 107 | 13 |
| 30 kDa | 8 | 450 | 66 | 8-13 | 22 | 7 |
| 10 kDa | 5 | 448 | 64 | 5-8 | 2 | 2 |
| 3 kDa | 3 | 413 | 44 | 3-5 | 35 | 20 |
| 1 kDa | 2 | 367 | 28 | 2-3 | 46 | 16 |
| | | | | < 2 | 367 | 28 |

### 6.2.2. Sample II

Results for the sequential filtration/ultrafiltration studies for Sample 2 presented in Table 6.8 and Figure 6.3. According to Table 6.8 and Figure 6.3, the bulk (around 50%) of the COD for influent stream is in the soluble form. The particulate part is 17% and 13% of the total COD is in 13-220 nm. The rest of the COD is seen to be distributed among other intervals and is negligible.

**Table 6.8 :** Cumulative and differential COD values after PSD – influent stream (Sample II).

| Separation Technique | Particle size (nm) | Cumulative COD (mg/L) | Size Category (nm) | Differential COD (mg/L) |
|---|---|---|---|---|
| *Total* | | 673 | | |
| *Filtration* | | | | |
| AP40 filter | 1600 | 560 | > 1600 | 113 |
| HV filter | 450 | 555 | 450–1600 | 5 |
| GV filter | 220 | 544 | 220–450 | 11 |
| *Ultrafiltration* | | | | |
| 100 kDa | 13 | 454 | 13–220 | 90 |
| 30 kDa | 8 | 418 | 8–13 | 36 |
| 10 kDa | 5 | 409 | 5–8 | 9 |
| 3 kDa | 3 | 358 | 3–5 | 51 |
| 1 kDa | 2 | 328 | 2–3 | 30 |
| | | | < 2 | 328 |

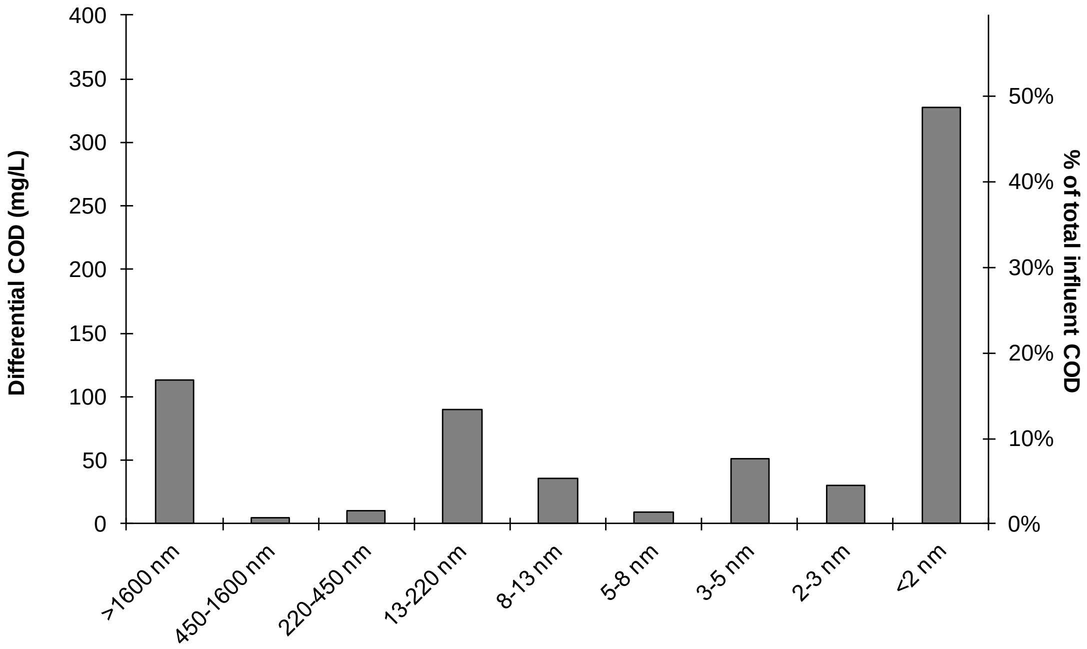



**Figure 6.3 :** PSD analysis and percent COD distribution of Sample II.

### 6.2.3. Comparison with the previous studies

The PSD-based COD fractionation obtained for textile industry is reviewed in Figures 6.4 and 6.5, which provide a clear indication that the COD variation according to different size categories exhibits similar trends for the textile industry. The bulk (around 50%) of the COD in textile wastewater consists of soluble organic matter (<2 nm) and only about 17% is particulate (>1600 nm). This COD profile is in agreement with some of the values summarized by Dulekgurgen *et al.* (2006).

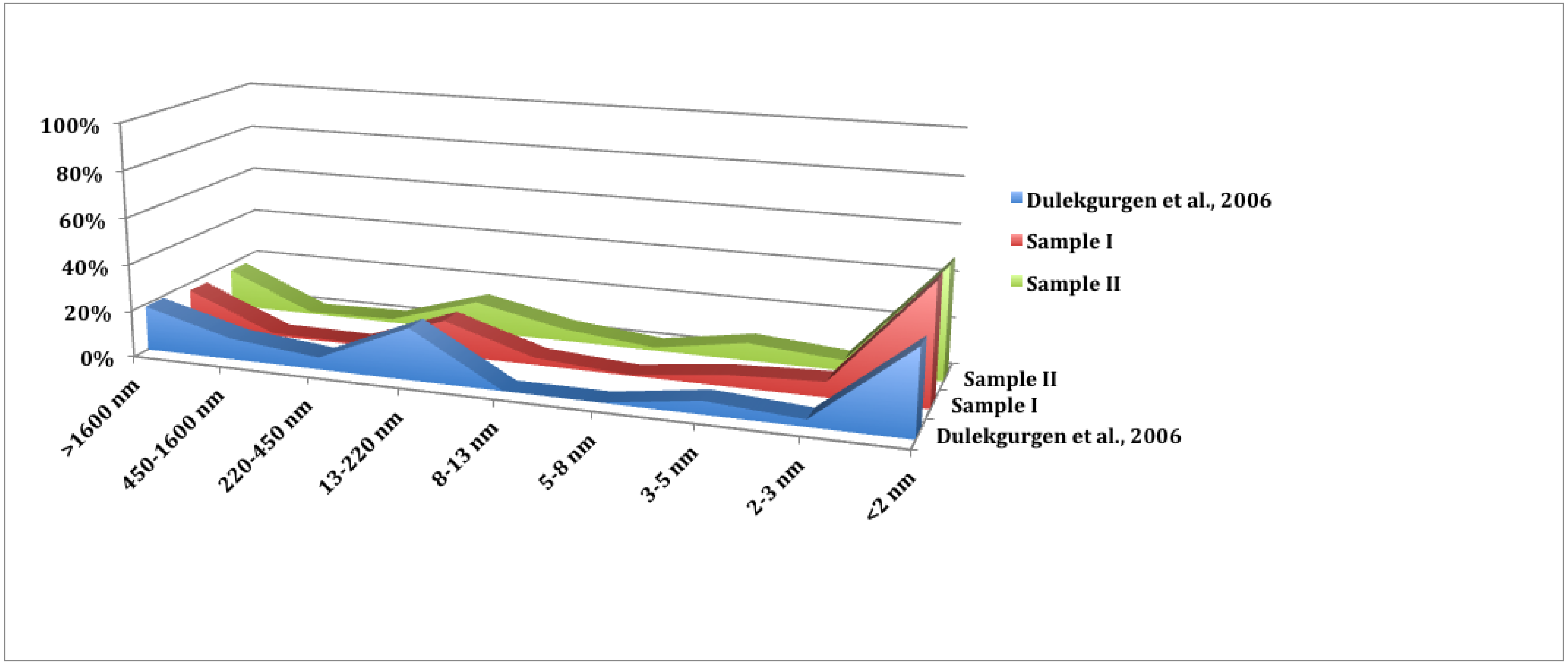



**Figure 6.4 :** Fingerprints of the textile industry samples based on differential COD values for selected particle size categories.

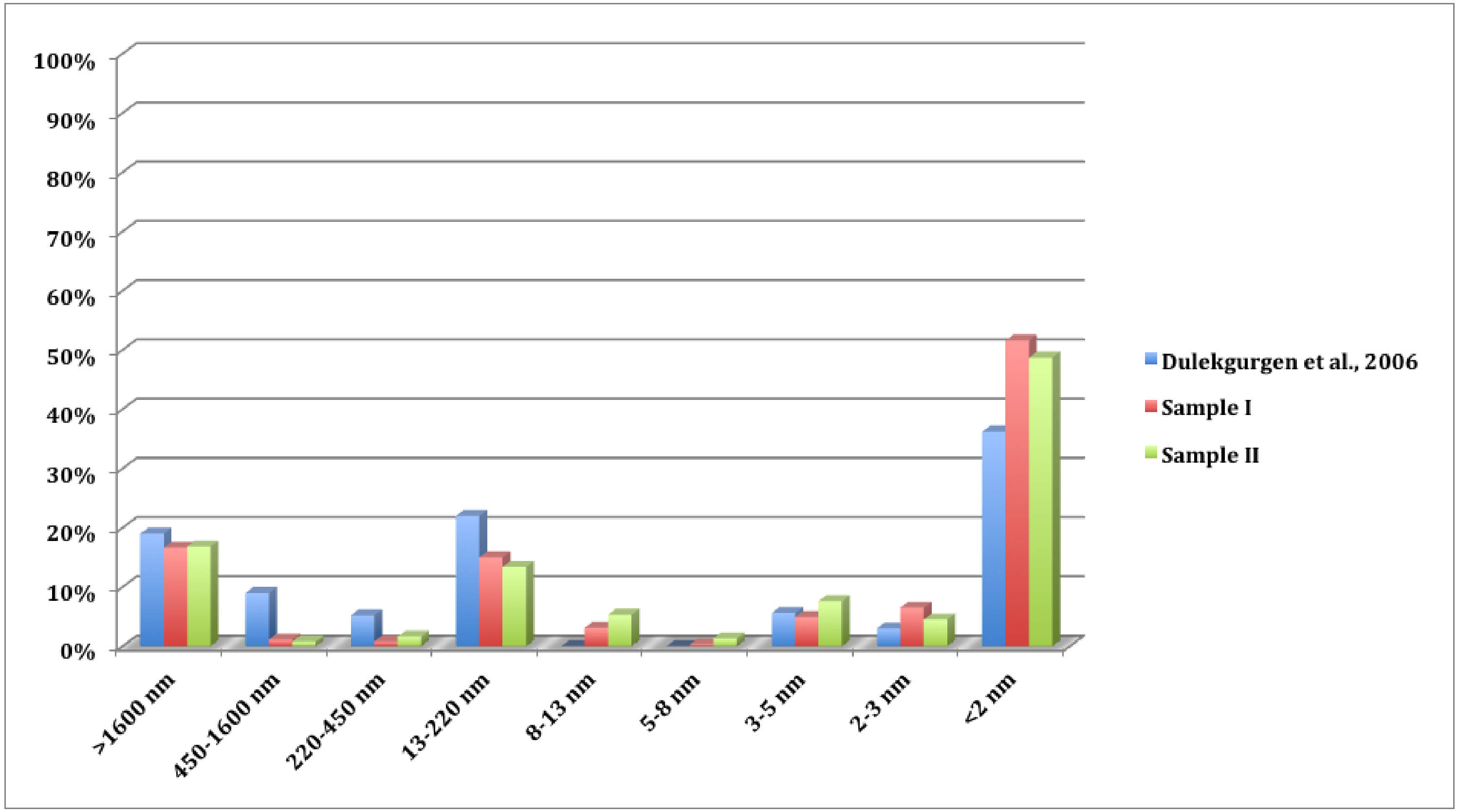



**Figure 6.5 :** Percent distribution of COD fractions for textile industry samples.

## 6.3. Sequential Filtration/Ultrafiltration for PSD-Based TOC Fractionation

### 6.3.1. Sample I

**Influent**

Results for the sequential filtration/ultrafiltration studies for TOC presented in Table 6.9 and Figure 6.6. According to Table 6.9 and Figure 6.6, most (51%) of the TOC for influent stream is in the soluble form. The particulate part is 17% and 15% of the total TOC is in 13-220 nm. The rest of the TOC is seen to be distributed among other intervals and is negligible.

**Table 6.9 :** Cumulative and differential TOC values after PSD – influent stream (Sample I).

| Separation Technique | Particle size (nm) | Cumulative TOC (mg/L) | Size Category (nm) | Differential TOC (mg/L) |
|---|---|---|---|---|
| *Total* | | 185 | | |
| *Filtration* | | | | |
| AP40 filter | 1600 | 154 | > 1600 | 31 |
| HV filter | 450 | 152 | 450–1600 | 2 |
| GV filter | 220 | 150 | 220–450 | 2 |
| *Ultrafiltration* | | | | |
| 100 kDa | 13 | 123 | 13–220 | 27 |
| 30 kDa | 8 | 117 | 8–13 | 6 |
| 10 kDa | 5 | 116 | 5–8 | 1 |
| 3 kDa | 3 | 107 | 3–5 | 9 |
| 1 kDa | 2 | 95 | 2–3 | 12 |
| | | | < 2 | 95 |

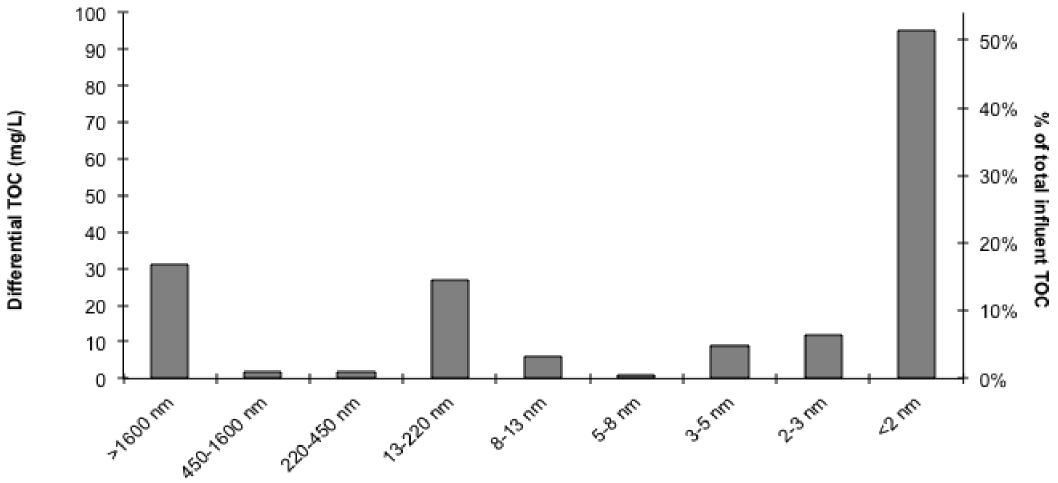



**Figure 6.6 :** PSD-based TOC fractionation for Sample I.

**Effluent**

**Table 6.10 :** Cumulative and differential TOC values after PSD – effluent stream (Sample I).

| Separation Technique | Particle size (nm) | Cumulative TOC (mg/L) | Size Category (nm) | Differential TOC (mg/L) |
|---|---|---|---|---|
| *Total* | | 54 | | |
| *Filtration* | | | | |
| AP40 filter | 1600 | 48 | > 1600 | 6 |
| HV filter | 450 | 46 | 450–1600 | 2 |
| GV filter | 220 | 44 | 220–450 | 2 |
| *Ultrafiltration* | | | | |
| 100 kDa | 13 | 37 | 13–220 | 7 |
| 30 kDa | 8 | 34 | 8–13 | 3 |
| 10 kDa | 5 | 33 | 5–8 | 1 |
| 3 kDa | 3 | 24 | 3–5 | 9 |
| 1 kDa | 2 | 14 | 2–3 | 10 |
| | | | < 2 | 14 |

Results for the sequential filtration/ultrafiltration studies for TOC presented in Table 6.10. According to Table 6.10, most (26%) of the TOC for influent stream is in the soluble form. The particulate part is 11% and 12% of the total TOC is in 13-220 nm. The rest of the TOC is seen to be distributed among other intervals and is negligible.

**Before and after biological treatment**

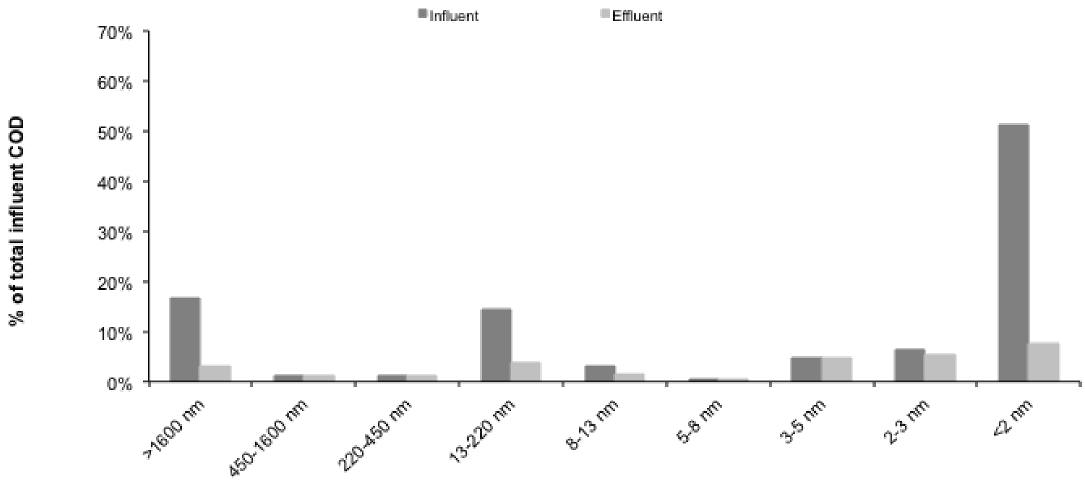



**Figure 6.7 :** PSD-based TOC fractionation before and after biological treatment.

Comparative presentation of the TOC profiles of the textile wastewater before and after biological treatment is reviewed in Fig. 6.7, which highlights the significant difference between the influent and effluent samples. The figures show that biological treatment effectively removed the soluble TOC, present as one of the significant fractions in the influent. For the particulate and the colloidal parts, which are the other significant parts of the wastewater, the considerable decrease observed at the effluent.

### 6.3.2. Sample II

**Table 6.11 :** Cumulative and differential TOC values after PSD – influent stream (Sample II).

| Separation Technique | Particle size (nm) | Cumulative TOC (mg/L) | Size Category (nm) | Differential TOC (mg/L) |
|---|---|---|---|---|
| *Total* | | 175 | | |
| *Filtration* | | | | |
| AP40 filter | 1600 | 146 | > 1600 | 29 |
| HV filter | 450 | 144 | 450–1600 | 2 |
| GV filter | 220 | 141 | 220–450 | 3 |
| *Ultrafiltration* | | | | |
| 100 kDa | 13 | 118 | 13–220 | 23 |
| 30 kDa | 8 | 108 | 8–13 | 10 |
| 10 kDa | 5 | 105 | 5–8 | 3 |
| 3 kDa | 3 | 91 | 3–5 | 14 |
| 1 kDa | 2 | 83 | 2–3 | 8 |
| | | | < 2 | 83 |

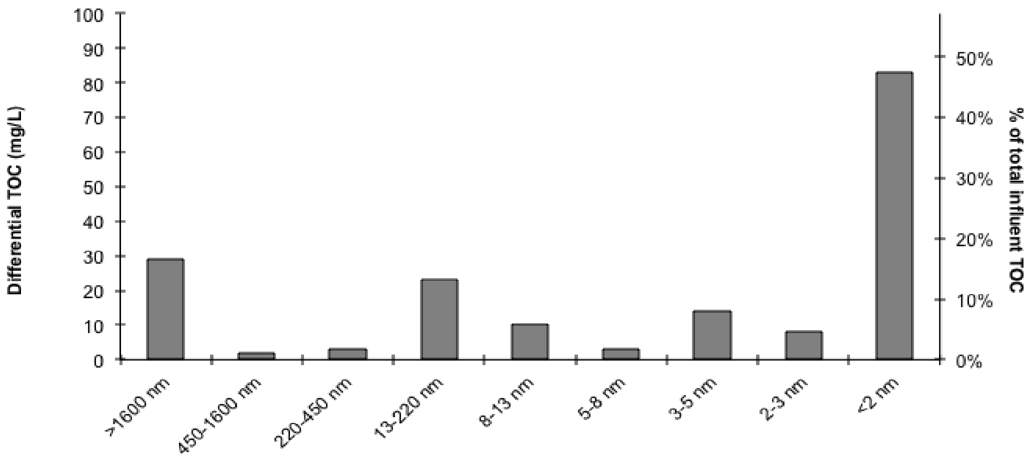



**Figure 6.8 :** PSD-based TOC fractionation for Sample II.

Results for the sequential filtration/ultrafiltration studies for TOC presented in Table 6.11 and Figure 6.8. According to Table 6.11 and Figure 6.8, most (47%) of the TOC for influent stream is in the soluble form. The particulate part is 17% and 13% of the total TOC is in 13-220 nm. The rest of the TOC is seen to be distributed among other intervals and is negligible.

### 6.3.3. Comparison with the COD

The PSD-based comparison between COD and TOC is reviewed in Figure 6.9, which provide a clear indication that the distribution among the size intervals for COD and TOC exhibits similar trends. As seen in Figure 6.9, most of the COD and TOC for influent stream are in the soluble form.

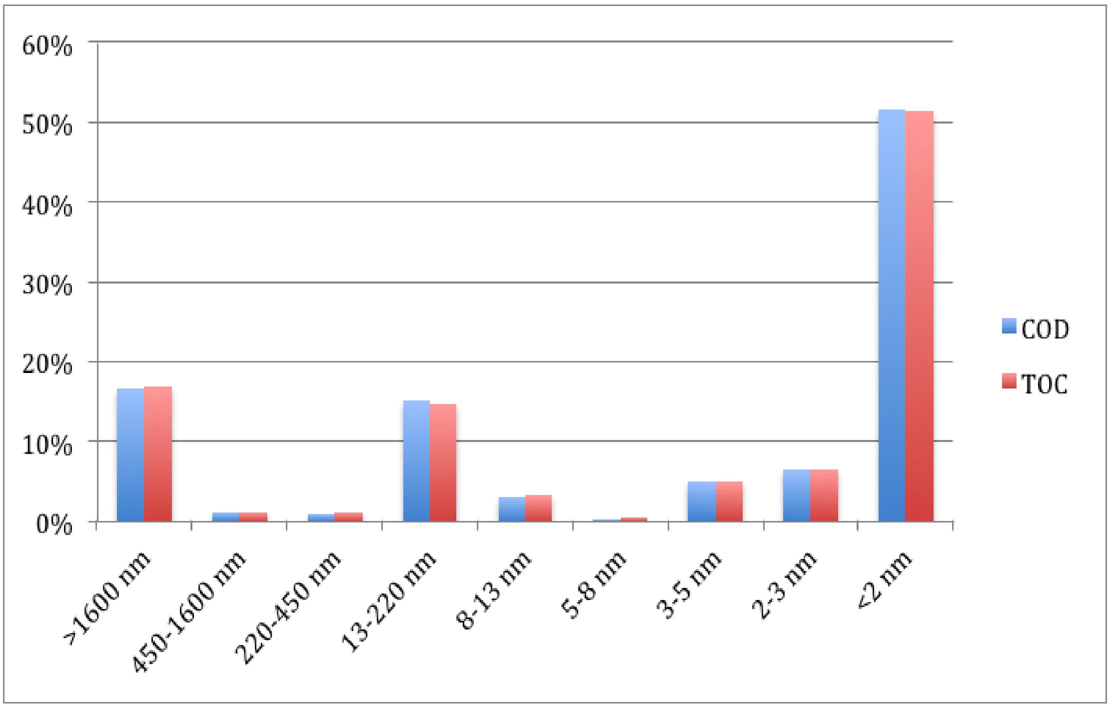



**Figure 6.9 :** PSD-based comparison between COD and TOC.

### 6.4. Sequential Filtration/Ultrafiltration for PSD-Based Color Fractionation

#### 6.4.1 Sample I

**Influent**

Results for the sequential filtration/ultrafiltration studies for color profile presented in Figure 6.10. According to Figure 6.10, most (70%) of the color for influent stream is in the soluble form. The rest of the color is seen to be distributed among other intervals and is negligible.

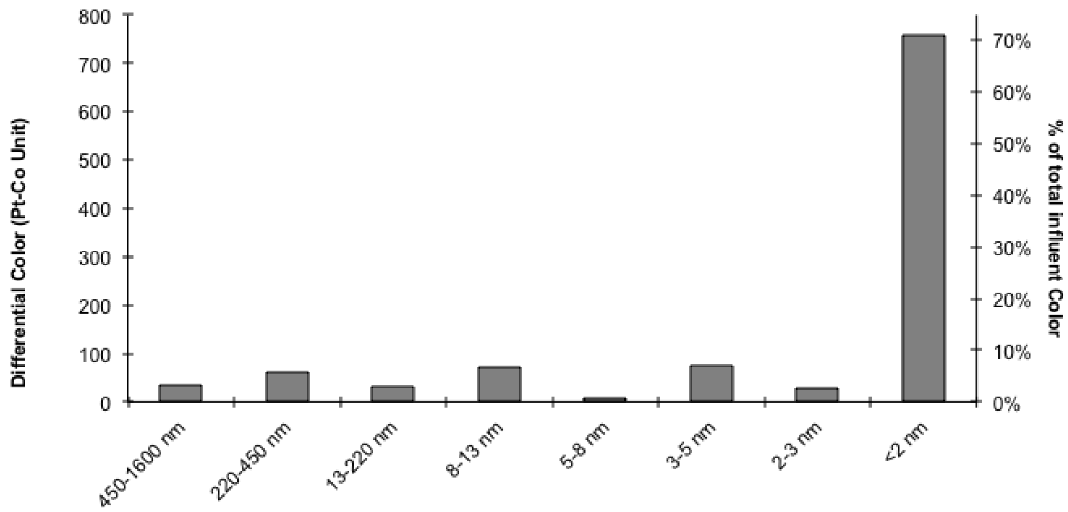



**Figure 6.10 :** PSD-based color fractionation for Sample I (Pt-Co Unit).

**Before and after biological treatment**

Comparative presentation of the color profiles of the textile wastewater before and after biological treatment is reviewed in Fig. 6.11. The figure shows that unlike COD, biological treatment slightly removed color (%30). Most of the color still remains in the effluent.

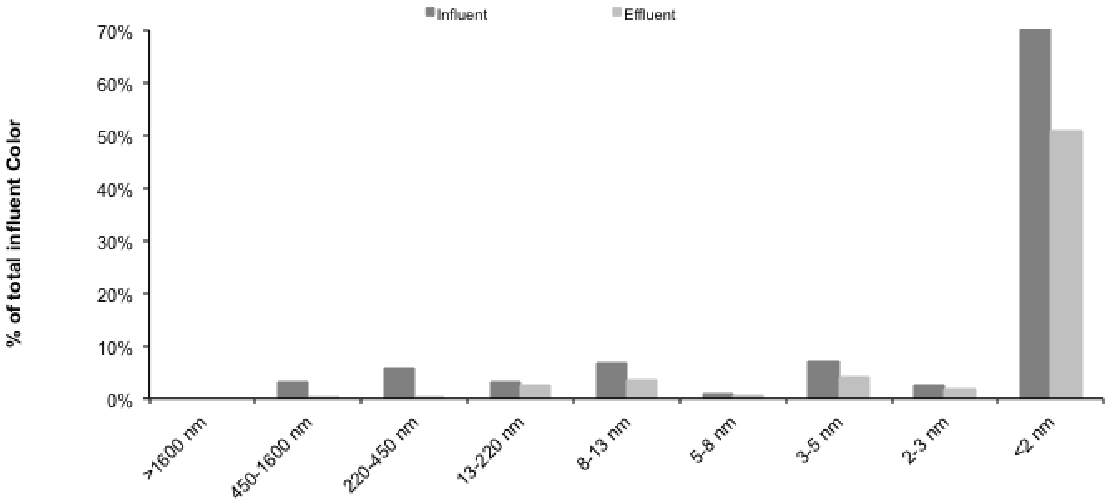



**Figure 6.11 :** PSD-based color fractionation before and after biological treatment.

### 6.4.2. Sample II

Results for the sequential filtration/ultrafiltration studies for color profile presented in Figure 6.12. According to Figure 6.12, most (%72) of the color for influent stream is in the soluble form. The rest of the color is seen to be distributed among other intervals and is negligible.

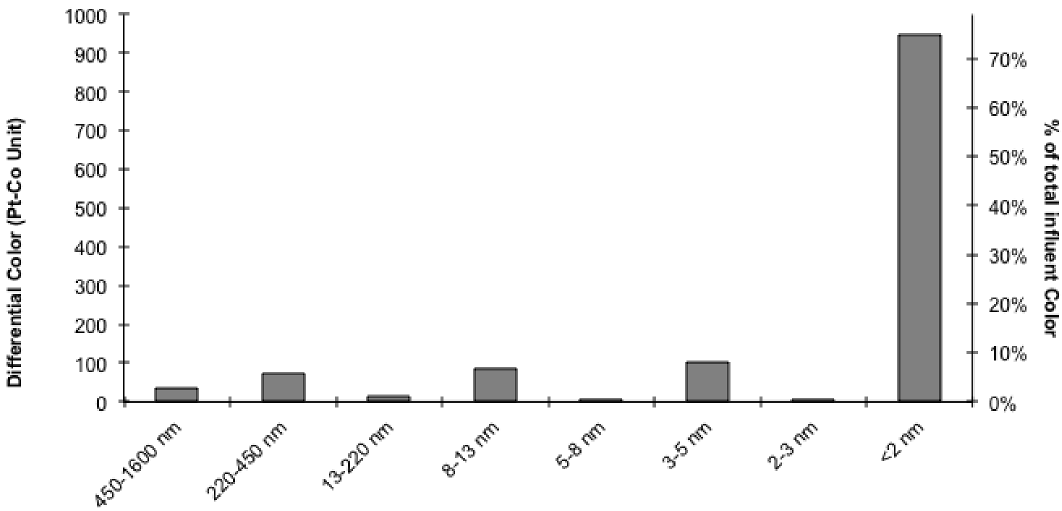



**Figure 6.12 :** PSD-based color fractionation for Sample II (Pt-Co Unit).

### 6.4.3. Comparison between samples and the previous studies

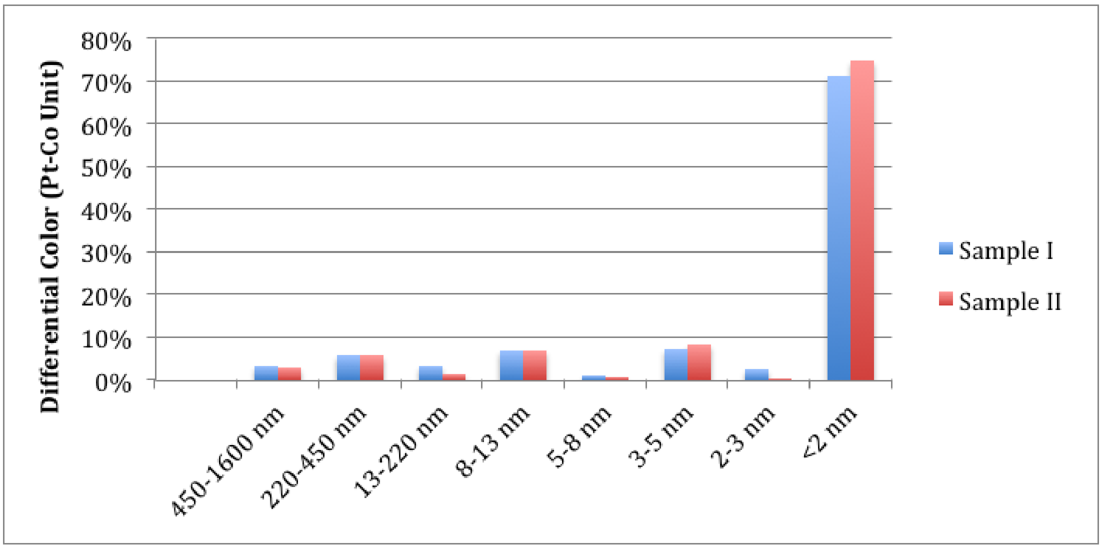



**Figure 6.13 :** PSD-based color fractionation for Sample I - II (Pt-Co Unit).

The PSD-based color fractionation obtained for textile industry is reviewed in Figure 6.13, which provide a clear indication that the color variation according to different size categories exhibits similar trends for Sample I and II. For both samples, most of the color for influent flow is in the soluble form.

This color profile is also in agreement with some of the values summarized by Doğruel *et al.* (2006). According to the study, most of the color profile is in 3-5 nm. Moreover, soluble part is the second most significant size interval.

### 6.5. Respirometric Analysis and Biodegradation Kinetics

The biodegradation characteristics of the samples taken from the influent were evaluated by model calibration of the respective OUR profiles. The OUR profiles of the raw and filtered (450 nm, 100 kDa, 1 kDa) samples are given in Figures. Moreover, the COD fractionation of the samples is reviewed in Table 6.12.

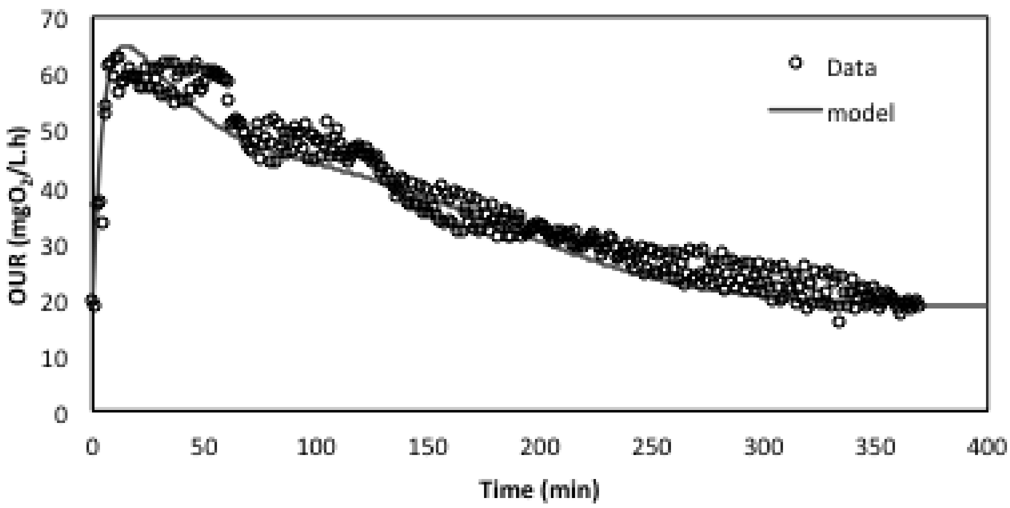



**Figure 6.14 :** The OUR profile of Raw Wastewater.

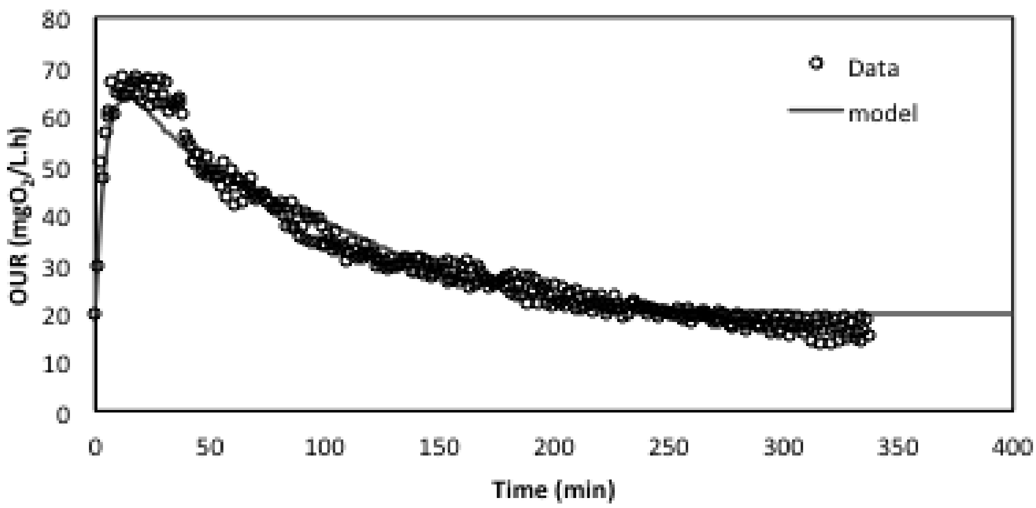



**Figure 6.15 :** The OUR profile of wastewater filtered through 0,45 nm.

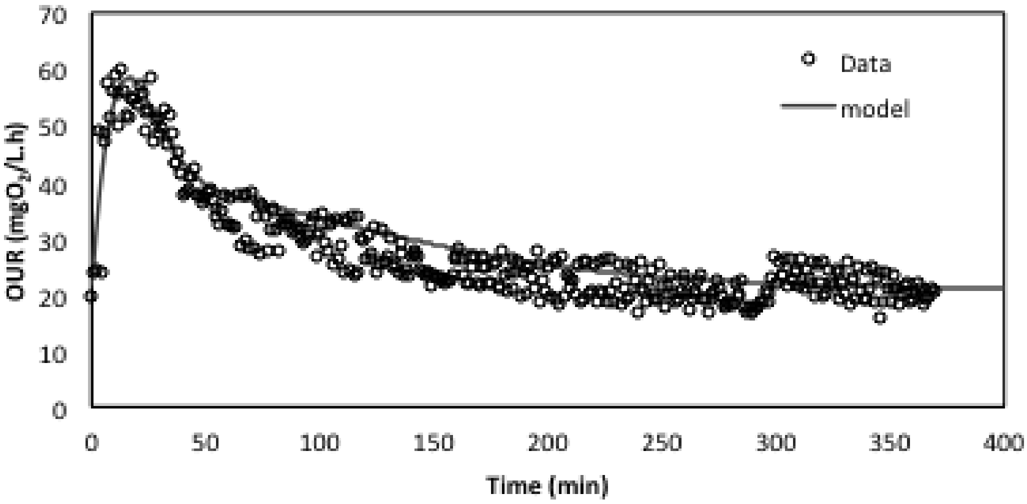



**Figure 6.16 :** The OUR profile of wastewater filtered through 100 kDa.

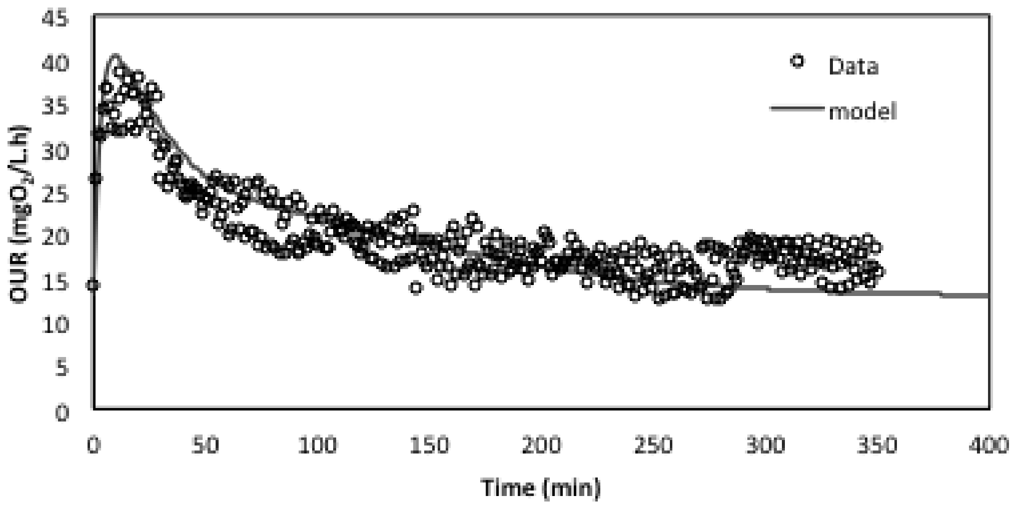



**Figure 6.17 :** The OUR profile of wastewater filtered through 1 kDa.

**Table 6.12 :** The COD fractionation of the samples.

| | Raw WW(mg/l) | 450 nm (mg/l) | 100 kDa (mg/l) | 1 kDa (mg/l) |
|---|---|---|---|---|
| $C_{S1}$ | 576 | 552 | 440 | 333 |
| $S_{S1}$ | 82 | 82 | 82 | 82 |
| $S_{H1}$ | 494 | 470 | 358 | 251 |
| $S_S/C_T$ | 11% | 11% | 11% | 11% |
| $S_H/C_T$ | 70% | 78% | 62% | 47% |

According to table, total COD mostly consists of soluble form. Moreover, $S_H$ is the most significant one among all fractions. For the raw wastewater sample, the biodegradable part is 576 mg/l with 81% contribution to the overall COD. The inert part is 135 mg/l with 19% contribution to the overall COD. Moreover, $S_I$ is 45 mg/l with 6% contribution to the overall COD.

The kinetic and stoichiometric parameters derived from model calibration of the corresponding OUR data are outlined in Table 6.13. As shown in table, a $Y_H$ value of 0.62 mg COD and a $b_H$ value of 0,12 $day^{-1}$ were found to characterize wastewater samples, as typical levels equally associated with textile wastewater; the same would apply to $f_{ex}$, with a quite accepted default value of 0.15 (Orhon et. al., 2001). Since, 30% of the organized industrial district is composed of other industries such as carpet, home furniture and plastic, the growth and hydrolysis rates are low possibly due to the accumulation and increased effect of inhibitory compounds likely to be present in the wastewater. Moreover, there may be slowly biodegradable organics present in wastewater.

**Comparison with the previous studies**

The results of OUR experiments provide a clear indication that the COD fractions according to their behaviors in the activated sludge process are in agreement with the studies done for textile wastewaters in the literature. For instance, Yildiz et al., 2007 studied biodegradation characteristics in textile wastewater. According to study, the total COD mostly consists of soluble form with %60 contribution to the overall

COD. Moreover, $S_H$ is the most significant part with 54% contribution to the overall COD.

The kinetic parameters are quite low due to the possible presence of inhibitory compounds and slowly biodegradable organics in wastewater. On the other hand, similarly low values are reported for other textile industry wastewaters. This study is in agreement with some of the values summarized by Orhon *et al.* (2001). Based on the study, even though results were not as low, the growth rate of 4.1 $d^{-1}$ experimentally assessed for the overall wastewater is lower than the average value of textile wastewaters.

**Table 6.13 :** Kinetic and stoichiometric parameters.

| Model Parameters | Unit | Raw | 0.45mm | 100 kDa | 1 kDa |
|---|---|---|---|---|---|
| Maximum specific growth rate, $\hat{\mu}_H$ | 1/day | 1.3 | 1.3 | 1.3 | 1.3 |
| Half saturation constant, $K_S$ | mg COD/L | 20 | 20 | 20 | 20 |
| Max.hydrolysis rate for $X_{S1}$, $k_{h1}$ | 1/day | 1.1 | 1.2 | 0.8 | 0.80 |
| Hydrolysis half sat.const. for $X_{S1}$, $K_X$. | mgCOD/mg COD | 0.03 | 0.03 | 0.03 | 0.03 |
| **State variables** | | | | | |
| Heterotrophic biomass, $X_H$ | mg COD/L | 2300 | 2500 | 2400 | 1660 |
| Activity | % | 64 | 68 | 58 | 48 |

Assumed: $Y_H$= 0.62 mg COD/mg COD; $f_{ES}$= 0.05; $f_{EX}$= 0.15 $b_H$: 0.24/day

## 7. CONCLUSION

In the present experimental work, the effect of biological treatment on the COD, TOC and color constituents in the textile wastewater was examined by employing PSD analysis (sequential filtration/ultrafiltration). Biodegradation characteristics were evaluated by means of oxygen uptake rate (OUR) and experimental results were used for model calibration.

The influent wastewater sample was characterized by a COD level of around 711 mg/L, with 185 mg/L of TOC and 1034 mg/l (Pt-Co) of color. The conventional characterization studies are in agreement with the studies done for textile wastewaters in the literature. According to study, textile wastewater which has been sampled from influent and effluent flow has a medium strength concentration given in literature.

The sequential filtration/ultrafiltration studies show that the bulk of the COD both for influent stream is in the soluble form. These results overlap with the previous studies, which have done in different industrial wastewaters. The most pronounced effect of biological treatment is observed in the soluble size range (< 2nm) with 48% contribution to the overall COD removal efficiency of 85%. PSD-based COD profile of the textile wastewater proves to be useful tool for evaluating the effect of biological treatment on the fate of COD components.

The PSD-based TOC profile of the biological treatment influent revealed similar size distribution characteristics as those of the COD parameter. Evaluation of the differential TOC profiles obtained for biological treatment influent and effluent samples reveals that biological treatment reduces the soluble TOC level from its initial value of 95 to 14 mg/l, translating into 43 contribution to the overall TOC removal performance.

The PSD of color constituent in the biological treatment influent and effluent streams underlines that biological treatment lowered the color content from 1034 Pt-Co to 677 Pt-Co, amounting to the color reduction of 30% on overall basis.

The respirometric experiments showed that the total COD mostly consists of soluble form and $S_H$ is the most significant one among all fractions. For raw wastewater, $S_H$ corresponded to 70% of the total COD and nearly 86% of the biodegradable COD content. The results are in agreement with the studies done for textile wastewaters in the literature. Furthermore, due to the possible effects of inhibitory compounds and the presence of slowly biodegradable compounds coming from industries, the kinetic parameters such as growth rate and hydrolysis rate are low. Even though these results rarely occur, in literature similar cases are present.

The results also showed that respirometry could be used as a useful complement of particle size distribution by ultrafiltration for the assessment of biodegradation characteristics of COD fractions within each operational size category; namely in particulate, colloidal and soluble portions. Moreover, by using this method, the interpretation of the potential and limitation of applied treatment alternatives can be determined.

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