

**CORRELATION BETWEEN COD FRACTIONATION
AND PARTICLE SIZE DISTRIBUTION FOR
DOMESTIC SEWAGE**

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**EVSEL ATIKSULARDA KOİ FRAKSİYONASYONU VE
PARTİKÜL BOYUT DAĞILIMI ARASINDAKİ
KORELASYONUN İNCELENMESİ**

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PREFACE

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LIST OF SYMBOLS

C_I	: Total Inert COD Concentration [MCOD/L ³]
C_S	: Total Biodegradable COD Concentration [MCOD/L ³]
C_T	: Total COD Concentration [MCOD/L ³]
NUR	: Nitrogen Utilization Rate [M/L ³ .T]
OUR	: Oxygen Utilization Rate [M/L ³ .T]
S_I	: Dissolved Inert COD Concentration [MCOD/L ³]
S_P	: Dissolved Inert Microbial Products [MCOD/L ³]
S_S	: Easily Biodegradable COD Concentration [MCOD/L ³]
S_T	: Total Dissolved COD Concentration [MCOD/L ³]
X_I	: Particulate Inert COD Concentration [MCOD/L ³]
X_P	: Particulate Inert Microbial Products [MCOD/L ³]
X_S	: Slowly Hydrolyzable COD Concentration [MCOD/L ³]
X_T	: Total Particulate COD Concentration [MCOD/L ³]
Θ_x	: Sludge Age [T]

CORRELATION BETWEEN COD FRACTIONATION AND PARTICLE SIZE DISTRIBUTION FOR DOMESTIC SEWAGE

SUMMARY

In raw wastewaters insoluble material forms a typical and significant fractionation of the organic pollution. Particulate matter forms over %50 of the organic load in the domestic sewage. In activated sludge systems, a part of these particulate organics is hydrolyzed and degraded. Depending on the retention time and efficiency of primary settlers, part of this suspended organic matter reaches the biological process. In some cases, low loaded activated sludge processes can be directly fed by non-settled wastewater to provide additional carbon source. In this study direct particle size measurement by sequential filtration and ultrafiltration is searched as a convenient method for wastewater characterization for appropriate treatment technology.

In this study a characterization study performed on the same domestic sewage for two sets from the influent of the WWTP and the effluent flow of the WWTP as composite samples. The first sample was taken on 18.01.2006 and the second sample was taken on 23.03.2006 which represents the winter conditions. The WWTP has trickling filters so that, it is not possible to evaluate the effluent flow characterization with the suspended activated sludge systems. Apart from these characterization studies, COD fractions have been profoundly observed. Sequential filtration/ultrafiltration has been used as a physical segregation tool. It also explores the correlation between particle size distribution (PSD) and COD fractionation, as an index for biological treatability. Profiles obtained through PSD based-COD fractionation serve as the fingerprints for domestic wastewater. PSD-based COD fractionation profiles identify the soluble range below 2 nm as the size interval housing both the soluble inert COD initially present in the wastewater and soluble easily biodegradable organic matter as also supported by the metabolic fractionation attained through the respirometric analyses and the inert COD determination with the method proposed by Orhon *et al.*, (1999).

As Atakoy WWTP is operating with trickling filter system it is not possible to compare the production of S_P with the S_P of an activated sludge system. Because of this reason a batch reactor was established as 3rd set and biomass was fed with domestic sewage till the system became to steady state.

At the end of the study it has been observed that conventional characterization of domestic sewage is in agreement with the previous studies for domestic sewage also it has been explored that particulate COD composes about % 65 of the raw wastewater which is in agreement with the study done by Dulekgurgen *et al.*, 2006. Another fraction in the wastewater inert particulate COD is about 10 % of the sewage and inert soluble fraction is about %5 of the raw wastewater. It also has been explored in sequential filtration/ultrafiltration studies that there is a homogenous distribution according to PSD based COD fractionation for the colloidal part of the sewage for different filter sizes.

EVSEL ATIKSULARDA KOI FRAKSİYONASYONU VE PARTİKÜL BOYUT DAĞILIMI ARASINDAKİ KORELASYONUN İNCELENMESİ

ÖZET

Ham atıksularda çözünmemiş yapıdaki partiküler maddeler, organik kirliliğin önemli bir bölümünü oluşturmaktadır. Bu oran evsel atıksularda organik yükün %50'sini oluşturabilmektedir. Aktif çamur sistemlerinde bu partiküllerin bir kısmı hidrolize uğrayarak giderilmektedirler. İlk çöktürme tanklarının verimine ve bekletme zamanına bağlı olarak bu tip askıda organik maddeler biyolojik prosese ulaşabilmektedirler. Bazı durumlarda aktif çamur sistemlerinde düşük organik yükünü arttırmak amacıyla ön çökeltme iptal edilerek çökeltilmemiş atıksu direk biyolojik prosese ek karbon kaynağı olarak verilebilir. Yapılan çalışmada en uygun artıma teknolojisinin belirlenmesi için atıksu karakterizasyonunda partikül boyut ölçümünün ardışık filtrasyon/ultrafiltrasyon metoduyla yapılmasının uygunluğu araştırılmıştır.

Bu çalışmada aynı evsel atıksu arıtma tesisinden 18.01.2006 ve 23.03.2006 tarihlerinde giriş ve çıkış akımlarından alınan örneklerde karakterizasyon çalışmaları uygulanmıştır. Örnekler alındıkları mevsim doğrultusunda kış koşullarını temsil etmektedirler. Arıtma tesisinde biyolojik proses damlatmalı filtre olduğundan dolayı çıkış akımını askıda aktif çamur sistemleriyle kıyaslamak doğru değildir. Karakterizasyon çalışmaları haricinde KOI fraksiyonları derinlemesine incelenmiştir. Ardışık filtrasyon/ultrafiltrasyon fiziksel ayırım aracı olarak kullanılmıştır. Ayrıca partikül boyut dağılımı ve KOI fraksiyonasyonu arasındaki korelasyon biyolojik arıtılabilirliğin bir göstergesi olarak incelenmiştir. Elde edilen partikül boyut dağılımı temelli KOI fraksiyonasyon profilleri evsel atıksuyun karakterinin ortaya çıkmasına yardımcı olmaktadır. PBD temelli-KOI fraksiyonasyon profillerinden çıkarılan tanıma göre 2 nm'nin altındaki boyuta sahip olan çözünmüş kısımda giriş akımında olan çözünmüş inert KOI ve çözünmüş kolay ayrılan organik madde olduğu

gözlenmiştir, bu sonuçlar, respirometrik analizler ve Orhon ve diğ., (1999) tarafından geliştirilmiş inert KOI deneyleriyle de desteklenmiştir.

Ataköy evsel atıksu arıtma tesisi damlamalı filtre sistemiyle işletildiğinden çıkış akımında sistemde oluşan mikrobiyal ürünleri bir aktif çamur sisteminin çıkış akımında oluşan mikrobiyal ürünlerle kıyaslamak mümkün değildir. Bu nedenle 3. set olarak kesikli bir reaktör kurulmuştur ve biyokütle evsel atıksuyla beslenerek mikrobiyal ürünlerin oluşumu sistem dengeye gelene kadar izlenmiştir.

Çalışmanın sonunda konvansiyonel karakterizasyon deneylerinin sonuçlarına bakıldığında atıksu karakterinin önceden yapılmış karakterizasyon çalışma sonuçlarıyla uyumlu olduğu gözlemlenmiştir. Ayrıca partikül kaynaklı KOI'nin toplam KOI'nin yaklaşık %65'ini oluşturduğu ve bu sonucunda Dülekürgen ve diğ., (2006) rapor ettiği sonuçla uyumlu olduğu gözlemlenmiştir. Diğer KOI fraksiyonu olan partikül inert KOI'nin toplam atıksuyun %10'unu ve çözünmüş inert KOI'nin ise toplam atıksuyun %5'ini oluşturduğu gözlemlenmiştir. Ayrıca yapılan ardışık filtrasyon/ultrafiltrasyon çalışmalarıyla PBD kaynaklı-KOI fraksiyonasyonunda atıksuyun koloidal kısmının değişik filtre boyutlarında homojen bir dağılım yaptığı gözlemlenmiştir.

1. INTRODUCTION

1.1 Significance of the Study

Exact wastewater characterization and after wastewater characterization treatment studies are necessary for the correct determination of biological treatment systems and design parameters. For this reason firstly it has been projected to make a detailed wastewater characterization.

Biodegradable part of the wastewater is composed of two main parts; readily biodegradable part and slowly biodegradable part. Slowly biodegradable part of the domestic sewage has a wide range and this makes it an important component of the domestic sewage. Settleable part of the slowly biodegradable component has the most important percent. According to literature studies; no study could have been established of the COD distribution on the particle size for the domestic sewage.

1.2 Aim and Scope of the Study

The aim of this study is to explore the correlation between physical segregation and biodegradability of the organic constituents. For this purpose, the domestic sewage samples were taken from the conventional biological WWTP in Ataköy. The domestic sewage before entering to the primary settler of the Ataköy WWTP was subjected to conventional wastewater characterization, sequential filtration and ultrafiltration experiments, and biological treatability studies (batch-inert COD experiments and respirometric measurements). The samples taken from the effluent of the WWTP were exposed to wastewater characterization and PSD-based fractionation to interpret the effect of biological treatment on the fate COD.

2. WASTEWATER CHARACTERIZATION

2.1 Definition of Organic Matter in Wastewaters

The significance of organic matter has changed for wastewater treatment in last 20 years. Nowadays organic matter in wastewaters is an important design parameter for denitrification, biological phosphorus removal and other processes such as it is in COD reduction (Dold *et al.*, 1980; Henze, 1992; Henze *et al.*, 1992). Particulate matter forms more than %50 of the organic load in domestic wastewater. In activated sludge systems most of these organic matters are hydrolysed and reduced biologically (Eliosov and Argman, 1995). Definition of these organic matter is very important which is mostly non-homogenous. Organic components in wastewater can be classified in three ways.

- Chemical characterization of chemical groups in components; ex. lipids, proteins, carbohydrates...etc. (Huelekian H. and Balmat J.L., 1959; Hunter J.V. and Huelekian H., 1965).
- Characterization of organic matter according to particle size distribution (Levine *et al.*, 1991; Balmat, 1957; Rickert D.A. and Hunter J.V., 1967)
- Characterization of organic contaminants according to their biodegradation rates in wastewaters.

First way is not very useful because it is very hard and not practical.

Activated sludge modelling depends on the utilization of COD because COD conveniently reflects the electron equivalence between organic substrate, active biomass and dissolved oxygen. The major prerequisite for modelling is a reliable wastewater characterization with COD fractionation, for the identification of organics with different biodegradation properties; this provides the necessary experimental support to the model, for an accurate prediction of the electron acceptor requirement and the excess biological sludge production (Orhon *et al.*, 1999). From this view, assessment of the inert fraction of the organic content of the wastewater is very important because it shows directly the other main fraction, biodegradable

organic matter, i.e. substrate available for microbial growth and electron acceptor utilization. A number of methods have so far been proposed for the estimation of inert COD fractions in wastewaters.

It has been necessary to understand the specific degradation mechanisms for specific groups of compounds better with the development of more detailed mathematical models (e.g., metabolic models). Guellil *et al.* (2001a) reported that the location of hydrolysis within the activated sludge floc differs for different chemical compounds. Protein hydrolysis generally resulted from the enzymatic activity of the extracellular polymeric matrix, whereas the glycolytic activity was mainly present in the organic colloidal fraction of the wastewater (Sophonsiri *et al.*, 2003). A more detailed analysis and modelling of hydrolysis is required for an understanding of the chemical composition for different particle size fractions. Dignac *et al.* (2000) appraised the fate of different organic compounds in an activated sludge treatment plant and reported that lipids are most easily removed followed by proteins and then carbohydrates. Others have identified carbohydrates as the most rapidly biodegradable fraction (Raunkjaer *et al.*, 1994).

2.2 Characterization of Particles According to their Size Distributions in Wastewater

As there are many technics to determine the particulate organic matter distinctions there is no standard way to determine the particle size distribution. One of the best ways to determine the particle size distribution is separating the organic matter such as solved and particulate structures (Levine *et al.*, 1985).

Size distribution for pollutants is important for the explanation of wastewater characteristics for 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. Filters with pore sizes of 450 nm and 1600 nm can show the size of particles that can be removed by chemical settling. Particles in wastewaters have conveniently been grouped into operational size categories, namely dissolved (<1 nm), 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.*, 2005).

According to Rozzi *et al.*, 1998 %TOC distribution and % absorbion fingerprints as a function of molecular cuts are very different TOC is composed of smaller fractions (<3.000 MWCO). The % absorbance distribution is much less homogenous and correlation between %TOC and %absorbance is very poor.

A necessary requirement for most water reuse applications is complete removal of particles (i.e., bacteria, protozoa, viruses) from the effluent of the biological treatment stage. In the past years, membrane filtration systems have been used for a secure retention of particles. A limiting factor for these membrane applications is membrane fouling, where fouling is directly related to the characteristics of soluble, colloidal, and particulate matter. For a microfiltration system (0.2 μm pore size) Pouet *et al.* (1994) have shown that fouling was mainly caused by the supracolloidal fraction defined as non-settleable particles $>0.05 \mu\text{m}$. Tardieu *et al.* (1998) have shown for an ultrafiltration system (molecular weight cut-off 300 kDa) that membrane fouling is mainly caused by small colloids. Thus, interactions between the specific particle size distribution in the reactor and pore sizes of the membranes used for particle retention need to be evaluated as a basis for process design and operation.

Larsen (1992) separated the dissolved organic matter into three categories as the diffusion of bacterial cell into membrane in the biofilm systems. These are organic substrate, S_A ; easily metabolised in the cell membrane, organic substrate can rapidly difusable into the biofilm, S_D , and non-difusable organic substrate X_S . These distributions are given in Figure 2.1.

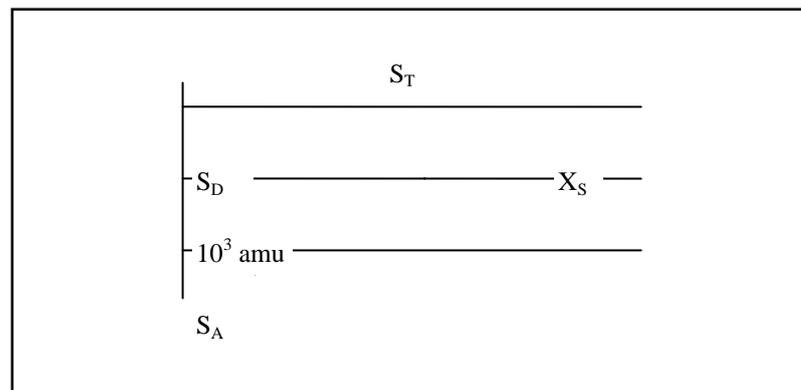


Figure 2.1: Fractionation of Organic Matter (Larsen, 1992)

It is right to separate the organic matter constituents such as Larsen's definiton. But to make this seperation advanced seperation technics are necessary such as gel filtration, chromatograph ultrafiltration, molecular screen and this is hard to do in application. Hydrolysis process will be necessary to minimize the particle size for the

diffusion into the cell membrane if the dissolved the particle size is bigger than Larsen's definition.

Separating the particles with membrane filtration is the most useful and the most preferred technic because this technic can be adapted to most situations with less equipments (Levine *et al.*, 1991). But this technic has some limitations. It is not possible to separate particle sizes under $0.01\mu\text{m}$. Organic mater contents can be developed in the forms of BOD, COD or TOC if particle size distribution is known. Levine *et al.* (1985) showed that contents of organic matter in domestic wastewaters, more than 50 % of the organic matter is bigger than $1\mu\text{m}$. The results in Figure 2.2 show that there is a net relation between COD and TOC but there is no net relation between COD/TOC and biological oxidation velocity in the hydrolysis of big particulate organics.

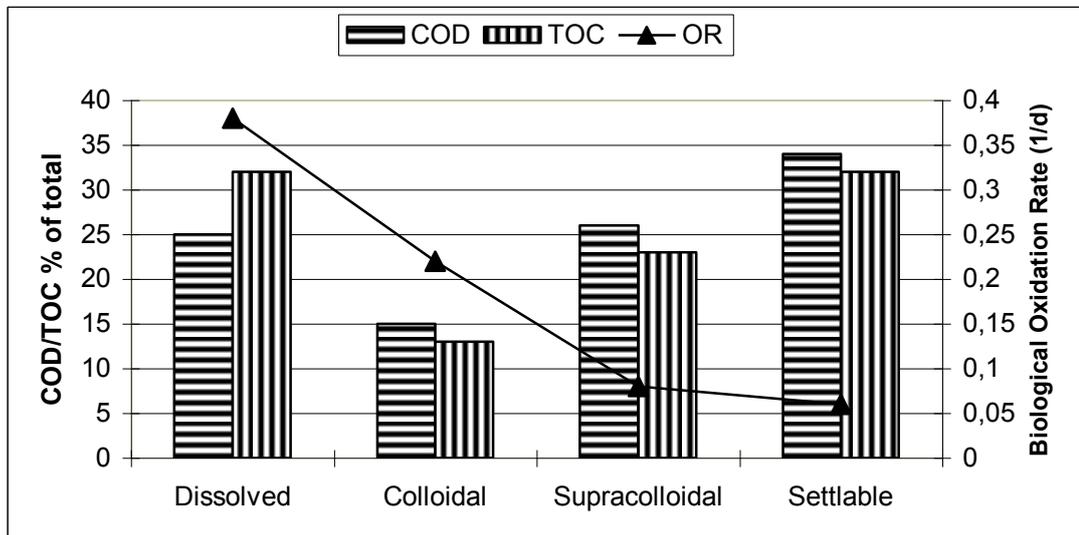


Figure 2.2: Composition of Organic Matter in Wastewater

If carbon source is in particulate structure than hydrolysis in wastewater treatment becomes a rate limiting process. Levine *et al.* (1991) told that particle size characterization can be used for a more efficient design in wastewaters containing particulate organic matter.

According to the results obtained by Sarner (1981) if suspended and colloidal particulates are present in the medium than dissolved organics' reduction become slower.

However Takahaski *et al.* (1969) defended that if particulate organic matter is present in the medium than organics' reduction become easier.

Biological treatment becomes more effective with the reduction of slowly biodegradable supracolloidal component (1-100 μm) and choosing the suitable kinetics particulate size distribution intervals for biological treatment. Retention time is the most important factor because of the rate limiting hydrolysis process. Selection of organic matter to the size factor increases the rate of easily biodegradable organic carbon component but decreases the denitrification capacity (Henze *et al.*, 1992).

According to Dogruel *et al.* (2005), PSD-based COD fractionation and color profiles seems to be a better way to understand the reactions taking place in the treatment process and to enhance the ability to interpret the results with a broader view rather than having a black-box type of evaluation based only on influent and effluent levels. PSD-based COD fractionation of the raw wastewater from a textile plant shows a specific size distribution character distributed over all size ranges, as a fingerprint for the selected sample.

Experimental data on particle size distribution is important for biological processes such as chemical and physical treatment systems. As a result researchers focus on particle size information for a better understanding of biological processes (Levine *et al.*, 1991; Sophonsiri and Morgenroth, 2004). Developments in this area can be accomplished after the introduction of mathematical models for activated sludge, adoption of chemical oxygen demand (COD) as the main parameter for organic substrate, and the introduction of COD fractions with different biodegradation characteristics (Ekama *et al.*, 1986; Henze *et al.*, 2000).

The reliability of mechanistic models which need the basic separation of the soluble and particulate COD fractions should be questioned without appropriate experimental support because physical segregation based on the particle size, have grown in complexity. COD is now the key parameter, especially for the expression of model components related to wastewater characterization (Orhon and Artan, 1994; Henze *et al.*, 2000). In these mechanistic models built on further differentiation in terms of biodegradability should be evaluated individually because each fraction may undergo different biochemical reactions (Wentzel *et al.*, 1999).

Conventional wastewater treatment depend on sedimentation for the decreasing of particle concentration before biological treatment (primary sedimentation) and for the removal of particles after biological treatment (secondary sedimentation). Alternative process formations have been suggested where direct influent filtration or chemically improved sedimentation are used to maximize the removal of organic matter before any biological treatment (Odegaard, 1998; van Nieuwenhuijzen *et al.*, 2001). Physical separation of organic matter can help to maximize energy generation

through anaerobic digestion, to reduce required energy input for aeration in the biological processes, and to build more compact biological reactors. Removal efficiencies and process selection for this pretreatment are directly related to particle characteristics in the incoming wastewater.

According to Dulekgurgen *et al.* (2006), particle size distribution of COD fractions serves as the fingerprint for wastewaters. PSD gives a different image for textile wastewater and domestic sewage. 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 than domestic wastewater. Yet, significant COD fractions are also present in a number of other size intervals, presumably due to different specific chemicals used in the process.

According to microbial degradation kinetics the soluble readily biodegradable COD fraction (S_S) consists of relatively small biodegradable particle that can be easily transported across cell membrane and then metabolized in minutes. Utilization of the particulate biodegradable COD (X_S) and the soluble slowly biodegradable COD (S_H) - or the rapidly hydrolyzable COD - fractions takes longer because these constituents consist of larger particles and need extracellular breakdown before their transport into the cells for biodegradation (Wentzel *et al.*, 1999; Hu *et al.*, 2002). The soluble inert COD fraction (S_I) consists a variety of compounds which are dissolved, thus can pass to the microbial cell interior, but can not be biodegraded because of their refractory nature. The soluble residual microbial product fraction (S_P) matches to the bulk of microbial end-products discharged from the cells without another utilization (Orhon and Çokgör, 1997; Wentzel *et al.*, 1999). COD fractionation is very important because biomass in activated sludge changes with particle size of these constituents. As a result, the wide range of biodegradation rates defined for different COD fractions is likely to have a correlation with physical categorization in terms of particle size and physical state in solution (Wentzel *et al.*, 1999).

For the quantitative characterization of the COD fractions in terms of biodegradability several methods, mostly relying on respirometry, have been proposed but most of these procedures are time-consuming and generally need acclimated biomass (Ekama *et al.*, 1986; Orhon *et al.*, 1998; Çokgör *et al.*, 1998; Orhon *et al.*, 1999; Carvalho *et al.*, 2001). On the other side, no single analytical method is available for the direct assessment of all particle size ranges. Furthermore, physical separation methods alone cannot separate between the biodegradable and non-biodegradable portions. For optimizing the COD fractionation, it would be more meaningful to use both methods in parallel.

According to the studies of Sophonsiri *et al.* (2003) for domestic sewage; 60% of the organic matter (measured as COD) in the primary effluent is larger than 10^3 amu and 45% is larger 1.2 μm . The continuous decrease of the COD concentration with decreasing particle size reveals that particles are well distributed over the measured size ranges. For the biological degradation of particulate organic matter, it can be assumed that macromolecules larger 10^3 amu require external hydrolysis before they can be taken up by the cell for oxidation and energy production (White, 2000).

According to a number of studies both the particle size distribution and also the chemical composition of municipal wastewater does not change significantly over time as at the same time wastewater flow and concentration changes (Sophonsiri *et al.*, 2003). Both Levine *et al.* (1985) and Guellil *et al.* (2001b) measured particle size distributions and demonstrated that these do not vary significantly from day to day. Heukelekian and Balmat (1959) evaluated lipids, amino acids, and carbohydrates in municipal wastewater and found that the composition did not significantly change between winter and summer. Similar results were obtained by Raunkjaer *et al.* (1994) for COD fractions taken during the day and during the night. However, they report a large variability for carbohydrate that was attributed to the easily degradable nature of carbohydrates and different residence times in the municipal sewer. Sophonsiri *et al.* (2003) assumed that the measured wastewater characteristics are representative of the specific waste stream based on these previous findings of the relative stability of the wastewater characteristics.

2.3 Biodegradation of Organic Matter in Wastewaters

At the beginning of 80's a shorter and selfer definition of organic matter had been necessary for the description of organic components' biodegradation and a better estimation of kinetic constants in the wastewaters (Dold *et al.*, 1980; Ekama *et al.*, 1986).

Organic pollution traditionally had been defined as BOD_5 , but defined as COD in the last years. In many countries COD is substituting with the TOC as a new application. But BOD_5 , COD and TOC are the parameters which can not give enough information about the chemical composition of organic pollution and present components for the microorganisms of activated sludge in wastewater. Biodegradable organic matter separated in two categories as easily biodegradable and slowly biodegradable (X_S and S_S). Inert organic matter is classified as dissolved and particulate (X_I and S_I).

The fractionation of the wastewater's chemical oxygen demand (COD) in classes of biodegradability variable with time and sampling point (Orhon *et al.*, 1995; Sperandio *et al.*, 2001). The watering down of domestic sewage by run-off waters, the donation of industrial water, the retention time in the sewer system can all donate to modifying the biodegradable potential of an urban wastewater (F. Lagarde *et al.*, 2005). Moreover, the fractions are not strictly comparable because their definition is based on their own biodegradation kinetics.

Task group (IAWQ), formed in 1983 made a new mathematical approach for the biological process of activated sludge. This group developed Activated Sludge Model No:1 to define the biological processes in wastewater treatment systems (Henze *et al.*, 1986). Format of the model is a matrix including the stoichiometry of the processes and kinetic informations. In this model, determination of model parameters become more important because organic matters are defined as components. For this direction firstly organic components can be determined experimentally (Henze *et al.*, 1986, Ekama *et al.*, 1986). Organic matter components in wastewater are given detailed in Figure 2.3. Slowly biodegradable organic matter X_S (Solfank *et al.*, 1991, Henze 1992) which forms the most part of the organic matter in wastewater can be determined experimentally but can be calculated with the equation below.

$$C_T = S_S + X_S + X_I + S_I + S_H$$

A lot of test technics had been developed for the better determination of organic matter. Batch experiments done with Oxygen Utilization Rate (OUR) and/or Nitrate Utilization Rate (NUR) measurements had been frequently used for the determination of organic matter (Kristen *et al.*, 1982), because these experiments can rapidly determine biodegradation of the organic carbon source in wastewater and can be done together as treatment process is working with the respiration experiments.

According to Reynolds *et al* (2002), optical techniques used with the assumption that oxygen demand is proportional to organic content is not necessarily the case since the specific nature of the oxygen demand (ie chemical or biochemical) will be heavily dependent upon the structure of the organic constituents.

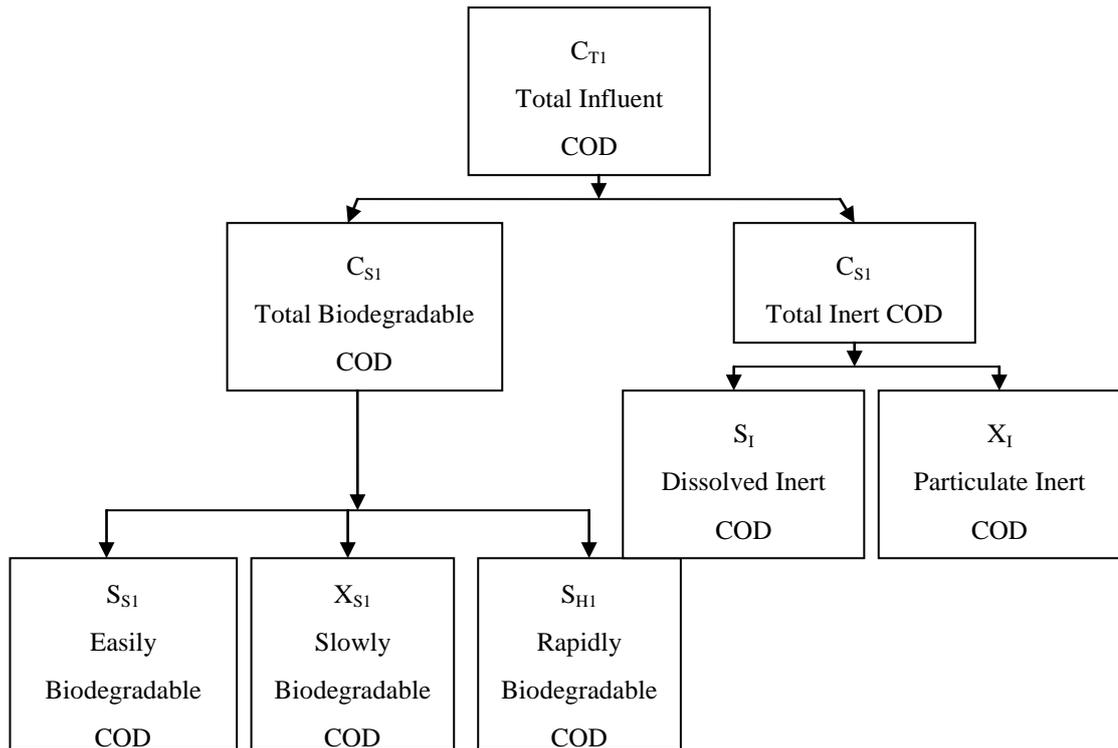


Figure 2.3: Organic Matter Components in Wastewaters

Classification on the basis of biodegradability may have a direct correlation with particle size and physical state in solution, showing 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 *et al.*, 1999, Dulekgurgen *et al.*, 2006).

2.3.1 Easily Biodegradable Organic Matter

Easily biodegradable organic matter constitutes 10-15% COD of the total COD in raw domestic wastewater (Henze, 1992). These components are generally low molecular weight organic components. Organic components which are directly metabolized are limited with volatile fatty acids, carbohydrates, alcohols, peptons and little molecules of aminoacids. Volatile fatty acids especially acetic acid makes up the important part of this component. Table 2.1 gives an example of easily biodegradable substrate component (Henze, 1992).

Table 2.1: Example of Easily Biodegradable Substrate Component for Domestic Wastewater (Henze, 1992)

Component	mg COD/l
Acetic Acid	25
Volatile Acids	10
Amino Acid	10
Alcohol	5
Simple Carbohydrates	10

Easily biodegradable component of organic matter are hydrolysed rapidly under aerobic and anoxic conditions. As a result of this in the channels most of these components are reduced while transporting (Solfrank *et al.*, 1983, Wentzel *et al.*, 1991). Important part of easily biodegradable organic matter is stored as PHB/PHV in biological phosphorus treatment systems under anaerobic conditions (Siebritz *et al.*, 1983, Wentzel *et al.*, 1991).

The measurement of this component had been indirectly given with the Oxygen Utilization Rate (OUR) by Ekama and Marais (1977), can be done with the method improved by Solfrank and Gujer (1991) and Kappaler and Gujer (1992). Nitrogen Utilization Rate (NUR) can also be used to find the rapidly biodegradable organic matter (Ekama *et al.*, 1986, Kristensen *et al.*, 1992).

50-70 % of the rapidly biodegradable COD is composed of volatile fatty acids, ethanol and glucose in raw domestic wastewater. Ultramembranes or gel filtration is a good way to separate the COD into its' low molecular weight components. Also ultrafiltration can be used in raw wastewater (Dold *et al.*, 1986). But dissolved COD components bigger than 1 μ m as molecular weight are not classified as rapidly biodegradable, they are classified as rapidly hydrolyzable organic matter (Henze *et al.*, 1992).

2.3.2 Rapidly Hydrolyzable Organic Matter

This component of the organic matter's dissolved part forms the 15-25 % of the raw domestic wastewater (Henze, 1992). Hydrolysis process can occur in a few hours for rapidly hydrolyzable organic matter under aerobic conditions. But channel systems can effect this component. During the transfer in the channels, suspended biofilms and biofilms on the wall have an important role on biodegradable components. For the channels flowing with the charming aerobic conditions becomes first for the biological oxidation and hydrolysis of rapidly biodegradable matter (Henze and Lindgreen, 1991). Change in the wastewater composition under pressure may become

slower under anaerobic conditions (Nielsen *et al.*, 1992).but biofilm inside the wall surface plays more important role under the pressure than under charming flow, and this can increase the velocity in the total. Heavy molecular weight but dissolved organic components are named as rapidly hydrolyzable components.

Rapidly hydrolyzable organic matter can be found in the continuous tests with the help of Oxygen Utilization Rate (OUR) (Solfrank and Gujer, 1991). Nitrification Utilization Rate (NUR) can be used in both batch and continuous tests (Kristensen *et al.*, 1992).

Nutrient removal processes are mostly limited by the availability of organic matter for denitrification and biological phosphorus removal (Sophonsiri *et al.*, 2003). Biodegradable organic matter in sewage is divided into readily biodegradable and slowly biodegradable fractions. Efficient treatment usually needs the use of both the readily and the slowly biodegradable organic matter to supply sufficient electron donor capacity (Sophonsiri *et al.*, 2003). Most of the slowly biodegradable organic matter is particulate, and extracellular hydrolysis is required to produce small molecules ($<10^3$ amu) which can be transported into bacterial cells where they are metabolized (White, 2000; Morgenroth *et al.*, 2002). Balmat (1957) showed that hydrolysis rates for large particles are up to four times slower than to hydrolysis rates for colloidal material. Even today, mechanisms of hydrolysis for different size particles are not well understood (Morgenroth *et al.*, 2002) and current mathematical models for wastewater treatment do not take into account different hydrolysis rates for different particle sizes (Henze, 2000). As a result, the hydrolysis rates in these mathematical models rely on the specific particle characteristics.

It is seen that particle size has a significant effect on hydrolysis in biofilm reactors. (Sophonsiri *et al.*, 2003). High rate biofilm reactors become an charming alternative to conventional activated sludge systems because they have higher biomass concentrations and can be built more dense. Anyway, biofilm reactors usually have to depend on the addition of an external organic carbon source as an electron donor for nutrient removal. Janning *et al.* (1997) told that only a small fraction of the organic matter in the wastewater is being utilized as an electron donor and the most of the particulate organic matter is removed during filter backwashing. Enzymatic hydrolysis most likely requires a direct contact between particles and bacteria. While small particles ($<1 \mu\text{m}$) are likely to penetrate the biofilm matrix (Drury *et al.*, 1993), large particles are restricted to the biofilm surface. A better understanding of the effect of particle size distributions and possibly even a modification of particle

characteristics is needed for an efficient application of biofilm reactors without the addition of an external carbon source.

2.3.3 Slowly Hydrolyzable Organic Matter

All the chemical components for the intracellular metabolism need to be hydrolysed by extracellular enzymes before transport into the cell are called slowly biodegradable components. Slowly biodegradable components can be in the particulate and the dissolved structure.

In Activated Sludge Model No:1 (Henze *et al.*,1987) and in original double substrate model (Dold *et al.*, 1980) most of the part of the biodegradable organic matter is this part (Figure 2.6). According to Activated Sludge Model No:1 40-60 % of the total COD belongs to this part in raw wastewaters.

In general, more complex, conjugated structures are less biodegradable and are associated with recalcitrant compounds present in wastewater. (Reynolds *et al.*, 2002).

Hydrolysis is the rate limiting step for the slowly hydrolyzable organic matter's biodegradation under aerobic or anoxic conditions. For most of the substrates' hydrolysis rates are changing as rapidly to slowly, slowly to very slowly, it is a better solution to separate these components into 2 or 3 groups. The changing hydrolysis rates according to electron acceptors could not be solved yet. Dold *et al.* (1980) discovered that hydrolysis occurs slower under anoxic conditions. This data is correlated with the results according to Henze and Mladenovski (1991); under aerobic and anoxic conditions hydrolysis is slower than the anaerobic conditions. Hydrolysis products are chemically alike the easily biodegradable components in raw wastewater. In the same metabolic way, it is not possible to separate organotrophic microorganisms with rapidly biodegradable components and metabolized group components.

In activated sludge model Ekama *et al.* (1986) preferred with bend made up; dynamic Oxygen Utilization Rate (OUR) experiments can be used to determine the slowly biodegradable organic matter components. Also batch OUR experiments can be used in this determination experiments (Kappler and Gujer, 1992).

Slowly hydrolyzable organic matter component can be determined at the same time with the COD mass balance, if all of the other components can be determined (Henze *et al.*, 1987).

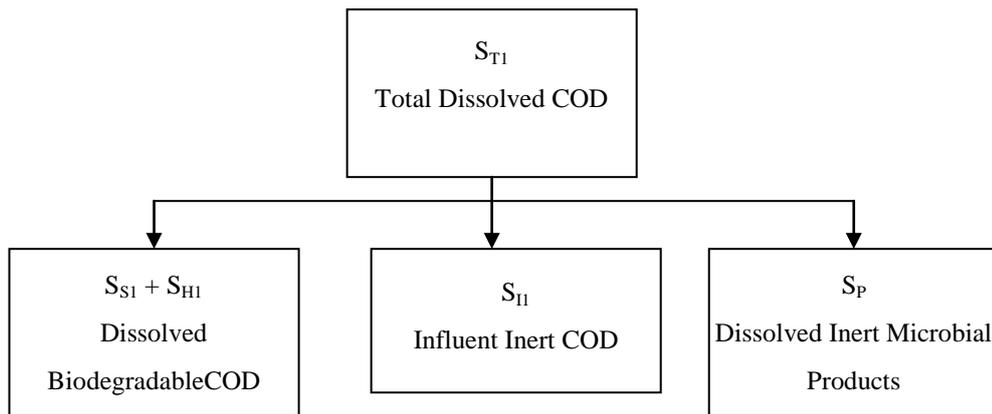


Figure 2.4: Dissolved COD Components in the Effluent Flow

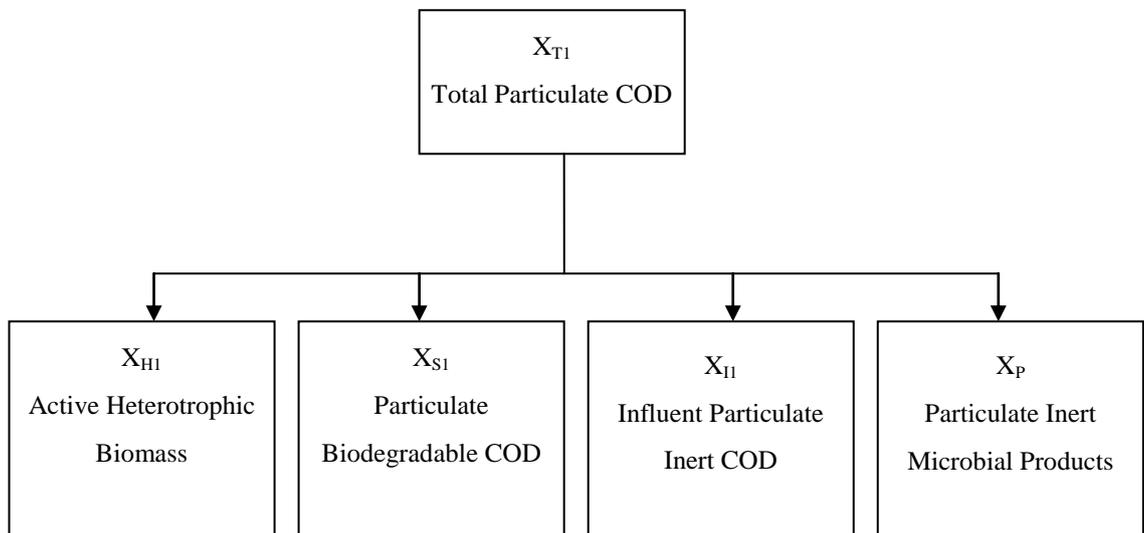


Figure 2.5: Particulate COD Components in the Effluent

2.3.4 Non-biodegradable, Inert Organic Components

In raw wastewaters non-biodegradable inert organic matter components exist in both dissolved and suspended forms.

2.3.4.1 Inert Dissolved Organics

As shown in Figure 2.3 raw wastewaters include dissolved inert organic matter, S_{I1} in the influent. During the activated sludge process inert dissolved organics are produced, S_P (Orhon *et al.*1989, Germirli *et al.*,1991, Solfrank *et al.*,1992). As a result of this in the effluent flow dissolved organic matter is much more than the influent flow. Dissolved organic matter components in the effluent flow are given in the Figure 2.4.

$$S_{IT}=S_{II}+S_P$$

If the contents of dissolved organic matter in the influent and effluent flows are compared it will be seen that effluent content is twice bigger than influent contents (Okutman, 2001).

A good modelling approach must include the formation of inerts during the decay of the cell and hydrolysis. This approach is used in ASM 1 (Henze *et al.*, 1987, Solfrank and Gujer, 1991). Inert dissolved organics are measured as COD.

2.3.4.2 Inert Particulate Organics

This organic component is alike its dissolved part. Particulate non-biodegradable organic component is held inside the biomass in the activated sludge flocs or held in the biofilms and only removed with the sludge in the treatment process. Figure 2.5 shows the particulate COD components in the effluent flow. Some of the particulate inert components may be present in the raw wastewater and some of them are produced during the activated sludge metabolism with the suspended organics. Suspended inerts produced are related with other components remained in the endogenous decay in the ASM 1 and the amount of inert suspended matter does not change with the treatment. Inert suspended organics produced during the activated sludge metabolism are modelled as a component of net biomass decay, this value is determined as 20% by McCarty and Brodesen (1962).

An important research effort has been devoted to the assessment of the initial particulate inert organics, X_{II} : a procedure developed by Ekama *et al.* (1986), involved the analysis of a laboratory-scale completely mixed activated sludge system with a sludge age of more than 5 days, where X_{II} was calculated by comparing the measured MLVSS concentration with the computed value on the basis of process kinetics. Henze *et al.* (1987) suggested a similar approach based upon the comparison of the observed and calculated sludge production. Later, Pedersen and Sinkjaer (1992) suggested an empirical method with the assumption that X_{II} will be roughly equal to the difference between the particulate portions of the COD and the ultimate BOD in the effluent of a low-loaded activated sludge plant. Obviously, this method only provides a crude approximation, as it used BOD₅ and COD together and did not account for the particulate residual COD generated during microbial activity (Orhon *et al.*, 1999). Kappeler and Gujer (1992) defined a more elaborate method using an experimental aerobic batch reactor and an evaluation procedure based upon model simulation and curvetting but the method ignored the generation of soluble residual microbial products, directly reflecting on the magnitude of the computed X_{II} .

value. Later, Orhon *et al.* (1994) proposed another procedure involving monitoring of the particulate COD in a batch reactor, both accounting for soluble and particulate inert products.

Particulate and dissolved inert organic matter components can be determined with the experiments (Kappeler and Gujer,1992).

Determining the organic matter components, control of treatment systems and using the automation for management makes it impossible which needs much and long working. Detailed definition of organic matters in wastewaters become more important with the improvement of biological phosphorus removal directly related to Volatile Fatty Acids (VFA's). This model includes biomass which has an important effect on COD contents and organic matters. Figure 2.6 shows the real composition of raw domestic wastewater used in ASM 1 (Henze,1992).

S_I	inert	↑ Dissolved ↓	inert	10
S_S	Easily Biodegradable		Easily biodegradable	60
			Rapidly hydrolysis	100
X_S	Slowly Biodegradable	↑ Particulate ↓	Slow hydrolysis	110
			Denitrification	20
			Denitrifying heterotrophs	59
X_I	Inert Particulate	Denitrifying autotrophs	1	
		inert	40	

Total COD 400 mg/l

Figure 2.6: Detailed Fractionation of Organic Material for Domestic Sewage
(Henze, 1992)

As seen in Figure 2.6 slowly biodegradable organic matter (X_S) forms important part of the wastewater in ASM 1. In this component heterotrophic biomass forms the 1/3 of total COD. More than half of the raw wastewater is not suitable for the bacterial metabolism to take inside rapidly and a hydrolysis step becomes necessary for the oxidation.

After a detailed definition of organic matter in raw wastewaters in Activated Sludge Model No:2 different organic components are defined which makes the model more complicated. As a result of organic matters detailed separation; processes like fermentation, storing, decay, hydrolysis and growth etc. are repeated for each group

of bacteria and this puts the model in a complicated structure. As a result of this new model includes so much unknown parameters that's why this model is not useful for the practical purposes.

3. DETERMINATION OF COD COMPONENTS IN WASTEWATERS

Particulate matter forms an important fraction of the organic matter entering sewage treatment plants. Definite wastewater characteristics are usually not determined while characterizing wastewater. Expressing the quantity of organic matter as chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), total organic carbon (TOC), or volatile suspended solids (VSS) is possible. Occasionally these parameters may be distinguished as settleable/ non-settleable or filtered/unfiltered. Most of the researchs on characterizing sewage are not established on the physical separation of particles but appraise their degradation kinetics in biological attempts leading to wastewater fractions that are related for mathematical modeling (Sophonsiri *et al.*, 2003). In mathematical models, different organic fractions are defined as: readily biodegradable, slowly biodegradable, soluble non-biodegradable, and particulate non-biodegradable (Henze, 2000). Anyway, the readily and slowly biodegradable organic fractions do not certainly fit to soluble and particulate organic fractions in the wastewater (Henze, 1992) even though some correlations have been reported (Mamais *et al.*, 1993).

A detailed estimation of particle size distributions or chemical composition for the purpose of wastewater characterization is time consuming and has received only limited attention (Levine *et al.*, 1985; Raunkjaer *et al.*, 1994). According to experiences; the use of gathered parameters (e.g., total and filtered COD) are usually sufficient for design and operation. However, these gathered parameters are enough as long as there are no big changes in wastewater characteristics or the types of treatment processes applied. As long as the introduction of new processes (e.g., membrane applications in wastewater treatment) and the application of new technologies typically applied for municipal wastewater treatment to other applications (e.g., agricultural wastewater treatment) the significance of particle size and chemical composition needs to be reappraised (Sophonsiri *et al.*, 2003).

3.1 Determination of Particulate and Dissolved Inert COD Components

The amount of the total organic matter in the effluent is determined by dissolved (S_{II}) and particulate (X_{II}) inert organic matter in the influent with dissolved (S_P),

particulate (X_p) metabolic products produced during biological treatment. Especially in the high COD wastewaters dissolved inert COD plays an important limit for the discharge limits.

There are many approaches for the determination of the inert COD components in the literature. Ekama *et al.* (1986), suggested a laboratory scaled system with a sludge age of 10-20 days and told that dissolved inert COD in the effluent would be equal to inert dissolved COD in the influent.

The structure of the dissolved inert products in the effluent can not be defined exactly. According to some studies dissolved microbial products are told to be permanent in the system but according to some of the other studies these products are biodegradable but it takes long time for their biodegradation.

The majority of the methods proposed for the calculation of the initial particulate inert COD fraction in wastewaters rely on simulations and experimental verifications using newly developed multicomponent activated sludge models (Henze *et al.*, 1987; Orhon and Artan, 1994).

Dissolved inert organic matters in the influent are experimentally determined by the ways defined by Kappeler and Gujer (1992) and Orhon *et al.* (1994). This experimental study is based on the COD measurement. With this method inert organics in the influent and microbial inert products can be determined separately. Experimental studies are done with raw wastewater reactor, filtered wastewater reactor and glucose reactor which has the same COD concentration as filtered wastewater reactor has. If filtered COD concentration has a big rate in the total COD than the experiments are done with the filtered wastewater reactor and glucose reactor which has the same COD concentration as filtered reactor. Less amount of biomass (10-50mg VSS/l) is added to each reactor which are acclimated with glucose and wastewater and COD values in the reactors are observed till the COD concentrations reach to a threshold constant COD concentration. At this point total biodegradable substrate is degraded and all the biomass is mineralised. Inert COD profiles for this technic are given in the Figures 3.1 and 3.2.

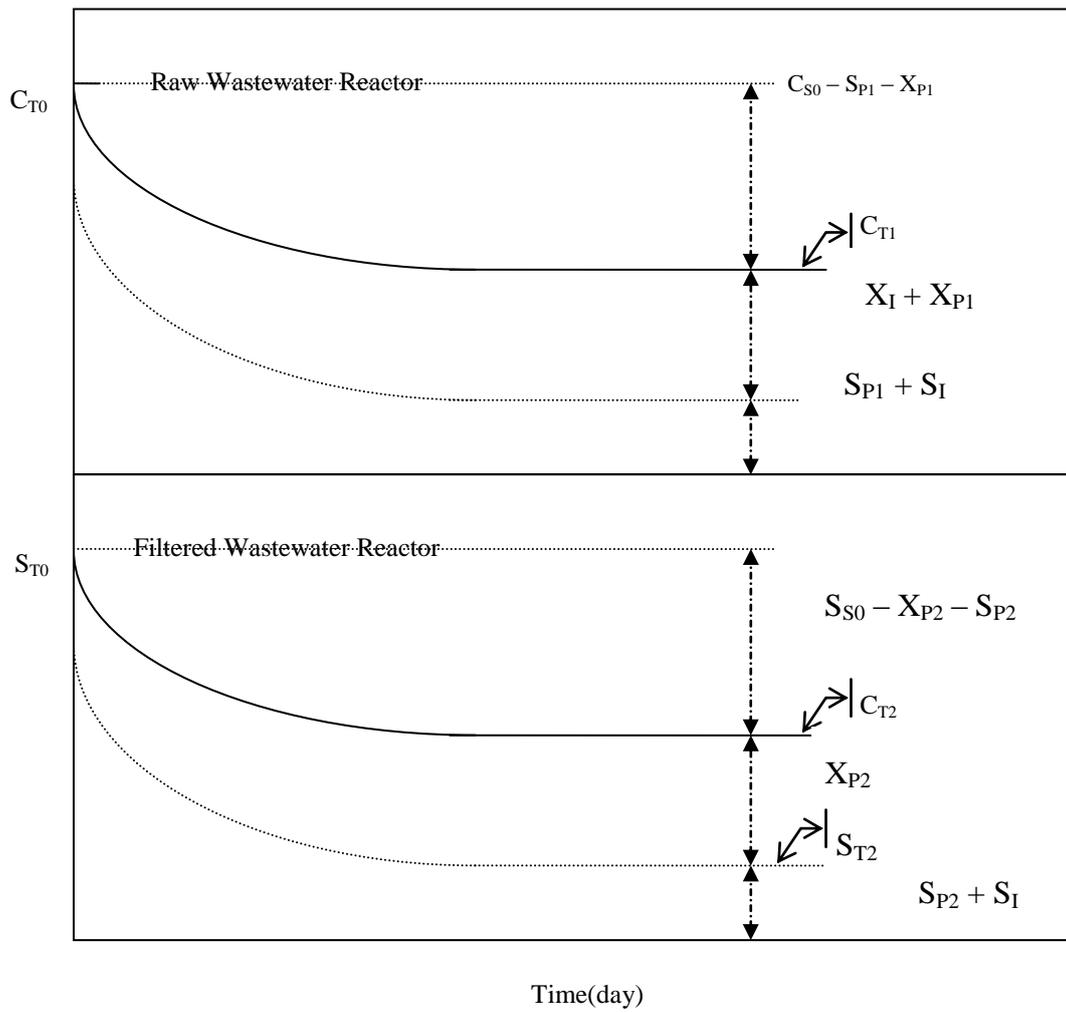


Figure 3.1: Raw Wastewater Reactor and Filtered Wastewater Reactor Inert COD Profiles

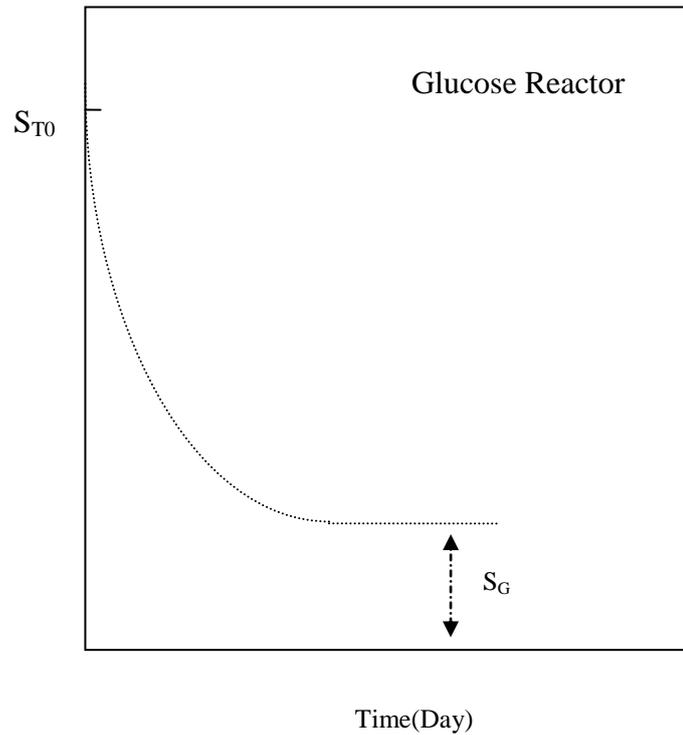


Figure 3.2: Glucose Reactor Inert COD Profile

In the glucose reactor which does not contain inert COD, remaining dissolved COD will only show the COD of dissolved metabolic products $(S_P)_G$. Then endogenous respiration biomass components converted to dissolved inert microbial product component, f_{ES} can be calculated as below;

$$Y_{SP} = \frac{(S_P)_G}{S_{G1}} \quad (3.1)$$

$$Y_{SP} = f_{ES} \cdot Y_H \quad (3.2)$$

$$Y_{SP} = \frac{(S_P)_G}{S_{G1}} = f_{ES} \cdot Y_H \quad (3.3)$$

$$f_{ES} = \frac{1}{Y_H} \frac{(S_P)_G}{S_{G1}} \quad (3.4)$$

In the filtered wastewater reactor, remaining dissolved COD under the same conditions $(S_T)_2$, will contain the inert COD in the wastewater and dissolved metabolic products $(S_P)_2$. Dissolved inert COD, S_{I1} , will be obtained with the calculations below;

$$S_{T2}=S_{P2}+S_I \quad (3.5)$$

Metabolic products formed in the system;

$$(S_P)_2=f_{ES} Y_H(S_{T1}-S_{I1}) \quad (3.6)$$

$$f_{ES} Y_H(S_{T1} - S_{I1})=(S_T)_2-S_{I1} \quad (3.7)$$

$$f_{ES} Y_H S_{T1}- f_{ES} Y_H S_{I1}=(S_T)_2-S_{I1} \quad (3.8)$$

$$S_{I1}- f_{ES} Y_H S_{I1}=(S_T)_2- f_{ES} Y_H S_{T1} \quad (3.9)$$

$$S_{I1}(1-f_{ES})=(S_T)_2- f_{ES} Y_H S_{T1} \quad (3.10)$$

Then dissolved inert COD, S_{I1} , can be calculated with the equation;

$$S_{I1}=\frac{(S_T)_2 - f_{ES} Y_H S_{T1}}{1 - f_{ES} Y_H} \quad (3.11)$$

Particulate COD remained on the reactor fed with filtered wastewater, is formed by the particulate metabolic products $(X_P)_2$ in the system. f_{EX} can be calculated with the equations below;

$$(X_P)_2= f_{EX} Y_H C_S \quad (3.12)$$

$$(X_P)_2=Y_{XP} (S_{T1}-S_{I1}) \quad (3.13)$$

$$(X_P)_2= f_{EX} Y_H C_S= Y_{XP} (S_{T1}-S_{I1}) \quad (3.14)$$

$$Y_{XP}=f_{EX} Y_H= (X_{P2})/S_{S1} \quad (3.15)$$

$$f_{EX} = \frac{1}{Y_H} \frac{(C_T)_2 - (S_T)_2}{(S_{T1} - S_{I1})} \quad (3.16)$$

In the reactor which fed with raw wastewater , the particulate COD (X_{T1}) remained in the reactor is equal to the total of particulate inert COD, X_{I1} and particulate metabolic products as a result of endogenous respiration. If $(X_T)_1$ is given as;

$$(X_T)_1 = (C_T)_1 - (S_T)_1 = X_{II} + (X_P)_1 \quad (3.17)$$

then;

$$C_{S1} = C_{T1} - X_{II} - S_{II} \quad (3.18)$$

$$(X_P)_1 = f_{EX} Y_H (C_{T1} - X_{II} - S_{II}) \quad (3.19)$$

Particulate inert COD, X_{II} ;

$$X_{II} = \frac{(X_T)_1 - f_{EX} Y_H (C_{T1} - S_{II})}{(1 - f_{EX} Y_H)} \quad (3.20)$$

can be calculated with the equation.

In this method most important coefficient is heterotrophic yield Y_H for the calculation of inert COD components. Heterotrophic yield may be different for each kind of wastewater, it may be useful to determine Y_H for the characterization.

Inert COD concentrations determined in the literature for domestic sewage is given in the Table 3.1.

Table 3.1: Determined inert COD rates for domestic sewage

Literature	S_I/C_T	X_I/C_T	f_{ES}	f_{EX}
Ubay Cokgor, 1997	0.04	0.10	-	-
Ubay Cokgor, 1997	0.04	0.06	-	-
Orhon <i>et al.</i> , 1994	0.02	0.07	-	-
Orhon and Karahan, 1999	0.07	0.03	0.13	0.23
Orhon and Karahan, 1999	0.06	0.06	0.10	0.26
Henze, 1992	0.02	0.19	-	-
Solfrank and Gujer, 1991	0.09	0.08	-	-
Ekama <i>et al.</i> , 1986	0.02	0.13	-	-

3.2 Easily Biodegradable COD, Determination of S_{S1}

Easily biodegradable COD is composed of VFA's, basic carbohydrates, alcohols, aminoacids and the components that can be directly absorbable for synthesis.

The enlarging use of treatment plant simulation models progressively generalised a improved definition of sewage organic matter into separate homogeneous compartments (Vanrolleghem *et al.*, 1999). Fractionation, based on the distinction between biodegradation kinetics, simulates nitrogen and carbon pollution removal in treatment plants (Spanjers *et al.*, 1998). It also foretells the organic matter behaviour in the receiving water body (Even *et al.*, 1998; Garnier *et al.*, 2001). As a result, respirometry has become a widely used tool, despite problems interpreting results (e.g. Spanjers *et al.*, 1998; Brouwer *et al.*, 1998; Spanjers *et al.*, 1999). The fractions corresponding to the various kinetics of degradation are only indirectly obtained by optimising the initial conditions and the model's parameters on experimental data. Modelling makes it possible to reproduce respiration rates, i.e. the conjugate of oxygen against time. Determining the fractions depends on both the model used and on the criteria of the implemented optimisation procedure, unless the characteristics of the respirogram provide for direct parameter extraction (Spanjers *et al.*, 1999).

Easily biodegradable organic matter can be determined by the respirometric measurement in continuous or batch systems under aerobic or anaerobic conditions. Respirometric methods depend on the measurement of the e^- acceptor wherever organic matter is the e^- donor. e^- acceptor (O_2) utilization rate, becomes slower after the easily biodegradable organic matter's utilization depending on organic matter's hydrolysis rate and reduces to the lower levels.

Generally e^- acceptor can be expressed as the equation below.

$$\frac{e^- \text{ acceptor quantity}}{\Delta t} = -(1-f_x Y) \frac{(C_{S0} - C_S)}{\Delta t} - (1-f_E).b.f_x.X \quad (3.21)$$

First term in the right side of the equation shows growth, second term shows endogenous respiration. In this equation;

Y= Yield (mg VSS/mg COD)

b= Endogenous decay rate (1/day)

f_E = Inert biomass component

$f_x = \text{COD/VSS}$

$X = \text{Active biomass concentration}$

$C_{S1} = \text{Biodegradable organic matter in the influent flow (mg/l COD)}$

$C_S = \text{Biodegradable organic matter in the effluent flow (mg/l COD)}$

Change of oxygen under aerobic conditions during time;

$$\frac{\Delta S_l}{\Delta t} = -(1 - f_x Y_H) \frac{C_{S1} - C_S}{\Delta t} - (1 - f_E) b_H f_x X_H \quad (3.22)$$

Ekama *et al.*, (1986) improved a respirometric method which measures Oxygen Utilization Rates (OUR) per time in batch reactor under aerobic or anoxic conditions.

The equations below were written with the approval of heterotrophic microorganisms growth on easily biodegradable substrate.

$$\frac{dX_H}{dt} = \mu_H \cdot X_H \quad (3.23)$$

$$\frac{dX_H}{dt} = Y_H \frac{dS_S}{dt} \quad (3.24)$$

With the help of the equations 3.23 and 3.24;

$$\frac{dS_S}{dt} = \frac{1}{Y_H} \mu_H X_H \quad (3.25)$$

is obtained.

$$\frac{dS_S}{dt} = \frac{C_{S1} - C_S}{\Delta t} \quad (3.26)$$

$$\frac{C_{S1} - C_S}{\Delta t} = \frac{1}{Y_H} \mu_H X_H \quad (3.27)$$

If we join the equations 3.22 and 3.27;

$$\frac{\Delta S_1}{\Delta t} = -\frac{(1-f_x Y_H)}{Y_H} \mu_H X_H - (1-f_E).b_H.f_x.X_H \quad (3.28)$$

equation is obtained.

In this method OUR profile goes on horizontal over the S_S during growth, easily biodegradable COD, to the end of this S_S rate slows down. Second plateau is seen during hydrolysis (Figure 3.3).

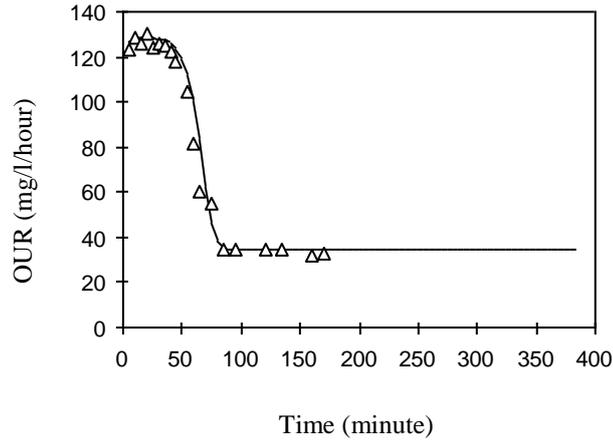


Figure 3.3: OUR Profile

At the start of the experiment with the approval of easily biodegradable organic matters' utilization in Δt time equations below can be written;

$$\frac{\Delta S_1}{\Delta t} \cong -\frac{(1-f_x Y_H)}{Y_H} \mu_H X_H \quad (3.29)$$

$$\text{OUR} = -\frac{\Delta S_0}{dt} \quad (3.30)$$

Joining these two equations together;

$$\text{OUR} = (1-f_x Y_H) \mu_H X_H \quad (3.31)$$

From the equations 3.27 and 3.31;

$$\text{OUR} \cong (1-f_x Y_H) \frac{C_{S1} - C_S}{\Delta t} \quad (3.32)$$

is obtained.

$$\text{OUR} = \frac{\text{OU}}{\Delta t} \quad (3.33)$$

If equations 3.26, 3.32 and 3.33 are joined together;

$$\frac{\text{OU}}{\Delta t} = (1 - f_X Y_H) \frac{dS_s}{dt} \quad (3.34)$$

$$\text{OU} = (1 - f_X Y_H) \int_0^t \frac{dS_s}{dt} \Delta t \quad (3.35)$$

$$\frac{\text{OU}}{1 - f_X Y_H} = \int_0^t \frac{dS_s}{dt} \Delta t \quad (3.36)$$

$$S_{s1} = \frac{\Delta O}{1 - f_X Y_H} \quad (3.37)$$

then equation 3.37 is found. ΔO value shows the area under the OUR profile in the Figure 3.3.

Easily biodegradable organic matter S_{s1} concentrations for domestic sewage reported in literature are given in the Table 3.2.

Table 3.2: Easily biodegradable organic matter concentrations reported in literature

Literature	C_T	S_{S1}	S_{S1}/C_T
Ubay Cokgor, 1997 (Kadikoy)	594	50	0.09
Ubay Cokgor, 1997 (Fethiye)	227	35	0.15
Ubay Cokgor, 1997 (Marmaris)	370	38	0.10
Ubay Cokgor, 1997 (Bodrum)	430	16	0.01
Ubay Cokgor, 1997 (Tuzla)	608	50	0.11
Ekama <i>et al.</i> , 1986	530		0.20
Henze, 1992			0.20
Solfrank and Gujer, 1991	320	45	0.14
Sozen, 1995	605	54	

PSD based COD fractionation can complete the missing parts of the currently used respirometric tests for biodegradability. Generation of the soluble microbial products could be better understood with the method of PSD-based COD fractionation which should be a part of all modeling efforts (Dulekgurgen *et al.*, 2006).

3.3 Determination of Slowly Biodegradable Dissolved COD (S_{H1}) and Particulate COD (X_{S1}) Components

In current time for Activated Sludge Models it is accepted that slowly biodegradable organic matter is reduced to easily biodegradable substrate with the hydrolysis process and growth process is accepted to continue like this.

Slowly biodegradable organic matter is composed of two parts as dissolved (S_{H1}) and particulate (X_{S1}).

Organic matter quantity measured in the filtered wastewater is composed of dissolved components then dissolved wastewater components can be given as below;

$$S_{T1} = S_{S1} + S_{H1} + S_I \quad (3.38)$$

Then S_H ;

$$S_{HI} = S_{T1} - S_{S1} - S_I \quad (3.39)$$

slowly biodegradable organic matter can be calculated by this way (Ubay Cokgor, 1997).

Components in the total raw wastewater can be given as below;

$$C_{T1} = S_{S1} + S_{HI} + S_I + X_{S1} + X_I \quad (3.40)$$

If the equations 3.38 and 3.40 are written together;

$$C_{T1} = S_{T1} + X_{S1} + X_I \quad (3.41)$$

equation is obtained. Then X_{S1} ;

$$X_{S1} = C_{T1} - (S_{T1} + X_I) \quad (3.42)$$

can be calculated.

4. MATERIALS AND METHODS

4.1 Preparation of the Experimental Programme

1. Collecting the studies from literature about domestic wastewater.
2. Choosing the wastewater treatment plant where the wastewater characterization and particle size distribution based COD fractionation will be determined.
3. Determining the sample intake point.
4. Determining the daily composite sample intake way.
5. Preparation of the experimental programme
6. Intake of the composite samples
7. Conventional Characterization of the samples
8. Determining the inert COD components
9. Sequential filtration/ultrafiltration and COD experiment of the filtrates
10. Oxygen Utilization Rates (OUR) analyses
11. Determination of S_p production
12. Correlation of the COD fractionation and Particle Size Distribution with the results achieved

4.2 Materials and Methods

Experiments were done on the composite samples taken from the influent and effluent of the wastewater treatment plant. Composite samples were taken as two sets

under winter conditions between 10.30 am and 3.30 pm which is quite representative of the wastewater character.

The conventional biological WWTP in Ataköy-Istanbul, is serving an entirely residential area. Ataköy WWTP (Orhon *et al.*, 1997; Okutman, 2001; Dulekgurgen *et al.*, 2006) was well studied previously regarding conventional wastewater characterization, as well as biological treatment applications.

Ataköy WWTP has a trickling filter system so that results obtained from the effluent flow of the system must be evaluated under this knowledge

4.2.1 Conventional Characterization

Conventional analyses were performed in duplicates and as described in the Standard Methods (APHA *et al.*, 1998), except for COD measurements, which were performed in duplicates and in accordance with the International Standard ISO 6060 (International Organization for Standardization, 1986). Millipore AP40 glass fiber filters with an effective pore size of approximately 1200~1600 nm were used for the measurement of suspended solids (SS) and volatile suspended solids (VSS).

4.2.2 Determination of Inert COD

With the aim of determining dissolved inert COD and particulate inert COD in domestic wastewater; a volumetric capacity of 3 liters reactors for raw wastewater, filtered wastewater and a glucose reactor which has an equivalence COD to the COD of filtered wastewater were set up and in COD parameters were followed over the time for these reactors. The test was conducted for a long time to enable the depletion of all biodegradable organics and mineralization of biomass.

For the determination of inert components of the wastewater biomass used in reactors were fed with the %50 glucose and %50 wastewater composition with an equivalent COD value. About 30 mg/l VSS acclimated biomass were added to the reactors. Formula 2533 (HACH Company) inhibitor was added to the reactors to prevent the possible nitrification.

Solution A and Solution B with a content given in the Table 4.1 were added to the glucose reactor to dispel the absence of the nutrient and trace material. Each of the three reactors were aerated at the same time for 45 days and their total and filtered COD were followed over the time.

Table 4.1: Components of Solution A and Solution B

Solution B	MnSO ₄ .3H ₂ O	0.5 g/l
	ZnSO ₄ .7H ₂ O	0.5 g/l
	FeSO ₄ .7H ₂ O	0.5 g/l
	MgSO ₄ .7H ₂ O	15 g/l
	CaCl ₂	2 g/l
Solution A	K ₂ HPO ₄	320 g/l
	KH ₂ PO ₄	160 g/l
	NH ₄ Cl	120 g/l

4.2.3 Sequential Filtration/Ultrafiltration

All filtration/ultrafiltration experiments were conducted 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 75 mL permeate was concluded to be enough to run COD experiments with two copies. Samples were filtered serially through conventional filters with pore sizes of 1200~1600 nm (Millipore AP40, glass fiber), 450 nm (Durapore[®] HV, polyvinylidene fluoride [PVDF]), and 220 nm (Durapore[®] GV, PVDF) (Millipore Corp., Bedford, MA 01730). Advised differential gas pressure in the manual is 0.7 atm and maximum temperature limit is +85 °C for the Durapore disposable filters. The pressure was hold about 0.35 atm as the filtration experiments were done 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 for all ultrafiltration membranes, recommended is +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 done at room temperature and at a pH range of 7.2-8.8. The pressure referred to the 100 kDa ultrafiltration membrane discs was 0.6 atm, and to the others was 1.2 atm. Figure 4.1 is the schematic presentation of the applied sequential filtration/ultrafiltration procedure.

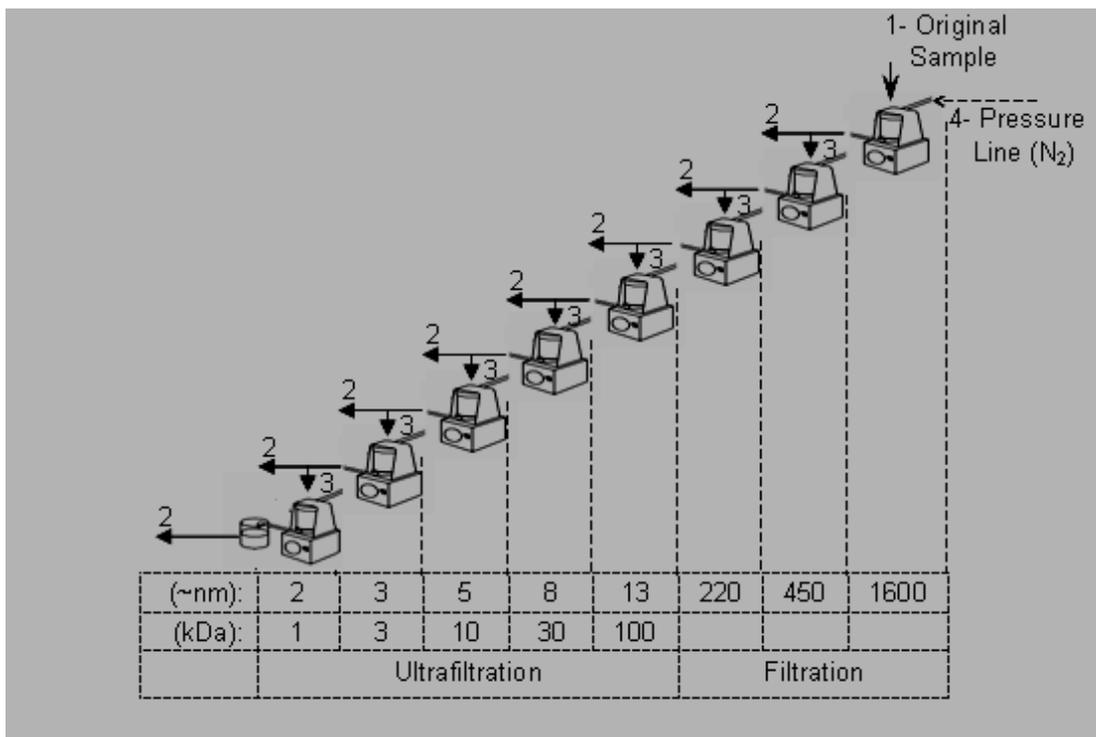


Figure 4.1: The schematic presentation of the applied sequential filtration/ultrafiltration procedure.

According to Figure 4.1 number one represents the non-settled, non-filtered but mixed original sample, number 2 represents aliquot of the filtrate from the previous step for COD experiments, number 3 represents aliquot of the filtrate from the previous step for the next filtration/ultrafiltration steps, number 4 represents N₂ gas line for the positive pressure.

Filtration/ultrafiltration has been used as an analytical tool in this study, and done as batches of 5 to 150 minutes, depending on the selected filter size. As expressed before, the filtrate volumes collected were very small (adjusted to obtain a final volume of 75 mL permeate after filtering through the last membrane disc) to allow for the analytical COD measurements and for enduring with the following filtration/ultrafiltration steps. All cleaning (consecutive washes with dI water, 70% ethanol, and finally 2 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 performed before and after filtering the samples, to be sure that there is no sign of fouling or effects like that were discovered through the flow-rate profiles.

4.2.4 Oxygen Utilization Rate (OUR) Analyses

OUR analyses were executed on Manotherm RA 1000 respirometry device.

A series of experiments was performed, primarily for the differentiation of the soluble COD (S_T) fractions of the influent entering to the on-site biological WWTP of the domestic sewage. The soluble readily biodegradable COD, S_S , was determined in accordance with the respirometric technique defined by Ekama *et al.* (1986).

RA 1000 respirometry device is composed of a 5 liters plexi-glass main reactor and a cell where OUR is measured.

The subjects that need attention while measuring;

- Aeration and mixing conditions must be enough in the main reactor
- Effluent oxygen value must be bigger than 2 mg/l
- No air bubble in the respiration cell
- Period time over the sample pump (46-48)
- Circulation pump is working on the respiration cell
- Control of pH and temperature.

Respirometric measurement principle; taking the sample from a mixed aerated main reactor to a mixed and a full cell than the measurement of the influent and effluent oxygen concentrations. Respiration rates;

$$r_t = \frac{Q}{V}(C - y) \text{ [mg/ lt / hr]} \quad (4.1)$$

can be calculated with the formula above.

r_t = respiration rate at the t moment [mg O₂/ lt / hr]

Q = flow rate of the sample [lt/hr]

V = cell volume [lt]

C(t) = Oxygen concentration at the t moment in the influent [mg/lt]

y(t+th) = Effluent concentration at the t+th moment [mg/lt]

t_h = HRT of the sample in the cell [s]

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). Activated sludge has been aerated for a few minutes before the wastewater addition to prevent the sudden fall in the oxygen concentration.

Heterotrophic biomass used in the respirometric measurements acclimated with domestic wastewater and fed as F/M 0,184 mg COD/mg VSS in the fill and draw reactors with a sludge age of (Θ_x) 20 days under laboratory conditions.

4.2.5 Determination of Soluble Microbial Products

Biomass was fed with 1 lt domestic wastewater in a batch reactor that the reactor's F/M became 0.135 mg COD/mg VSS. At the same moment aeration and mixing of reactor had started. Samples were taken from the mixture of the reactor then filtered with 450 nm filters. COD measurements were executed on the filtrates of 450 nm membranes. Samples were taken at the periods which were determined before and which are representative of the soluble microbial products.

5. RESULTS AND DISCUSSIONS

5.1 Conventional Characterization

5.1.1 SET 1

The results of the conventional characterization of the domestic sewage for set 1 (18.01.2006) determined in this study are summarized in Table.5.1.

The COD of the raw wastewater is 415 mg/l, suspended solids concentration is 305 mg/l, TKN of the raw wastewater is 42 mg/l and TP of the wastewater is 8 mg/l. According to influent wastewater characterization; total COD, VSS, TKN and TP of the wastewater is in the medium concentration and has a neutral pH.

Table 5.1: Conventional characterization of domestic sewage (SET 2)

Parameter	Unit	SET.1 (18.01.2006)	
		Influent	Effluent
		Value	Value
Total COD	mg L ⁻¹	415	130
Settled COD	mg L ⁻¹	305	
Filtered (1600 nm) COD	mg L ⁻¹	145	100
Filtered (450 nm) COD	mg L ⁻¹	120	80
SS	mg L ⁻¹	180	25
VSS	mg L ⁻¹	165	25
TDS	mg L ⁻¹	1185	1345
TKN	mg L ⁻¹	42	30
NH ₃ -N	mg L ⁻¹	25	25
TP	mg L ⁻¹	8	4
pH	---	7.7	8.0
Alkalinity	mgCaCO ₃ L ⁻¹	400	385
Chloride	mg L ⁻¹	430	500

5.1.2 SET 2

The results of the conventional characterization of the domestic sewage for set 2 (23.03.2006) determined in this study are summarized in Table 5.2.

The COD of the raw wastewater is 340 mg/l, suspended solids concentration is 155 mg/l, TKN of the raw wastewater is 38 mg/l and TP of the wastewater is 7 mg/l. According to influent wastewater characterization; VSS, TKN and TP of the

wastewater is in the medium concentration, total COD is in the weak concentration and has a neutral pH.

Table 5.2: Conventional characterization of domestic sewage (SET 2)

Parameter	Unit	SET.2 (23.03.2006)	
		Influent	Effluent
		Value	Value
Total COD	mg L ⁻¹	340	95
Settled COD	mg L ⁻¹	225	
Filtered (1600 nm) COD	mg L ⁻¹	115	80
Filtered (450 nm) COD	mg L ⁻¹	100	70
SS	mg L ⁻¹	155	30
VSS	mg L ⁻¹	145	30
TDS	mg L ⁻¹	1265	1320
TKN	mg L ⁻¹	38	25
NH ₃ -N	mg L ⁻¹	20	19
TP	mg L ⁻¹	7	4
pH	---	7.4	7.7
Alkalinity	mgCaCO ₃ L ⁻¹	375	365
Chloride	mg L ⁻¹	410	455

5.1.3 Comparison with the Previous Studies

The results of conventional characterization for the domestic sewage samples, determined in this study and reported in the previous ones, are summarized in

Table.5.3 The domestic sewage was also characterized in two studies (Orhon *et al.*, 1997; Okutman, 2001). The average values determined by both Okutman (2001) and Orhon *et al.* (1997) for the same domestic sewage agree with the ones reported for the domestic wastewaters entering to the other major conventional biological WWTPs in Istanbul (Orhon *et al.* 1997).

Comparative evaluation of the values presented in Table 5.3 clearly reveals that the samples evaluated in this study are quite representative, since their conventional characteristics, updated here, are reasonably close to the average characteristics reported in the previous studies of Orhon *et al.* (1997) and Okutman (2001).

Table 5.3: Conventional Characterization of the Domestic Sewage

Parameter	Unit	Previous Studies			This Study			
		Influent		Effluent	Influent		Effluent	
		Range	Average		Value	1 st Sample	2 nd Sample	1 st Sample
Total COD	mg L ⁻¹	295-535	406	440	415	340	130	95
Settled COD	mg L ⁻¹			340	305	225		
Filtered (1600 nm) COD	mg L ⁻¹			155	145	115	100	80
Filtered (450 nm) COD	mg L ⁻¹	70-147	107	115	120	100	80	70
SS	mg L ⁻¹	122-247	190	180	180	155	25	30
VSS	mg L ⁻¹	118-227	178	160	165	145	25	30
TDS	mg L ⁻¹	2600-3300	2874		1185	1265	1345	1320
TKN	mg L ⁻¹	36-47	41		42	38	30	25
NH ₃ -N	mg L ⁻¹	19-34	27		25	20	25	19
TP	mg L ⁻¹	6-12	8		8	7	4	4
pH	-	7.2-7.9	7.6	7.2	7.7	7.4	8.0	7.7
Alkalinity	mgCaCO ₃ L ⁻¹			400	400	375	385	365
Chloride	mg L ⁻¹	400-450	450	430	430	410	500	455

5.2 Sequential Filtration/Ultrafiltration for PSD-Based COD Fractionation

The results obtained for the PSD-based COD fractionation are outlined in tables. In these tables, the cumulative values for a given filter size reflect the COD of the filtrate and this way, each of them defines the total COD below the selected filter size. The differential COD, between the two consecutive filter sizes, might then be obtained as the difference of the two corresponding absolute 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.

5.2.1 SET 1

Table 5.4: Size distribution of the COD content of domestic sewage (SET 1)

Separation Technique	18.01.2006 (Set 1)			
	Cumulative COD (mg L ⁻¹)		Differential COD (mg L ⁻¹)	
	Influent	Effluent	Influent	Effluent
<i>Total</i>	415	130		
<i>Filtration</i>				
AP40 filter	145	100	270	30
HV filter	120	80	25	20
GV filter	115	60	5	20
<i>Ultrafiltration</i>				
100 kDa	85	50	30	10
30 kDa	65	45	20	5
10 kDa	60	35	5	10
3 kDa	50	25	10	10
1 kDa	40	20	10	5
			40	20

Results for the sequential filtration/ultrafiltration studies for set 1 presented in Table 5.4. According to Table 5.4 bulk of the COD for influent flow is in the particulate form.

5.2.2 SET 2

Results for the sequential filtration/ultrafiltration studies for set 2 presented in Table 5.5. According to Table 5.5 bulk of the COD for influent flow is in the particulate form.

Table 5.5: Size distribution of the COD content of domestic sewage

Separation Technique	23.03.2006 (Set 2)			
	Cumulative COD (mg L ⁻¹)		Differential COD (mg L ⁻¹)	
	Influent	Effluent	Influent	Effluent
<i>Total</i>	340	95		
<i>Filtration</i>				
AP40 filter	115	80	225	15
HV filter	100	70	15	10
GV filter	90	60	10	10
<i>Ultrafiltration</i>				
100 kDa	75	50	15	10
30 kDa	60	45	15	5
10 kDa	50	40	10	5
3 kDa	40	25	10	15
1 kDa	35	20	5	5
			35	20

5.2.3 Comparison with the Previous Studies

The PSD-based COD fractionation obtained for domestic sewage is plotted in Figures 5.1 and 5.2, which provide a clear indication that the COD variation according to different size categories exhibits similar trends for the domestic sewage.

The bulk (around 65%) of the COD in domestic sewage consists of particulate organic matter (1600 nm) and only about 15% is soluble (<2 nm). This COD profile is in agreement with some of the values summarized by Dulekgurgen *et al.* (2006).

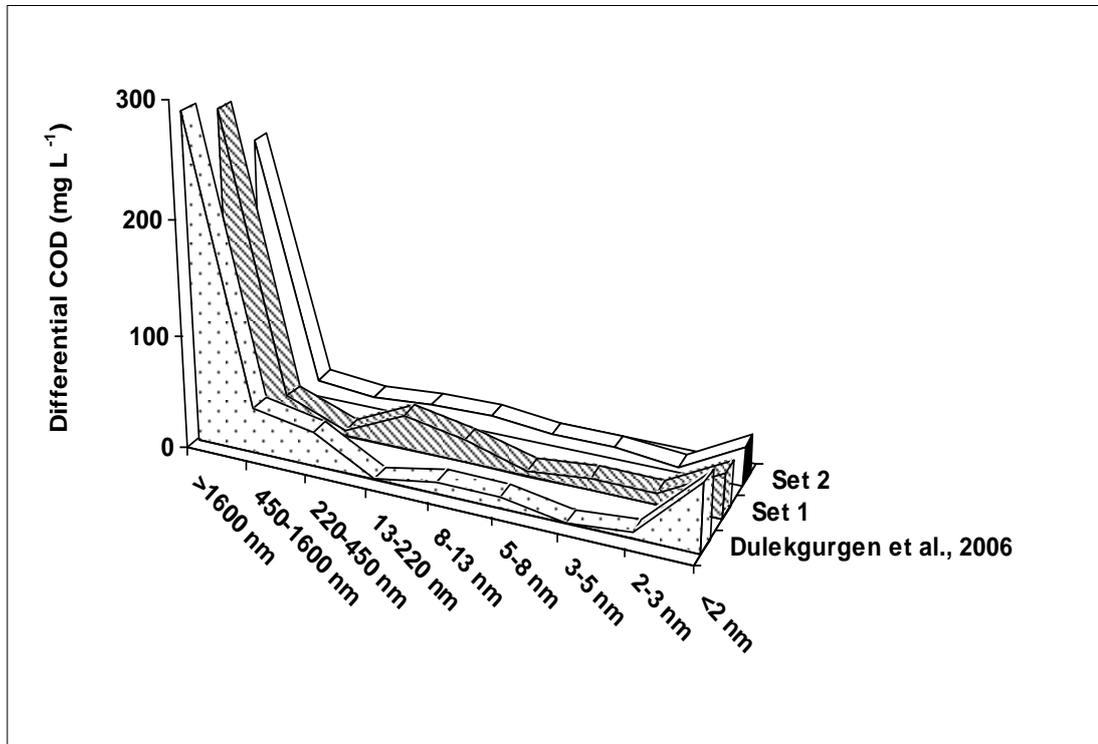


Figure 5.1: Fingerprints of the domestic sewage samples based on differential COD values for selected particle size categories

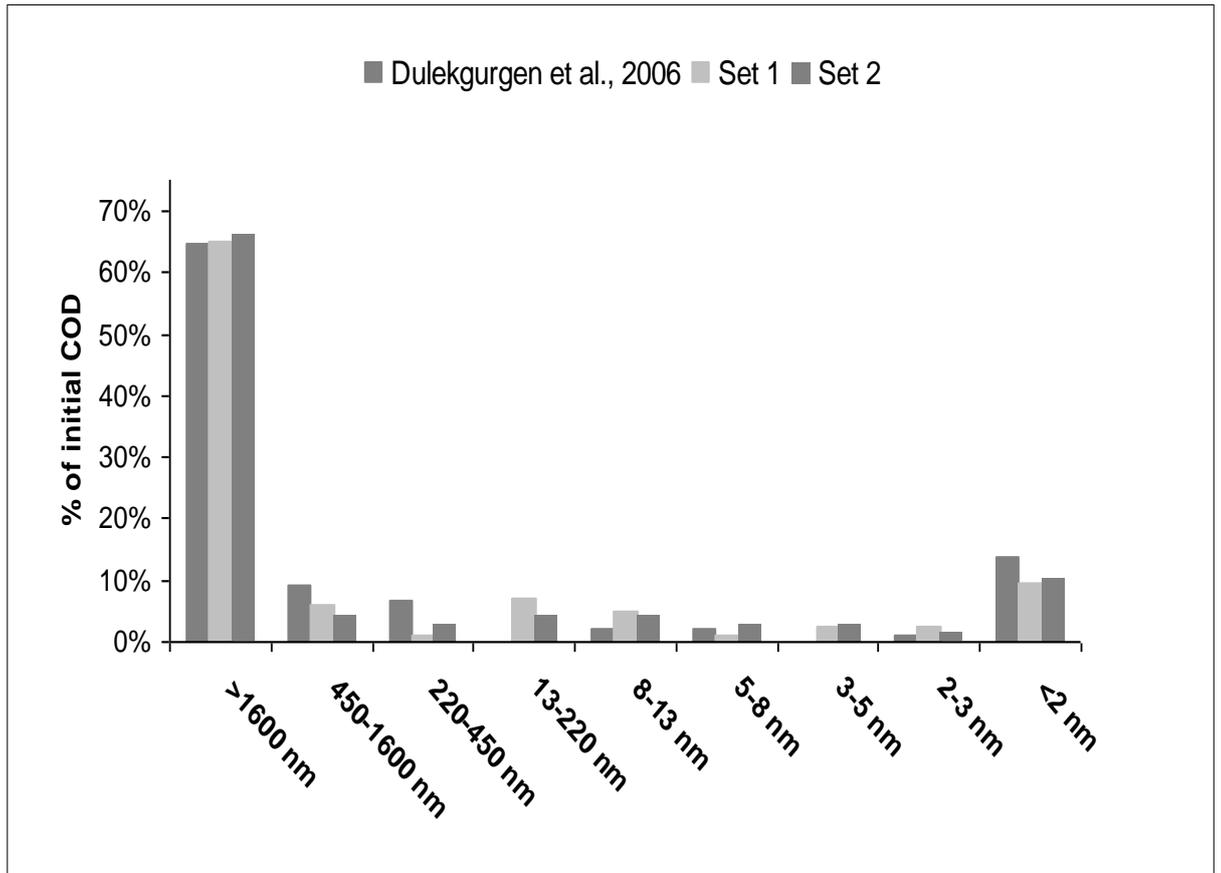


Figure 5.2 Percent distribution of COD fractions for domestic sewage samples

5.3 Determination of Inert COD

5.3.1 SET 1

Inert COD components of the domestic sewage were determined with the method proposed by Orhon *et al.* (1991).

According to the results of the experiments particulate inert COD value for raw domestic sewage is 45 mg/l and dissolved inert COD is 15 mg/l.

The experiments were carried on till the COD values of the reactors have a stationary value for the aim of determination of the inert COD components in raw domestic sewage. COD results are given in the Figures 5.3 and 5.4

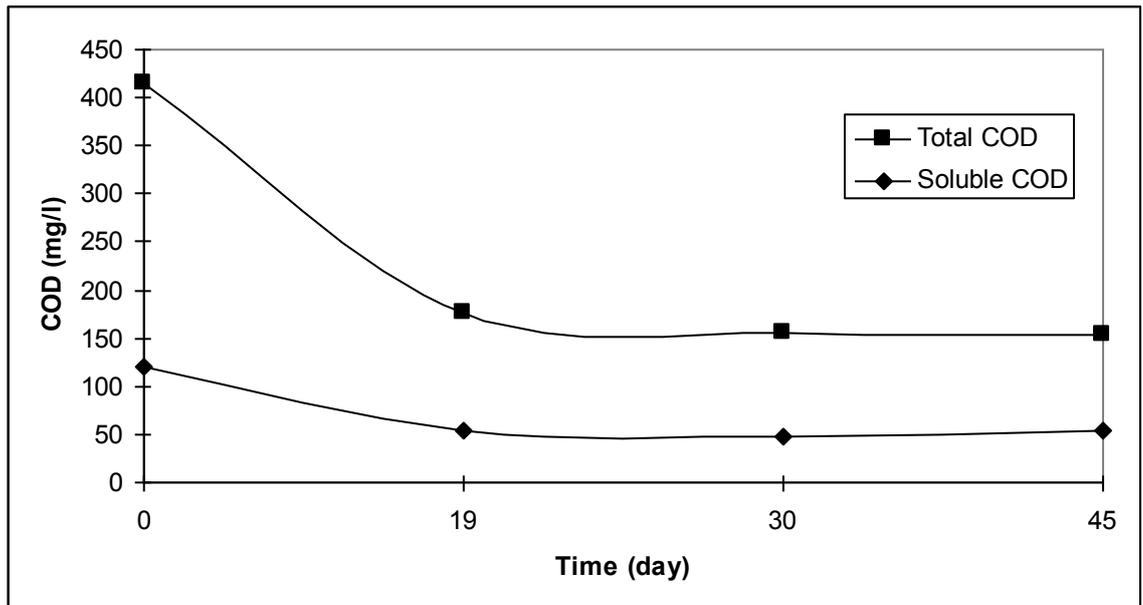


Figure 5.3: COD Profile for the reactor fed with total wastewater

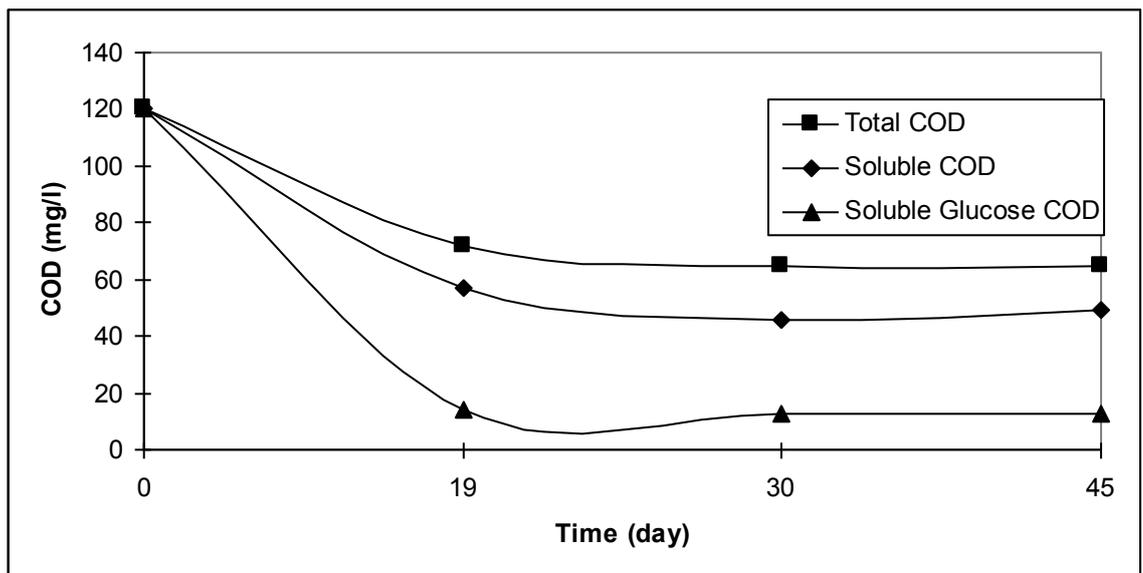


Figure 5.4: Profile for the reactors fed with filtered wastewater and glucose

Experimental datas and calculation method used for determination of inert COD components for domestic sewage are given below;

$$Y_H = 0.67 \text{ g COD/g COD}$$

$$S_{T1} = 120 \text{ mg/l}$$

$$(S_T)_2 = 26 \text{ mg/l}$$

$$(S_P)_G = 13 \text{ mg/l}$$

$$S_G = 120 \text{ mg/l}$$

$$(C_T)_2 = 65 \text{ mg/l}$$

$$(C_T)_1 = 415 \text{ mg/l}$$

$$Y_{SP} = \frac{(S_P)_G}{S_{G1}} = 0.108$$

$$f_{ES} = \frac{(S_P)_G}{S_{G1}} \cdot \frac{1}{Y_H} = 0.161$$

$$S_{II} = \frac{(S_T)_2 - f_{ES} \cdot Y_H S_{T1}}{1 - f_{ES} \cdot Y_H} = 15 \text{ mg/l}$$

$$X_{P2} = (C_T)_2 - (S_T)_2 = 16 \text{ mg/l}$$

$$S_{S1} = S_{T1} - S_{II} = 105 \text{ mg/l}$$

$$Y_{XP} = \frac{(X_P)_2}{S_{S1}} = 0.151$$

$$f_{EX} = \frac{1}{Y_H} \cdot \frac{(C_T)_2 - (S_T)_2}{S_{T1} - S_{II}} = 0.22$$

$$X_{T1} = (C_T)_1 - (S_T)_1 = X_{II} + (X_P)_1 = 101 \text{ mg/l}$$

$$X_{II} = \frac{X_{T1} - f_{EX} \cdot Y_H (C_{T1} - S_{II})}{1 - f_{EX} \cdot Y_H} = 45 \text{ mg/l}$$

5.3.2 Comparison with the Previous Studies

The results of inert COD experiments of the domestic sewage samples, determined in this study and reported in the previous one, are summarized in Tables 5.6 and 5.7. % COD fractionation of the domestic sewage found in this study and Okutman's(2001) study are summarized in Tables 5.6 and 5.7. From these results it is seen that both of the experimental results for the same domestic sewage are very similar.

Table 5.6: COD Fractions of Domestic Sewage

	COD Fractions (mg/l)						
	C _T	S _T	X _T	S _S + S _H	S _I	X _S	X _I
This Study	415	120	295	105	15	250	45
Okutman,2001	425	120	305	110	10	265	40

Table 5.7 % Fractions of Domestic Sewage

	COD Fractionation (%)						
	C _T	S _T	X _T	S _S + S _H	S _I	X _S	X _I
This Study	100	29	71	25	4	60	11
Okutman,2001	100	28	72	26	2	63	9

5.4 Oxygen Utilization Rate (OUR) Analyses

Oxygen Utilization Rate (OUR) analyses were executed with a F/M ratio of 0.184 gCOD/gVSS for raw wastewater and 0.044 gCOD/gVSS for AP 40 filtered wastewater. Readily biodegradable organic matter (S_S) has been calculated as 20 mg/l with the method of Ekama *et al.*(1986). In these calculations Y_H was chosen as 0.67 gcellCOD/gCOD for domestic sewage. The figures of OUR analyses are given in the Figure 5.5, Figure 5.6 and Figure 5.7 and related calculations are given below them.

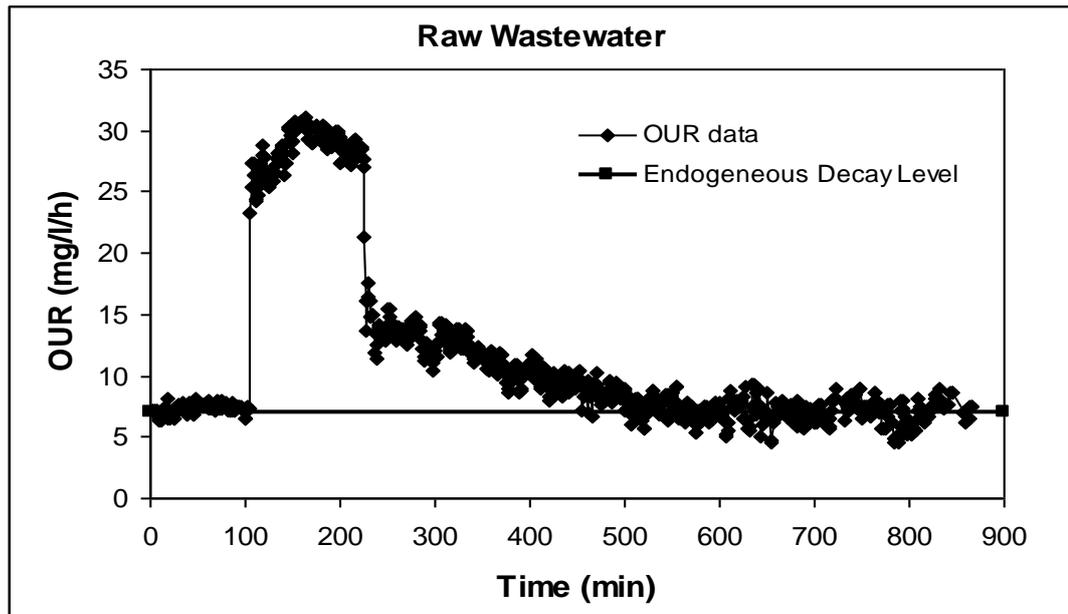


Figure 5.5: OUR profile evaluated for raw wastewater.

Assuming Y_H as 0.67 gCOD/gCOD,

Net oxygen consumption is 63.2 mg/l,

Total Biodegradable COD= C_S = 287 mg/l

Total Inert COD = C_I = 340-287 = 53 mg/l

CS = [Net oxygen consumption/ (1- Y_H)]*(2000 ml/1250ml)

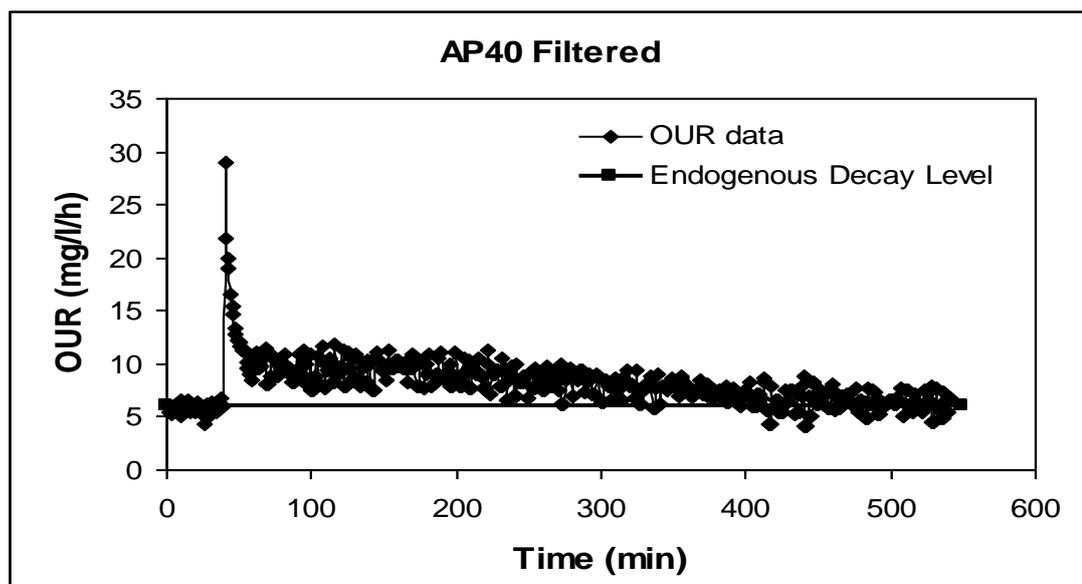


Figure 5.6: OUR profile evaluated for AP40 filtered wastewater

Assuming Y_H as 0.67 gCOD/gCOD,

Then net oxygen consumption is 12.2 mg/l

Total soluble biodegradable COD calculated as, $C_s = 93$ mg/l.

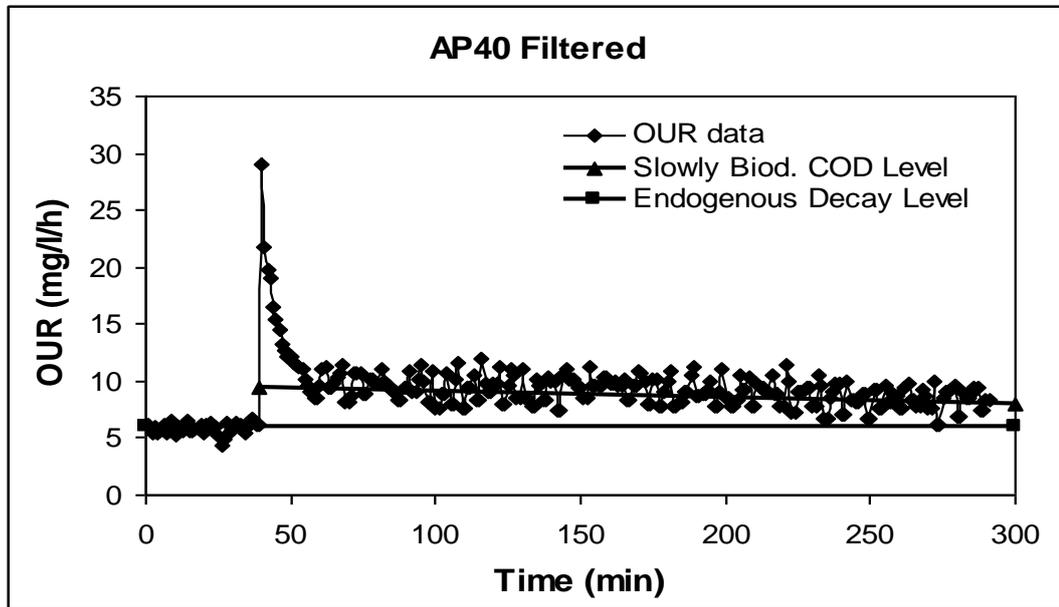


Figure 5.7: OUR profile evaluated for AP40 filtered wastewater (Determination of S_s)

Net oxygen consumption is 2.6 mg/l,

Then readily biodegradable COD = $S_s = 20$ mg/l

Total soluble COD = 115 mg/l

Soluble Inert COD = $S_I = 115 - 93 = 22$ mg/l

Particulate Inert COD = $X_I = C_I - S_I = 53 - 22 = 31$ mg/l

5.5 Determination of Soluble Microbial Products

Atakoy WWTP has a trickling filter system so that it was not going to be possible to evaluate the soluble microbial production of this system with an activated sludge system. This experiment was done to see the soluble microbial production if Atakoy had an activated sludge system. According to the COD results shown in Table 5.8 and in Figure 5.7, it can be seen that the content of soluble microbial products is about 20 mgCOD/l for raw domestic wastewater which has a total COD concentration of 540 mg/l.

Table 5.8: Production of S_p

SAMPLE	COD (mg/L)
RAW	540
0,45 μm	130
0'	130
10'	110
20'	95
30'	80
60'	60
120'	50
180'	40
240'	35
300'	30
360'	31
1440'	52
1680'	49

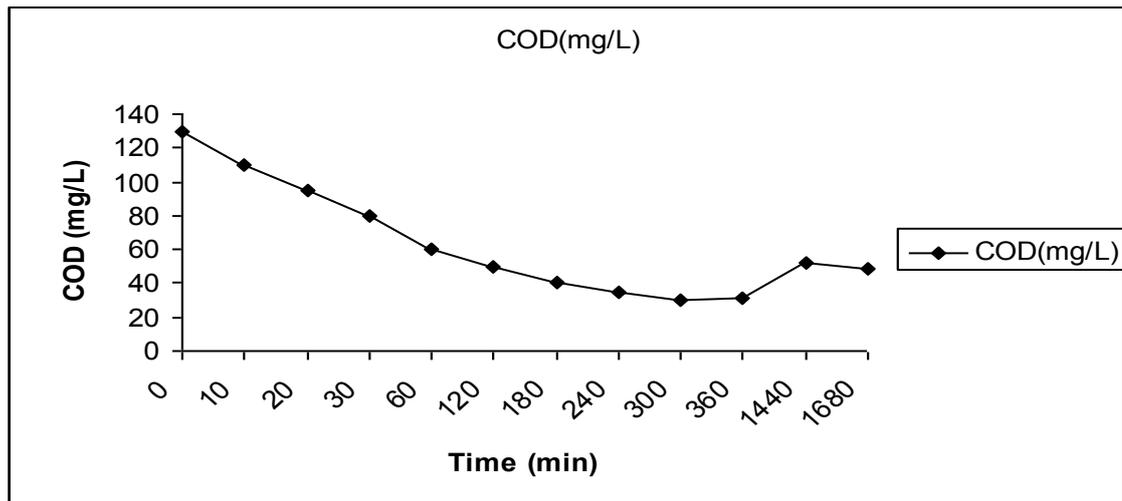


Figure 5.8: Production of S_p

6. EVALUATION

In the designing of treatment systems, wastewater characterization is one of the most important steps from the view of biological treatment. This characterization study is composed of determination of parameters which are important for biodegradability, COD fractions, kinetic and stoichiometric coefficients.

In this study characterization study performed on the same domestic sewage for two sets from the influent of the WWTP and the effluent flow of the WWTP as composite samples. The first sample was taken on 18.01.2006 and the second sample was taken on 23.03.2006 both representing the winter conditions.. Apart from these characterization studies, COD fractions have been profoundly observed. Sequential filtration/ultrafiltration has been used as a physical segregation tool. It also explores the correlation between particle size distribution (PSD) and COD fractionation, as an index for biological treatability. Profiles obtained through PSD based-COD fractionation serve as the fingerprints for domestic wastewater. PSD-based COD fractionation profiles identify the soluble range below 2 nm as the size interval housing both the soluble inert COD initially present in the wastewater and soluble inert microbial products generated during biological treatment as also supported by the metabolic fractionation attained through the respirometric analyses and the inert COD determination with the method proposed by Orhon *et al.* (1999)

Conventional characterization for domestic sewage for this study is in agreement with the results reported in the literature.

For the COD fractionation of domestic sewage reported in the literature it is seen that S_I/C_T is between 0.02-0.20, S_S/C_T is between 0.04-0.32, X_S/C_T is between 0.24-0.79 X_I/C_T is between 0.08-0.17. The COD fractions found in this study are; $S_I/C_T=0.04$ and 0.06, $S_S/C_T=0.06$, $X_S/C_T=0.6$ and $X_I/C_T= 0.09$ and 0.10. These results show that COD fractionation of this study is quite representative.

The sum of S_S+S_I (mg COD/l) is approximately the same as the COD (mg/l) value of filtrate of the 2 nm membrane. As described before filtrate of 2 nm sewage is in the soluble form and we can see that S_S and S_I is in the soluble form for domestic sewage which is in agreement with Dulekgurgen *et al.* (2006) for textile wastewater.

Set 3 was executed to determine the S_p production of final sewage sample. Biomass was fed with domestic sewage and it was found that steady state conditions achieved after 30 hours corresponding to 20 mg/l of S_p production.

Atakoy WWTP has a trickling filter system and the effluent COD according to Set 1 is 130 mg COD/l. According to COD fractionation for this study it can be seen that if Atakoy WWTP was operated with an activated sludge system then the effluent COD would be around 50 mgCOD/l.

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