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EVALUATION OF TOC CONCEPT IN INDUSTRIAL WASTEWATER AT SART AS

Master in Environmental Technology - Specialization
Water Science and Technology

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ABSTRACT

Approximately 98 % of the industrial wastewater that SART receives comes from offshore activities. Unlike municipal waste water, this wastewater contains relatively high Total Organic Carbon (TOC), and very little Nitrogen (N) and Phosphorus (P). The objective is to reduce TOC, and therefore nutrients N and P are added to the biological reactor. For the chemical and the biological processes, Dissolved Air Flotation (DAF) units are coupled with activated sludge. Combining chemical and biological processes is effective in reducing harmful components in the wastewater.

In order to follow biodegradation on samples with different TOC concentrations, three laboratory bench tests were considered. Sludge washing of activated sludge and flocculation tests on selected water samples was done before start up of the bench tests. Samples before start up and at the end of each bench test were sending externally for Hydrocarbon (HC) analyses. During bench experiments more than 90 % of the initial DOC concentration was degraded within 3 days showing good effectiveness of activated sludge process. GC/MS results showed that most of the compounds identified before cycles belonging to glycol and glycol ethers that are known to be rapidly degraded.

Overview of Advanced Oxidation Processes (AOP) for treating slowly biodegradable components is given.

Keywords: Industrial wastewater, TOC, DOC, Biodegradation, Activated sludge, VSS, Flocculation, Coagulation, Dissolved Air Flotation, AOP

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ABBREVIATIONS:

AOP	Advanced Oxidation Processes
BOD	Biochemical Oxidation Demand
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
COD	Chemical Oxidation Demand
C1	Single- Carbon Compounds
C2	Double carbon compounds
DAF	Dissolved air flotation
DOC	Dissolved Organic Carbon
DS	Dissolved Solids
EC	Electrical Conductivity
GC/MS	Gas Chromatography – Mass Spectrometry
HC	Hydrocarbons
KLIF	Norwegian state pollution authorities
MLVSS	Mixed Liquor Volatile Suspended Solids
MLSS	Mixed Liquor Suspended Solids
NPOC	Non Purgeable Organic Carbon Method
PV	Permanganate Value
PAH	Polycyclic Aromatic Hydrocarbons
RO	Reverse Osmosis
RBCOD	Readily Biodegradable Soluble Substrate
SART	SAR Treatment AS
TC	Total Carbon
TS	Total Solids
TDS	Total Dissolved Solids

TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TOD	Total Oxygen Demand
TSS	Total Suspended Solids
SS	Suspended Solids
SRT	Sludge Retention Time
SBCOD	Slowly Biodegradable Particulate Substrate
VSS	Volatile Suspended Solids
2, 4, 5 - T	2, 4, 5 - Trichlorophenoxyacetic Acid
2, 4 – D	2, 4 - Dichlorophenoxyacetic Acid

INTRODUCTION

Industrial wastewaters are composed of a broad spectrum of organic and inorganic compounds depending on the type of industry. ”*Industrial wastewaters are always priority issue for the protection of the environment. They should be considered as the most significant components of any water quality management programs*”*[1]*. The objective of discharge requirements is protection of the environment. It should associate correctly with the wastewater characteristics and with the specific treatment scheme *[1]*.

The thesis contains a combination of laboratory work and theoretical work on biodegradation.

Laboratory work was done on:

- Determining Total Organic Carbon (TOC) concentration on different water samples at SAR Treatment AS (SART).
- Small and large scale flocculation tests on selected water samples.
- Sludge washing of activated sludge.
- Small scale simulation test on biodegradability.

Due to complexity and high cost of Gas Chromatography – Mass Spectrometry (GC/MS) analysis of Hydrocarbons (HC), samples before and after each bench test were send to external laboratory for HC scanning.

The objective of the thesis is:

a. Detailed analyses of TOC content in the waste water at SART.
b. Investigation on biodegradation of HC.
c. Investigation on which part of the TOC is easily biodegradable.
d. Technical potential for treatment of slowly biodegradable TOC.

1. BACKGROUND AND LITERATURE REVIEW

1.1. WASTEWATER CHARACTERSITICS AND TOC INTRODUCTION

Large number of microorganisms and compounds in wastewater are able to create pollution that can be displayed in many ways. Therefore entire wastewater chemical and microbial analysis is not done, but the wastewater components are determined in terms of categories such as organic material, inorganic material and microbial content *[2]*.

1.1.1. Organic constituents

The wastewater organics consist of a large number of compounds which can be oxidized both chemically and biologically to yield CO_2 and water.

Oxidation of glucose is given as an example (Equation 1).

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O \qquad \text{(Eq. 1)}$$

In order to indicate the amount of organic material present in the wastewater, oxidation reactions are carried out both microbialy and by use of chemical oxidation agents. These are known as non specific tests.

If biological oxidation is applied, the test parameter is biochemical oxidation demand (BOD). The terms chemical oxidation demand (COD), permanganate value (PV) or the total oxygen demand (TOD) are used for chemical oxidations *[2]*.

The advantages and disadvantages of each of these tests are summarized in Table 1.

Table 1: Advantages and disadvantages of the non- specific test parameters *[2]*.

Test	Advantages	Disadvantages
BOD	Very simple and well known. Gives information on carbonaceous and nitrogenous oxygen demand.	Time-consuming incubation period. Poor reproducibility and sensitive to inhibition by many industrial wastes.
PV	Demands inexpensive apparatus and data are available within 40 min. It has good reproducibility.	Not many of the organic components are oxidized by the mild oxidation conditions. Some inorganic components can contribute a high oxygen demand.
COD	Demands inexpensive apparatus and data are available within 3 hours. It has good reproducibility.	It cannot oxidize ammonia. Great number of non - biodegradable organic components exerts an oxygen demand. Obstructions by higher concentrations of chloride ions.
TOC	Data are available in minutes. It has excellent reproducibility.	Demands expensive apparatus and experienced technician. Not much comparative data is available.

1.1.2. Inorganic nonmetallic compounds

Inorganic compounds which contribute to serious pollution are limited in industrial wastewater and can be detected by performing simple analyses *[2]*.

- **Nitrogen (N) and phosphorus (P)**

N and P are known as nutrients because they are essential for the growth of microorganisms, animals and plants. N and P are considered the two major nutrients of importance. They occur in wastewater in the following forms: Ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), orthophosphate (PO_4^{3-}). They come from different sources such as manufacturing processes, animal wastes from farms and effluents from sewage treatments *[2]*.

- **pH**

Significant quality parameter for wastewaters is the hydrogen - ion concentration. Expressing the hydrogen ion concentration is by pH.

"*pH is defined as negative logarithm of the hydrogen - ion concentration*" *[3]*.

$pH = -\log_{10} (H^+)$ (Eq. 2)

The pH concentration range tolerable for most biological life is typically pH 6 – 9. For treated wastewater effluents pH varies between pH 6.5 - 8.5 *[3]*.

- **Alkalinity**

"Alkalinity in wastewaters results from the presence of hydroxides [OH^-], carbonates [CO_3^{2-}] and bicarbonates [HCO_3^-] of elements such as calcium, magnesium, sodium, potassium and ammonia" [3].

Calcium and magnesium bicarbonates are the most usual *[3]*. The significance of alkalinity is based on its capacity to resist acid/base influences. Conventional titration with acid to an end pH of 4.5 is used to measure the alkalinity. Higher alkalinity indicates greater buffer capacity *[4]*.

1.1.3. Metallic constituents

Macro and micro amounts of metals are required for living organisms for their proper growth. They can however be toxic above certain concentrations. The following metals are of importance in waters: Arsenic (As), Lead (Pb), Cadmium (Cd), Copper (Cu), Chromium (Cr), Nickel (Ni), Zinc (Zn), Molybdenum (Mo), Tin (Sn), Vanadium (V), Mercury (Hg) and Barium (Ba) *[3]*.

1.1.4. Physical characteristics

- **Wastewater solid content characterization**

Total solids (TS) = *Suspended Solids (SS) + Dissolved Solids (DS)*
Total solids (TS) = *Organic TS + inorganic TS = Volatile TS +Fixed TS*
Suspended Solids (SS) = *Organic SS + inorganic SS = Volatile SS + Fixed SS*
Dissolved Solids (DS) = *Organic DS + inorganic DS = Volatile DS + Fixed DS*

The terms volatile TS, SS, DS as well as fixed TS, SS and DS refer respectively to the organic and inorganic solid content *[5]*. All matter that remaining as residue after evaporation of water at 103 – 105 °C is total solids (TS). TS are further classified as Suspended Solids (SS) which are non filterable and Dissolved Solids (DS) which are filterable through a 0.45 μm nominal pore size filter. The Suspended Solids fraction consists of the settleable solids which represent the approximate measure of the sludge quantity that will be removed by sedimentation.

The Dissolved Solids (DS) fraction contains colloidal (0.001-0.45 μm) and truly dissolved solids. For removing of the colloidal fraction coagulation followed by sedimentation is common. Further classification of the TS, SS and DS is on the basis of their volatility at 600 °C. At this temperature the organic fraction will oxidize and inorganic fractions remain as ash *[6]*.

- **Temperature**

Temperature is important parameter because of chemical and biological reaction rates and possible impact on aquatic life. For example, increased temperature can influence changes in the fish species near receiving waters. In warm water oxygen is less soluble compared with cold water.

"The increase in the rate of biochemical reactions that accompanies an increase in temperature, combined with the decrease in the quantity of oxygen present in surface water, can often cause a serious depletions in dissolved oxygen concentrations in the summer months "[3].

Rapid change in temperature can influence high mortality rate of aquatic life. High temperature conditions can bring growth of wastewater fungus and undesirable plants *[3]*.

Temperature control is essential in the biological treatment system. This is where the biological process brings the temperature from ambient 10-15 degrees up to 35-45 degrees*[7]*.

- **Conductivity**

"The Electrical conductivity (EC) of water is a measure of the ability of a solution to conduct electrical current"[3].

Conductivity increases with the increasing ion concentration. The capability of the water for irrigation can be determined by electrical conductivity. By measuring the electrical conductivity, estimation can be made for using of salinity of treated wastewater for irrigation. Expression of the electrical conductivity in SI units is as milisimens per meter (mS/m). EC is used as a surrogate of total dissolved solids (TDS) and also salinity *[3]*.

- **Density**

Density (ρ) is determined as mass per unit volume expressed in SI units as g/L or $kg/m^{3.}$ Because of the potential of density currents in sedimentation tanks, chlorine contact tanks etc. density represents significant physical characteristic of wastewater *[3]*. Sometimes specific gravity parameter of the wastewater is used instead of the density of wastewater.

$S_w = \rho_w / \rho_0$ (Eq. 3)

S_w = specific gravity of the wastewater

ρ_w = density of the wastewater

ρ_0 = density of water

S_w and ρ_w parameters are dependent of the temperature and the total solids concentration in wastewater *[3]*.

1.1.5. Biological characteristics

Biological characteristics of waste water are essential in controlling diseases caused by microorganisms. Bacteria, viruses, archae, algae, fungi, protozoa and rotifers are microorganisms found in wastewaters *[3]*.

Tables 2 and 3 provide the comparisons of the composition of domestic sewage and some industries wastewater.

Table 2: Composition of untreated domestic sewage *[2]*.

Parameter	**Manchester (UK)**	**Mafraq (Abu Dhabi town)**	**Campina Grande (NE Brazil)**	**Amman (Jordan)**	**Nairobi (Kenya)**
BOD (mg O_2/l)	240	228	240	770	520
COD (mg O_2/l)	520	600	570	1830	1120
PV (mg O_2/l)	----	75	---	---	---
Suspended solids (mg/l)	210	198	392	900	520
Ammonia(as N) (mg/l)	22	35.2	38	100	33
Ph	7.4	7.6	7.8	---	7.0
Temperature (°C)	14	---	26	22	24

Table 3: Composition of untreated effluents from industries *[2]*.

Parameter	Pharmaceuticals (India)	Textiles (India)	Beet-sugar waste (USA)	Coke –oven liquor (UK)
BOD_5	15250	2000	930	1200
COD (mg O_2/l)	28540	5000	1601	3900
Suspended solids	5400	4000	1015	950
Ammonia (as N)	-----	-----	6.3	4.5
pH	9.3	12.0	7.1	5.5
Total N	5166	---	16.4	490

Municipal wastewaters are generally the same with low organic load and high content of ammonia. Industrial wastewaters depending of the source have average or high organic load and high suspended solid concentration but little or no ammonia. They are generally more concentrated compared with domestic sewage in the terms of COD. The COD can have different values starting from 500 - 100.000 mg/l, according to the type of the industry. However, COD of majority of industrial effluents is in the range of 1000 – 2000 mg/ l *[1]*.

1.1.6. Introduction of Total Organic Carbon (TOC)

"Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality"[8].

As Metcalf & Eddy indicates, to measure the pollution characteristic of waste water the TOC tests can be used. These tests are very fast and reliable to complete. The time interval is around 5 – 10 minutes *[3]*.

"The test methods for TOC utilize heat and oxygen, ultraviolet radiation, chemical oxidants or some combination to convert organic carbon to carbon dioxide which is measured with an infrared analyzer or by other means"[3].

A continuous on-line TOC analyzer has been developed lately. These TOC analyzers can detect TOC concentration in the ppb (parts per billion) range. They have found use in microfiltration and Reverse Osmosis (RO) treatment units, for uncovering residual TOC in the treated effluent. When valid relationship is established among results from TOC and BOD tests, applying of TOC test for process control is recommended *[3]*.

1.2. BACTERIAL GROWTH

"*Bacterial growth is a complex process involving numerous anabolic (synthesis of cell constituents and metabolites) and catabolic reactions (breakdown of constituents and metabolites)"[9].*

1.2.1. Bacterial growth in a batch reactor

Bacterial growth in a batch reactor is characterized by phases shown on Figure 1. Four growth phases can be distinguish as substrate is consumed *[3]*.

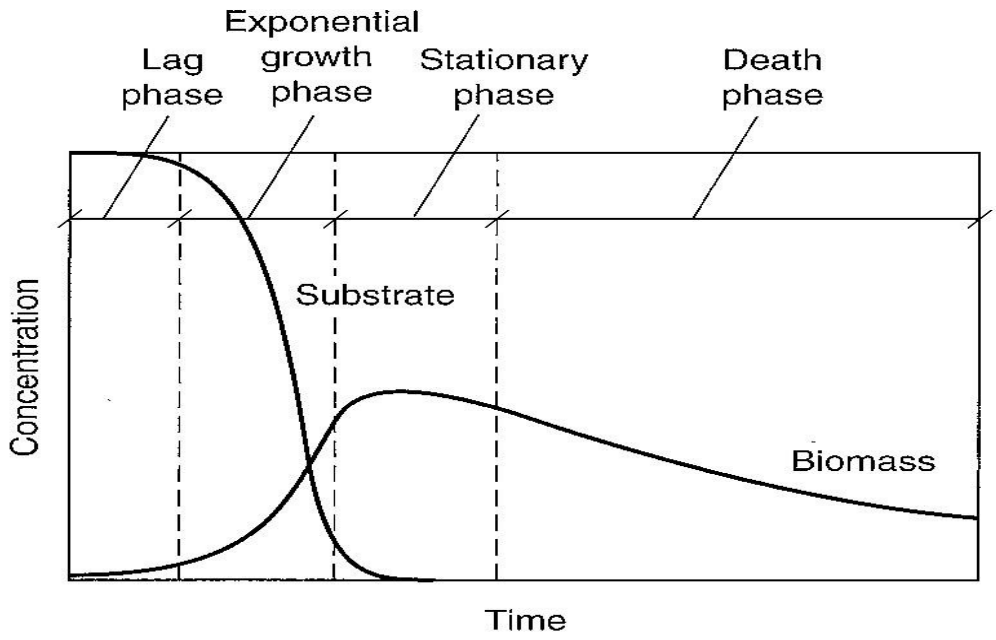


Figure 1: Bacterial growth in a batch reactor with biomass and substrate changes versus time *[3]*

a) The lag phase

Lag phase is the first phase where rate of growth is essentially zero *[9]*. The lag phase corresponds with the acclimation of organisms into a new environment. During this phase enzyme induction can happen and/or the cells can be acclimating to salinity, pH and temperature changes *[3]*.

b) The exponential phase

"During the exponential growth phase, bacterial cells are multiplying at their maximum rate, as there is no limitation in substrate and nutrients. The biomass growth curve increases exponentially during this period. The only factor that affects the rate of exponential growth is temperature" [3].

The biomass increase rate in this phase is proportional to the initial cell concentration and can be presented by a first – order reaction:

$$\frac{dX}{dT} = \mu X \qquad \text{(Eq. 4)}$$

In Equation 4, the first-order rate constant (μ) is noted as the specific growth rate *[2]*.

c) The stationary phase

"During the stationary phase the biomass concentration remains relatively constant with time. In this phase, bacterial growth is no longer exponential and the amount of growth is offset by the death of the cells"[3].

There are several reasons for reaching the stationary phase. First reason is when carbon or important nutrient is completely consumed. *"When a carbon source is used up it does not necessarily mean that all growth stops. This is because dying cells can lyse and provide a source of nutrients. Growth on dead cells is called endogenous metabolism"[9].* Another reason for the stationary phase is when the waste products inhibit the growth or are toxic to cells *[9]*.

d) The death phase

The final phase in the batch reactor is the death phase. The death phase is characterized with no growth, because the substrate has been depleted and due to the cell death there is a decrease of biomass concentration *[3]*.

1.2.2. Effect of substrate concentration on microbial growth

As it can be seen from the Figure 1, there is decline in bacterial growth at the end of exponential growth. As N,J,Horan stated, this decline is regarding to the depletion of a growth-limiting nutrient that can be the organic carbon, nitrogen, phosphorus or any other factor essential for bacterial growth *[2]*.

Jacques Monod was first who described the relationship between specific growth rate of the microorganism and the substrate concentration (Figure 2).

$$\mu = \mu_m \frac{S}{K_s + S}$$ (Eq. 5) *[2]*

μ is known as the specific growth rate

μ_m is the maximum specific growth rate

S is the concentration of the growth limiting substrate

K_s is a saturation coefficient *[2]*.

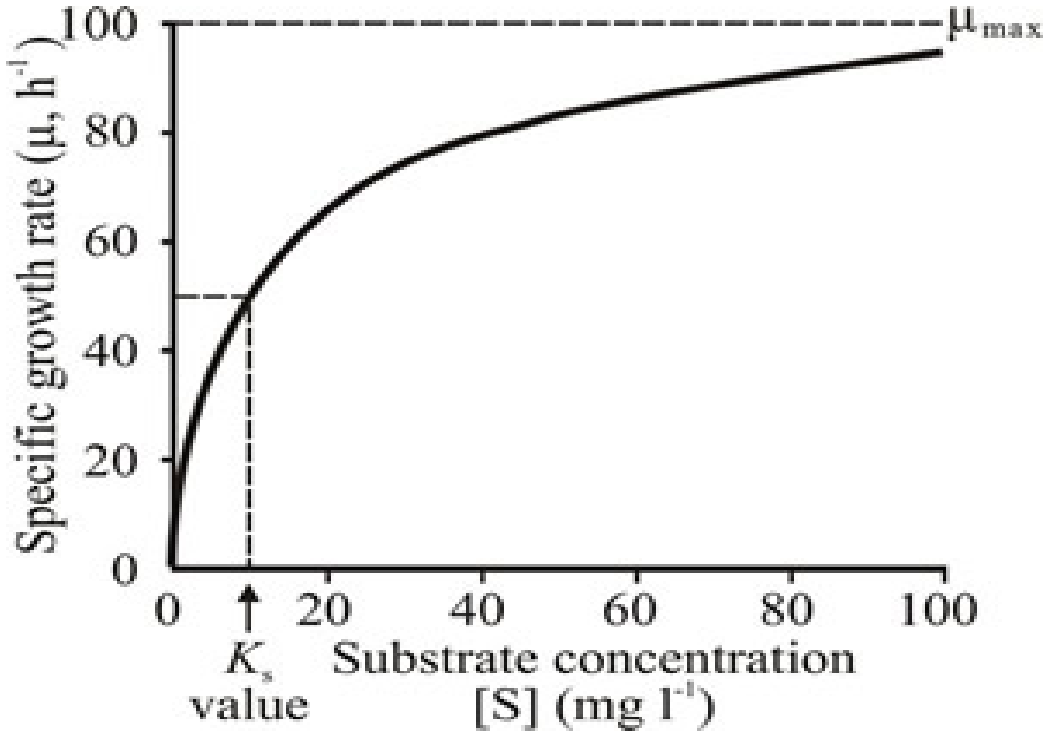


Figure 2: Relationship between substrate concentration and bacterial growth *[10]*

The result of the competition among microorganisms for a limited supply of food can be described by saturation coefficient K_s*.[2]*. Saturation coefficient is defined as *"the substrate concentration at which growth occurs at one half the value of* μ_m*"[9]*. The preference of organism towards substrate is greater as the value of K_s *i*s lower *[2]*.

Substituting the Equation 5 in Equation 4, result in expression (Equation 6) that according to N.J.Horan allows providing the kinetics of elimination of substrate for microorganisms growing at various substrate concentrations *[2]*.

$$\frac{dX}{dt} = \frac{\mu_m S}{K_s + S} X \qquad \text{(Eq. 6)}$$

There are two limiting cases for the Monod equation *[9].* The first case the substrate concentration is high in comparison with K_s indicating zero order of the microorganisms' growth rate:

$$\frac{dX}{dt} = \mu_m \quad X \qquad \text{(Eq. 7) } [2]$$

The second case occurs at low substrate concentration compared to K_s, resulting in first order dependence on substrate concentration *[9]*:

$$\frac{dX}{dt} = \frac{\mu_m S}{K_s} X \qquad \text{(Eq. 8) } [2]$$

Equation 8 may be used for activated sludge systems that are described by low substrate concentration with microorganisms showing a high saturation coefficient *[2]*.

1.2.3. Bacterial growth and biomass yield

"In biological treatment processes, cell growth occurs concurrent with the oxidation of organic and inorganic compounds. The ratio of the amount of biomass produced to the amount of substrate consumed (g biomass/g substrate) is defined as the biomass yield, and typically is defined relative to the electron donor used " [3].

$$\text{Biomass yield } Y = \frac{\text{g biomass produced}}{\text{g substrate utilized (i.e.,consumed)}} \qquad \text{(Eq. 9)}$$

The yield for aerobic heterotrophic reactions with organic substrates can be written as g biomass / g organic substrate *[3]*.

1.3. BIODEGRADATION

"Biodegradation can be defined as the biologically catalyzed reduction in complexity of chemicals" [11].

This process cover conversion of organic compounds into less complex metabolites by biotransformation or conversion of organic substrate into inorganic minerals, H_2O, CO_2 (aerobic) or CH_4 (anaerobic) by mineralization. Bacteria and fungi have been studied for their capability to degrade pollutants such as halogenated hydrocarbons, polycyclic aromatic hydrocarbons and nitro aromatic compounds. The initial transformation stages are done with specific enzymes. These enzymes are converting pollutants to metabolites, which can be integrated within more central bacterial pathways *[12]*.

There are six major divisions of enzymes presented in Table 4.

Table 4: Divisions and distribution of enzymes by Enzyme Commission (EC) in the University of Minnesota Biocatalysts / Biodegradation Database (UM-BBD) *[13].*

EC no.	Enzyme class	No. of class in UM-BBD
1	Oxidoreductase	260
2	Transferase	30
3	Hydrolase	60
4	Lyase	50
5	Isomerase	14
6	Ligase	10

In order for biodegradation to occur the following conditions must be met:

a) An organism with the necessary enzymes must exist in the environment where the chemical is contained.
b) The chemical must be available to the organism.
c) If the enzyme catalyzing the degradation is extracellular, for functioning of the catalyst, the bonds must be exposed.
d) If the enzyme catalyzing the degradation is intracellular, the molecule must penetrate to the internal sites where the enzyme acts.
e) Environmental conditions must enable proliferation of the potentially microorganisms *[11]*.

The incapacity of a microorganism to function or his absence from a particular environment means that the compound will disappear slowly. If the above conditions are not satisfied, the pollutant will be long lived. When microorganisms are not functioning, act slowly or don't exist , the pollutants will be persistent *[11]*.

1.3.1. Acclimation

"Prior to the degradation of many organic compounds, a period is noted in which no destruction of the chemical is evident "[11]. This period is named as acclimation period or the lag time.

One of the definitions related with acclimation is the time interval between chemical entrance into the environment and the initial loss detected. As it can be seen on the Figure 3, during the acclimation period the concentration of the 2, 4, 5- Trichlorophenoxyacetic acid (2, 4, 5-T) is not changed, after which the rapid destruction takes place.

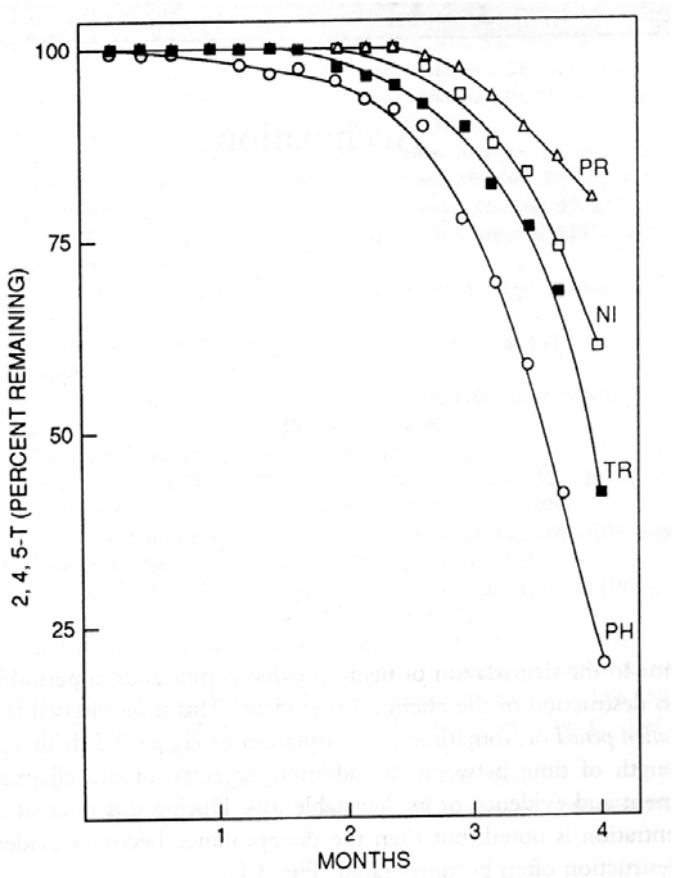


Figure 3: Soil degradation of 2, 4, 5 –T in Puerto Rico (PR), Nigeria (NI), Trinidad (TR) and Philippines (Ph)

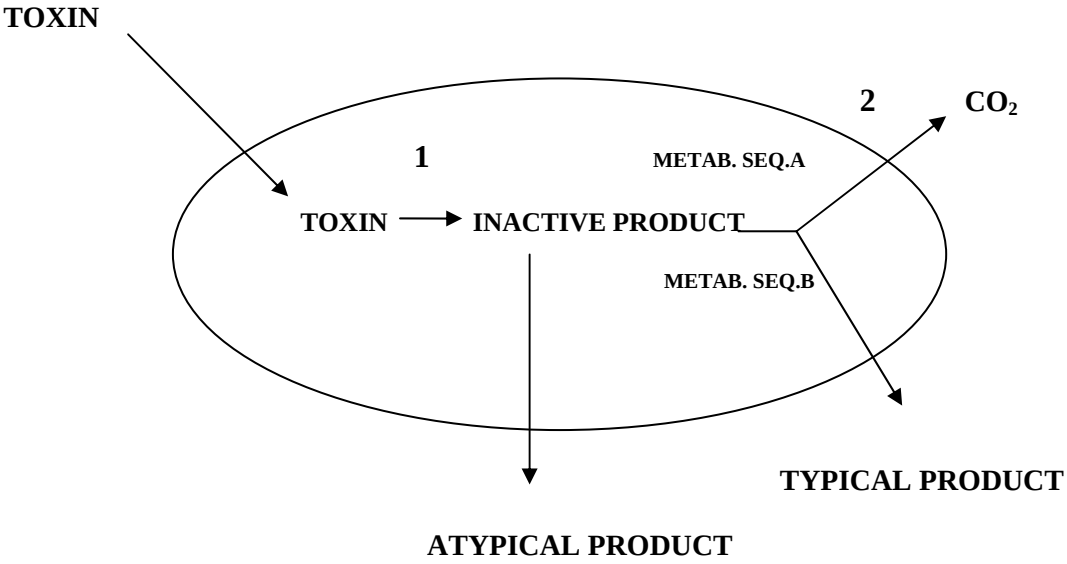
Presence of a lag phase is evident for most of the chemicals degraded in the environments *[14]*. Acclimation period length can vary from minutes to months. At the beginning of detectable biodegradation, the acclimation phase is considered finished. The most common causes of the acclimation are the following mechanisms: Proliferation of small populations, toxicity, predation by protozoa, appearance of novel genotypes and diauxic growth *[11]*.

The size of a lag time is affected by the following factors: a) Initial chemical, b) Initial biomass density, c) Temperature, d) pH, e) Nutrients, f) e^- acceptor availability g) Grazing, h) Growth history *[14]*.

1.3.2. Detoxification and activation

Detoxification is defined as induced changes in a molecule that makes it less harmful to species during biodegradation *[14]*. This is one of the microorganisms' most important roles in pollutants transformation. With detoxification the toxicologically active substance is inactivated, with the enzymatic steps usually occurring within the cell. The following processes which result in detoxification are only the first step in Figure 4 *[11]*.

Detoxification reactions are following:
- Hydrolytic cleavage
- Hydroxylation
- Dehalogenation
- Demethylation and dealkylations
- Methylation
- Nitroreduction
- Deamination
- Ether cleavage
- Amidification of nitriles
- Conjugations to a metabolic intermediate *[14]*



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1. DETOXICATION REACTION

2. MINERALIZATION

Figure 4: Fate of detoxified chemicals *[11]*

One of the most unwelcome microbial transformations aspects is the production of toxicants *[11]*. Activation is a process during biodegradation consisting of formation of toxic products from less toxic substrates *[14]*. Activation may occur in active microorganism environments such as water, wastewater and soil. Products formed can be subject to rapid or slow mineralization, or persistence for a long period as shown on Figure 5 *[11]*.

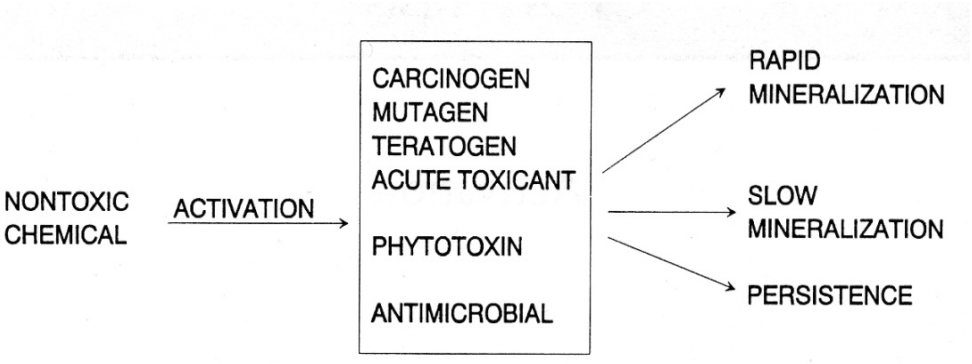


Figure 5: Activation associated processes *[11]*

Biosynthesis of carcinogens, mutagens, teratogens etc are the consequences of activation*[11]*.

Activation reactions are:

- Dehalogenation (TCE → VC)
- Halogenations
- Nitrosations of sec-amines
- Epoxidations
- Phsophothionate conversion to phosphates
- Oxidation of thioesters
- Hydrolysis of esters to acids *[14]*.

1.3.3. Kinetics of biodegradation

Kinetics of biodegradation is important for the evaluation of the organic pollutant persistence and exposure assessing *[11]*.

The following classes of kinetics exist:

- Non-growth related kinetics
- Growth related (autocatalytic) kinetics *[14]*.

a) **Non-growth related kinetics**

Models for Non-growth kinetics relates to the variable substrate concentration. Non - growth zero order kinetics (Equation 10) is used when there is constant supply of limiting nutrients, low water solubility and high biomass and substrate concentrations. Non-growth first order kinetics (Equation 11) are used in environmental fate models and when the soluble substrate is bellow K_S and μ-k_d is close to zero *[14]*.

Differential form for zero order kinetics is:

$$\frac{dS}{dt} = -k_2 \qquad \text{(Eq. 10)}$$

Differential form for first order kinetics is:

$$-\frac{dS}{dt} = k_1 \cdot S \qquad \text{(Eq. 11)}$$

K_1 - first order rate constant *[11]*.

b) **Growth related kinetics**

Individual dynamic expressions for biomass (*X*) and substrate (*S*) are used by growth related (autocatalytic) models. Some models are utilized to reflect substrate limitations and some models although involve biomass do not take into account the density of the degrading population as variable. Secondly mentioned are:

– Logarithmic model

– Logistic model ($k= \mu_{max}/K_S$) *[14]*

Logarithmic kinetics (Equation 12) of disappearance of substrate may be written as:

$$\frac{dS}{dt} = \mu_{\max} \cdot \left(S_0 + X_0 - S\right) \quad \text{(Eq. 12)}$$

S_0 is initial concentration of the substrate

X_0 is the substrate amount needed for initial population production

S is substrate concentration

Logarithmic kinetics conditions are completed when $S_0 >> K_S$.

When $S_0 << K_S$, different kinetics of growth apply. Growth on substrate concentrations much beneath K_S is known as logistic growth (Equation 13). Logistic kinetics can be expressed as:

$$-\frac{dS}{dt} = dS \cdot \left(S_0 + X_0 - S\right) \quad \text{(Eq. 13) } [11]$$

1.3.4. Thresholding

"Metabolic thresholds are the lowest substrate concentrations that sustain growth of bacteria" [14]. One of the evidence for thresholding comes from studies of biodegradable synthetic compounds in water. According to these studies, during the test period below certain concentration biodegradation doesn't take place, or the biodegradation rate is less than expected. Mineralization data of 2, 4-dichlorophenoxyacetic acid (2, 4 – D) added at different concentrations in river water is shown on figure 6 *[11]*.

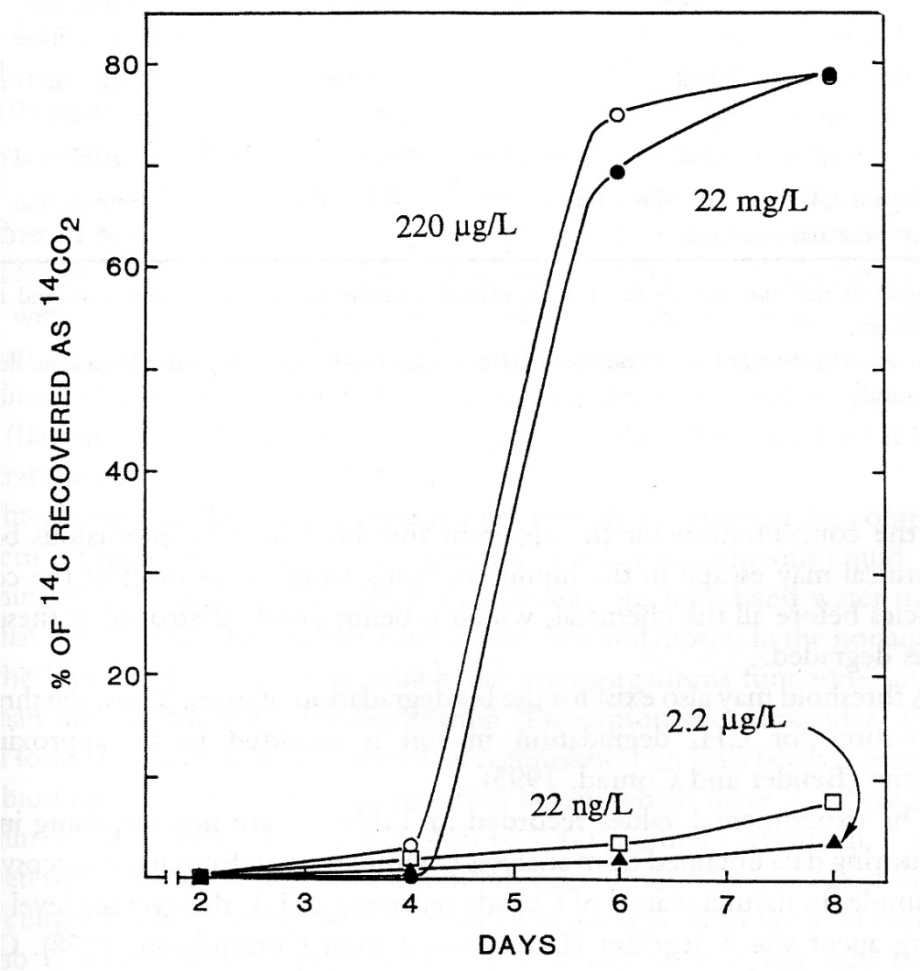


Figure 6: Example of mineralization of 2, 4 – D after addition at different concentrations *[11]*

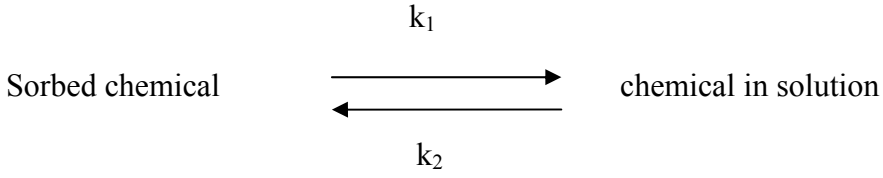
In a standard growth models, decay rates and maintenance requirements assign the threshold value *[14]*.

1.3.5. Sorption

Some substances which are attacked by microorganisms, however, are not being biodegraded, although they are biodegradable. There are several reasons for this: a) Microbial proliferation and metabolism are precluded when the concentration of the toxins are high b) Too low concentration of nutrients for microbial growth and too low substrate concentration for microorganism's replication c) Lack of readily available form of substrate for the microorganisms *[11]*.

"The term sorption is used to include both adsorption and absorption" [11]. The term adsorption is associated to the solutes retention by the solid material surface, while absorption is associated with solutes retention within the mass of the solid.

Microenvironment adjacent to the solid material is the zone where sorption occurs. Many organic compounds can be sorbed by soil components, wastewaters, sediments etc. Factors like pH, temperature, type and concentration of solutes, type and quantity of clay minerals, the amount of organic matter can affect sorption of organic compounds. Although sorption reduces the biodegradation rate, it doesn't prevent it totally. Microorganisms can use sorbed molecules as C- source, energy, N-source ant other elements, resulting in transformation of compounds. How sorbed molecules are becoming available to microorganisms it's still confusing. Three hypotheses are explaining the mechanism of utilization. According to first hypothesis, *"The organism use the chemical that is initially in solution, and it also metabolizes the compound that enters the aqueous phase as a result of spontaneous desorption from the solid" [11]*. Equilibrium exists between sorbed chemical and chemical in ambient liquid:

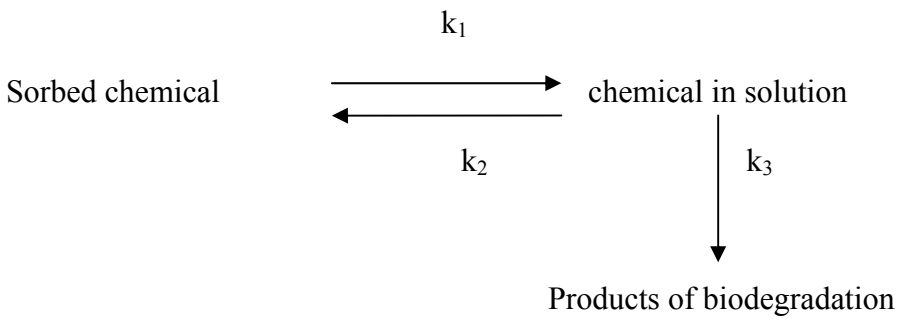


(k_1) desorption rate constant

(k_2) adsorption rate

The second hypothesis explains that metabolites excreted by microorganisms facilitate desorption so that biodegradation rate is larger than the spontaneous desorption rate when microorganisms are lacking. In compliance with the third hypothesis, microorganisms utilize directly the sorbed compound because of the same surface adherent.

For the biodegradation of sorbed compounds, several models have been proposed. The main assumption of these models is that substrate has to be in an aqueous solution so that it can be metabolized. In one of the early models there is use of desorption rate constant (k_1), adsorption rate (k_2) and biodegradation rate (k_3) *[11]*.



If the compound is toxic or a toxic intermediate, the sorption can have positive kinetic effects *[14]*.

1.3.6. Cometabolism

Cometabolism is defined as *"Transformation of an organic compound by a microorganism that is unable to use the substrate as a source of energy or of one of its constituent's elements" [11].* Variety of organic compounds is known to be transformed cometabolically, with the cometabolic product mostly excreted to the environment *[14].*

Explanations for cometabolism are:

1. Initial enzymes are present and they convert the substrate to a product which is not converted further.
2. The initial substrate is converted into products that inhibit further metabolism.
3. Necessity of a second substrate to initiate a particular reaction *[11] [14]*.

1.3.7. Aerobic versus anaerobic microorganisms in biodegradation

The dominant metabolic pathways are determined by the presence or absence of oxygen*[15]* . Much more is known about biodegradation under aerobic conditions, compared with anaerobic degradation *[13]*.

Some of the general trends are given below:

- Aerobic lag times are shorter than equivalent anaerobic lag times which can last 6 months to 1 year before biodegradation occurs.
- Aerobic degradation proceeds in pure cultures and anaerobic degradation involve complex bacterial consortia
- High energy xenobiotics seem to be degraded much faster by aerobes, because of the high energy yield, larger number of generated ATP equivalents, and generation of more biomass.
- Kinetics of degradation is higher for aerobic guilds than anaerobic consortia.
- Organic compounds like Alkanes demand oxygenase activation by introducing molecular oxygen derived from oxygen atom(s).
- Other organic compounds require anaerobic reduction (eg. Dehalogenation), or at least, pre-anaerobic degradation intensify the process kinetics before aerobic mineralization *[15] [13]*.

1.3.8. Metabolic logic and pathway maps

a) C1 Metamap

Single- carbon compounds (C1), are metabolized with short and simple metabolism by microorganisms such as methanothrops and methylothrops .These compounds pass through three intermediates *[15]*. Single- carbon compounds are transformed by enzymes into the following intermediates: methanol, formaldehyde and formate, as it can be seen on Figure 7. After that oxidation and assimilation processes can proceed *[13]*.

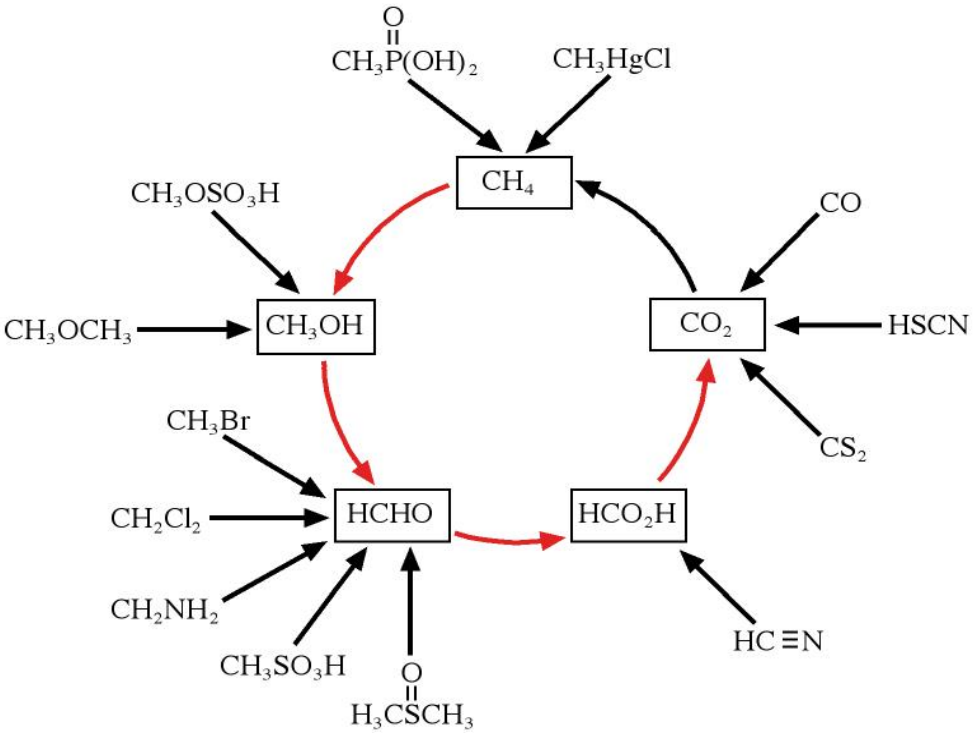


Figure 7: C1 Metamap *[16]*

b) C2 Metamap

Double carbon compounds like Ethyne, Ethene and Ethane can be transformed to one or more of the nine metabolic intermediates from ethanol to oxalic acid as shown in Figure 8 *[15]*.

"Ethene and ethyne are catabolized by bacteria, with functionalization of the carbon atoms leading to the loss of the carbon-carbon multiple bond"[13]. Ethene is oxidized to an epoxide and after hydrated to ethylene glycol ($C_2H_6O_2$) *[15] [13]*.

Acetaldehyde will be produced from the acting of alkyne metabolism mechanism on the ethyne *[13]*. In the case of halogenated double carbon compounds, the functional groups are taken away by dehalogenation to give glycolate *[15]*.

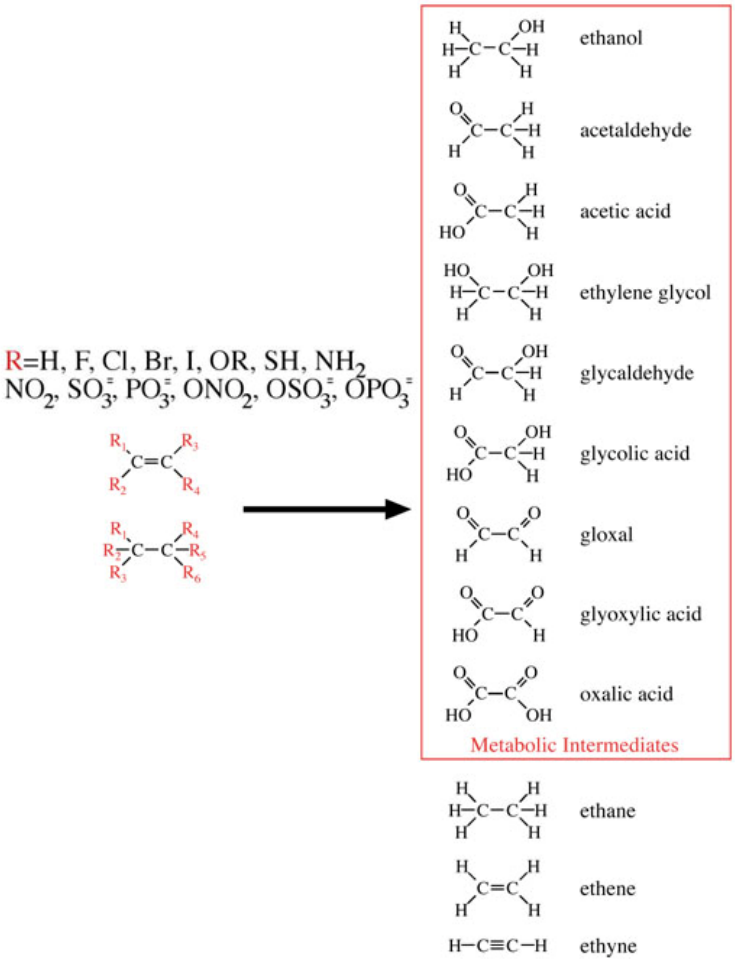


Figure 8: C2 Metamap *[17]*

c) Cycloalkane Metamap

"Cycloalkanes are alkanes that contain rings of carbon atoms. Simple cycloalkanes are named like acyclic (noncyclic) alkanes, with the prefix cyclo – indicating the presence of a ring" [18].

Example for cycloalkanes metamap is illustrated through Cyclohexane in Figure 9. Biodegradation of cyclohexane progress by monooxygenation to create cyclic alcohol - cyclohexanol. Dehydrogenation gives a ketone. Next step is the reaction called Baeyer - Viliger monooxygenation by inserting oxygen atom into the ring structure. After the cyclic

ester formation, hydrolysis of the ring ester and further metabolism of the remaining carboxylic acid follows *[13] [15]*.

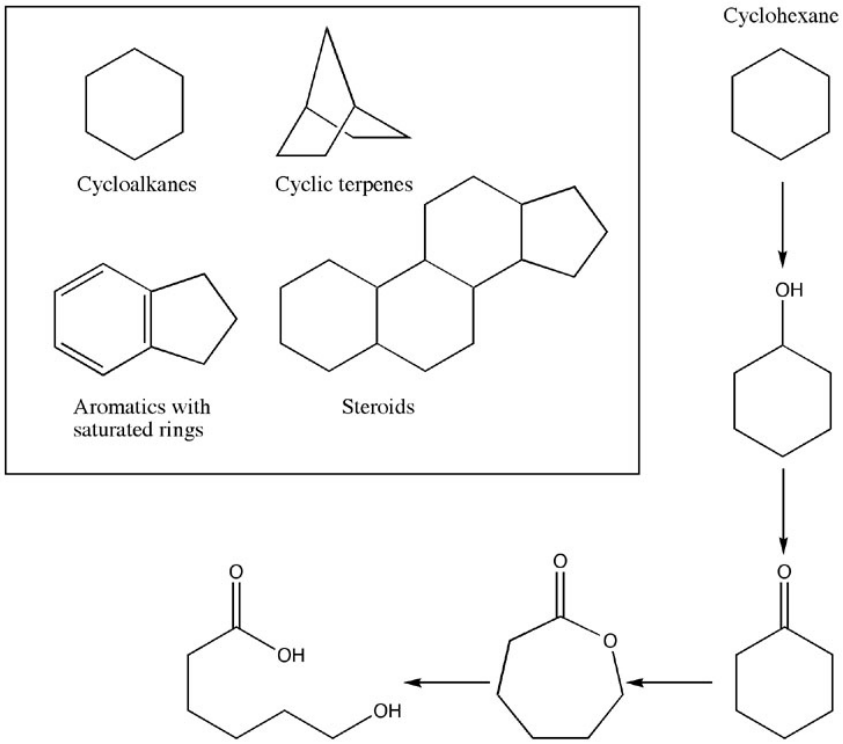


Figure 9 Cycloalkane Metamap *[19]*

d) BTEX Metamap: Aerobic Metabolism

"Monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene, collectively known as BTEX, are commonly found in gasoline and are highly volatile substances " [12].

Aerobic metabolism of BTEX compounds has been investigated especially under aerobic conditions, as shown on Figure 10. Oxygen activating enzymes for oxidation of BTEX compounds are dioxygenases or monooxygenases in different organisms. For example, toluene is oxidized by dioxygenases to cis-1,2-dihydroxydihydro-3-methyl-3,5-cyclohexadiene. This intermediate is oxidized by dehydrogenase to 3-methylcatechol.

Dioxygenase – dependant pathways capture more overall energy compared with monooxygenase – dependent pathways *[13]*.

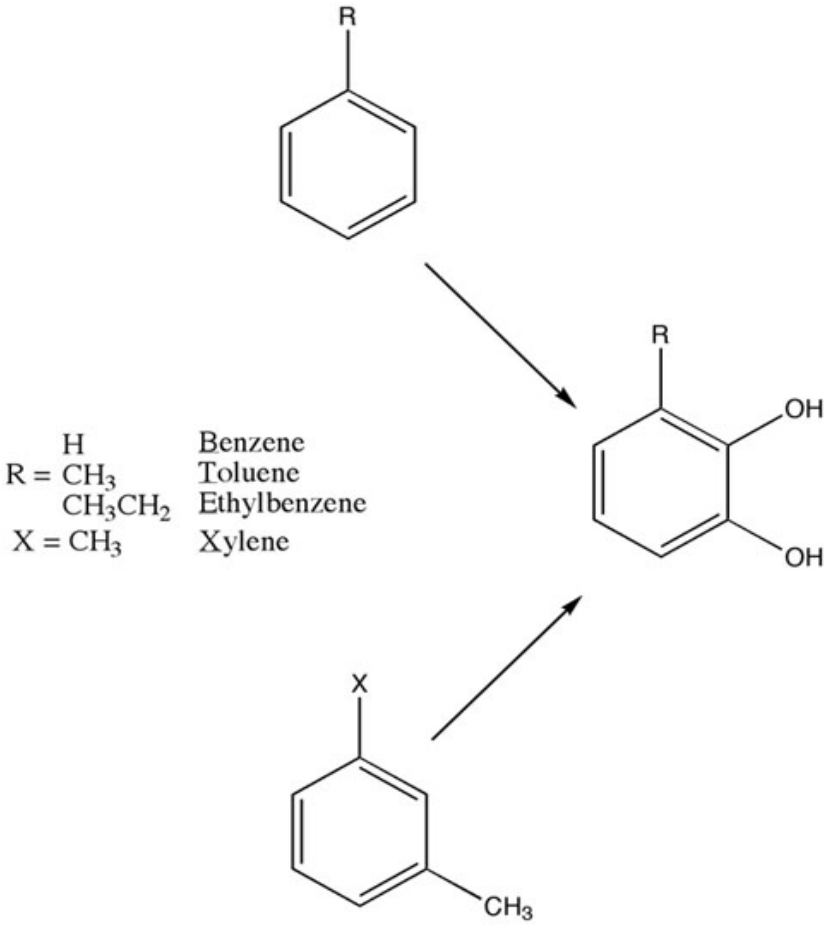


Figure 10: BTEX Metamap *[20]*

Ethylbenzene often comes in contact with the environment resulting from petroleum industrial discharges or spills. Ethylbenzene is an example of n-alkylbenzenes (C2-C7), that is been utilized by Pseudomonas sp. strain NCIB 10643. Dioxygenation is the initial step of aerobic degradation of Ethylbenzene, followed by extradiol ring cleavage *[21]* (Figure 11) .

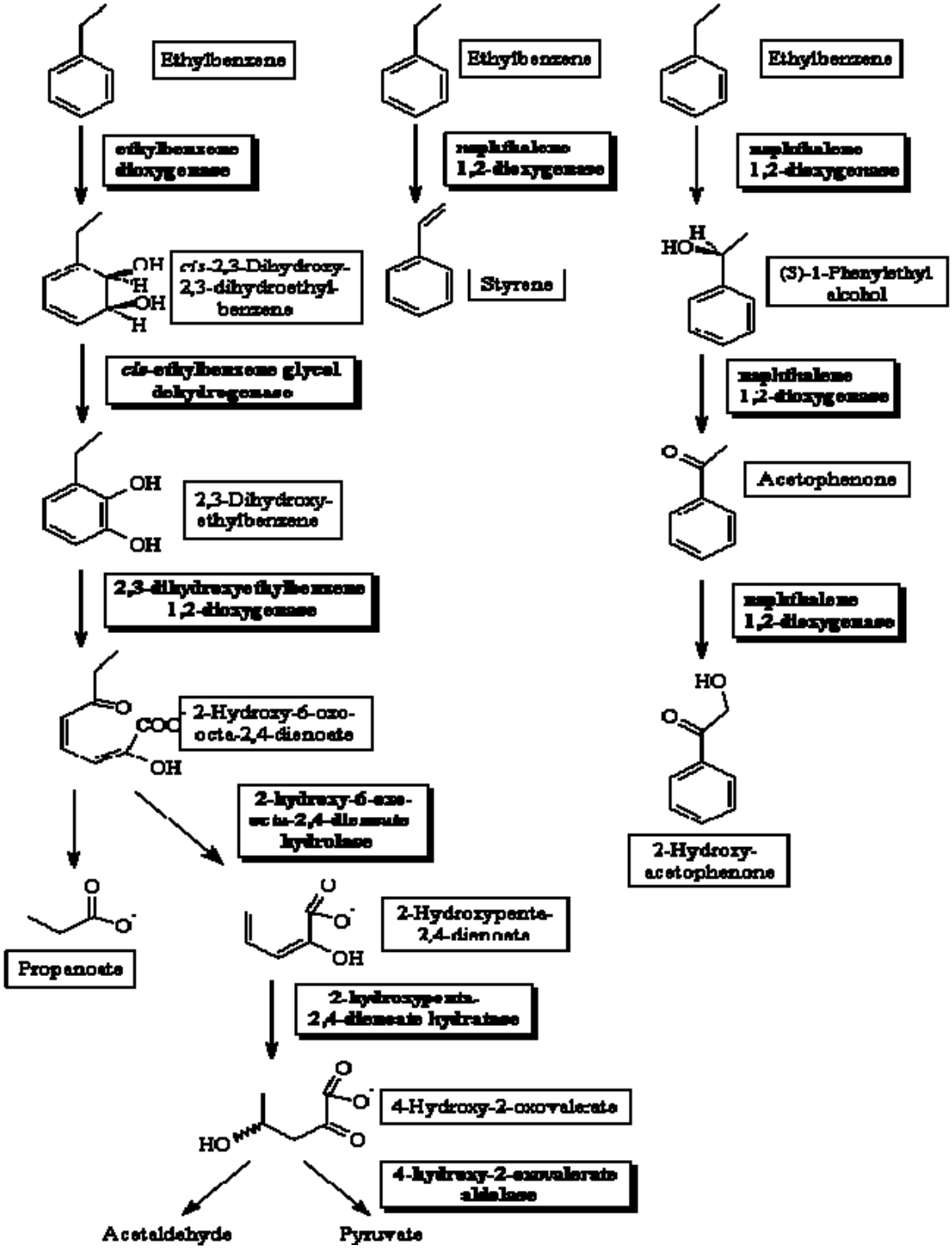


Figure 11: Ethylbenzene pathway map *[21]*

e) PAH Metamap

PAHs or Polycyclic aromatic hydrocarbons are containing two or more benzene rings in their structure .Compared with monoaromatics they are more hydrophobic and therefore lower solubility. PAHs come in contact with the environment from discharges from oil refineries, accidental oil spills or domestic runoffs *[12]*.

In case of naphthalene (Fused benzene – ring PAHs), dioxygenation by naphthalene dioxygenase will result in dihydrodiol (not shown in figure 12, top) *[13]*. Enzymatic dehydrogenation on dihydrodiol intermediate will give naphthalene catechol. The existence of the two hydroxyl groups activates the catecholic ring. These facilities a ring cleavage reaction by mono-and dioxygenases and three carbon units pare away. The resulting *ortho*-hydroxyaromatic acid (salicylate) can be oxidatively decarboxylated to a second catechol*[15]*. The reaction can be repeated to deconstruct the next aromatic ring *[13]*.

In petroleum industry there are examples of non aromatic five and six member rings fused to aromatic rings. One simple example is Acenaphtene (Figure 12, bottom). Acenaphtene degrade by hydroxylation of nonaromatic ring first, followed by second hydroxylation and dehydrogenation to give diketone. Oxygen insertion is a key reaction that results in a naphthalene dicarboxylic acid followed by dioxygenation and decarboxylation to make approximate pathway to naphthalene metabolism *[13]*.

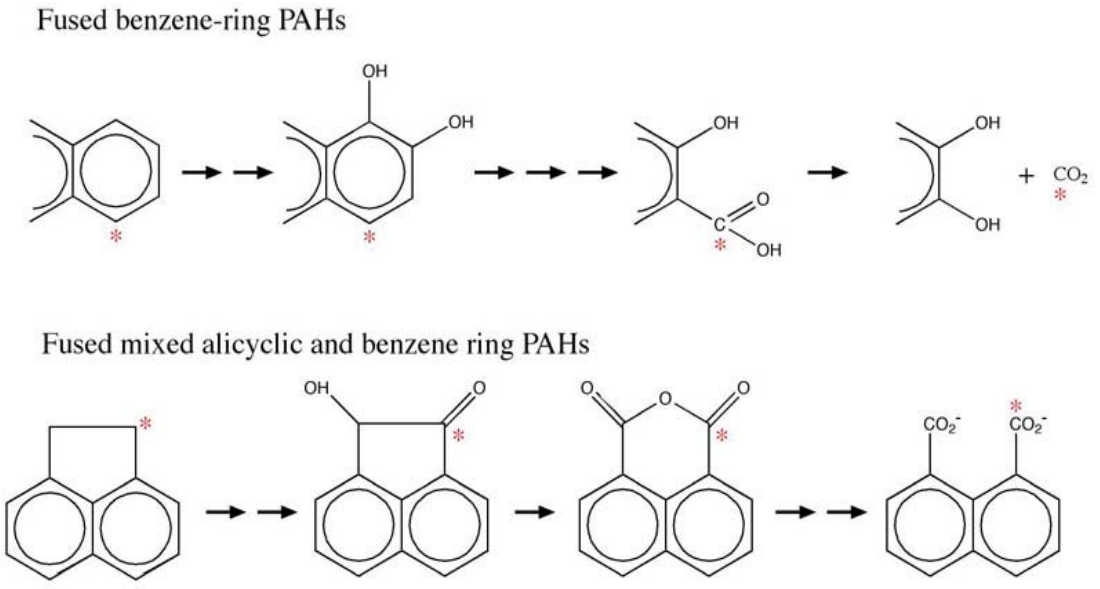


Figure 12: PAHs metamap of fused benzene ring PAHs and Fused mixed alicyclic and benzene ring PAHs *[22]*

1.4. SAR TREATMENT WASTEWATER PLANT

1.4.1. Characteristic of the plant

SAR Treatment owned by SAR AS (60%) and Nature Technology Solution AS (40%) is one of the leading companies in Norway within environmental technology. SAR Treatment provides treatment of industrial wastewater from the offshore industry, ships and onshore activities. The company purifies big quantities of waste water like oil-contaminated water, ballast water, engine-room slop and heavy-metal-contaminated waste water. Variety of methods is used to treat these contaminated fluids such as flocculation/coagulation of oil, heavy metals and suspended particles, as well as biodegradation of dissolved organic compounds. SAR Treatment has permission to handle 60,000 m3 of waste water annually *[23]*.

Figure 13 provides schematically an explanation of the SAR treatment plant.

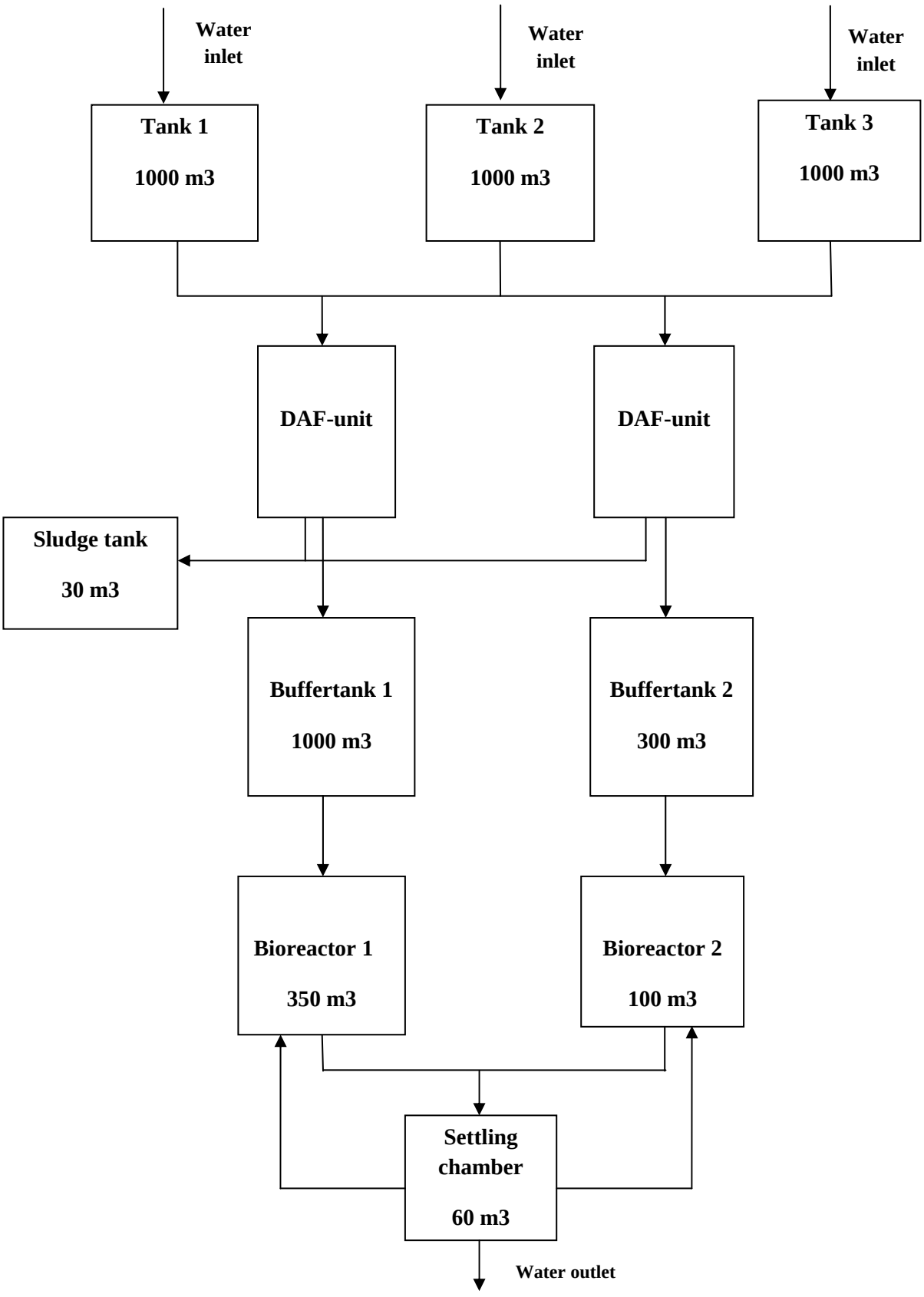


Figure 13: SART Water treatment flowchart

1.4.2. Overview of unit processes at SART

a) Physical process

For separation of wastes consisting of liquids and solids, physical treatment is usually the first step. This treatment process consists of a range of separation methods that have been used in the industry.

Typical physical treatment processes are:

- Screening
- Adsorption
- Sedimentation
- Clarification
- Evaporation
- Centrifugation
- Filtration
- Distillation
- Stripping
- Membrane filtration
- Flotation *[24]*

"Sedimentation is the most widely used method for removal of floating and coarsely dispersed oils from wastewater"[25].

Oil particles can be separated by gravity, due to the difference in density between oil and water *[25]*. SAR Treatment uses sedimentation, which relies on gravity to achieve separation (Figure 14).

Figure 14: Gravity separator tanks *[26]*

Oil, which has lower density than water, will form an apparent boundary layer on the top of the tank. Suspended solids which are the larger particles, will settle to the bottom of the tank.

Three gravity separation tanks of 1000 m^3 each are implemented in the SAR treatment plants which allow suspended solids removal.

b) Chemical process

- Coagulation and Flocculation

"Coagulation and flocculation can enhance the precipitation process and assist in separation of suspended solids from liquids"[24].

Every colloidal particle is surrounded by electrical double layers, which can stabilize a colloid particle. (Figure 15) .The inner layer (Stern layer), is made up of ions with the opposite charge of the colloidal particle *[27]*. The outer region is diffusive layer. Notional boundary (Slipping plane) exists within the diffusive layer, making the particle acts as a single unit *[28]*.

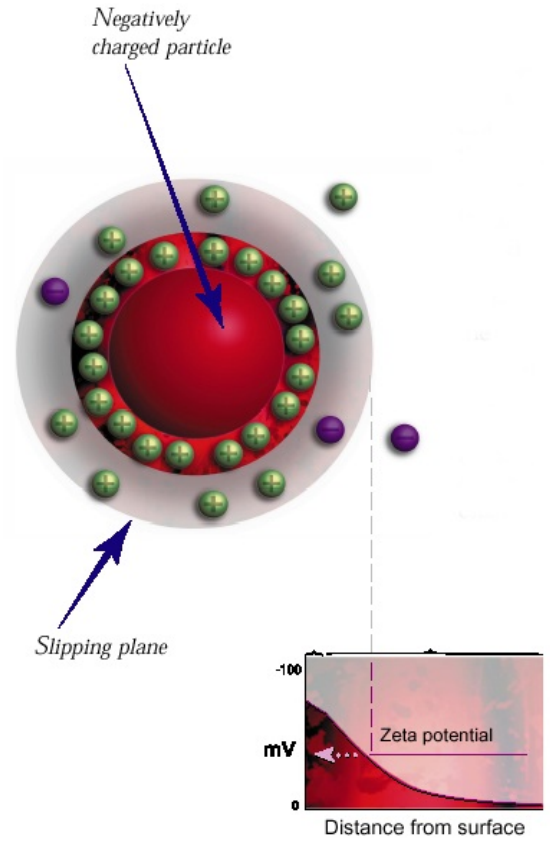


Figure 15: Negatively charged colloid particle *[28]*

The potential at slipping plane is known as the Zeta Potential.(Figure 16) which is the overall charge around the particle. In order to maintain a stable colloid, double layer needs a charge of 30 mV. As it can be seen from the figure 16, particles with zeta potentials more positive than +30mV and more negative than -30mV are considered stable *[28]*. The colloid particles will form a floc in a stable colloid system because of the electric attraction between them *[27]*.

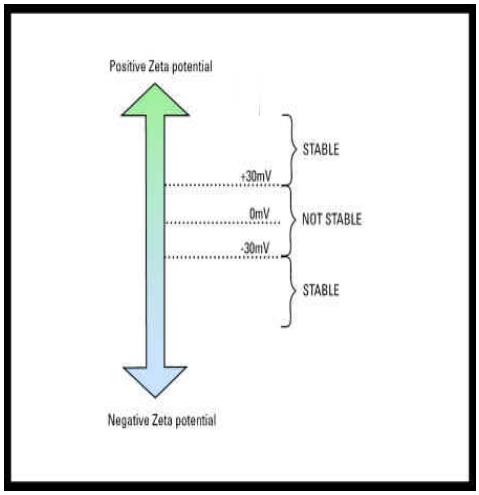


Figure 16: Zeta potential of the particle *[28]*

Clay, silica, heavy metals and organics are colloids found in wastewater. Due to lack of insufficient settling time during the treatment, colloids require coagulation for increasing the particle size and settling rates. According to *Løklingholm, M.S.* coagulation is a process described as rapid mixing of added coagulant, neutralizing charges to effect agglomeration and settling, and flocculation is process described as gentle agitation/mixing in order to allow bridging of flocculants chemical and forming of large settle able flocks from agglomerated colloids *[27]*. Some of the coagulants and flocculants used in clarification of water are aluminum salts and iron salts *[24]*.

- **(DAF) Dissolved air flotation**

Dissolved air flotation (DAF) removes hydrocarbons and protects the biological treatment that follows DAF. The DAF process consists of two different stages:

a) The chemical stage, where emulsion breaking and formation of solid aggregates (coagulation and flocculation) occurs.
b) The physical stage, where aggregates from the liquid phase are separated by introducing of air bubbles *[29]*.

From Figure 17 after treating feed water with chemicals, it is send to a flotation tank from where the portion of the effluent is recycled with recycle pump into a small pressure vessel (Air drum).

Here compressed air is introduced that will saturate the pressurized effluent water with air. The pressure release will result in air bubbles being released. The bubbles will attach to suspended matter which floats to the surface and skimmed off by mechanical device *[30]*.

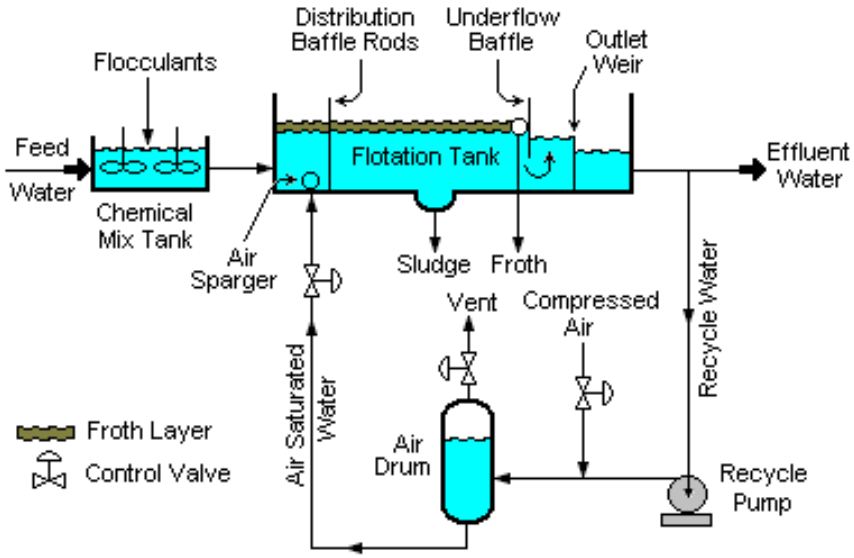


Figure 17: A typical dissolved air flotation unit (DAF) *[31]*

DAF units typically remove more than 95 percent of the oil and 75 percent of the solids. So DAF greatly reduces loads on downstream biological treatment unit *[32]*.

Two DAF units are implemented at the SAR Treatment plant, both of them connected with sludge tanks of 60 m^3 volumes each. At the inlet of the flotation tank, samples are taken to the lab (1-2 times a week) to determine the amount of TOC removed by coagulation/flocculation. At the outlet of each of the DAF units, samples are taken for TOC measurement to check the effectiveness of DAF units.

c) Biological process

Physical and chemical treatment methods contribute to partial removal of wastewater organic material. For effective removal of organic content in industrial effluents, there is need of biological treatment as well. *"The activated sludge process is by far the preferred treatment scheme for this purpose" [1]*.

SAR treatment plant has two bioreactor tanks 120 m^3 and 350 m^3 each, and settling chambers of 2 x 60 m^3 allowing settled sludge to be recycled to the inlet of the two bioreactors. Bioreactors are equipped with sensors which measure pH and temperature. Analyses are done in order to estimate the content of N and P that needs to be added as nutrients in reducing TOC.

In the bioreactors the oxygen concentration is due to the equilibrium among oxygen addition and oxygen consumption. Therefore to avoid limitations, dissolved oxygen must be in excess. Dissolved oxygen concentrations lower than necessary will affect growth and TOC removal rate, and higher concentration than needed will affect the economics of the process *[33]*.

- **Activated sludge:**

The activated sludge process shown in Figure 18 is treatment system combined of an aerobic bioreactor where with help of aeration the biomass is kept in suspension and a second part known as clarifier where biomass and particles are settled *[1]*. Sludge that is most settled is recycled back to the inlet of the aerobic bioreactor, therefore retention of high biomass concentrations is allowed *[34]*.

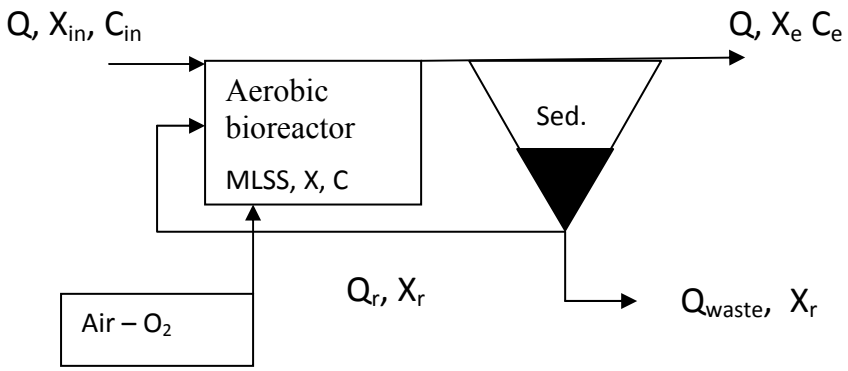


Figure 18: Activated Sludge Mass Balance

Equations for mass balance of the activated sludge

Hydraulic retention time (HRT): $t_H = \frac{V}{Q}\frac{(volume)}{(volume\ out)}$ (Eq. 14)

Solids retention time (SRT): $t_C = \frac{V \cdot X}{Q_{waste} \cdot X_r}\frac{(mass)}{(mass\ out)}$ (Eq. 15)

Presumptions:

Steady state: dX/dt = 0

Sterile influent: $X_{in} = 0$

Finished solids separation; $X_e = 0$

Correlation between growth rate and Sludge Retention Time can be determined by finding solution of the mass balance for biomass

$$\mu - k_d = \frac{Q_{waste} \cdot X_r}{X \cdot V} \Rightarrow \mu - k_d = \frac{1}{SRT}$$ SRT is reversed of growth rate. (Eq. 16)

The growth rate is given by Monod's equation: $\mu = \frac{\mu_{\max} \cdot C}{K_S + C}$

$$\frac{\mu_{\max} \cdot C}{K_S + C} - k_d = \frac{1}{SRT} \Rightarrow \quad C = \frac{K_S(k_d + 1/SRT)}{\mu_{\max} - (k_d + 1/SRT)}$$ (Eq.17)

Sufficient SRT is selected so that certain treatment efficiency can be accomplished *[35]*.

- **Biomass concentration**

The biomass is the amount of growth (substrate removal), decay and waste. Biomass concentration is determined by finding solution of the mass balance for substrate:

$$V\frac{dC}{dt} = Q(C_{in} - C_e) - \frac{\mu XV}{Y}$$ (Eq.18)

as well as

$$\mu - k_d = \frac{1}{SRT} \Rightarrow \mu = k_d + \frac{1}{SRT}$$ (Eq.19)

When steady state is assumed and μ (from Equation 19) is replaced will result in Equation 20.

$$0 = Q(C_{in} - C_e) - \frac{XV}{Y}\left(k_d + \frac{1}{SRT}\right) \quad \rightarrow X = \frac{Q(C_{in} - C_e)Y}{V\left(k_d + \frac{1}{SRT}\right)} = \frac{Q(C_{in} - C_e)Y \cdot SRT}{V(SRT \cdot k_d + 1)} \text{ (mg/l)}$$ (Eq.20)

The equation for biomass indicates when more substrate that is taken away and when the longer SRT is, the biomass concentration is higher.

The total mass of biomass is the product of bioreactor volume and concentration:

Biomass production: $MX = V \cdot X = \frac{Q(C_{in} - C_e)Y \cdot SRT}{(SRT \cdot k_d + 1)}$ (mg) (Eq.21) *[35]*

- **Sludge concentration in the bioreactor**

The sludge in a bioreactor includes biomass and non viable organic and inorganic compounds. The inorganic compounds are represented by metals, sand and clay that are existent in the influent. The organic compounds are dead cells residues (unbiodegradable) as well as unbiodegradable particulate organic components in the wastewater.

Mixed Liquor Suspended Solids (MLSS) corresponds to the total solids concentration in a bioreactor and the organic solids concentration in a bioreactor is known as Mixed Liquor Volatile Suspended Solids (MLVSS). The inorganic and unbiodegradable organic solids from the wastewater accumulate in the sludge (MLSS) in compliance with SRT. They do not take part in reactions in the bioreactor. The key assumption in a bioreactor when a fraction of the organisms die is that the rest of the living cells degrade the main organic fraction of the organisms (around 80 – 90 %) while the residue (10 – 20 %) corresponds to organic solids (f_d) that are unbiodegradable and they accumulate in the bioreactor. The endogenous residue accumulation represents a function of organism's concentration, SRT and the rate of decay.

The composition of the organic sludge in the bioreactor is:

Organic fractions = Biomass + Unbio. Org. + Endogenous residue

$$MLVSS = X + X_{i,R} + X_{E,R} \quad \text{(Eq.22)}$$

By analysing the MLVSS/MLSS ratio which is between 0.7 and 0.8, the inorganic fraction can be determined *[35]*.

1.5. CHROMATOGRAPHY – MASS SPECTROMETRY

Gas chromatography – mass spectrometry (GC/MS) is a powerful tool being used for the analysis of complex organic and biochemical mixtures *[36]*. GC/MS instruments are utilized for the identification of components found in the natural and biological systems *[37]*.

1.5.1. Gas chromatography-mass spectrometry (GC/MS) instrument

The GCMS instrument consists of two parts, Gas Chromatography (GC) and Mass Spectrometer fraction (MS) (Figure 19).

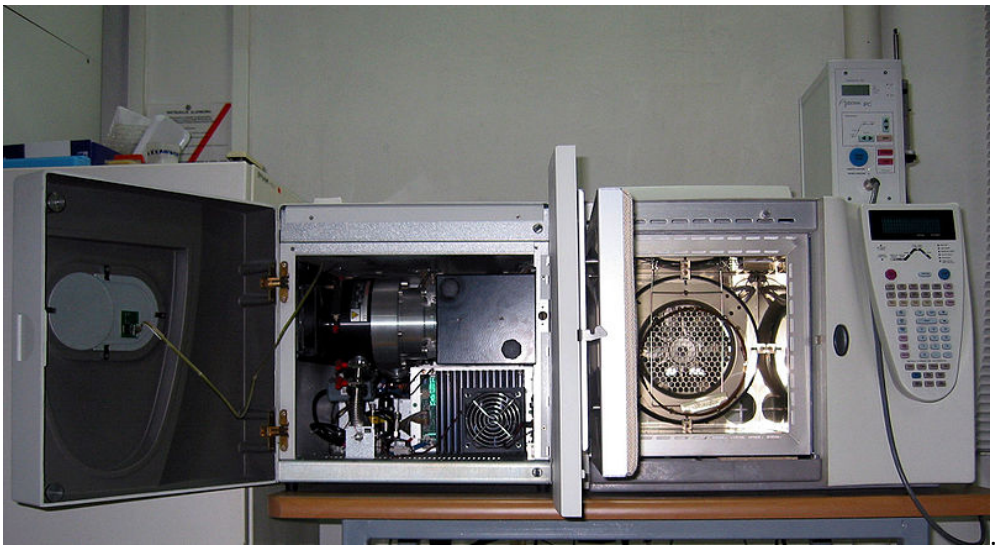


Figure 19: GC/MS Instrument *[38]*

The GC fraction separates the chemical mixtures by their volatility and the MS is used for qualitative analyses of the chemicals.

a) Gas chromatography (GC) consists of:

Injection port – Solvent is injected into the GC. Then by the help of inert gas, the sample is carried through the instrument. By heating the injection port up to 300° C, the chemicals become gases.

Oven – Oven represents the external part of the GC. Molecules through the column are passing by heating of the column up to 320° C.

Column – Column is a 30 meter long thin tube inside the oven. Chemicals are transported through the column by the help of inert gas and are separated based on their volatility *[39]*.

b) Mass Spectrometer (MS) consists of:

Ionization Source – After entering the MS…*"the molecules are blasted with electrons, which cause them to break into pieces and turn into positively charged particles called ion"[39]*. This is essential, because in order to pass through the filter the particles must have charge *[39]*. Electron- impact ionization and chemical ionization are most common ion sources used in GCMS analyses *[37]*.

Filter – Electromagnetic field is filtering the ions based on mass. The range of masses allowed through the filter is selected by technicians.

Mass Detector – Number of ions with a specific mass is given by mass detector. This message is forwarded to a computer where mass spectrum is produced

c) Computer

Received data is plotted on a graph called a mass spectrum. Mass spectrum represents the number of ions with different masses. It consists of x-axis which is a mass and the y-axis which represents abundance or quantity *[39]*.

1.6. ALTERNATIVE TECHNOLOGIES FOR TREATMENT OF SLOWLY BIODEGRADABLE TOC

Advanced oxidation processes (AOP) can be useful when components in wastewater are chemically stable and / or they have low biodegradability. Even AOPs are using different reagent systems, they have in common that they all produce HO• radicals that are very reactive, not highly selective and powerful oxidants by which the organic compounds are attacked at high rate *[40]*. "Hydroxyl radicals are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and no selectively with nearly all electron-rich organic compounds" *[41]*.

$$\text{AOPs} \longrightarrow \text{HO}\bullet \longrightarrow CO_2 + H_2O + \text{inorganic ions} \qquad \text{(Eq.23)}[40]$$

Radical addition (Eq.24), hydrogen abstraction (Eq.25) and electron transfer (Eq.26) are types of hydroxyl radicals attacks on organic compounds *[41]*.

$$R + HO\bullet \rightarrow ROH \qquad \text{(Eq.24)}$$

$$R + HO\bullet \rightarrow R\bullet + H2O \qquad \text{(Eq.25)}$$

$$Rn + HO\bullet \rightarrow Rn\text{-}1 + OH^- \qquad \text{(Eq.26)}$$

R – Organic compound *[41]*

Reaction rate constants for ozone and hydroxyl radicals with various organic compounds are presented in Table 5.

Table 5: Reaction rate constants (k, M^{-1} s^{-1}) of ozone compared with hydroxyl radical *[42]*.

Compound	O_3	HO•
Chlorinated alkenes	10^3- 10^4	10^9- 10^{11}
Phenols	10^3	10^9- 10^{10}
N-containing organics	10- 10^2	10^8- 10^{10}
Aromatics	1 - 10^2	10^8- 10^{10}
Ketones	1	10^9- 10^{10}
Alcohols	10^{-2}- 1	10^8- 10^9

Methods for generating hydroxyl radicals can be divided into non-photochemical and photochemical.

1.6.1. Non – Photochemical Methods

Non – photochemical methods generate HO• radicals with no use of light energy:

1. Ozonation at elevated pH (pH>8.5)
2. Ozone + hydrogen peroxide (O_3/H_2O_2)
3. Ozone + catalyst (O_3/CAT)
4. Fenton system (H_2O_2/Fe^{2+})

- **Ozonation at higher pH**

Ozone's decomposition rate is increased at higher pH levels. Molecular ozone reactions combined with HO• radicals reaction can oxidize organic species. Three molecules of ozone gives two $OH^{\cdot}$ radicals that have 10^6 to 10^9 faster rate of attack than corresponding molecular ozone (Eq.27).

$$3\,O_3 + OH^- + H^+ \longrightarrow 2OH^{\cdot} + 4O_2 \qquad \text{(Eq.27)}$$

Electricity cost for generation of ozone is the capital operating cost for the ozone oxidation process *[42]*.

- **Ozone + hydrogen peroxide (O_3/H_2O_2)**

Hydrogen peroxide is the simplest peroxide. "Oxidizing capacity of hydrogen peroxide is so strong that it is considered a highly reactive oxygen species" *[43]*

B adding this strong oxidizer to ozone, decomposition cycle of ozone is initiated by HO• radicals that are formed. Two ozone molecules give two HO• radicals

$$2O_3 + H_2O_2 \longrightarrow 2OH^{\cdot} + 3O_2 \qquad \text{(Eq. 28)}[42]$$

Some studies suggesting that best treatment efficiency were achieved when hydrogen peroxide was added after oxidation with ozone *[42] [44]*.

- **Ozone + catalyst (O_3/CAT)**

Heterogeneous and homogeneous catalysts are investigated as possibility of acceleration of ozonation reactions. A significant result in destruction of the compounds was carried out by metal oxides and metal ions such as Fe_2O_3, MnO_2, Al_2O_3–Me, Fe^{2+}, TiO_2–Me, etc. *[42]*.

In some studies that were investigating AOP for chlorobenzenes oxidation in wastewater, concluded more efficient reduction of TOC achieved with ozone + catalyst compared with ozonation at high pH alone *[42] [45]*.

- **Fenton system (H_2O_2/Fe^{2+})**

" Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or waste waters. Fenton's reagent can be used to destroy organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE)" [46].

In the presence of hydrogen peroxide, Fe (II) is oxidized very fast to Fe (III), a hydroxyl anion and a hydroxyl radical.(Eq. 29) Iron (III) is reduced back to iron (II), a proton and peroxide radical by the same hydrogen peroxide (Eq.30) *[46]*.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \quad \text{(Eq.29)}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + OOH\cdot \quad \text{(Eq.30)}[46]$$

Fenton system is used for wastewater treatment because iron is not toxic and highly abundant element and hydrogen peroxide is easy to manage and environmental gentle *[42]*.

1.6.2. Photochemical Methods

Complete oxidation reactions of organics resistant to non photochemical methods can be done with addition of UV radiation. This is because many organic compounds absorb UV (in the range of 200 – 300 nm) and due to photolysis decompose or they turn into more reactive compounds with chemical oxidants *[42]*.

Photochemical methods are:

1. Ozone and UV radiation (O_3/UV)
2. Hydrogen Peroxide and UV radiation (H_2O_2/UV)
3. Ozone, hydrogen peroxide and UV radiation (O3/H2O2/UV)
4. Photo-Fenton and Fenton-like systems
5. Photocatalytic oxidation (UV/TiO2)*[42]*.

- **Ozone and UV radiation (O_3/UV)**

Photolysis of the ozone is the first reaction when AOPs are using combination of ozone and UV during which hydroxyl radicals are produced *[40]*.

$$H_2O + O_3 \xrightarrow{hv} 2HO\bullet + O_2 \quad \text{(Eq.31)}$$

$$2HO\bullet \longrightarrow H_2O_2 \quad \text{(Eq.32)}[40]$$

If organics in waste water absorb greatly UV, then no additional effects will be given by UV to ozone. *[42]*. Total mineralization of organics with short molecular chain can be done by ozone and UV*[42] [47]*. The efficiency of Ozone and UV in removing tetrachloroethylene from water compared to ozonation and photolysis alone was investigated by Peyton et al. *[42] [48]*.

- **Hydrogen Peroxide and UV radiation (H_2O_2/UV)**

Photolysis of hydrogen peroxide produces hydroxyl radicals.

$$H_2O_2 \xrightarrow{hv} 2HO\bullet \quad \text{(Eq.33)}$$

Hydrogen peroxide anion that is in an acid base equilibrium with H_2O_2, absorbs UV in the wavelength of 254 nm.

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad \text{(Eq.34)}$$

$$HO_2^- \xrightarrow{hv} HO\bullet + O^{\cdot -} \quad \text{(Eq.35)}$$

H_2O_2/UV was investigated and proved successful in destruction of chlorophenols and other chlorinated compounds *[42]*.

- **Ozone, hydrogen peroxide and UV radiation (O_3/H_2O_2/UV)**

Addition of Hydrogen peroxide to O_3/H_2O_2 speed up ozone decomposition resulting in increased HO • radicals production *[42]* .

$$2O_3 + H_2O_2 \xrightarrow{hv} 2\,HO\bullet + 3O_2 \quad \text{(Eq.36) [40]}$$

These processes are expensive. Costs vary with wastewater flow rate, concentration and type of contaminants and the required removal level *[42]*.

- **Photo-Fenton and Fenton-like systems**

Addition of Fe^{3+} ions to H_2O_2/UV results in a photo – Fenton type oxidation process. At lower pH around 3 due to acidic environment $Fe(OH)^{2+}$ is produced. When this complex is exposed to UV is decomposed and results in HO• and Fe^{2+} ions (Equation 37).

$$Fe^{3+} + H_2O \longrightarrow Fe(OH)^{2+} + H^+ \quad \text{(Eq.37)}$$

$$Fe(OH)^{2+} \rightleftharpoons Fe^{3+} + OH^- \quad \text{(Eq.38)}$$

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + HO\bullet \quad \text{(Eq.39) [42]}$$

The efficiency of these systems is due to Photo reduction of ferric ion and efficient use of light quanta *[42]*. Due to its simplicity, these kind of reactions are used often to eliminate obstinate components *[40]*.

2. METHODOLOGY

2.1. METHODS FOR DETERMINING TOC CONCENTRATIONS

Direct Non Purgeable Organic Carbon (NPOC) method and difference method are two methods for determining TOC. This is because there are inorganic carbon components together with the organic substances in an aqueous sample. Authentic TOC results will come from the selection of appropriate determination method according to predomination of the carbon compounds in the sample. The instruments on the market can detect TOC by either NPOC method or difference method.

- Direct determination - (NPOC) method

Removing of the inorganic carbon compounds (TIC) from the sample is the first step in NPOC method. Removal of TIC can be externally-outside the TOC analyzer, or internally in the TIC reactor part. Removal of the TIC is done by addition of acid to pH 2, and afterwards purging the carbon dioxide produced by an auxiliary gas. After purging, by injection the sample into the digestion unit of the analyzer, the remaining component of the organic carbon is identified. Due to its simple handling and reliability, NPOC method has become approved as the most frequent method of TOC determination.

- Difference method

The difference method requires two measurements. First, part of the sample is injected into the TIC reactor. Here usually with addition of acid and in a stream of carrier gas, the carbonate-derived portion of CO_2 is detected as TIC. Second step takes place in the digestion unit of the analyzer, where untreated sample is introduced and the total carbon (TC) is determined. Thus TOC is calculated as:

TOC = TC – TIC *[49]*.

"*The method has been standardized worldwide through a large number of standards. Besides the ASTM and EPA standards, the international standard ISO 8245 and the European standard EN 1484 are the conventions most frequently considered" [49]*.

Comparisons of the two methods are given in Table 6.

Table 6: Advantages and disadvantages of direct and difference TOC determining method *[49]* .

Method	**Advantage**	**Disadvantage**
Difference method	Volatile organic compounds in the samples are detected as well.	Unsuitable at high TIC concentrations (TIC >> TOC). Measurement times are long.
Direct-NPOC method	Favorable at high TIC concentrations (TIC >> TOC). Gives quick results.	Volatile organic compounds in the samples are not detected.

2.2. OVERVIEW OF THE ANALYTICAL TECHNIQUES AT SART

Description of the various analytical techniques used at SAR treatment plant.

➢ TOC and total N measurements

For the measurement of TOC and Nitrogen content SAR Treatment is using multi N/C® 2100 Analyzer produced by Analytic Jena AG (Figure 20). TOC/TN_b analyzer gives data of total carbon and total nitrogen from every wastewater sample.

" Characteristics multi N/C® 2100:

- *Focus Radiation NDIR-Detector®*
- *VITA® Flow Management System**
- *Easy Cal®**
- *Auto-protection*
- *Catalytic high-temperature oxidation up to 950°C*
- *Valve-free direct-injection technology*
- *Suitable also for small injection volumes*
- *Upgradable for simultaneous TN_b determination*
- *A catalyst for simultaneous TOC/TN_b determination in the entire measurement range*
- *Option of HT 1300 or double furnace technology for solid analysis*
- *Compact system with integrated, fully automated auto sampler " [50]*

***model-specific**

Figure 20: TOC/TN_b analyzer *[50]*

➢ Density measurements

For density measurements of wastewater samples a hydrometer device is used (Figure 21). Hydrometer is composed of a long-necked glass bulb that is weighted and sealed. Liquid density is determinate by depth of the flotation *[51]*.

Figure 21: Hydrometer *[52]*

Sometimes SART also use a weight and measure the weight of one liter of the wastewater.

- Photometer for determining the content of P in water samples

Photometer is an instrument that measures the electromagnetic radiation from ultraviolet to infrared range and along with the visible spectrum *[53]*. SAR treatment for this purpose uses Spectroquant® NOVA 60 (Figure 22).

"Spectroquant® NOVA 60 is an instrument for the routine analysis of all water types and is capable of measuring both the ready-to-use cell tests as well as inexpensive reagent tests" [54].

Figure 22: Spectroquant® NOVA 60 Photometer *[55]*

- JAR testing

Jar test or coagulation test are used for simulating full scale coagulation and flocculation processes (Figure 23). It is performed in laboratory to determine optimum chemical (coagulant) dosage. The Jar tests can be used for selection of the most effective coagulation chemical and its optimum dosage *[56]*.

For doing the Jar test analyses SAR Treatment is using coagulants PAX L60 and Polymer, and for pH adjusting HCL and NaOH are used. Specifications of PAX XL 60, Polymer, HCL and NaOH are given in Appendixes C, D, E and F.

Figure 23: JAR test model *[57]*

- pH and conductivity measurement

For this purpose SAR Treatment is using instrument pH 100 produced from WWR. Conductivity is measured by "Combo pH & EC" By Hanna.

- Alkalinity measurement

For alkalinity measurement pH 100 apparatus is used.

If SART is unsure on the biological degradation of wastewater, small scale biological lab experiments are done. Measure the TOC after addition of the test water mixed with biomass and water from the biological rector. TOC is measured after 24 and 48 hours. This will give an idea if the water is biologically treatable.

2.3. LAB WORK AT SART FOR TOC CONCENTRATIONS

To get an overview of the TOC concentrations for wastewater at SART, a total 40 samples were analyzed, 5 from each month starting from July 2010 till February 2011. TOC in each sample was determined by using direct determination - NPOC method.

First step in removal of inorganic carbon compounds (TIC) from the sample was dilution of 2.5 ml sample with distillated water in 50 ml test tube and acidifying by adding 0.5 ml of hydrochloric acid (Figure 24).

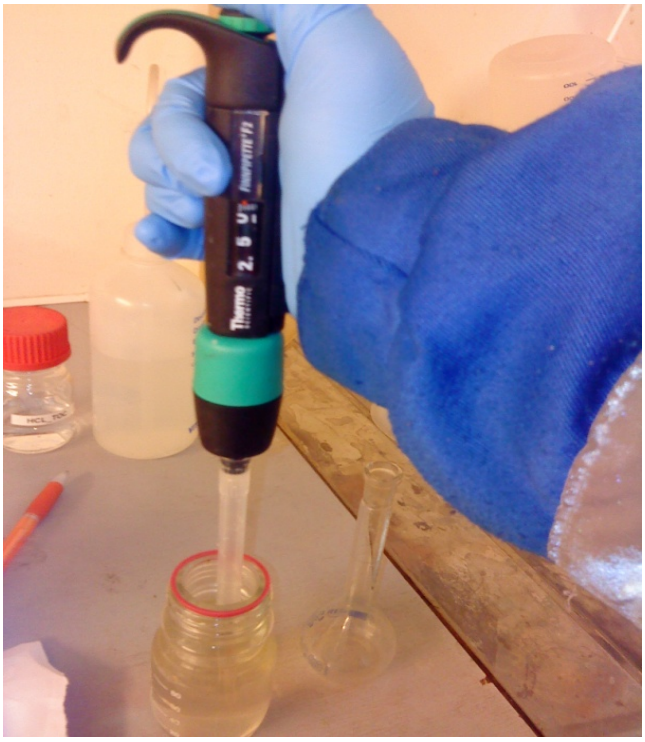


Figure 24: Dilution of the sample

After that purging hose was inserted into the test tube purging the carbon dioxide generated by additional gas. Purging lasted for two minutes. This step was done externally - outside the TOC analyzer (Figure 25).

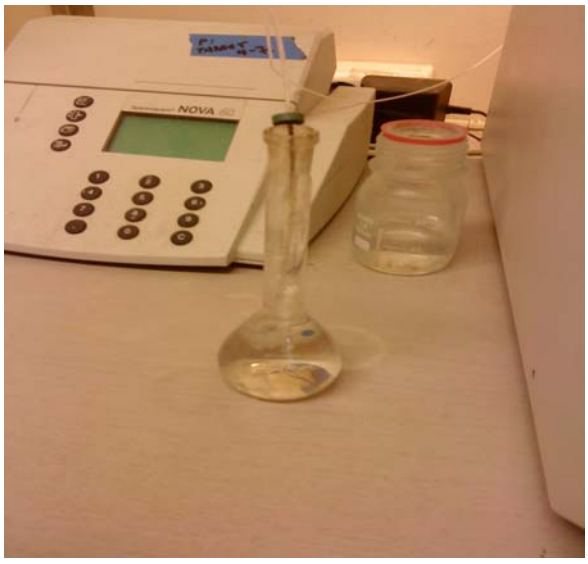


Figure 25: Removing of inorganic carbon compounds (TIC) from the sample

After TIC removal the MultiWIN evaluation software was started. Micro liter syringe of 500 µL was used for taking the sample and injecting into the digestion unit of the analyzer. In this way the remaining component of the organic carbon was determined *[49]*. The injection procedure consisted of two steps. Figure 26 shows injecting the sample in the TC port of the apparatus for 5 seconds. For another 10 more seconds (Figure 27) the syringe stayed in the port before it was removed and the port was closed.

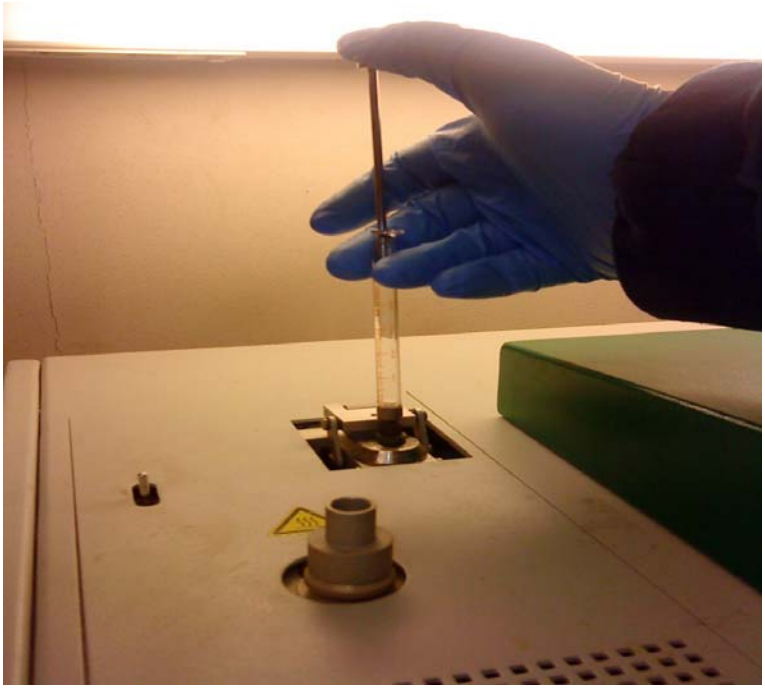


Figure 26: Injecting the sample in the TC port of the analyzer

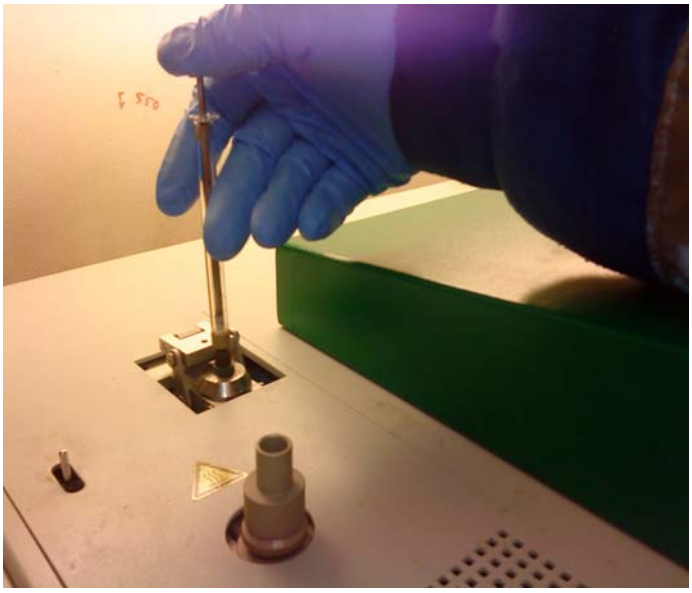


Figure 27: Second step of injection procedure of the sample

The procedure was repeated twice more for each sample. The MultiWIN evaluation software is set up for 2(2-3) repetitions, and it takes the average of the 2 closest values in the 3 repetitive measurements *[49]*.

2.4. JAR TESTING AT SART

2.4.1. Small scale flocculation method

Small scale flocculation methods were done in order to find out the potential reaction.100 ml of each sample was taken in a sample glass (Figure 28), followed by addition of 200 µl PAX XL 60 per 100 ml sample. Addition of PAX was done by 100 – 1000 µl automatic pipette. After that the sample glass was rapid mixed and the pH was measured. The next step was to adjust pH to 7 with NaOH, after which flocks in the water could easily be seen in Figure 29. The last step was addition of 3 ml of Polymer, which was injected with syringe in the water sample followed by slow mixing (Figure 30).

Figure 28: Water sample in a sample glass

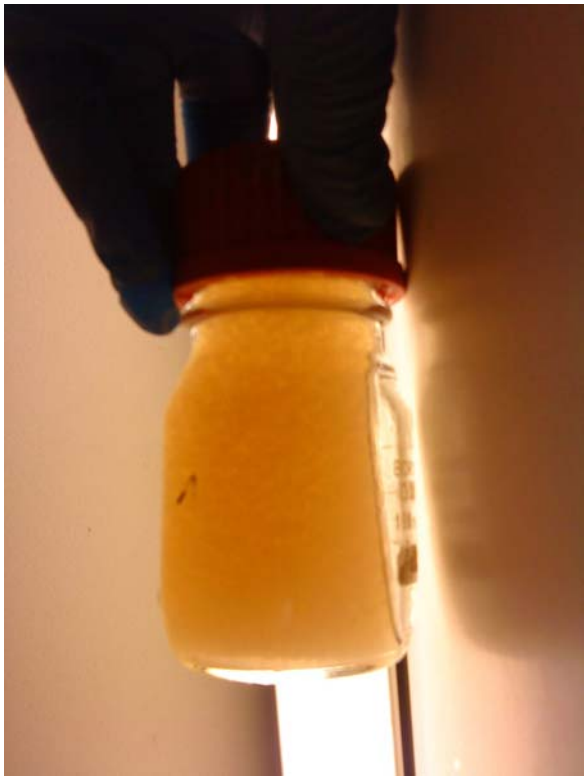


Figure 29: Flocks in the water

Figure 30: Comparison of water samples, before and after small scale flocculation

2.4.2. Large scale flocculation method

Large scale flocculation tests were done on the same samples which later were sent to the UIS for Small Scale Simulation Test on biodegradability. A 2 L flask was used where 1500 ml of water sample was introduced followed by addition of 2000 µl PAX XL 60 per 1000 ml sample. Addition of PAX was done by 0.5 – 5 ml automatic pipette. Thereafter the sample was placed into jar test, and mixed at 100 ppm. (Figure 31). pH was measured by pH meter - pH 100.The mixing was typically about 1 min. Next step was adjusting the pH to 7 with NaOH, after which flocks in the water could easily be seen (Figure 32). The last step was addition of 3 ml of Polymer, which was injecting with syringe into the water sample. Mixing was then reduced to 30 r/min to provide gentle agitation and the flocks were allowed to settle. The sample settled for some time (Figure 33) before transferred to a sample tube (Figure 34) *[56]*.

The TOC of the flocculated sample was measured using NPOC method for determining TOC concentration on the sample after flocculation.

Figure 31: Rapid mixing of the sample

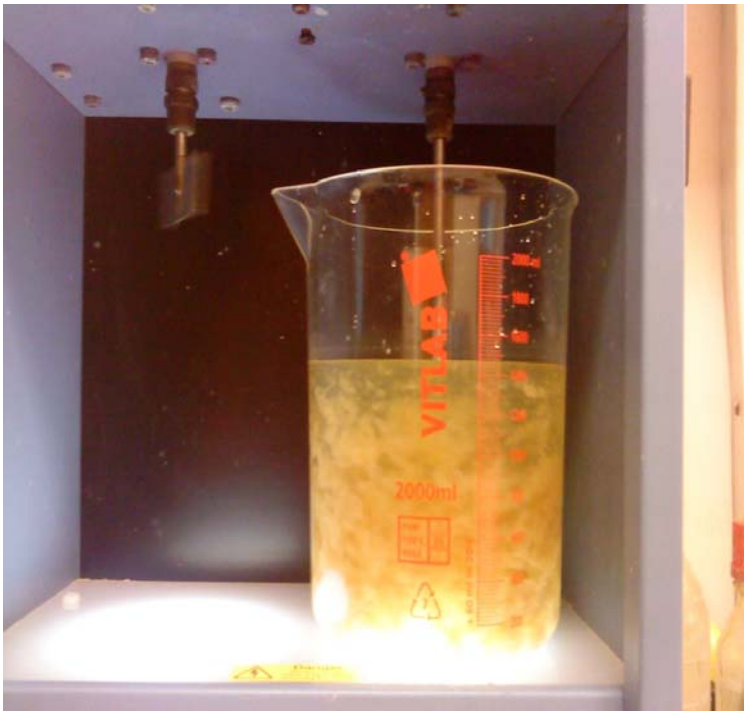


Figure 32: Flocks in the water

Figure 33: Settling of flocks before taking the sample for biodegradation test

Figure 34: Taking sample for biodegradation test

2.5. SMALL SCALE SIMULATION TESTS ON BIODEGRADABILITY

Small scale simulation tests on biodegradability were done in order to follow the degradation in the bioreactor at SART. 1 liter of sample water was saved for GC/MS scanning for hydrocarbons before start up and ends of each cycle of the bench tests.

2.5.1. Experimental procedure

Sludge washing on the activated sludge was done at SART before start up of each of the laboratory bench tests. By doing sludge washing, the TOC is removed from the water leaving only bacteria. The purpose of doing this is that no TOC should be left in the water phase but only clean sludge that is thereafter used for doing laboratory bench test. The activated sludge was collected from the bioreactor tank at SART (Figure 35).

Figure 35: Adding 1000 ml sludge in the measuring cylinder

The procedure for sludge washing was addition of 1000 ml sludge from bioreactor into measuring cylinders and settling the sludge for approximately 1 hour (Figure 36). After settling, the clear phase was decanted out of cylinders (Figure 37), before refilled with seawater up to 1000 ml and mixed. Seawater was stored for 24 hours at room temperature before addition to the cylinders.

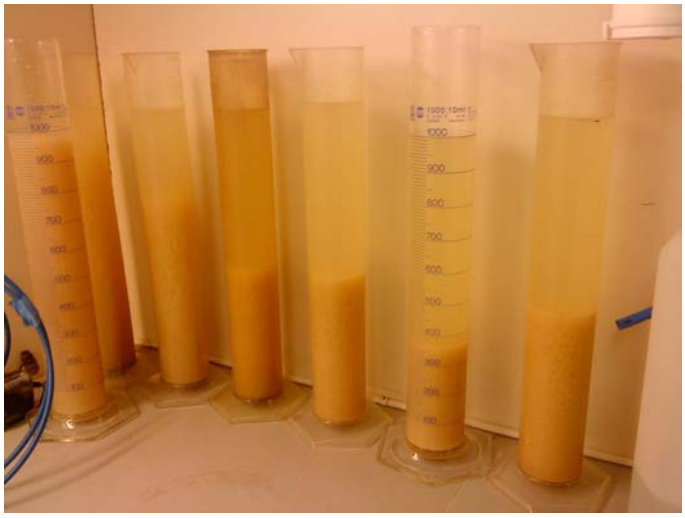


Figure 36: Settling of the sludge

The steps settling, decanting and refilling with seawater were repeated three more times. For the final washing step after decanting, the settled sludge from all cylinders was poured off into sample bottle and taken to the laboratory for start up of the bench tests (Figure 38).

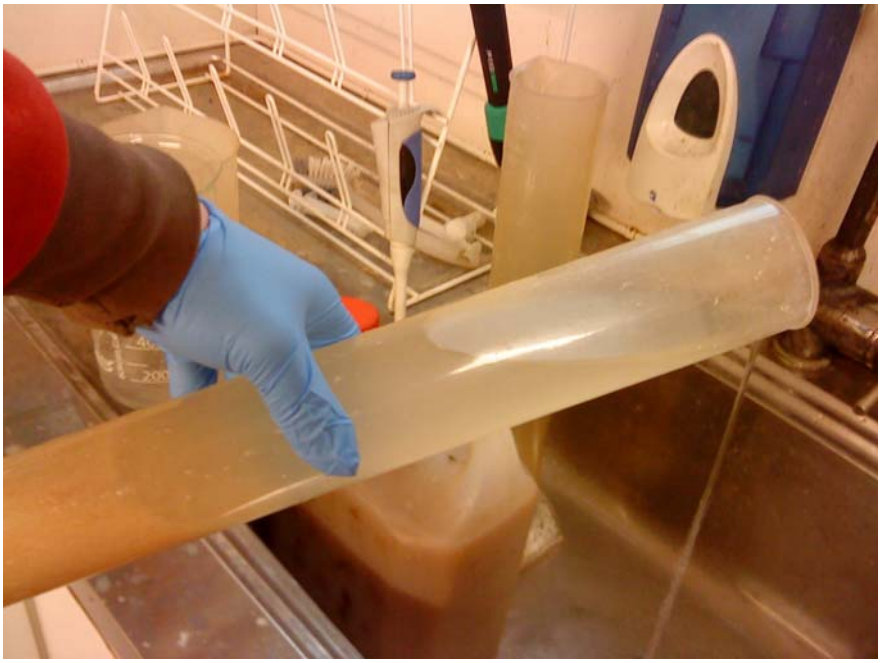


Figure 37: Pouring out the clear phase

Figure 38: Transferring sludge into sample bottle

The laboratory bench test consisted of five by 1800 ml flasks. First flask was used for blank control, second for negative control and last three flasks were run in parallel where the degradation of the flocculated wastewater sample was monitored. All of the flasks were equipped with magnetic stirrers for establishing sufficient mixing and uniform distribution of biomass and substrate in the flasks. Oxygen in the flasks was provided by air diffusers for sufficient oxygen supply (Figure 39) *[33]*.

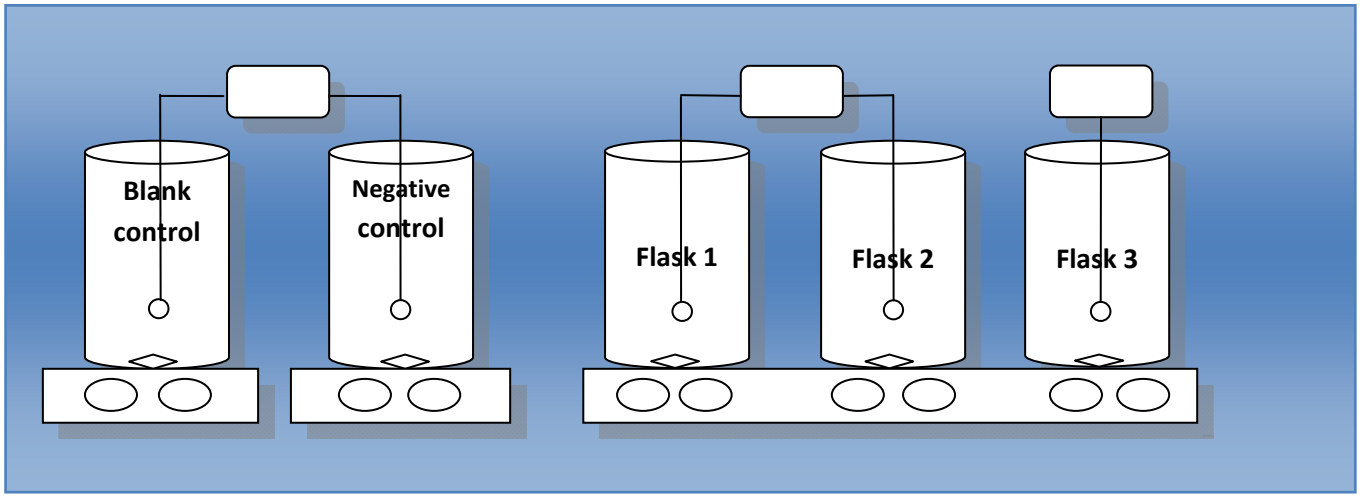


Figure 39: Schematic diagram of the bench test

Legend:

Stirring and temperature control, Magnetic stirrer, Air pump, Air diffuser

Before the start up of the tests, the temperature on the hotplate magnetic stirrers was adjusted to around 34 °C to simulate the temperature in the bioreactor at SART (Figure 40).

Figure 40: Adjusting the temperature on hotplate magnetic stirrers to 34 °C

In order to avoid temperature shock on the bacteria, flocculated wastewater was stored to room temperature 24 hours before each run of the bench tests. Biomass was distributes equally to all 5 flasks corresponding to the level in sample bottle (Figure 41), following by addition of seawater in the flasks.

Figure 41: Sludge for distribution in flasks

Macronutrients, micronutrients, vitamins and amino acids were mixed in separate flask with flocculated wastewater sample so the pH could be adjusted to 7 (Using NaOH), to avoid low pH before distribution to the flasks. Optimum pH range of microorganisms is pH 7 - 8. pH outside this range may reduce growth, treatment rate and even kill bacteria*[33]*. Flocculated wastewater sample was distributed in 3 flasks in parallel and in one for the negative control (Figure 42) and diluted till 1800 ml by seawater. The blank control consisted of biomass, nutrients and seawater without wastewater sample. In the flask for blank control seawater was added together with nutrients till 1800 ml. Aeration of the bench test was started and it was left during the night (Figure 43).

Figure 42: Distribution of the flocculated water with nutrients in each flask

Figure 43: Laboratory bench test

Total of three bench experiment were done. Table 7 shows the bench test content before start of the experiments *[58]*.

Table 7: Bench test configuration

Bench test		**Content**
Negative control		Biomass, nutrients, flocculated water and seawater
Blank Control		Biomass, nutrients and seawater
Test control	**Flask 1**	Biomass, nutrients, flocculated water and seawater
	Flask2	Biomass, nutrients, flocculated water and seawater
	Flask3	Biomass, nutrients, flocculated water and seawater

From the beginning of each cycle of bench test, the total suspended solids and volatile suspended solids were measured daily to follow the biomass growth. The retained filtrate from TSS/VSS analyzes was filtered daily through 0.22 µm Nylon acrodisc filters, and TOC of filtrate was measured as Dissolved Organic Carbon (DOC). DOC is a general description of the organics capable to pass through 0.22 µm size filter *[59]*. Dissolved oxygen (DO) was measured during the first day and parameters temperature and pH were measured a couple of times daily. In test flasks VSS growth and DOC removed were corrected for the blank.

2.5.2. Analytical procedures during the bench test

- **Calculation of flocculated sample volume (Vs)**

Addition of the flocculated water sample volume (Vs) for each bench run was calculated according to the mass balance.

$$C_s \times V_s = C_0 \times V_0 \quad \text{(Eq.40)}$$

Where:

C_s - Concentration of the flocculated water sample

V_s - Volume of the flocculated water sample

C_o - Initial concentration of the flocculated water sample

V_o - Initial Volume of the flasks

C_o for every run was set at 1200 mg/l.

Addition of macronutrients was calculated according to ratio C: N: P 100:20:5. After calculations 2 ml/L of 40 % Urea $(NH_2)_2CO$ was added as a source of N and 0.4 ml/L of 75% Phosphoric acid (H_3PO_4) was added as a source of P. 1 ml of micronutrients and 0.2 ml of Vitamins and Amino acids were added together with macronutrients in each flask. Specification of 75 % Phosphoric acid is given in Appendix G, and specifications for micronutrient solution in Appendix H.

- **Temperature and pH**

Temperature on the hotplate magnetic stirrers was adjusted to 34 °C to simulate the temperature at bioreactor at SART. Temperature together with pH was monitored with instrument Metrohm 744 pH meter.

- **Dissolved Oxygen (DO)**

Dissolved oxygen was measured with WTW Multi 3410.

- **Analyses of TSS and VSS**

TSS analyses were done using Whatman glass microfiber filters GF/F - 47 mm with 1 um pore size. First filters were dried at 105 ºC for at least 15 minutes prior to weighting to assure completely dryness. After drying, the filters were cooled in desiccator and weight was measured as m_{filter}. The appropriate sample volume was allowed to settle for around 30 minutes prior to filtration and the clear liquid was filtered first while the settled solids were added after so the filtering procedure went much faster. The filtered liquid was used for dissolved organic carbon analysis. Determination of TSS was after drying the filters with support dishes for a minimum of 2 hours in oven at 103-105°C and cooling them in desiccator.

After cooling, filter + solids weight was measured and was noted as $m_{filter + solids.}$

Calculation of TSS:

$$TSS\left[\frac{mg}{l}\right] = \frac{m_{filter+sample} - m_{filter}}{V_{sample}} \quad \text{(Eq.41)}$$

For determination of VSS, the filters with porcelain dishes were combusted in muffle oven at 550°C for 30 minutes. After combustion the dishes with filters were cooled for a short time in air before transferred to desiccator. The weight of filters and ignited residual was measured on analytical balance and noted as $m_{filter + ignited}$ residual.

Calculation of VSS:

$$VSS\left[\frac{mg}{l}\right] = TSS - \frac{m_{filter+ignited\,residual} - m_{filter}}{V_{sample}} \quad \text{(Eq.42) [60]}$$

- **Dissolved Organic Carbon (DOC)**

For Dissolved Organic Carbon measurements, 1 ml of filtered liquid from TSS analyses was taken with syringe and filtered through 25 mm W/0.2 µm Nylon membrane Syringe filters. After 1:20 dilution, the samples were taken to SART where TOC of filtrate was measured as DOC.

- **Calculation for DOC degradation**

By using the equation below the degradation percentage was calculated.

$$D_t = \left[1 - \frac{C_t - C_{bl(t)}}{C_0 - C_{bl(o)}}\right] \cdot 100 \quad \text{(Eq.43)}$$

Where:

D_t = percentage of DOC degradation at time t,

C_0 = DOC starting concentration

C_t = DOC concentration at time t,

$C_{bl\,(0)}$ = starting concentration of DOC in the blank,

$C_{bl\,(t)}$ = concentration of DOC in the blank at time t *[61]*

3. RESULTS AND DISCUSSION

3.1. RESULTS FROM LAB WORK ON DETEMINING TOC CONCENTRATION

TOC concentrations on 40 water samples were analyzed at SART. According to Figure 44, TOC concentration in receiving water at SART ranges from 2000 to over 10000 mg/l.

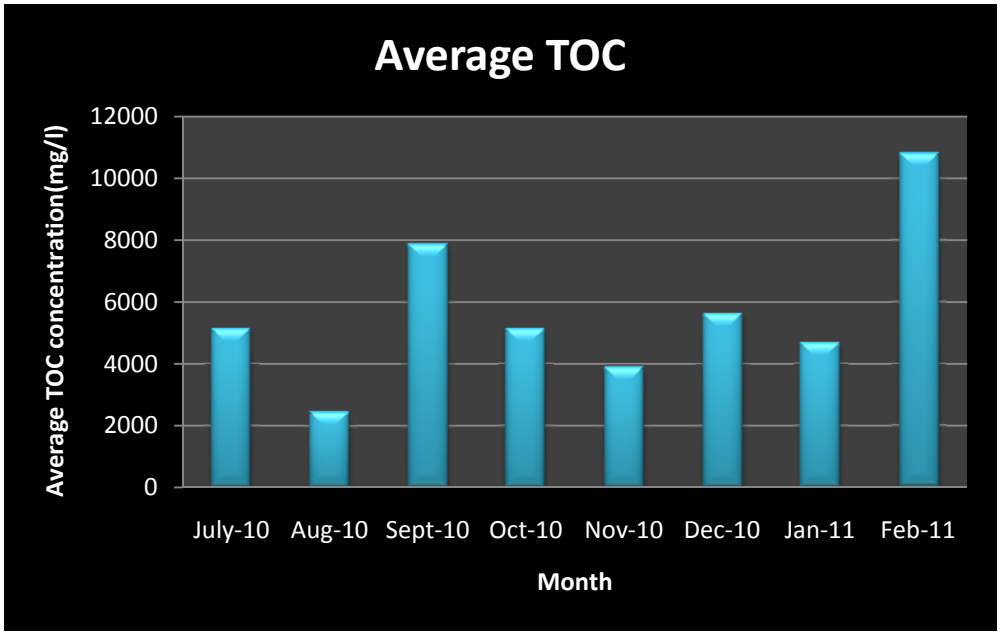


Figure 44: Average TOC during period of 8 months

3.2. RESULTS FROM JAR TEST

Table 8 shows TOC concentration after flocculation and filtering on selected samples. These samples with various TOC concentrations were used as C_{sample} for the three bench tests at UiS in order to follow the HC degradation. As degradation of sample with the highest TOC concentration (12000 mg/l) during the first run went very fast (in two days) for the second and third run, therefore, C_{sample} with less TOC concentration were chosen.

Table 8: TOC concentration after flocculation

Cycle No.	Sample ID	TOC concentration (mg/l) after flocculation (C_{sample})
1	STR10-219	12000 mg/l
2	STR10-256 and STR10-155	2500 mg/l
3	Water taken from DAF outlet unit mixed with water from mixing chamber	1900 mg/l

3.3. RESULTS FROM SMALL SCALE TESTING FOR BIODEGRADABILITY

3.3.1. First bench cycle

For the first bench test, sample with relatively high concentration of carbon was chosen (C_s = 12000 mg/l) and 250 ml biomass was added in each flask. After aeration for one day, 4 g Sodium Azide (NaN_3) was added in the negative flask control for biological inactivation of bacteria. Initial DOC in test flasks was unfortunately not calculated during the first day. This was however performed later by (1:10) dilution of 2 ml sample substrate by 18 ml de-ionized water in 22 ml vial. Thereafter the normal procedure for DOC measurements was followed.

a) Discussion

Results from this cycle were not as expected. They were therefore considered inaccurate due to analytical errors in VSS measurements and not being able to biologically inactivate bacteria in the negative control flask. Results from this cycle are presented in Appendix A. What was interesting is that DOC removal rate was very rapid with most of the organics removed by day 2 (Figure A8 in Appendix A). However, this was a good learning experience and led to the following changes in the next run by:

a. Reducing the initial C_{sample} and initial biomass concentration
b. Increasing the accuracy in VSS analysis
c. Measuring initial VSS and DOC concentrations
d. Measuring DO concentrations during the first day
e. Autoclaving of the negative control flask before addition of NaN_3

3.3.2. Second bench cycle

For the second bench test, sample with less carbon was chosen (C_s = 2500 mg/l) and less biomass (150 ml) was added in each flask compared with the first bench run. After addition of the test compound, foam started to occur but was stabilized by adding 3 ml of foam inhibitor. Initial concentrations of DOC and VSS were measured in all flasks approximately 1 hour after feeding. During the first day of measuring DO concentrations it was established that the test flasks were anoxic with DO concentrations at around 0.5 mg/l. Pumps were not efficient to provide enough oxygen which resulted in reducing the initial carbon and biomass concentrations in third cycle.

a) Results from second bench cycle

- **Environmental factors**

Temperature and pH are presented in Figure 45 and Figure 46. As mentioned earlier, temperature on the hotplates with magnetic stirrers was adjusted to around 34 °C before the start up of the bench tests to simulate temperature at SART full scale bioreactor.

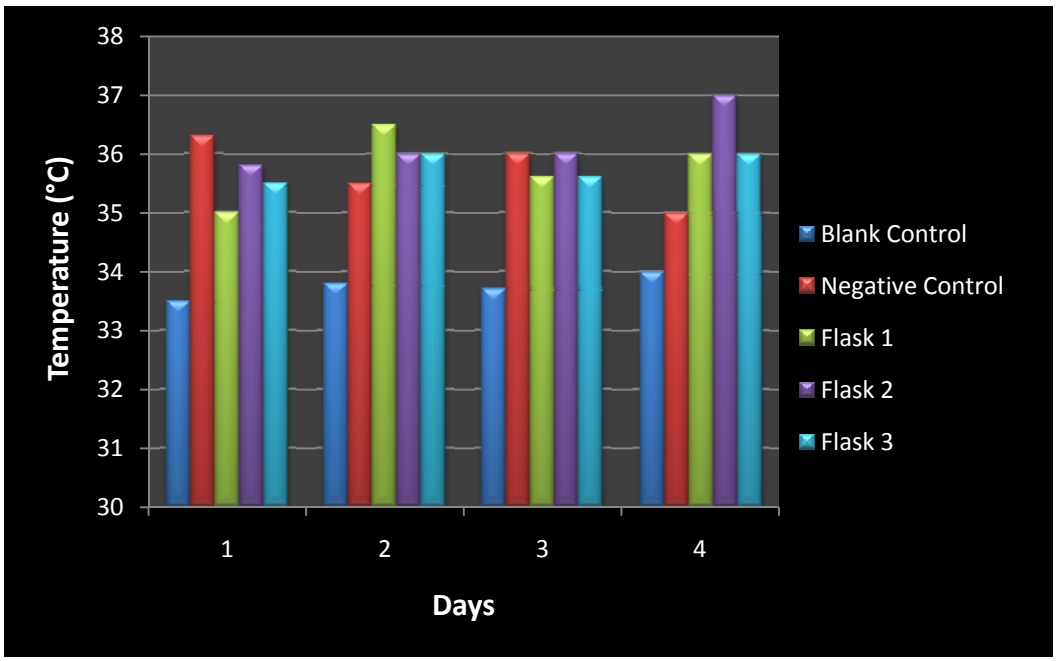


Figure 45: Temperature during second bench run

Figure 46 shows pH values in test flasks between 7 and 8.

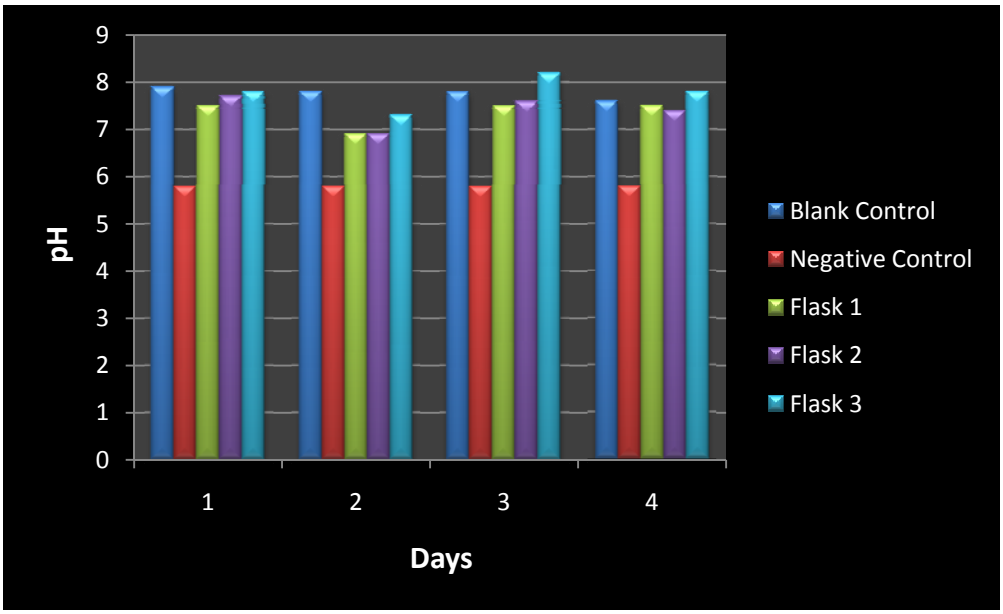


Figure 46: pH during second bench run

- **Correlation between VSS and DOC**

In the blank control test (Figure 47), DOC differences of 50 mg/l were noticeable.

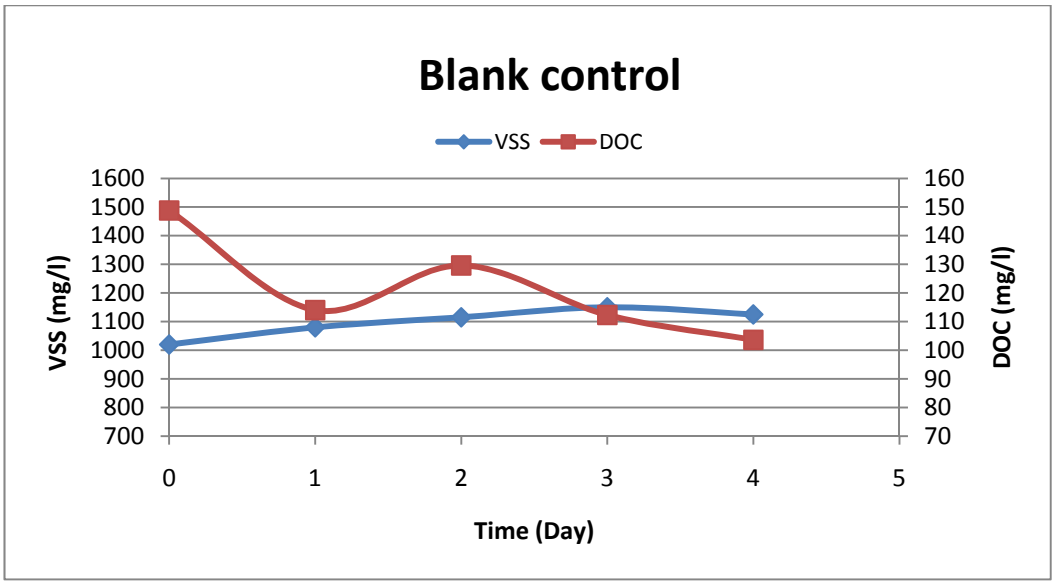


Figure 47: Blank control during second bench run

For the second run, negative flask control (Figure 48) was autoclaved for 1 hour at 120 °C followed by addition of 5 g Sodium Azide. Despite autoclaving and addition of chemicals there was still noticeable increase in the biomass growth during the first day. Additional 5 grams of Sodium Azide was added after the first day followed by a slight decrease in biomass. The pH during the second run was kept below 6 by addition of HNO_3 (Figure 46).

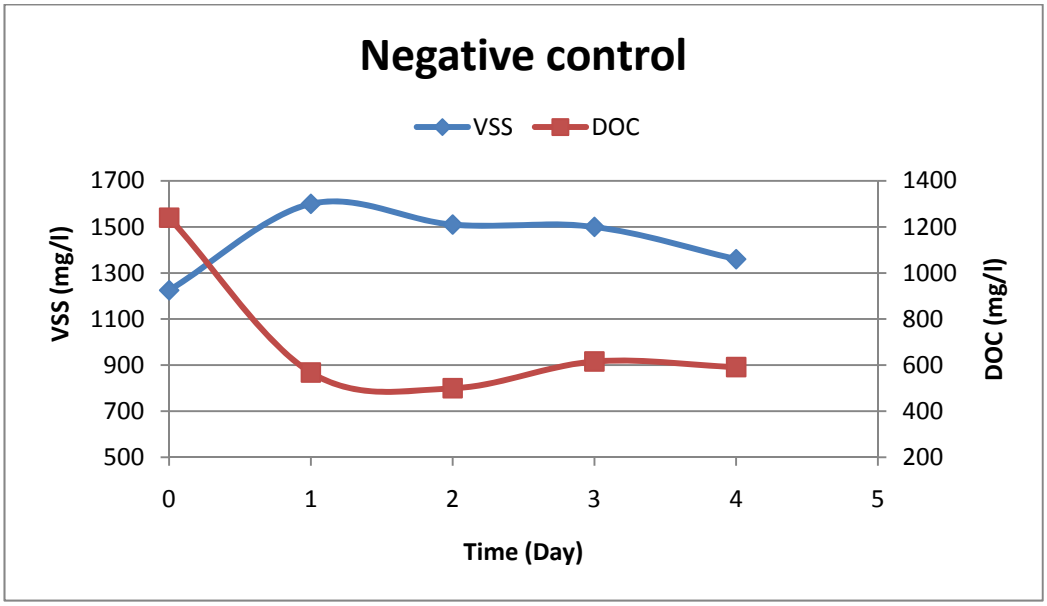


Figure 48: Negative control during second bench run

Figures 49, 50 and 51 are representing test flasks where rapid increase in VSS corresponds to utilization of readily biodegradable soluble organics (RBCOD).

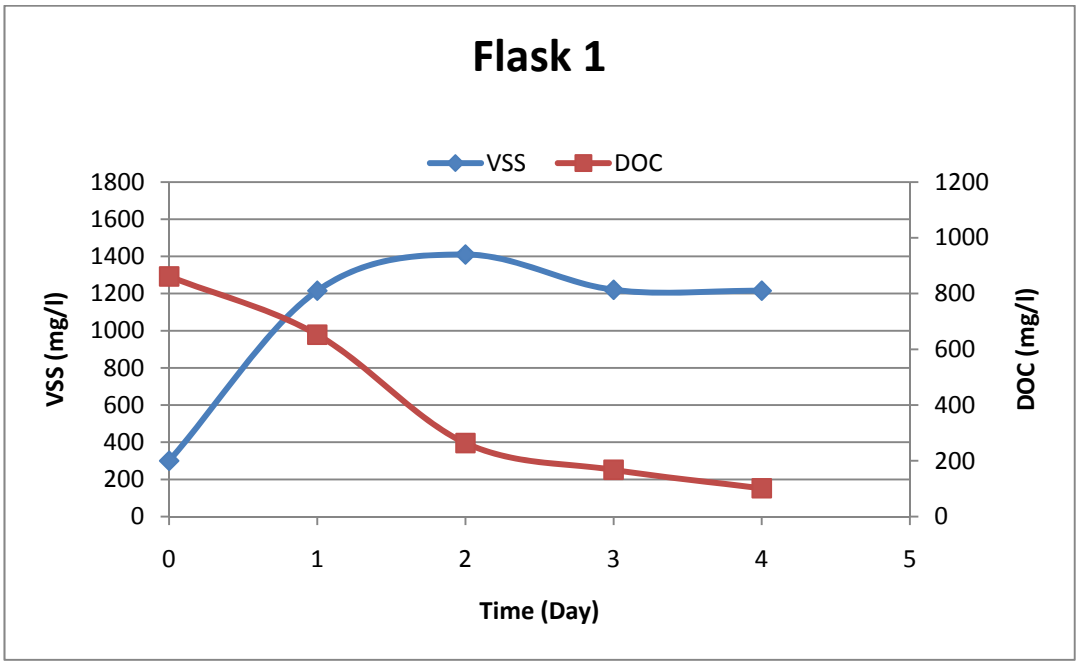


Figure 49: Test flask 1 during second bench run

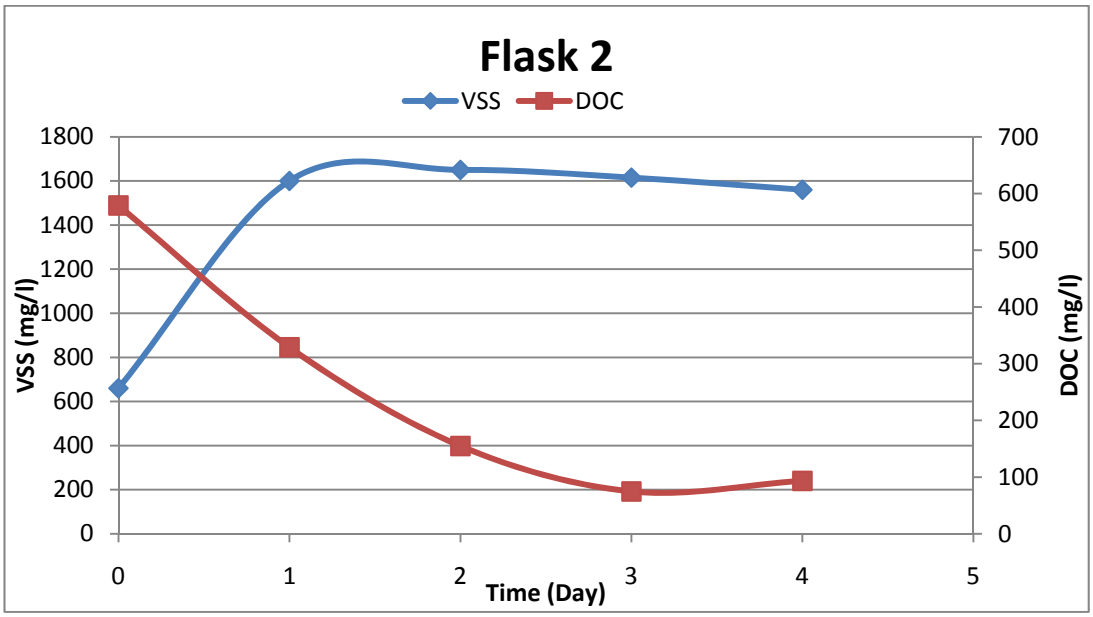


Figure 50: Test flask 2 during second bench run

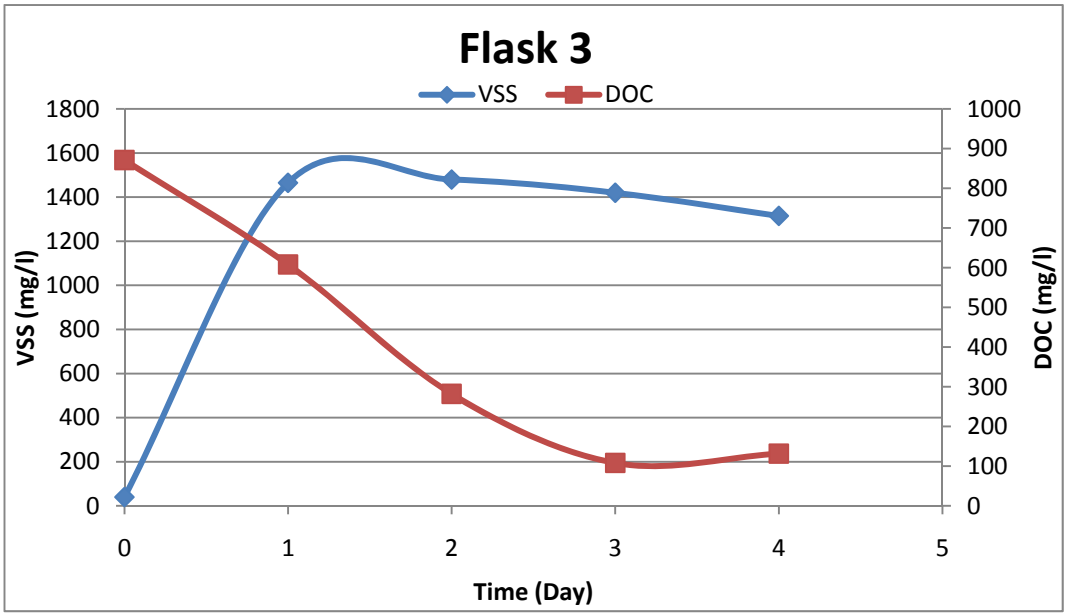


Figure 51: Test flask 3 during second bench run

Figure 52 show that the degradation curve reached a plateau after 2.5 days with more than 90% DOC removal. Average DOC removals from the test flasks gives DOC concentration below 200 mg/L after 2.5 days (Figure 53) *[58]*.

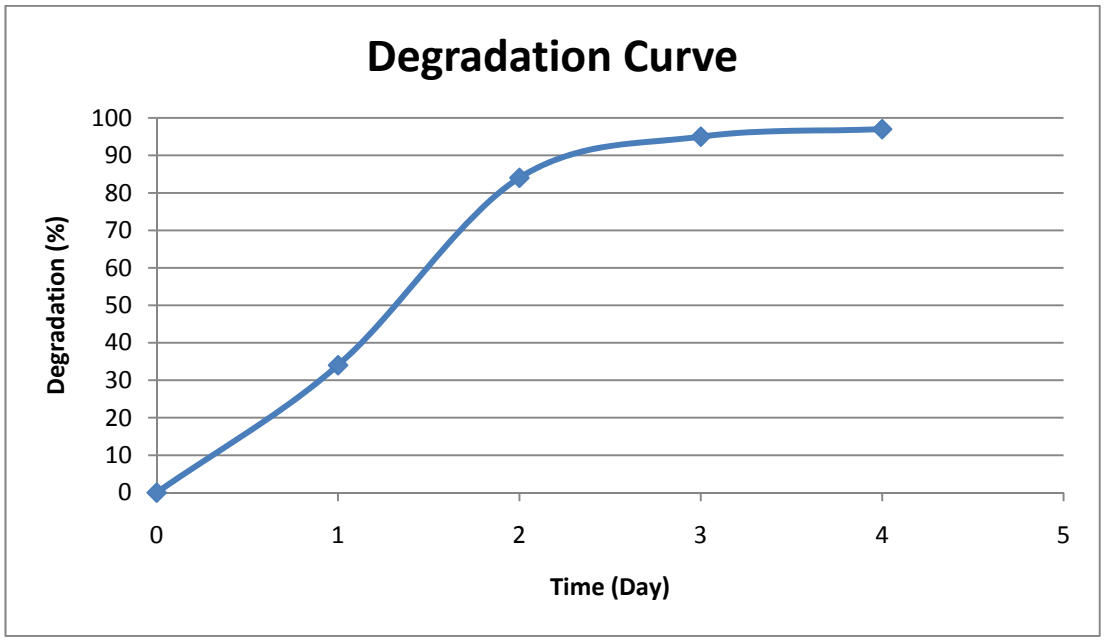


Figure 52: Degradation curve for the test sample

Figure 53 represents average VSS growth and average DOC removal in the test flasks with standard errors.

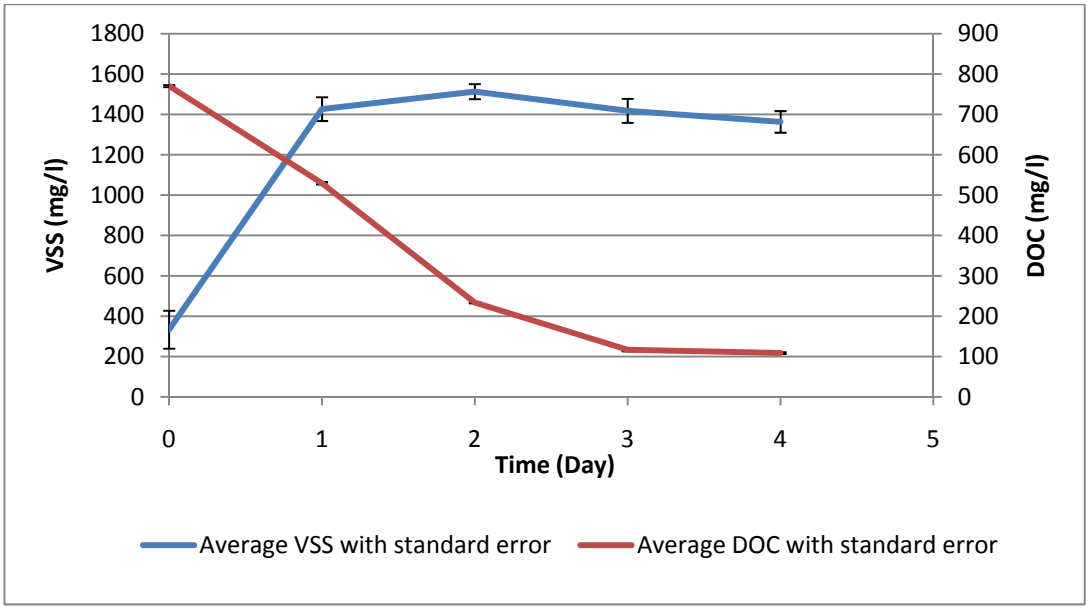


Figure 53: Average VSS growth and average DOC removal in test flasks with standard errors

b) Discussion

This run was ended after day 4 due to low DO and assuming constant removal of DOC. For third cycle sample with less carbon and less sludge was therefore used and was operated during 10 days. During second cycle of bench test the temperature was stable in the range of 35 – 37 °C. Temperature significantly influence biological growth rate. The biological growth rate is increasing exponential as a function of temperature *[33]*. PH was within the optimum pH range (Figure 46). When pH dropped below 7 and increased above 8 it was adjusted to 7 with NaOH / HNO_3. Optimum pH range for microorganisms is pH 7 – 8 with acceptable range of about 6 – 9. PH outside this range may lower growth and removal of TOC significantly, and even kill bacteria. In addition, high pH can cause salts to precipitate causing problems for the process and enhance sludge production *[33]*.

The results from VSS analyses were considered accurate. Degradation of substrate that occurred in blank control was probably due to residual DOC from biomass (i.e. DOC adsorbed to biomass during sludge washing). From the negative control flask after analyzing the DOC concentration, no decrease in substrate was observed after day one during the second run. Due to the growth of VSS in the negative control flask of the second cycle, for the third cycle was performed autoclaving of the negative flask together with air diffuser and air hose, followed by lowering the pH below 2 with HNO_3.

In the beginning of the degradation process, as it can be seen from the Figures 49 to 51, there is rapid uptake of substrate resulting in large increase in VSS and decrease in DOC. This corresponds with day 2 in Flasks 1 and 3 and somewhere after 1,5 days in flask 2.

During this period the bacteria in the wastewater are consuming the readily biodegradable soluble substrate (RBCOD). RBCOD is taken rapidly by the sludge and metabolized at high rate *[62]*. The period after day 2 should correlate with utilization of slowly biodegradable particulate substrate. (SBCOD). "SBCOD requires to be adsorbed and stored by the organisms, breaking down to simpler chemical units by extracellular enzymes and then absorbing and metabolizing by the organism " *[62]*.

Calculation of degradation curve gave more than 90 percent DOC removal during the first 2.5 days meaning rapid degradation (Figure 52).

During the experiment there were some errors due to analyses of the samples and errors from the TOC instrument. Figure 53 presents calculated standard errors for the mean VSS growth and mean DOC removal. It shows higher content of variation of results calculating the average VSS growth compared with lower content of variation of results for average DOC removal given by the instrument.

3.3.3. THIRD BENCH CYCLE

For the third bench test, sample with further less carbon (C_s = 1800 mg/l) and less biomass (30 ml) were added in each flask compared with the second bench run. Reduction in carbon source and biomass were due to ineffectiveness of the pumps providing insufficient oxygen into the flasks resulting in low DO concentrations. After addition of the test compound foam occurred and was stabilized by addition of 3 ml foam inhibitor. Initial concentrations of VSS and DOC were measured in all flasks approximately 1 hour after feeding. For the negative control test after autoclaving, C_s and seawater was added to the1800 ml and 2 mol HNO_3 was added to bring the pH below 2. Additional, air from the pump was filtered before distributing it to the flask,

a) Results from third bench cycle

- Environmental factors

Figure 54 shows that temperatures during the third cycle were in the range of 34 to 37, except for the blank that was bellows 34.

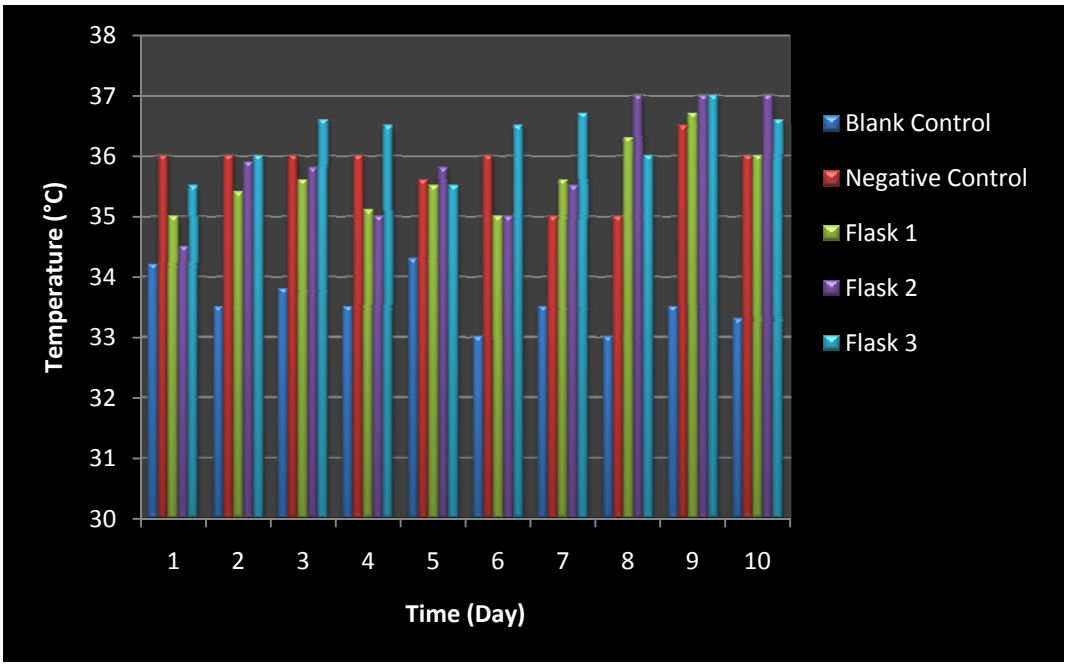


Figure 54: Temperature during third bench run

As observed from the Figure 55, pH in test flasks was within the range of 7 – 8 except for days 7 and 8 in flasks 2 and 3 where pH dropped to around 6.5.

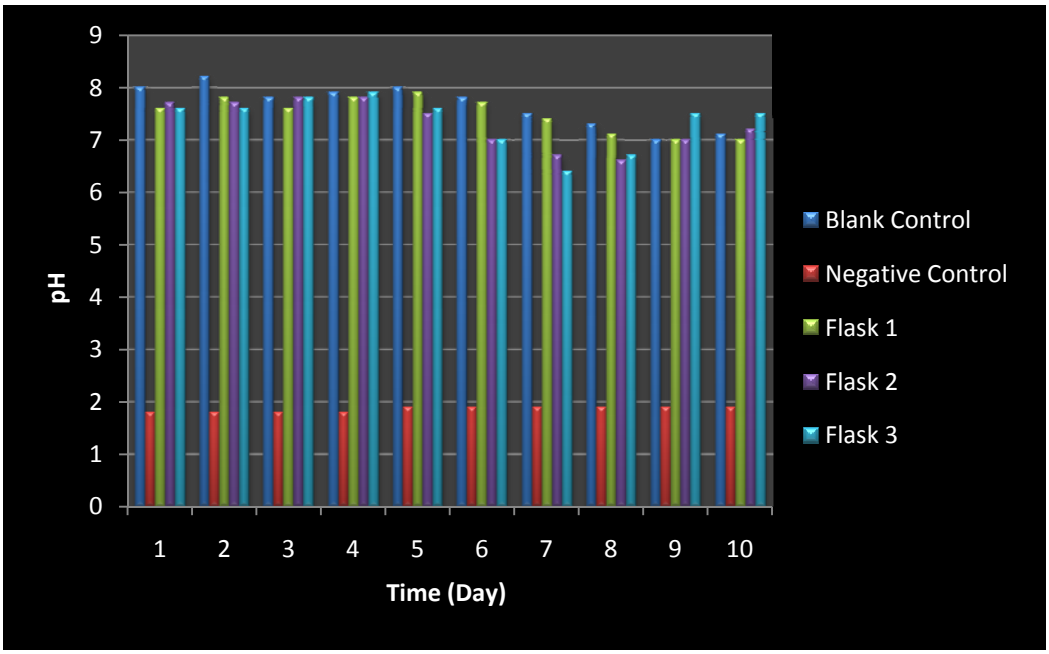


Figure 55: pH during third bench run

Figure 56 shows the bench test during the third cycle.

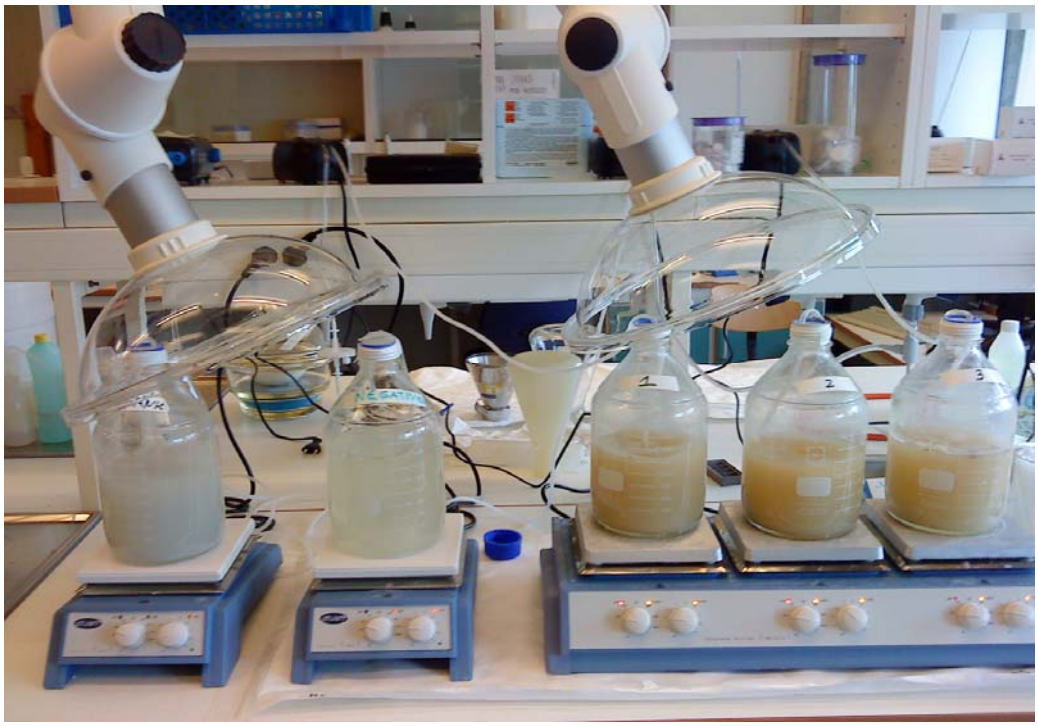


Figure 56: Bench test during third run

- **Correlation between VSS and DOC**

In the blank control test, a change of 160 mg/l DOC was noted (Figure 57).

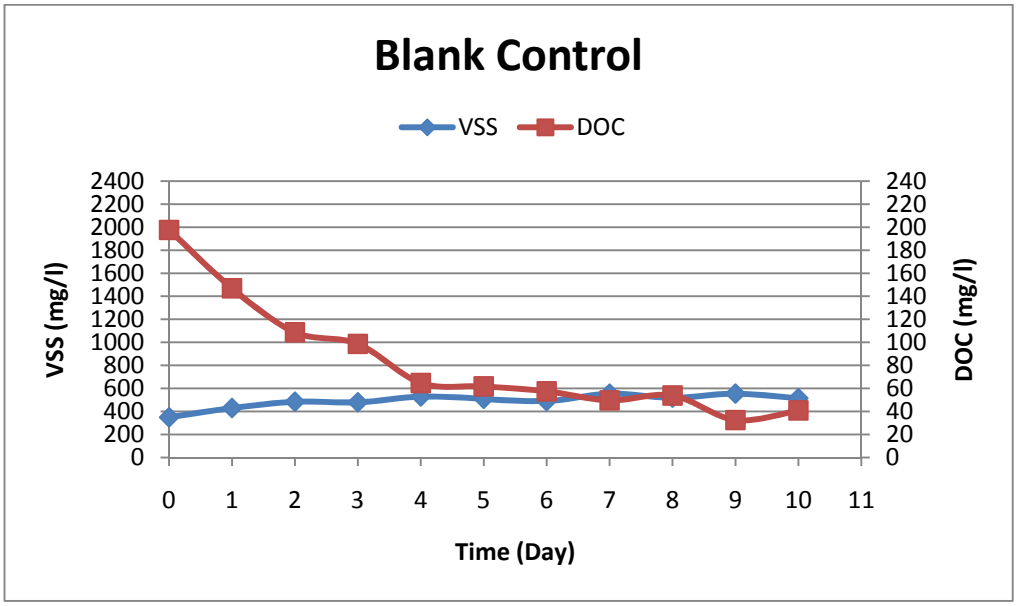


Figure 57: Blank control during third bench run

The pH distribution for the negative control is shown in Figure 55. During the third cycle in the negative control flask there was no growth of VSS and very slight decrease of DOC as seen in Figure 58.

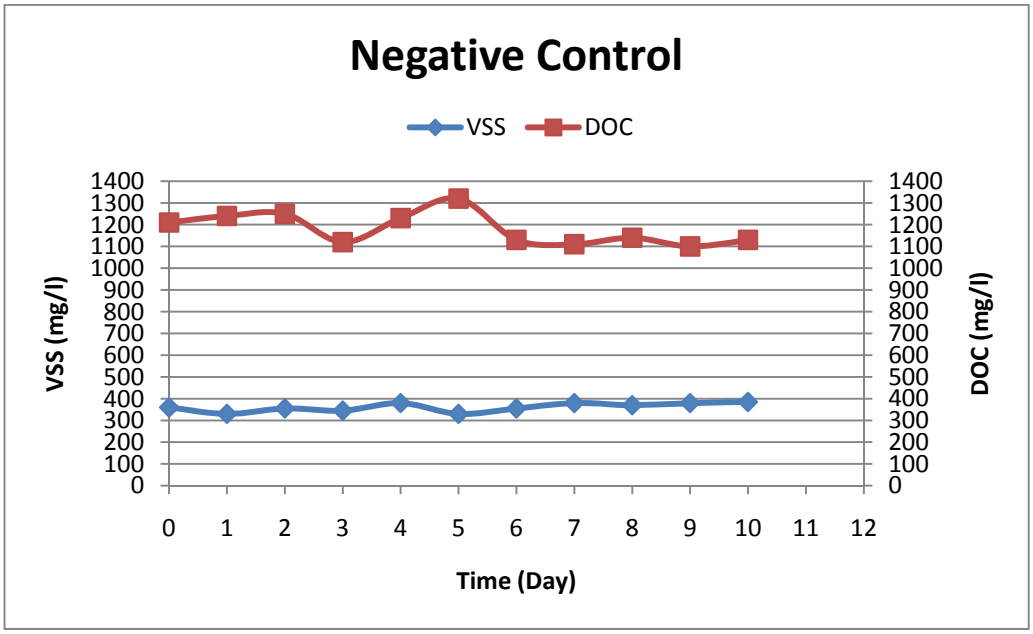


Figure 58: Negative control during third bench run

For the test flasks from Figures 59, 60 and 61 there is rapid increase in VSS corresponding to utilization of readily biodegradable soluble organics (RBCOD).

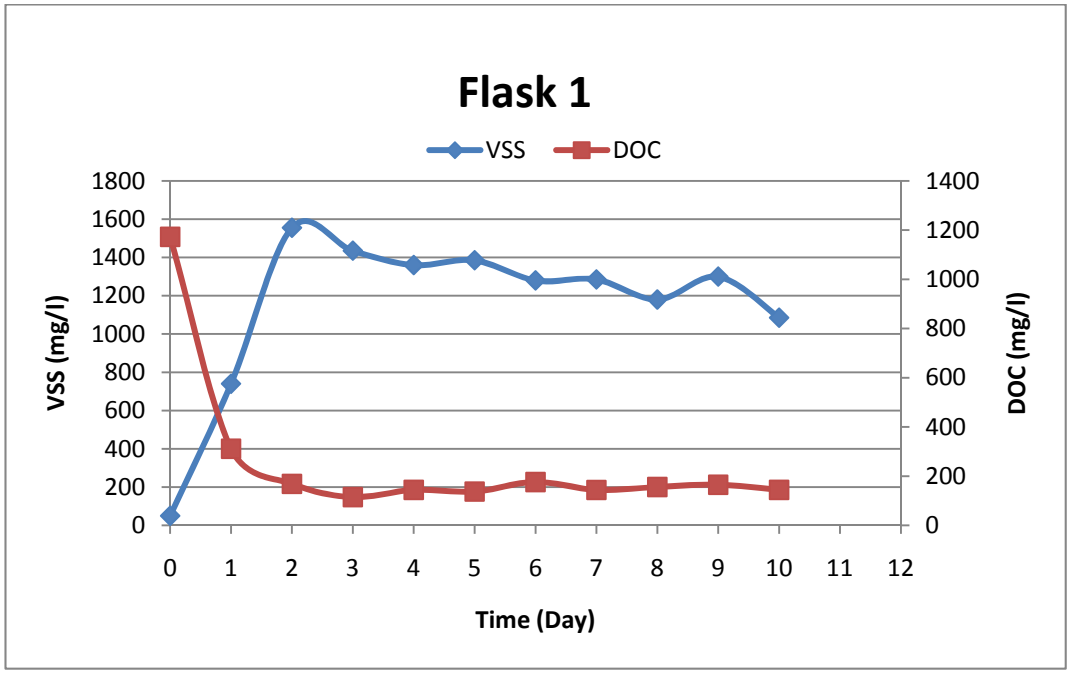


Figure 59: Test flask 1 during third bench run

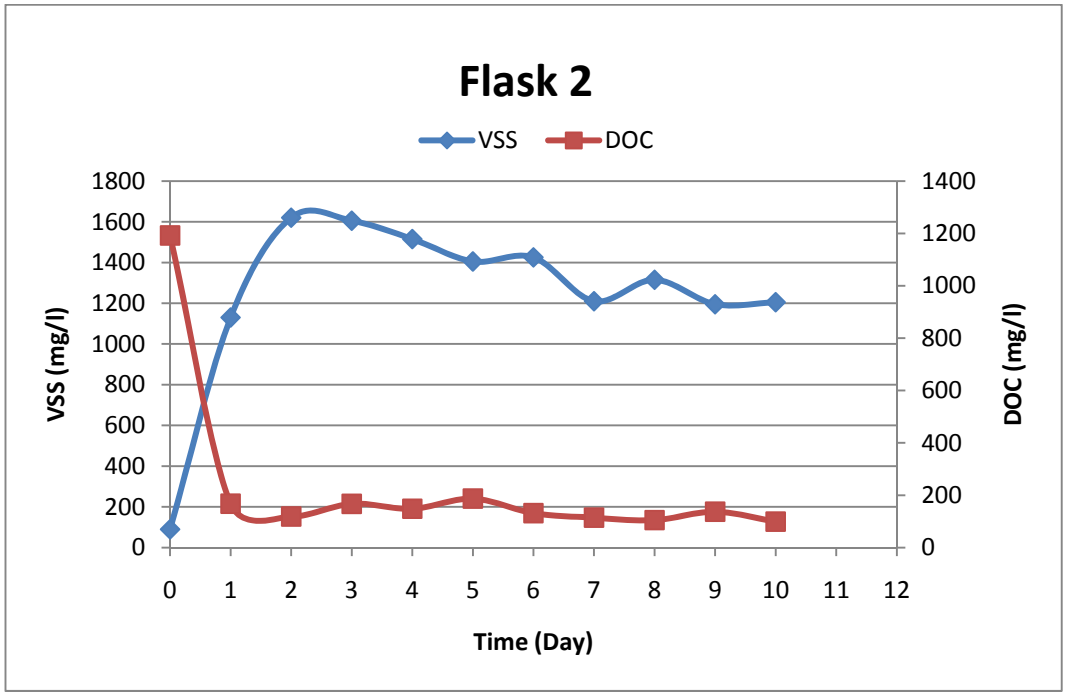


Figure 60: Test flask 2 during third bench run

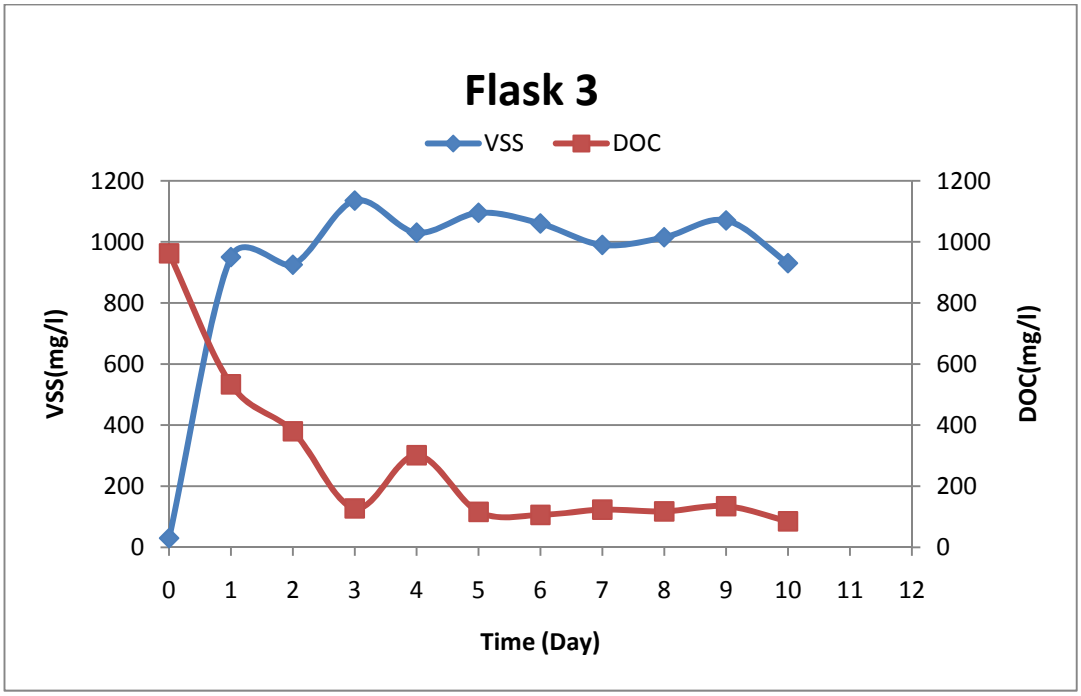


Figure 61: Test flask 3 during third bench run

Calculation of DOC degradation gave more than 90% DOC removal after 2.5 – 3 days of batch test (Figure 62). Average DOC concentration from the test flasks presented with standard error after 2.5 - 3 days was below 200 mg/L (Figure 63) indicating rapid degradation*[58]*.

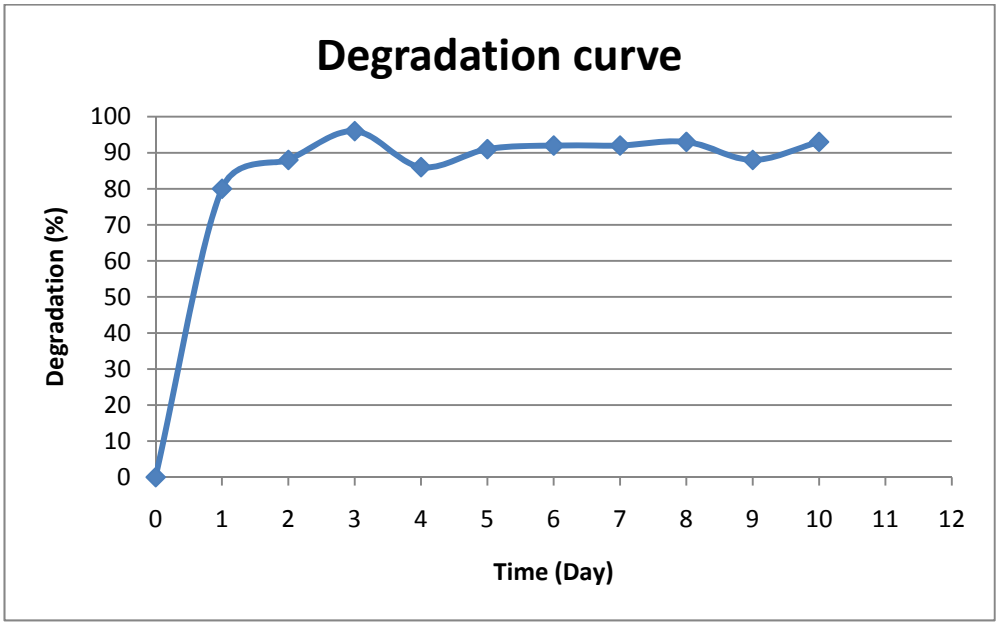


Figure 62: Degradation curve for the test sample

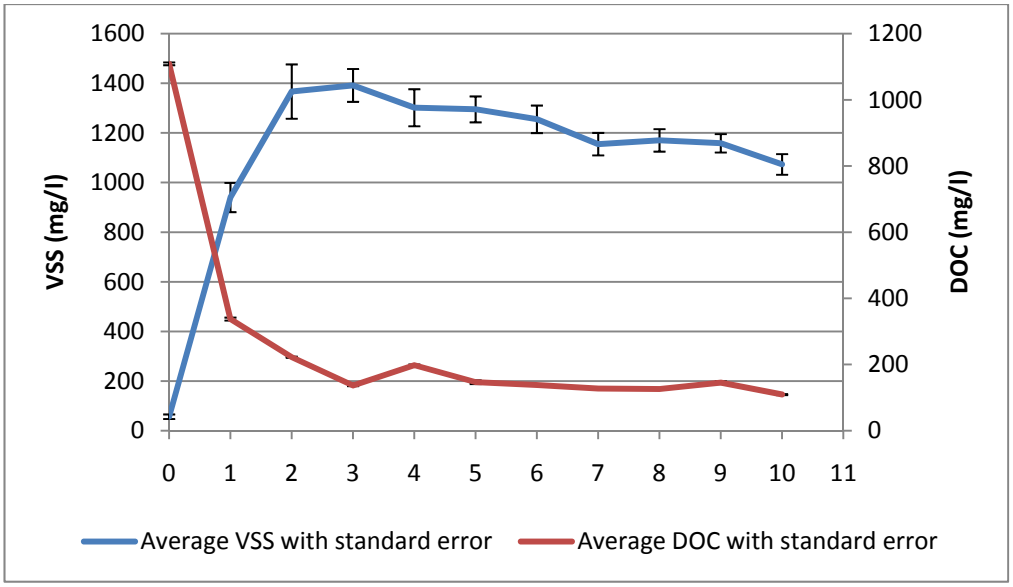


Figure 63: Average VSS growth and average DOC removal in test flasks with standard errors

b) Discussion

The results from third cycles are considered accurate. Temperatures were within the range of 34-37 ºC. A pH drop for days 7 and 8 in flasks 2 and 3 was probably due to nitrification process in activated sludge. Nitrification is a two step process where group of bacteria known as Nitrosomonas oxidize ammonium to nitrite (Equation 44) and then another group of autotrophic organisms known as Nitrobacter oxidize nitrite to nitrate (Equation 45)*[4]*. During the nitrification process acid is produce that lowering the pH. The pH drop was neutralized by addition of 0.1 mol NaOH.

$$NH_4^+ + 1.5\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+ \quad \text{(Eq. 44)}$$

$$NO_2^- + 0.5O_2 \longrightarrow NO_3^- \quad \text{(Eq. 45)}$$

Elimination of Volatile Organic Compounds (VOC) from activated sludge system correlate with biodegradation, adsorption onto solids and air striping removal. Use of oxygen is very effective in prediction of VOCs elimination by air stripping *[63]*. During this experiment, bacteria in negative control flask were biologically inactivated successfully and the observed slight decline in DOC is probably due to small content of VOCs air striping contributing to the overall degradation process.

Degradation in test flasks gave rapid increase in VSS and decrease in COD due to utilization of RBCOD. RBCOD are considered small molecules which are utilized relatively fast by the biomass *[35]*.

They pass straightforwardly through the cell wall and are metabolized at high rates resulting in a rapid uptake equivalent to a VSS increase *[62]*. The visible constant removal of DOC after day 2 (day 3 in Flask 3), represents utilization of slowly biodegradable particulate organics, SBCOD. SBCOD are large complex molecules and suspended particles that prior to uptake must be hydrolyzed to simple compounds, RBCOD *[35]*.

SBCOD is first adsorbed onto microorganisms followed by storage. The stored organic compounds helped by extracellular enzymes are broken down, passed through the cell wall and metabolized. The enzymatic breakdown rate is very slow and is around one tenth of the RBCOD rate *[62]*. That is why utilization of SBCOD is slower than utilization of RBCOD. The growth rate of biomass is lower as organics are not directly received. During this phase there is more death of bacteria than growth, corresponding to slow decline in VSS.

DOC degradation curve gave more than 90 percent removal of DOC after 2.5 – 3 day indicating rapid degradation (Figure 62).

3.4. RESULTS FROM GC/MS ANALYSES

Analyses of samples before and after each bench cycle were performed externally at ALS Laboratory Group Norway AS for screening of semi volatile compounds using GC/MS. Following method was used: Samples were extracted with n-hexane and analyzed by GC / MS. After separations in gas chromatographic column organic compounds were determined by looking at the characteristic mass of the / those compounds (GC-MS). Mass spectrum can compare the components in a library of mass spectrums from organic compounds or with spectra of equal reference values. In this way an appropriate organic compound in the sample can be determined qualitatively.

Although additional time for GC / MS analyses was required by the external laboratory, they have managed to identify the compounds only in the samples from first two bench cycles. The second sample from the third bench cycle was unfortunately misplaced by the external laboratory and no results from this cycle were given back.

Without signal from the internal standard, the following semi-volatile compounds where identified and presented in tables 9 –12.

Table 9: Identified compounds before the start up of the first bench cycle

Peak No	Sample before first bench cycle No. N00145482
1	Butoxyethanol
2	Butoxypropanol
3	Phenol
4	2-Ethyl-1-hexanol
5	Methylphenol
6	1-octanol
7	Isooctane
8	Butoxyethoxyethanol (glycol)
9	Octanoic acid
10	Hydroxypropoxyethanol (glycol)
11	Alkane
12	Glycol
13	Triethylene glycol monododecyl ether (or similar)
14	Octaethylene glycol
15	Glycols and glycolmonoether

Table 10: Identified compounds at the end of the first bench cycle

Peak No	Sample after first bench cycle No. N00145483
16	Benzothiazole
17	Dodecamethylcyclohexasiloxane
18	Phenol
19	2-Ethyl-1-hexanol
20	Tetrahydroquinoline
21	Benzophenone
22	Alkane
23	TCEP (tris(2-carboxyethyl)phosphine)
24	N-Butyl-benzenesulfonamide
25	Alkene
26	Bisphenol A
27	Diisooctyl phthalate
28	Squalene or similar

Table 11: Identified compounds at the beginning of the second bench cycle

Peak No	Sample before second bench cycle No. N00145484
1	Butoxyethanol
2	Butoxypropanol
3	Phenol
4	2-Ethyl-1-hexanol
10	Hydroxypropoxyethanol (glycol)
11	Alkane
12	Glycol
13	Triethylene glycol monododecyl ether (or similar)
14	Octaethylene glycol
15	Glycols and glycolmonoether

Table 12: Identified compounds at the end of the second bench cycle

Peak No	Sample after second bench cycle No. N00145485
29	Glycol ether
30	Indole
21	Benzophenone
25	Alkene
31	Pentadecanoic acid
27	Diisooctyl phthalate
32	Phthalate esters (technical mix)
33	Polypropylene glycol

Because of the internal standard not visible in chromatograms due to high signal of the substances, semi quantification with internal standard is not possible. The extracts from the samples N00145482 and N00145484 were evaporated and the residue was weighed.

N00145482: 18 mg/l.

N00145484: 135 mg/l *[64]*.

Chromatograms are in Appendix B.

3.4.1. Discussion

Results presented are from qualitative GC/MS analyzes without concentrations of the organic compounds before and after the experiments. At the beginning of the degradation process both RBCOD and SBCOD are present. From Tables 9 and 11 similar compounds were detected in the samples before degradation. Compounds identified are belonging to glycols, glycol ethers, phenols, fatty alcohols, fatty acids and alkanes. They all have been found to be easy biodegradable compounds, RBCOD. Assumption is made that similar compounds could be expected in the third experiment as well. Slowly biodegradable compounds, SBCOD, were detected as well but due to the overlap of the chromatogram peaks they are not shown in the tables (see chromatogram). Most of the compounds identified as RBCOD are glycols and glycol ethers. Means & Anderson followed the aerobic biodegradation of ethylene glycol using five different procedures where ethylene glycol was rapidly degraded in all tests *[65]*. According to some laboratory studies on biodegradation of glycol ethers it was found that these compounds have very good biodegradation characteristics and they are expected to go through rapid degradation in activated sludge systems *[66]*.

At the end of the degradation process RBCOD are utilized and only SBCOD and some unbiodegradable compounds are left. Compounds in Tables 9 and 11 are identified as organo sulfur compounds, cyclic siloxanes, amides, benzophenone compounds and phthalate esters. Most of them are SBCOD and some of them are stable against biodegradation. Incomplete removal of Benzophenone has been reported from wastewater treatment process showing recalcitrance of this compound *[67]*. Benzothiazole is reported as a toxic and slowly biodegradable compound *[68]*. Biodegradation of different sulfonamides were investigated using a respirometric and activated sludge simulation tests and it was concluded that sulfonamides cannot be placed as readily biodegradable compounds *[69]*.

According to Rene Huppmann et all, cyclic siloxanes like dodecamethyl cyclohexasiloxane and tetradecamethyl cyclohexasiloxane are highly volatile and very stable to biochemical degradation *[70]*.

A type of Pentanoic acid was found to be a byproduct of Phenol to catechol degradation pathway *[71]*.

4. CONCLUSION AND RECOMMENDTAIONS

This research proved that biological treatment using activated sludge is very effective in removal of organics from industrial wastewaters. According to the bench tests results, wastewater received at SART is very biodegradable. Although using wastewater samples with various TOC concentrations ranked from 1900 to 12000 mg/l, DOC removal rate was very rapid with approximately 90 percent of DOC removed within 2 - 3 days. Taking into consideration the VSS growth and DOC removal in test flasks and degradation curves the wastewater from SART is composed of around 90 % of RBCOD and the rest is slowly biodegradable particulate organics and unbiodegradable substrates. During the third cycle it was found that small percent of air striping of VOCs probably contribute to the overall degradation process.

Results from the GC/MS analyze shows that most of the compounds identified before each cycle is belonging to glycol and glycol ethers that are known to be rapidly degraded. Biodegradability of slowly biodegradable particulate organic compounds like organo sulfur compounds, cyclic siloxanes, amides, benzophenone compounds etc can be improved by use of Advanced Oxidation Processes.

Recommendation for future research is that Oxygen Utilization Rate (OUR) measurements are performed during bench tests. These results can be used to distinguish more precise the RBCOD from SBCOD substrate utilization. Performing bench test for evaluating effectiveness of AOP in destroying compounds correlate as SBCOD can be done and calculation of biodegradation parameters and implementation of experimental data in AQUASIM software for parameter estimation (μ_{max}, K_s and $Y_{x/s}$) is also recommended.

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APPENDIX A

Results from first bench cycle

- **Environmental factors**

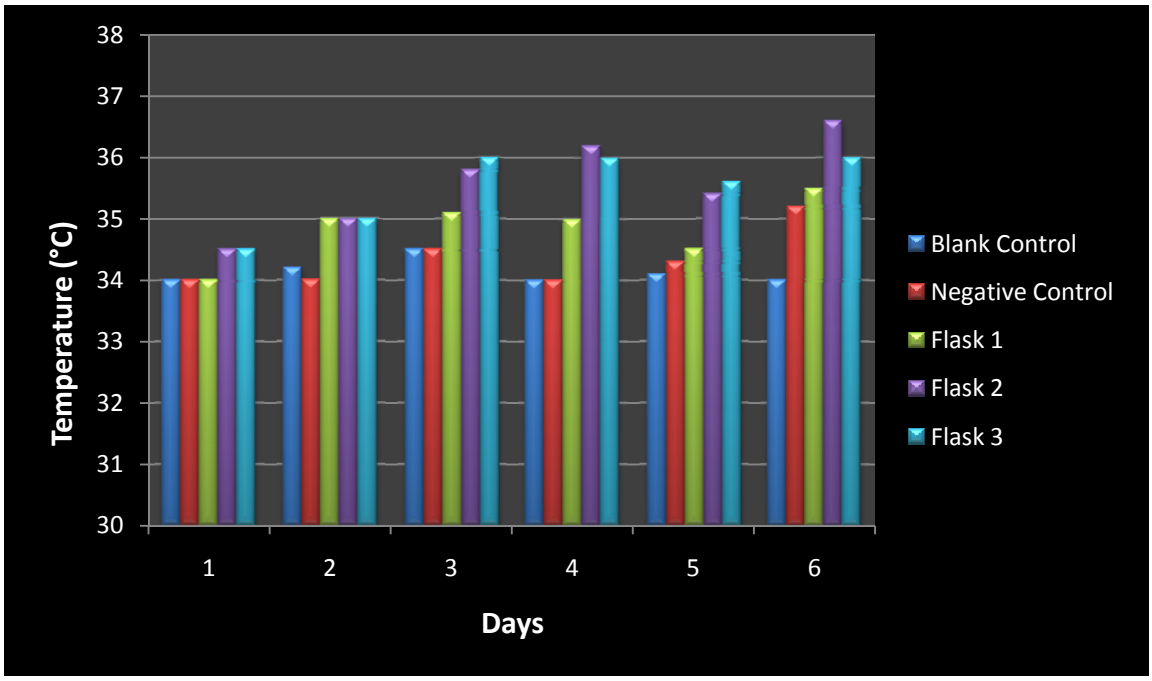


Figure A1: Temperature during first bench run

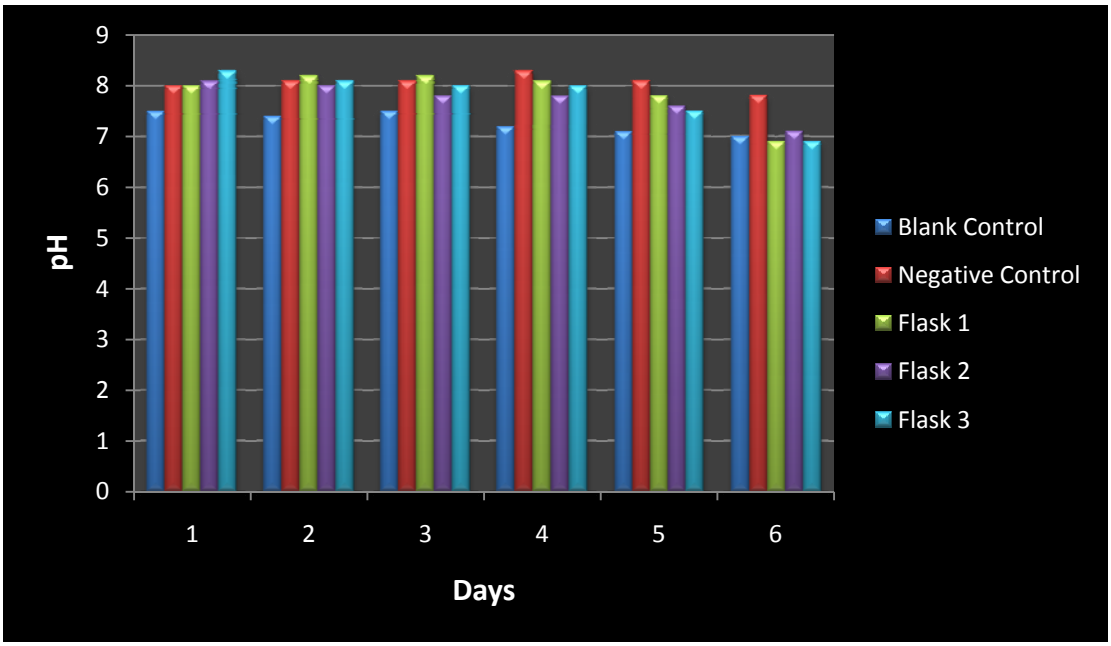


Figure A2: pH during first bench run

- **Correlation between VSS and DOC**

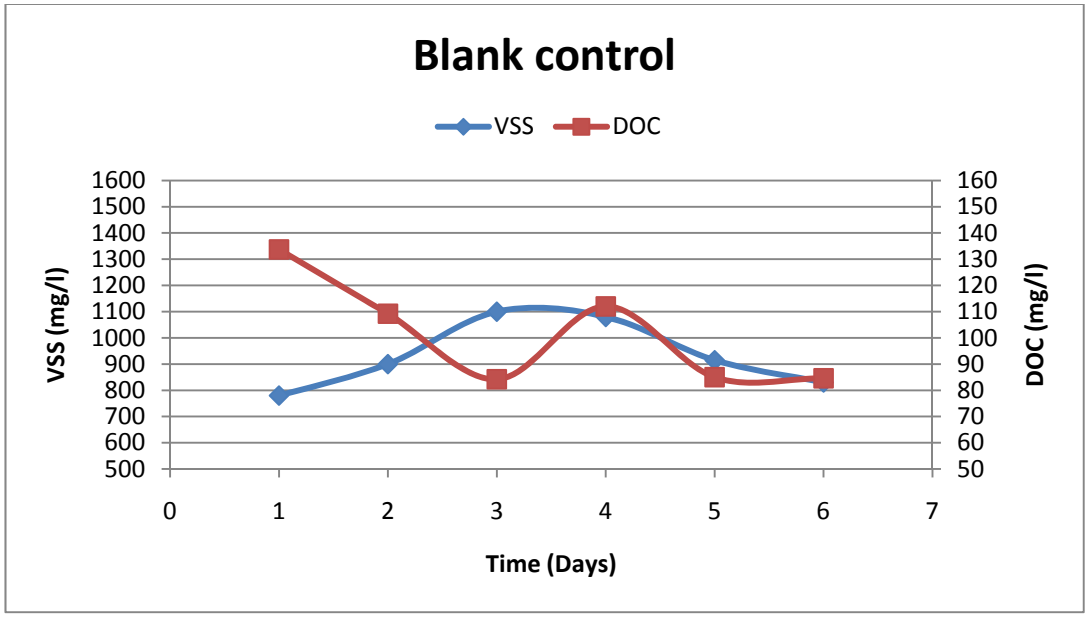


Figure A3: Blank control during first bench run

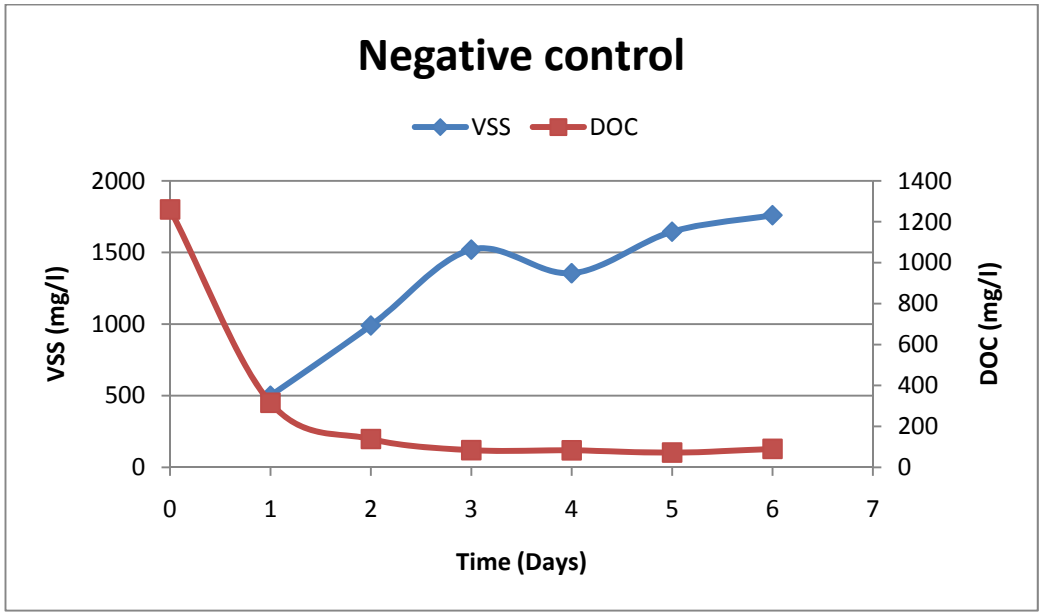


Figure A4: Negative control during first bench run

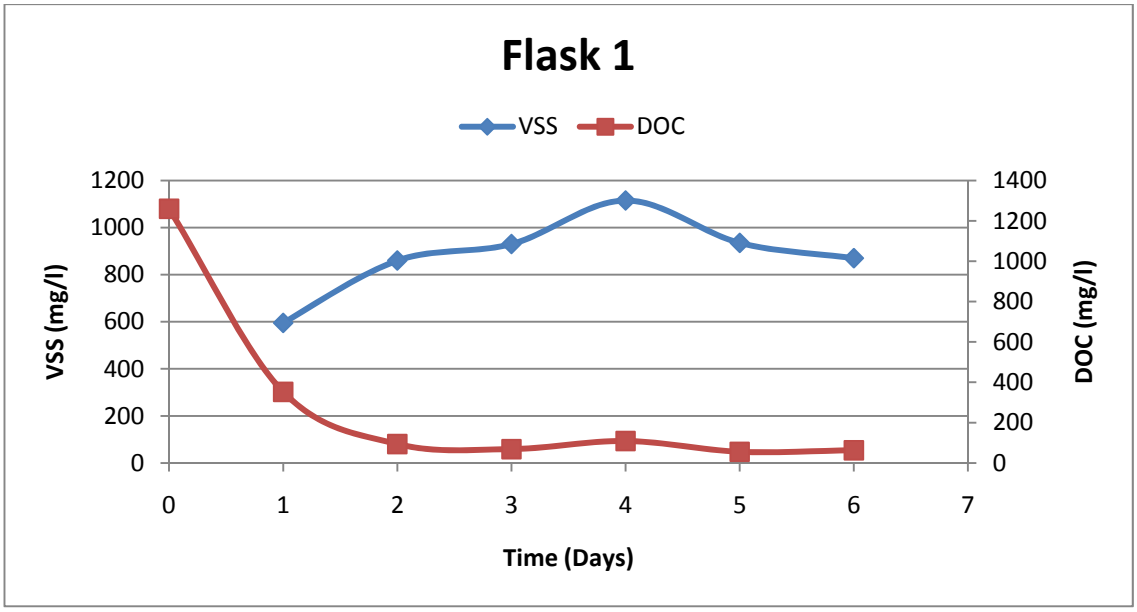


Figure A5: Test flask 1 during first bench run

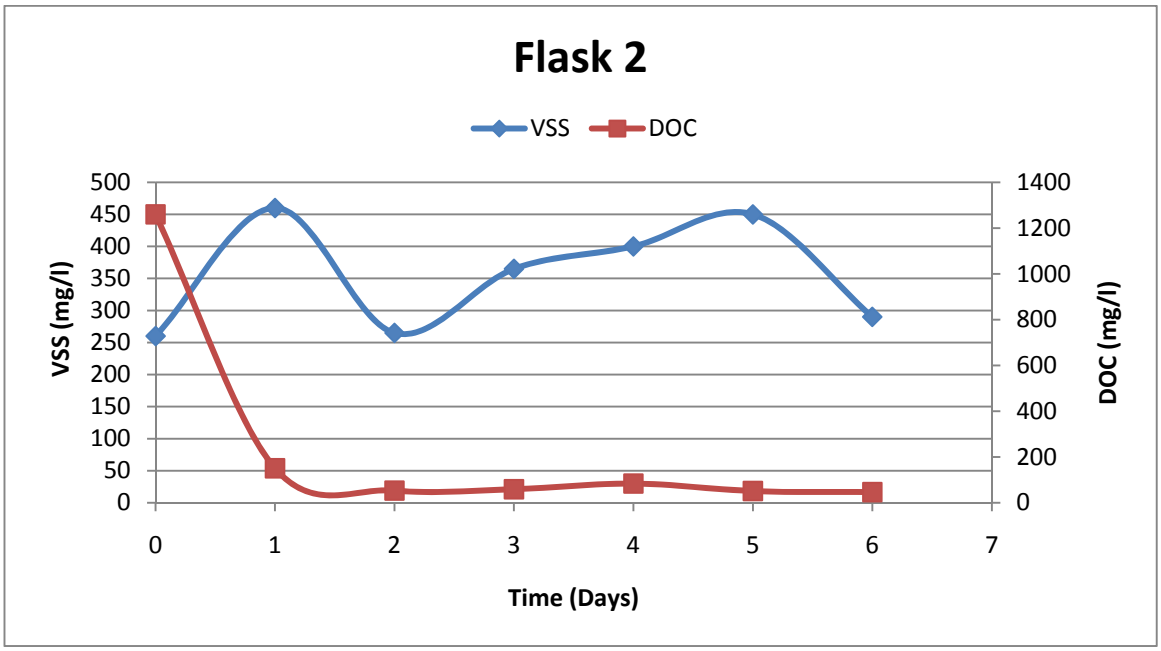


Figure A6: Test flask 2 during first bench run

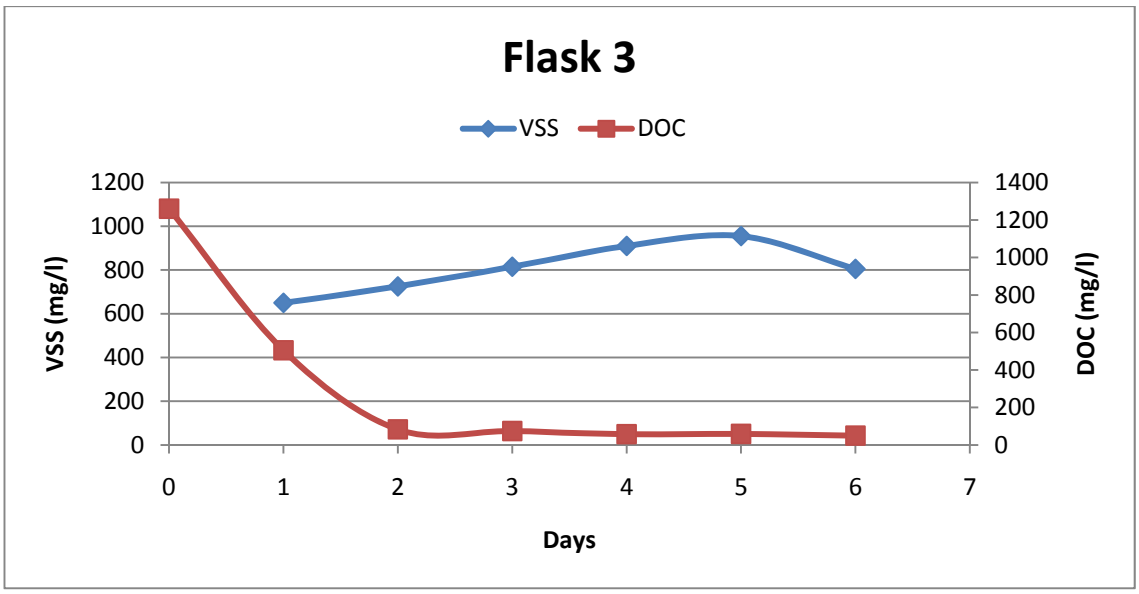


Figure A7: Test flask 3 during first bench run

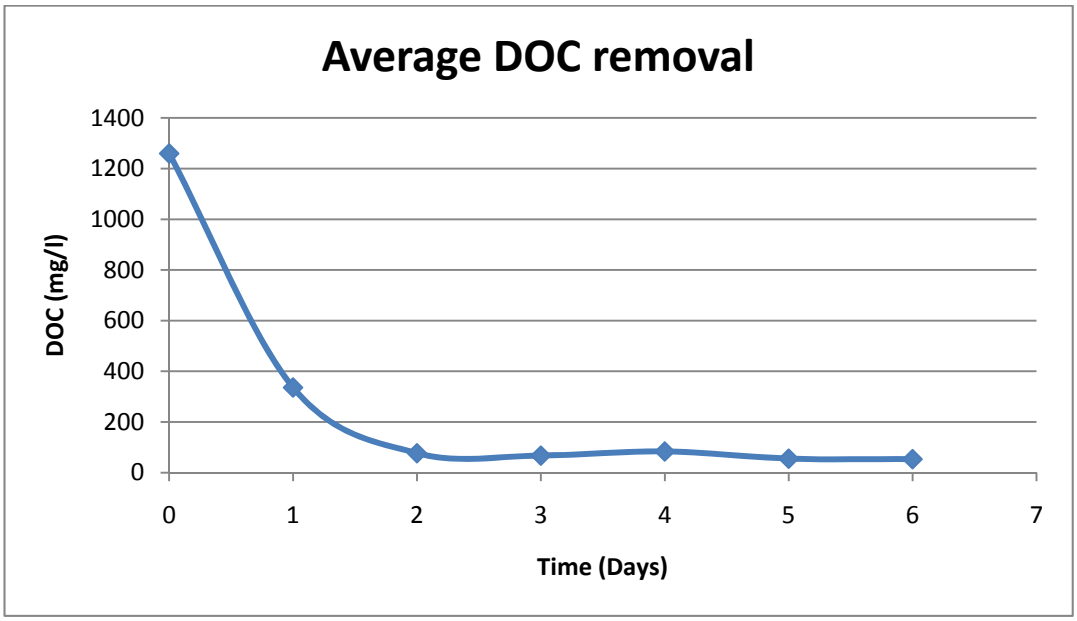


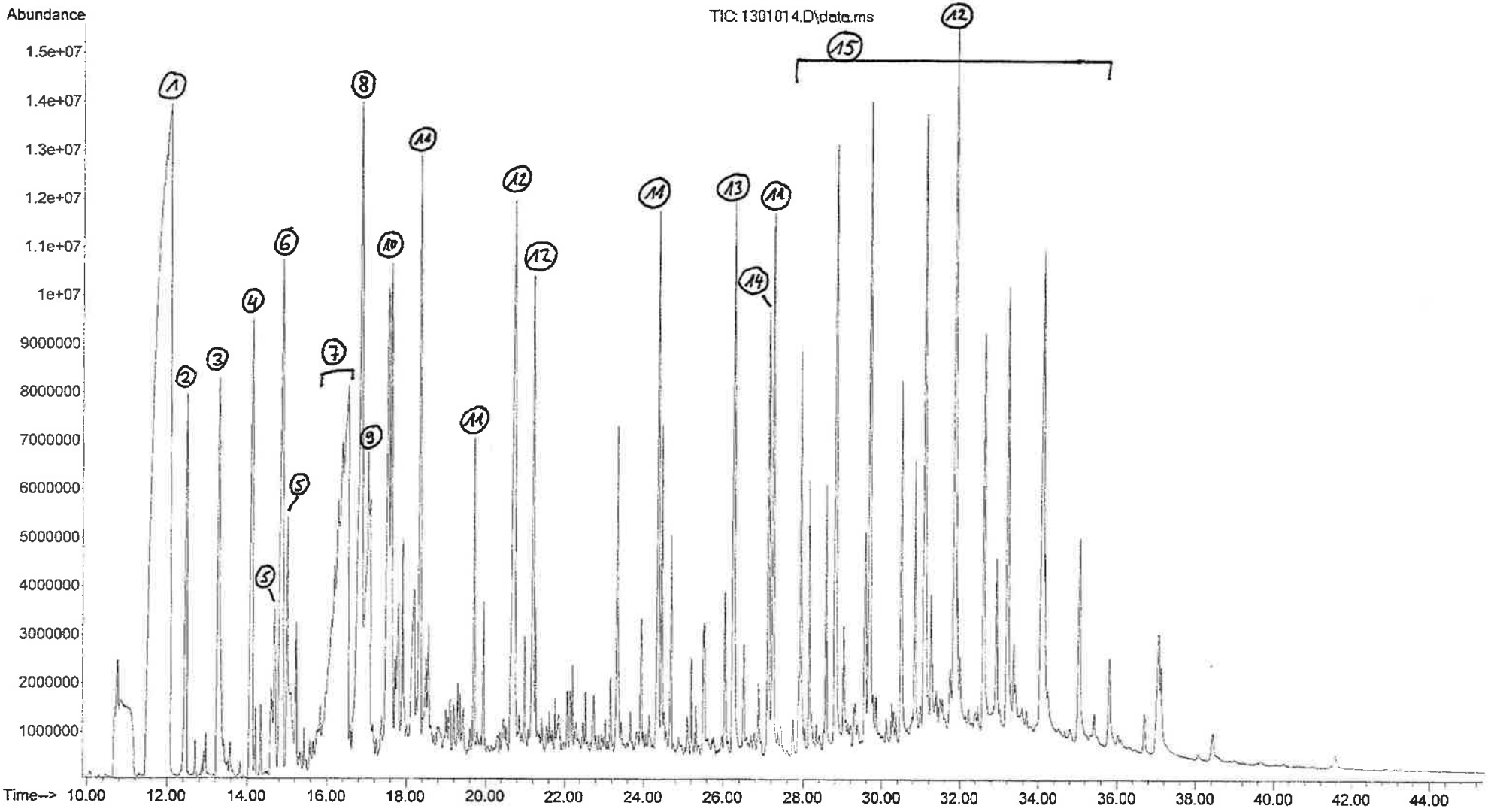
Figure A8: Average DOC removal during first bench run

Appendix B

GC/MS Chromatograms

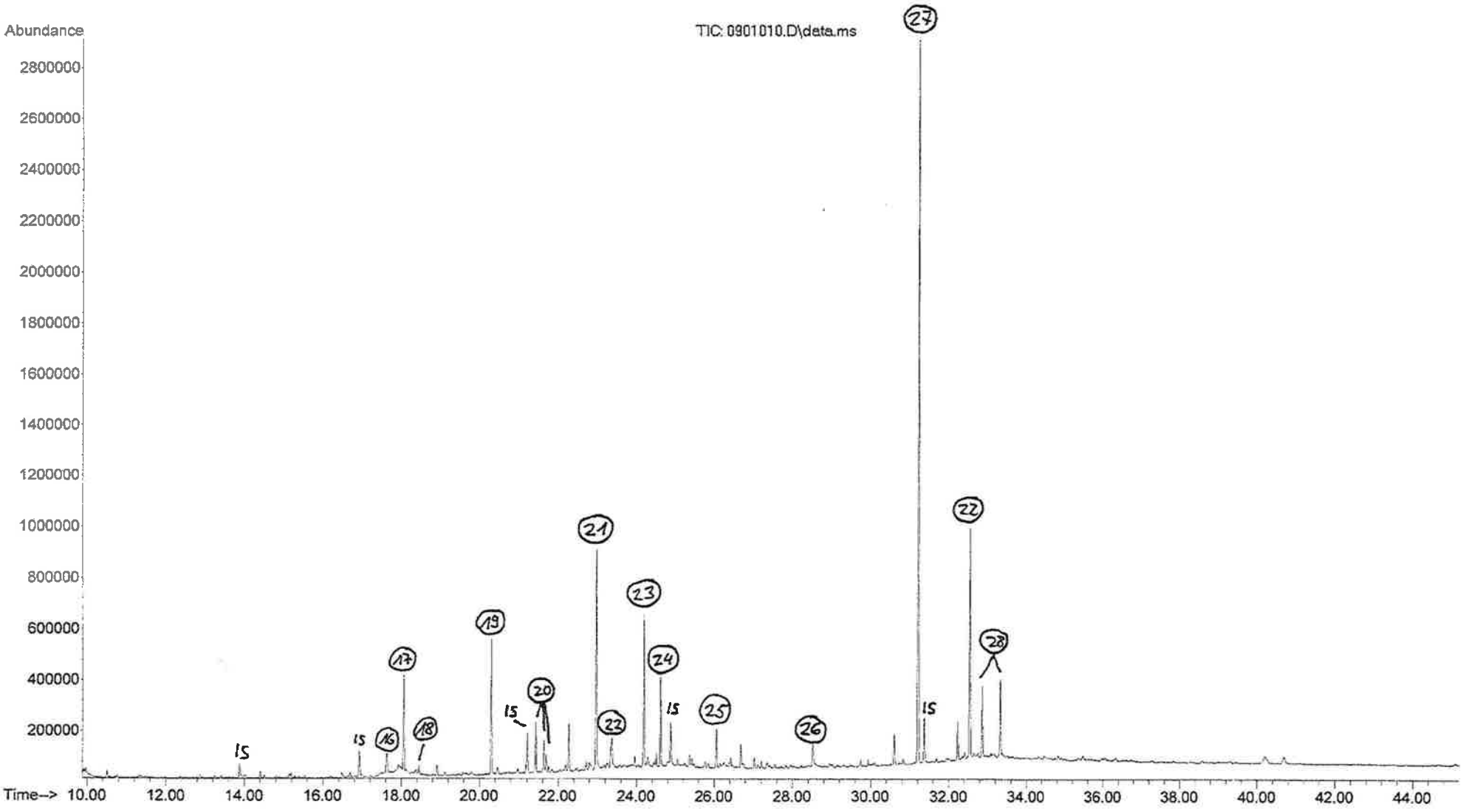
N0014 5482

File :R:\GC7\data0211\pak\pak23ma\1301014.D
Operator :
Acquired : 24 May 2011 8:08 using AcqMethod SCREEN60
Instrument : Instrumen
Sample Name: 3350-06
Misc Info : 722mL; 1mLEV:1µgIS PAK
Vial Number: 13



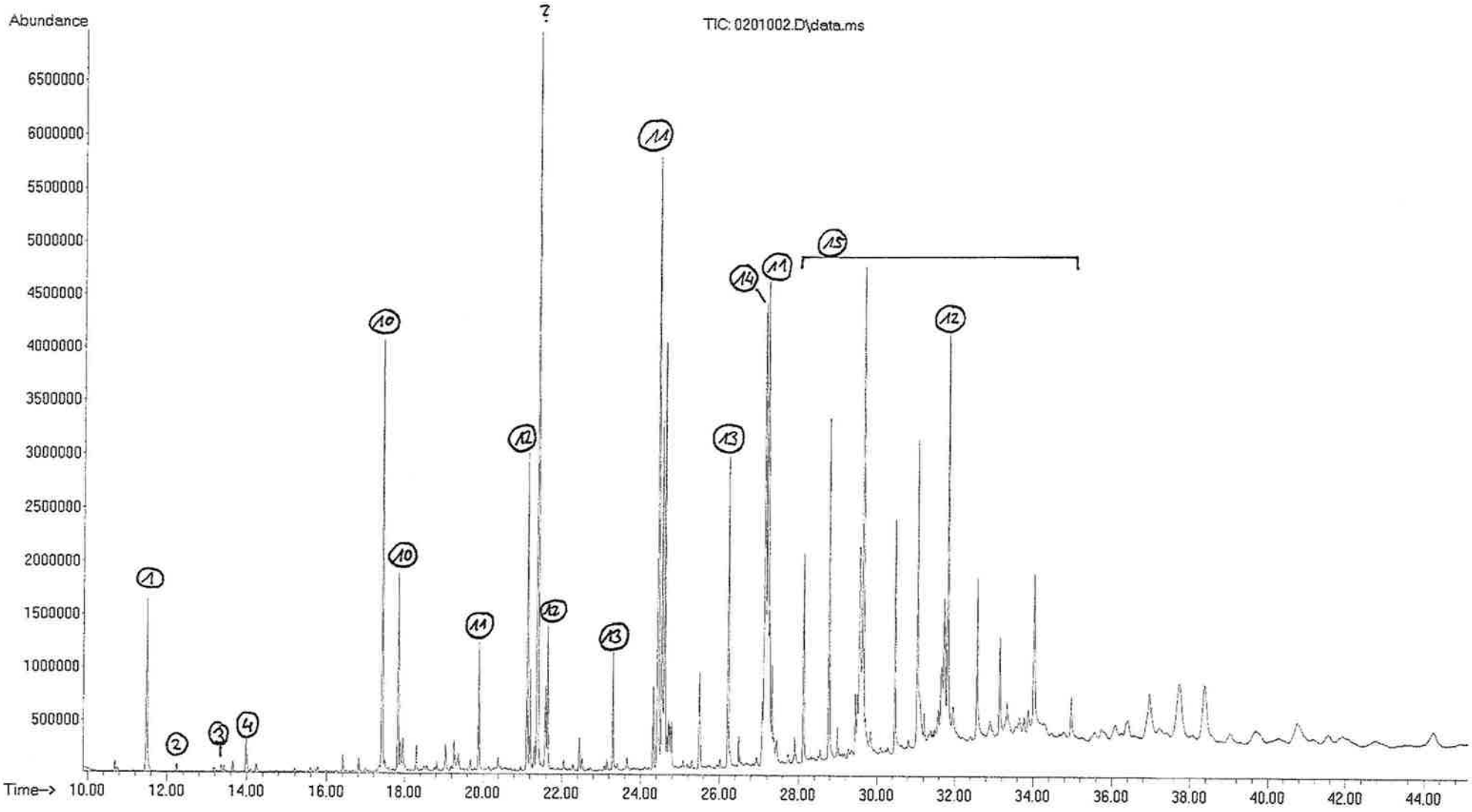
N00145483

File :R:\GC7\data0211\pak\pak23ma\0901010.D
Operator :
Acquired : 24 May 2011 3:14 using AcqMethod SCREEN60
Instrument : Instrumen
Sample Name: 3350-07
Misc Info : 746mL:1mLEV; 1µg IS PAK
Vial Number: 9



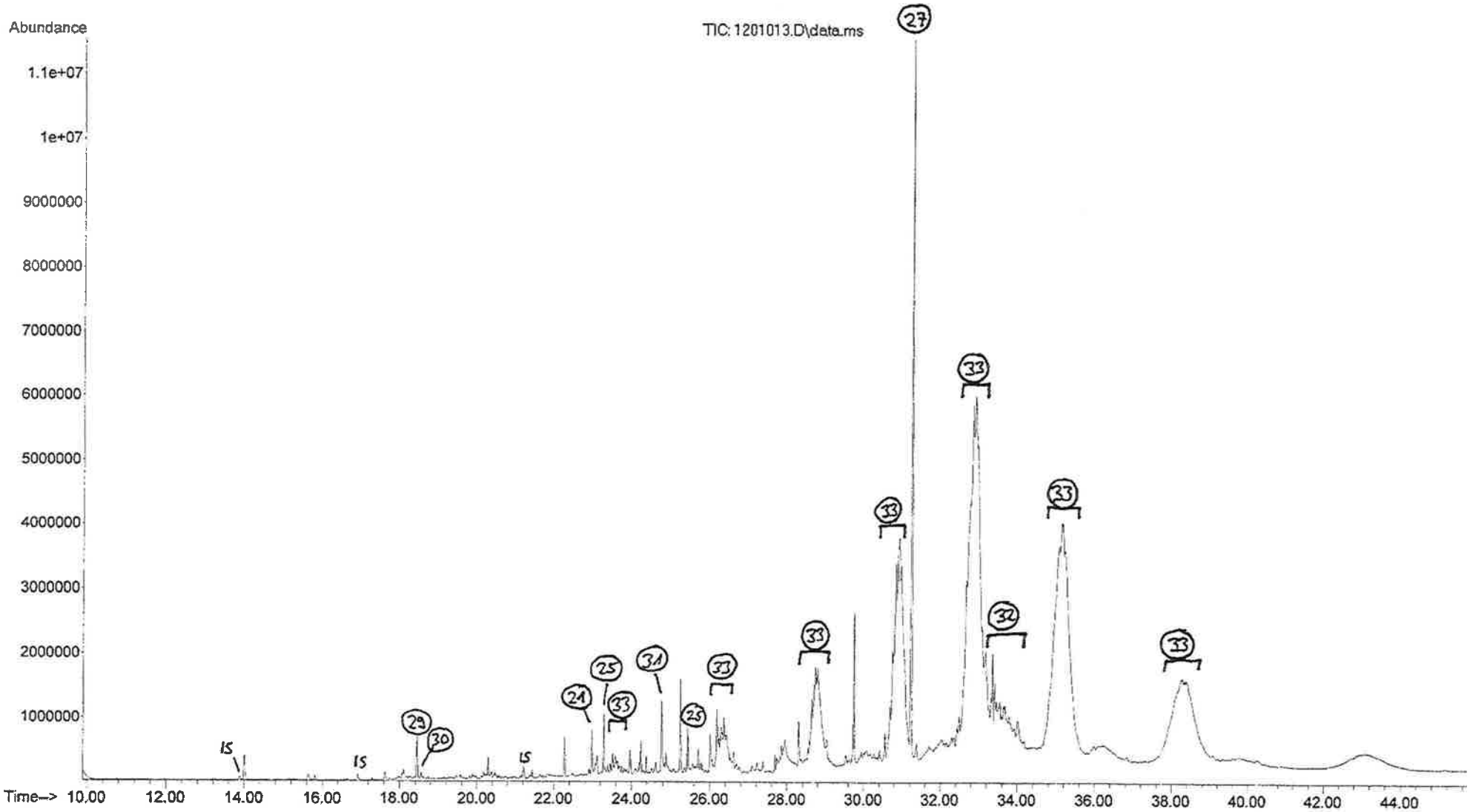
N00145484

File :R:\GC7\data0211\pak\pak25ma\0201002.D
Operator :
Acquired : 25 May 2011 9:41 using AcqMethod SCREEN60
Instrument : Instrumen
Sample Name: 3350-08 1:20
Misc Info :
Vial Number: 2



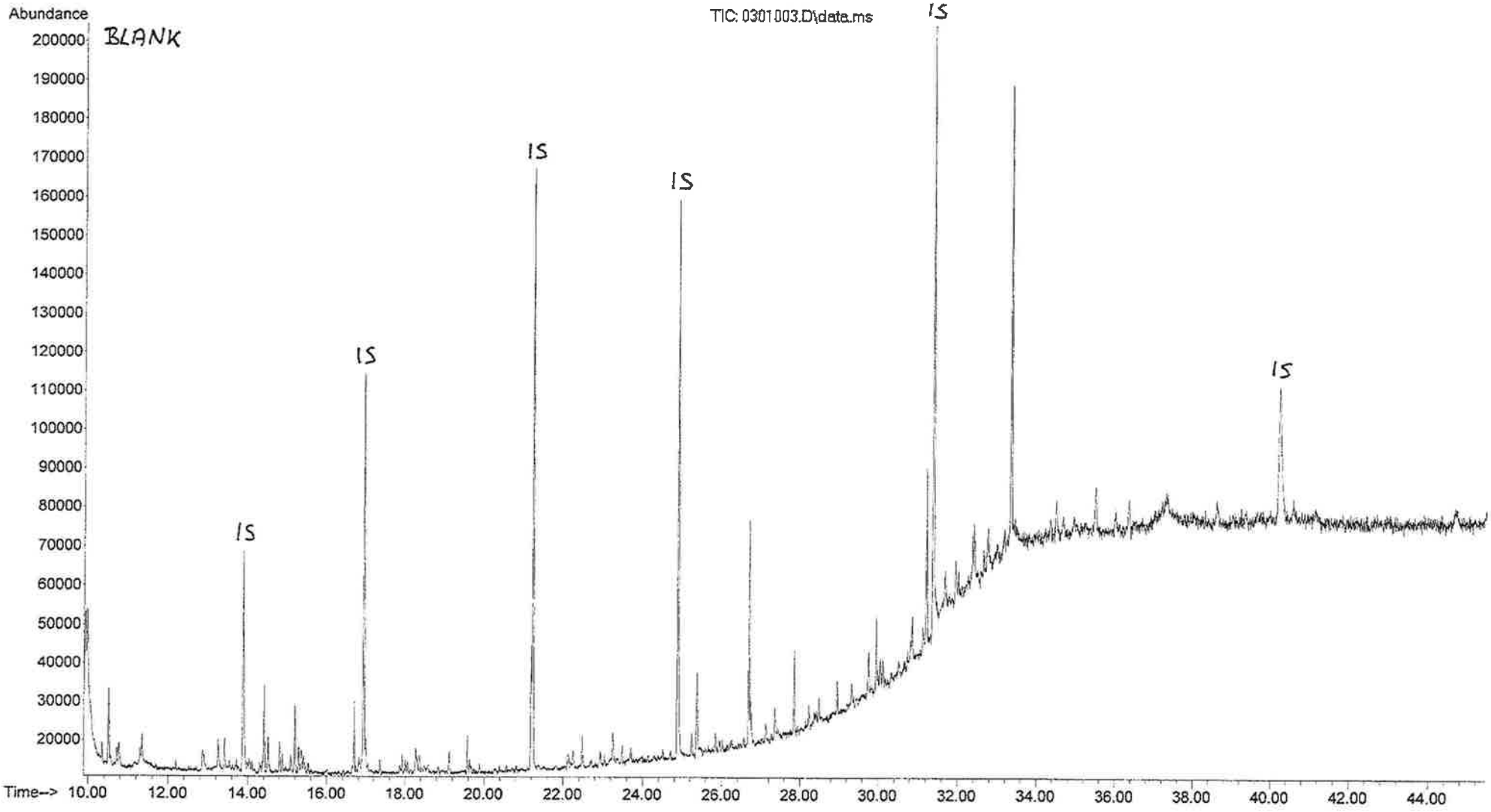
N00145485

File :R:\GC7\data0211\pak\pak23ma\1201013.D
Operator :
Acquired : 24 May 2011 6:54 using AcqMethod SCREEN60
Instrument : Instrumen
Sample Name: 3350-09
Misc Info :
Vial Number: 12



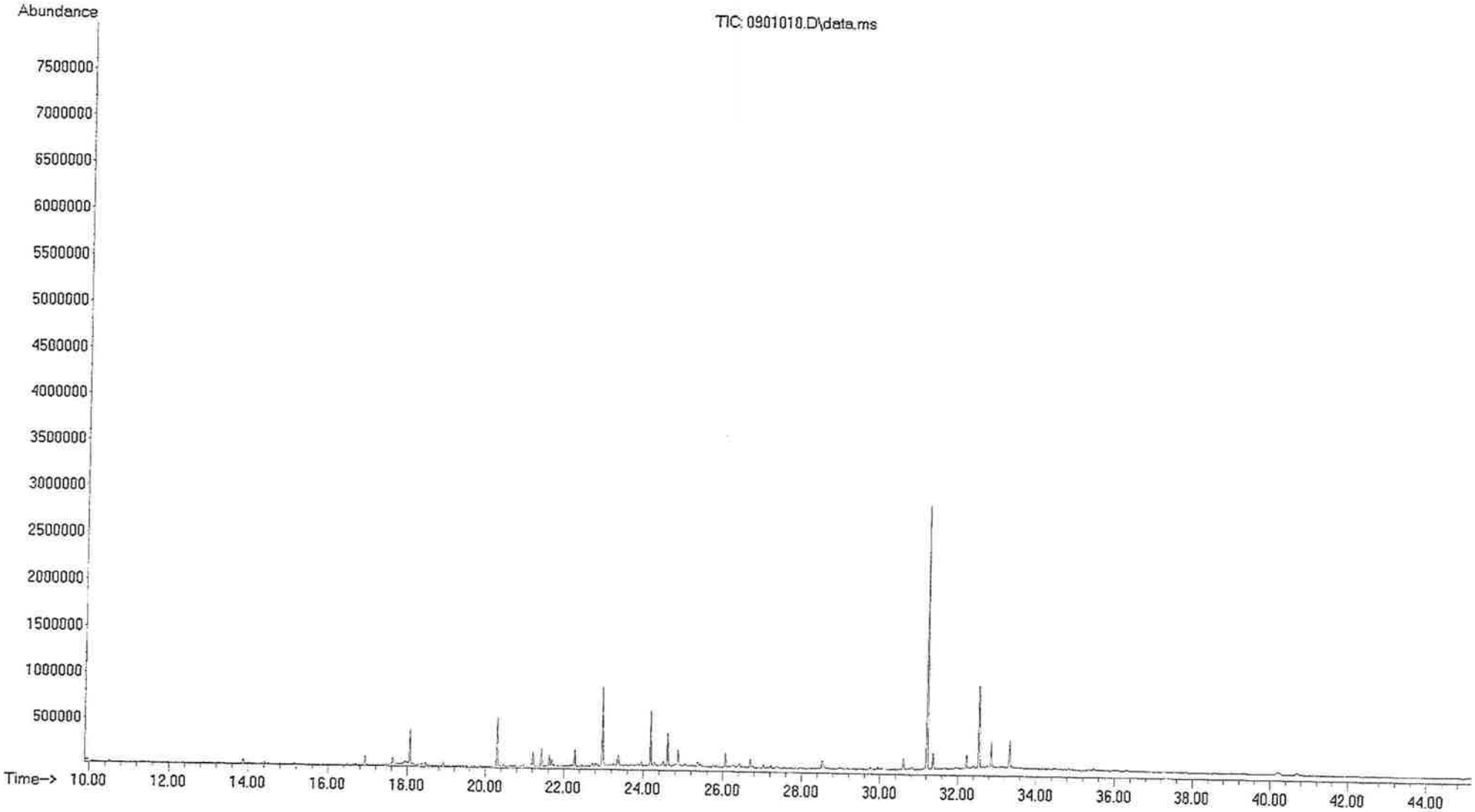
BLANK

File :R:\GC7\data0211\pak\pak23ma\0301003.D
Operator :
Acquired : 23 May 2011 18:33 using AcqMethod SCREEN60
Instrument : Instrumen
Sample Name: BW 3350
Misc Info :
Vial Number: 3



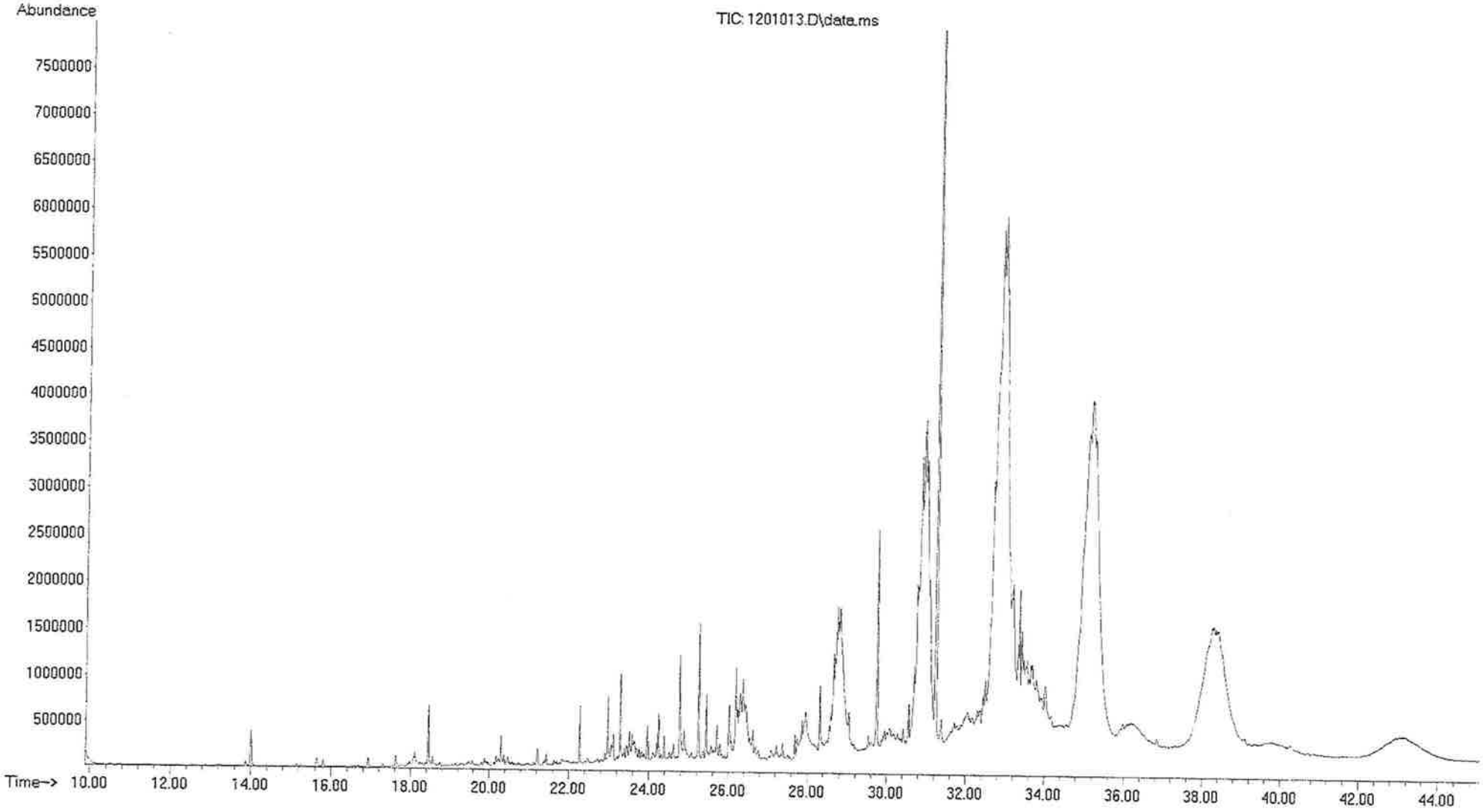
File :R:\GC7\data0211\pak\pak23ma\0901010.D
Operator :
Acquired : 24 May 2011 3:14 using AcqMethod SCREEN60
Instrument : Instrumen
Sample Name: 3350-07
Misc Info : 746mL:1mLEV: 1µg IS PAK
Vial Number: 9

N00145483 - titles.



N00145485 - tilles.

File :R:\GC7\data0211\pak\pak23ma\1201013.D
Operator :
Acquired : 24 May 2011 6:54 using AcqMethod SCREEN60
Instrument : Instrumen
Sample Name: 3350-09;731mL;1mLEV;1µg IS PAK
Misc Info :
Vial Number: 12



Appendix C

Specifications on PAX XL-60

HMS-DATABLAD
KEMWATER TM PAX-XL60

1. Identifikasjon av kjemikaliet og ansvarlig firma

Utgitt dato	06.12.2005
Kjemikaliets navn	KEMWATER TM PAX-XL60
Kjemisk navn	Polyaluminiumkloridhydroksidsilikat
Deklarasjonsnr.	23573
CAS-nr.	1327-41-9
EC-nr.	215-477-2
Kjemikaliets bruksområde	Fellingsmiddel for rensing av drikke- og avløpsvann.

Produsent

Firmanavn	Kemira Chemicals AS
Besøksadresse	Øraveien 14
Postnr.	1630
Poststed	Gamle Fredrikstad
Land	N
Telefon	69358585
Telefaks	69358595
E-post	kemira.no@kemira.com
Hjemmeside	www.kemira.no
Org. nr.	941559190
Kontaktperson	Tore Hunn
Nødtelefon	22591300

2. Stoffblandingers sammensetning og stoffenes klassifisering

CAS-nr.	EC-nr.	Komponentnavn	Innhold	Merking/klassifisering	Anm.
1327-41-9	215-477-2	Polyaluminiumkloridhydroksidsilikat	30	Xi; R36/38	
7732-18-5	231-791-2	Vann	70		

Kolonneforklaring	CAS-nr. = Chemical Abstracts Service; EU (Einecs- eller Elincsnummer) = European inventory of Existing Commercial Chemical Substances; Ingrediensnavn = Navn iflg. stoffliste (stoffer som ikke står i stofflisten må oversettes hvis mulig). Innhold oppgitt i; %, %vkt/vkt, %vol/vkt, %vol/vol, mg/m3, ppb, ppm, vekt%, vol%
Symbolforklaringer	T+ = Meget giftig, T = Giftig, C = Etsende, Xn = Helseskadelig, Xi = Irriterende, E = Eksplosiv, O = Oksiderende, F+ = Ekstremt brannfarlig, F = Meget brannfarlig, N = Miljøskadelig.

3. Viktigste faremomenter

Farebeskrivelse	Irriterer øyne og huden. Produktet er ikke brannfarlig. Store utslipp kan innvirke negativt i vannmiljø pga lokal pH-senkning.

4. Førstehjelpstiltak

Innånding	Frisk luft. Skyll nese, munn og svelg med vann.

Hudkontakt	Fjern forurenset tøy. Skyll huden med mye vann. Kontakt lege hvis irritasjon vedvarer.
Øyekontakt	Skyll øyeblikkelig med vann i 10-15 min. Hold øynene åpne. Gni ikke i øyet! Kontakt lege.
Svelging	Drikk straks et par glass vann eller melk. Fremkall ikke brekninger. Kontakt lege ved vedvarende symptomer.
Informasjon til helsepersonell	Hvis lege skal kontaktes, anvendes dette HMS-datablad som informasjonskilde.

5. Tiltak ved brannslukning

Passende brannslukningsmiddel	Ikke brannfarlig, velg slukningsmiddel etter omgivelsene.
Uegnet brannslukningsmiddel	Ingen restriksjoner
Brann- og eksplosjonsfarer	Ikke brannfarlig. Ved oppvarming dannes giftige og etsende gasser (saltsyregass).
Personlig verneutstyr	Bruk selvforsynt åndedrettsvern, friskluftmaske og beskyttelsesklær. Risiko for dannelse av giftige gasser.

6. Tiltak ved utilsiktet utslipp

Sikkerhetstiltak for å beskytte personell	Bruk vernebriller og hansker ved håndtering, se pkt 8. Evakuer overflødig personell. Øyespyleflaske skal være tilgjengelig.
Sikkerhetstiltak for å beskytte ytre miljø	Større mengder må ikke tømmes i kloakk og dem opp for spredning av utslipp til ytre miljø. Nøytraliser med kalk og absorbèr i sand.
Metoder til opprydding og rengjøring	Gjør rent med vann.
Andre anvisninger	Ved større utslipp til vann, kontakt politi/redningstjeneste.

7. Håndtering og oppbevaring

Håndtering	Håndter produktet slik at søl og damp ikke oppstår.
Oppbevaring	Lagres på containere/tanker merket "IRRITERENDE". Skal ikke lagres i temperatur under 0°C. Ved langtidslagring bør temp.ikke overstige +20°C . Bruk glassfiberarmerte polyestertanker med Deracane 411/45 ECR-glass innerskikt (sperreskikt). Lagringsstabilitet: Stabilt i minst 6 mnd.
Spesielle egenskaper og farer	Irriterende

8. Eksponeringskontroll og personlig verneutstyr

Eksponeringskontroll

Begrensning av eksponering på arbeidsplassen	Sørg for god ventilasjon. Beskyttelse mot sprut. Vask hendene godt ved kontakt med produktet. Nøddusj skal finnes på stedet
Åndedrettsvern	Gassmaske med patron for partile (P2).
Håndvern	Hansker av naturgummi, neopren, nitril, PVC eller viton. Gjennomtrengningstid > 8 timer.
Øyevern	Bruk tettsittende vernebriller. Øyespyleflasker skal være tilgjengelig.
Annet hudvern enn håndvern	Fullstendig kjemikaliebestandig dress og støvler ved behov.

9. Fysiske og kjemiske egenskaper

Tilstandsform	Flytende
Lukt	Ubetydelig
Farge	Svakt gulfarget klar væske
Løselighet i vann	Fullstendig løselig ved 20°C
Løselighet i fett	Ikke fettløslig
Relativ tetthet	1300-1330 kg/m3
Smeltepunkt/smeltepunktsintervall	-25
Smeltepunkt/smeltepunktsintervall	**Verdi:** °C
Kokepunkt/ kokepunktintervall	100-120
Kokepunkt/ kokepunktintervall	**Verdi:** °C

pH (handelsvare)	pH 1 - 2
Luftreaktivitet	Log Pow <<3

10. Stabilitet og reaktivitet

Forhold som skal unngås	Unngå høye temperaturer og frysing.
Materialer som skal unngås	Stål, galvaniserte overflater. Unngå kontakt med kloritt, hypokloritt, sulfitt, nitritt, nitrat og ulegert stål.
Farlige spaltningsprodukter	Ved oppvarming >200°C kan saltsyregass dannes.
Stabilitet	Produktet er stabilt ved normal lagring.

11. Opplysninger om helsefare

Toksikologisk informasjon

Oral toksisitet	LD50, rotte (mg/kg) >2000

Øvrige helsefareopplysninger

Generelt	Damp virker irriterende på slimhinner, øyne og åndedrettsorganer
Innånding	Innånding av aerosoler kan gi sviing, hoste og pustebesvær.
Hudkontakt	Irritasjon, rødflammethet og eksemlignende besvær
Øyekontakt	Damp kan virke irriterende på øyne
Svelging	Svelging kan gi magesmerter og oppkast. Kan virke irriterende i munn, svelg og mage.

12. Miljøopplysninger

Toksikologisk informasjon

Akvatisk kommentarer	Bioakkumuleres ikke. Log pow <<3

Øvrige miljøopplysninger

Økotoksisitet	LC50/96h/Danio rerio: > 1000 mg/l EC50/48h/Daphnia magna: 98 mg/l IC50/72h/Alga:Ikke relevant i algetest da fosforet felles ut som aluminiumfosfat. Dessuten er aluminium maskert av algevekstmedium i testen (pkt. 16.4). NOEC Danio rerio:>1000 mg/l NOEC Daphnia magna: 40 mg/l (= 3.6 mg total Al/l, både i løslig og utfelt form) Da langtidsløseligheten (28 dager) ligger i området 0.006 - 0.035 mg/Al/l, blir ikke stoffet klassifisert som farlig for miljøet. Klassifiseres ikke som giftig eller skadelig i vannmiljø (pkt. 16.4).
Persistens og nedbrytbarhet	Bionedbrytbarhet er ikke relevant for et uorganisk produkt som dette. Da produktet mineraliseres umiddelbart ved normale betingelser, ansees produktet å være lett nedbrytbart. Ved hydrolyse dannes ufarlig aluminiumhydroksid i pH-område 5-7. Denne fellingen anses som ufarlig for alge, daphnia og fisk.
Bioakkumulasjonspotensial	Bioakkumuleres ikke. Log pow <<3
Andre skadevirkninger / annen informasjon	Ved normale doseringsmengder vil det ikke oppnås konsentrasjonsnivåer som virker toksisk på vannlevende organismer. Hvis fosfat finnes, dannes metallfosfater. Ved unormalt høye konsentrasjoner som følge av utslipp vil pH-verdien synke i vannfasen og vannets buffringsevne reduseres, og i så fall kan dette skade vannlevende organismer (fisk). Store utslipp kan virke negativt i et vannmiljø pga lokal pH-senkning.

13. Fjerning av kjemikalieavfall

Avfallskode EAL	060314
NORSAS	7132
Produktet er klassifisert som farlig avfall	Ja
Annen informasjon	Spill og rester fortynnes med vann og nøytraliseres med kalk (hydratkalk). Rester kan eventuelt behandles som spesialavfall der Kemira Chemicals A/S tar varen i retur for gjenbruk og sluttdisponering. Emballasje kildesorteres eller destrueres i henhold til gjeldende norsk regelverk.

14. Opplysninger om transport

Varenavn (nasjonalt)	Polyaluminiumkloridhydroksidsilikat løsning
UN-nr.	3264
Farlig gods ADR/RID	Ja, Klasse:8 Fare nr.:80
Farlig gods IMDG	Ja, Klasse:8 Emballasjegruppe:III
Farlig gods ICAO/IATA	Ja, Klasse:8 Emballasjegruppe:III
Fareseddel	8
Andre relevante opplysninger	Produktet er klassifisert som farlig gods da det er svakt etsende på metaller iflg ADR-test 2800 (3) (f).

15. Opplysninger om lover og forskrifter

Faresymbol

Sammensetning på merkeetiketten	Polyaluminiumkloridhydroksidsilikat: 30 %, Vann: 70 %
EC-nr.	215-477-2
R-setninger	R-36/38 Irriterer øynene og huden.
S-setninger	S26 Får man stoffet i øynene, skyll straks med vann og kontakt lege. S28 - Får man stoff på huden, vaskes straks med vann. S36 Bruk egnede verneklær S37 Bruk vernehansker. S39 Bruk vernehansker og ansiktsskjerm.
Referanser (Lover/Forskrifter)	1. Klassifisering og merking av farlige kjemikalier i Norge (stofflisten). 2. Administrativ norm for arbeid med kjemikalier. 3. Forskrift om vern mot eksponering for kjemikalier på arbeidsplassen (kjemikalieforskriften). 4. Databladforskriften, revidert forskrift nr 1323 per 16.07.02. 5. Lov om transport av farlig gods.

16. Andre opplysninger av betydning for helse, miljø og sikkerhet

Erstatter HMS-datablad av	10.07.2005
Liste over relevante R-setninger (i seksjon 2)	R36/38 Irriterer øynene og huden.
Viktigste kilder ved utarbeidelsen av HMS-databladet (ikke norske)	1. Hommel, Handbuch der gefährlichen Güter 2. European Standard SS-EN 883 3. NIVA Study G 003/1-3 4. Fraunhofer-Institute for Molecular, Germany. Ecotoxicology-study pkt. 12. 5. Säkerhetsdatablad Kemwater TM PAX-XL60 25.10.2002 Skjelmose/Wall
Opplysninger som er nye, slettet eller revidert	Endringer i pkt. 2
Leverandørens anmerkninger	Innholdet i dette HMS-databladet er basert på de opplysninger som vi er kjent med ved bladets siste utgave.

Appendix D

Specifications on Polymer- Polyacrylamide

HELSE-, MILJØ- og SIKKERHETSDATABLAD Superfloc emulsjoner anioniske (4812RS, 4814RS)

1. Identifikasjon av stoffet / produktet og av selskapet / foretaket

Utgitt dato	30.03.2005
Revisjon	01.03.2008
Kjemikaliets navn	Superfloc emulsjoner anioniske (4812RS, 4814RS)
Kjemisk navn	Anionisk polyakrylamid
Deklarasjonsnr.	60956
Kjemikaliets bruksområde	Flokkuleringsmiddel for rensing av avløpsvann og/eller slamavvanning.

Importør

Firmanavn	Kemira Chemicals AS
Besøksadresse	Øraveien 14
Postnr.	1630
Poststed	Gamle Fredrikstad
Land	N
Telefon	69358585
Telefaks	69358595
E-post	kemira.no@kemira.com
Hjemmeside	http://www.kemira.no
Org. nr.	941559190
Nødtelefon	22591300

2. Farlige egenskaper

Farebeskrivelse	Irriterer huden.

3. Sammensetning /opplysning om innholdsstoffer

Komponentnavn	Identifikasjon	Merking/klassifisering	Innhold
Petroleum destillater	CAS-nr.: 64742-47-8 EC-nr.: 265-149-8	Xn; R65	22 - 25
Ammoniumhydroksyd	CAS-nr.: 1336-21-6 EC-nr.: 215-647-6	C,N; R34, R50	0.15 - 0.9 %
Etoksilater oleyl amin	CAS-nr.: 26635-93-8	Xn,N; R22, R38, R41, R50/53, R51, R52	1.2 - 1.6 %
Alkohol (C12-16) etoksilater	CAS-nr.: 68551-12-2	Xn,N; R22, R38, R41, R50	0 - 3.6 %
Alkohol (C10-16) etoksilater	CAS-nr.: 68002-97-1	Xn,N; R22, R38, R41, R50	0 - 3.6 %

Kolonneforklaring	CAS-nr. = Chemical Abstracts Service; EU (Einecs- eller Elincsnummer) = European inventory of Existing Commercial Chemical Substances; Ingrediensnavn = Navn iflg. stoffliste (stoffer som ikke står i stofflisten må oversettes hvis mulig). Innhold oppgitt i; %, %vkt/vkt, %vol/vkt, %vol/vol, mg/m3, ppb, ppm, vekt%, vol%
FH/FB/FM	T+ = Meget giftig, T = Giftig, C = Etsende, Xn = Helseskadelig, Xi = Irriterende, E = Eksplosiv, O = Oksiderende, F+ = Ekstremt brannfarlig, F = Meget brannfarlig, N = Miljøskadelig.

4. Førstehjelpstiltak

Innånding	Flytt ut i frisk luft. Gå til lege hvis det oppstår problemer.

Hudkontakt	Ta av forurenset tøy. Skyll med store mengder vann. Kontakt lege hvis problemer oppstår.
Øyekontakt	Skyll øyeblikkelig med vann i 10-15 min. Hold øynene åpne.
Svelging	Kontakt lege snarest. Gi aldri noe i munnen til en bevisstløs person.

5. Tiltak ved brannslukning

Passende brannslukningsmiddel	Bruk vann, karbondioksyd eller tørt kjemikalie.
Personlig verneutstyr	Bruk beskyttelsesklær og friskluftmaske.
Annen informasjon	Beholdere i nærheten av brann bør flyttes eller kjøles med vann.

6. Tiltak ved utilsiktet utslipp

Sikkerhetstiltak for å beskytte personell	Unngå kontakt med hud og øyne. Spill gir glatte flater.
Sikkerhetstiltak for å beskytte ytre miljø	Må ikke slippes ut i omgivelsene.
Metoder til opprydding og rengjøring	Lekkasjer av oppløst polymer skylles med vann. Varmt vann gjør skyllingen lettere.
Andre anvisninger	Med fare for forurensning av drikkevann, må politi og helsevesen varsles.

7. Håndtering og lagring

Oppbevaring	For å unngå nedbryting av produktet og korrosjon av utstyret, må jern-, kobber- eller aluminiumbeholdere ikke benyttes. Fastleggelsen av flammepunkt for materialer av denne type skal, ifølge visse bestemmelser og vitenskapelige normer, utføres ved hjelp av en Pensky-Martens prøvemetodetype, lukket kopp.Denne metoden indikerer et flammepunkt over 200F (93°C). Derfor bør det utvises forsiktighet ved lagring og omgang med materialet. Lagringstemp.: <32°C
Spesielle egenskaper og farer	Utspedde løsninger som er laget for bruk, må ikke betraktes som ufarlig vann pga produktets egenskaper.

8. Eksponeringskontroll / personlig verneutstyr

Administrative normer

Komponentnavn	Identifikasjon	Enhet	Norm år
Petroleum destillater	CAS-nr.: 64742-47-8 EC-nr.: 265-149-8	8 t.: 165 ppm Verdi: 1200 mg/m3	2003

Eksponeringskontroll

Begrensning av eksponering på arbeidsplassen	Unngå søl. Risiko for glatte gulv/overflater.
Åndedrettsvern	Sørg for egnet ventilasjon.
Håndvern	Beskyttelseshansker (PVC, neopren, butylgummi).
Øyevern	Tettsittende vernebriller. Øyespyleflaske med rent vann.
Annen informasjon	Spising, røyking og drikkefontener ikke tillatt nær arbeidsstedet. Vask ansikt og hender grundig med vann og såpe før du spiser, drikker eller røker.

9. Fysiske og kjemiske egenskaper

Tilstandsform	Flytende væske
Lukt	Oljelignende lukt
Farge	Mørkegrønn til melkaktig
Løselighet i vann	Begrenset av viskositet
Relativ tetthet	**Verdi:** 1.03 -1.06
Smeltepunkt/smeltepunktsintervall	**Verdi:** < -20 °C
Kokepunkt/ kokepunktintervall	Som vann
pH (bruksløsning)	**Verdi:** < 9.5
Flammepunkt	**Verdi:** > 100.6 °C

10. Stabilitet og reaktivitet

Farlige spaltningsprodukter	Termisk dekomponering kan frigi gasser av ammoniakk, svoveloksyd, karbondioksyd, nitrogenoksyd og karbonmonoksyd.

11 Toxikologisk information

Toksikologisk informasjon

Oral toksisitet	LD50, rotte mg/kg > 5000
Akutt dermal toksisitet	LD50, kanin mg/kg > 2000
Innåndingstoksisitet	LC50, 4h rotte mg/l > 20.0
Andre toksikologiske data	Petroleum destillater: Akutt LD50 oralt rotte > 5 g/kg t Akutt LD50 dermal kanin > 3.16 g/kg Ammoniumhydroksyd: Akutt LC50-(1hr)-rotte 7338 ppm Etoksilater oleyl amin: Akutt LD50 oral rotte 1500 mg/kg Alkohol (C10-16) etoksilater: Akutt LD50 oral rotte 1600-2500 mg/kg Akutt LD50 dermal kanin > 2000 mg/kg Alkohol (C12-16) etoksilater: Akutt LD50 oral rotee 1600 - 2500 mg/kg Akutt LD50 dermal kanin > 2000 mg/kg

Øvrige helsefareopplysninger

Hudkontakt	Kan forårsake mild hudirritasjon.
Annen informasjon	Lokale virkninger på hud og øyne: Ammoniumhydroksyd Akutt øyeirritasjon - gir alvorlige skader Akutt dermal irritasjon - korrosiv Petroleum destillater Akutt dermal irritasjon - ikke irriterende Akutt øyeirritasjon - ikke irriterende Alkohol (C10-16) etoksilater Akutt øyeirritasjon kanin - gir alvorlige skader akutt dermal irritasjon kanin - irriterende Alkohol (C12-16) etoksilater Akutt dermal irritasjon - irriterende Akutt øyeirritasjon - gir alvorlige skader Etoksilater oleyl amin Akutt dermal irritasjon - irriterende Akutt øyeirritasjon - gir alvorlige skader

12. Miljøopplysninger

Øvrige miljøopplysninger

Økotoksisitet	Testresultater alger: Green Algea (Selenastrum capricornutum), 72 h, IC50: > 100 mg/l Testresultater fisk: Zebra Fish (Brachydanio rerio), 96 h, LC50: > 100 mg/l Testresultater virvelløse dyr: Water Flea (Daphnia magna), 48 h, EC50: > 100 mg/l
Mobilitet	Relativ liten mobilitet.
Persistens og nedbrytbarhet	På grunn av høy polymerstruktur er biodegradering av et slikt produkt lav.
Andre skadevirkninger / annen informasjon	Utspedde løsninger som er lagret for bruk, må ikke betraktes som ufarlig vann pga produktets egenskaper.

13 Fjerning av kjemikalieavfall

Avfallskode EAL	070112
NORSAS	7152
Produktet er klassifisert som farlig avfall	Ja
Egnede metoder til fjerning av kjemikaliet	Må leveres til godkjent mottak for farlig avfall.

14.Transportinformasjon

15. Opplysninger om lover og forskrifter

Faresymbol

Sammensetning på merkeetiketten	Petroleum destillater: 22 - 25 %, Ammoniumhydroksyd: 0.15 - 0.9 %, Etoksilater oleyl amin: 1.2 - 1.6 %, Alkohol (C12-16) etoksilater: 0 - 3.6 %, Alkohol (C10-16) etoksilater: 0 - 3.6 %
R-setninger	R38 Irriterer huden.
S-setninger	S81 Spill er meget glatt.
Referanser (Lover/Forskrifter)	1. Klassifisering og merking av farlige kjemikalier i Norge (stofflisten). 2. Administrativ norm for arbeid med kjemikalier. 3. Forskrift om vern mot eksponering for kjemikalier på arbeidsplassen (kjemikalieforskriften). 4. Databladforskriften, revidert forskrift nr 1323 per 16.07.02. 5. Lov om transport av farlig gods.

16 Andre opplysninger

Liste over relevante R-setninger (i seksjon 2 og 3).	R22 Farlig ved svelging. R34 Etsende. R38 Irriterer huden R41 Fare for alvorlig øyeskade. R50/53 Meget giftig for vannlevende organismer, kan forårsake uønskede langtidsvirkninger i vannmiljøet. R50 Meget giftig for vannlevende organismer. R51 Giftig for vannlevende organismer. R52 Skadelig for vannlevende organismer. R65 Farlig: kan forårsake lungeskade ved svelging.
Viktigste kilder ved utarbeidelsen av HMS-databladet (ikke norske)	EEC-EINECS: Alle dette produktets bestanddeler er oppført på Den Europeiske Lagerliste med eksisterende Kjemiske Stoffer (EINECS) eller er polymerer, hvis bestanddeler er i EINECS, i overensstemmelse med Rådsdirektiv 67/548/EFs endringer. USA-TCCA: Dette produktet fremstilles i overensstemmelse med alle bestemmelser i Loven om kontroll med kjemiske stoffer, 15 U.S.C.2601 et.seq. CANADA-DLS: Stoffene i dette produktet er rapportert til canadisk miljø i overensstemmelse med punkt 25 i den canadiske miljøbeskyttelesloven og er oppført på den lokale stofflista.
Leverandørens anmerkninger	Gjelder for produktene: 4812RS og 4814RS
Ansvarlig for HMS-datablad	Kemira Chemicals AS

Appendix E

Specifications on 25% HCL

HELSE-, MILJØ- og SIKKERHETSDATABLAD SALTSYRE > 25 %

1. Identifikasjon av stoffet / produktet og av selskapet / foretaket

Utgitt dato	02.11.2005
Revisjon	19.10.2007
Kjemikaliets navn	SALTSYRE > 25 %
Kjemisk navn	Hydrogenkloridløsning
Synonymer	Saltsyre 30%. Saltsyre 33-35%.
Deklarasjonsnr.	30 %: under deklarering. 33-35 % : 70214.
EC-nr.	231-595-7
Indeksnr.	017-002-01-X
Kjemikaliets bruksområde	pH-regulerende midler, industrirengjøringsmidler, prosesskjemikalier.

Nedstrømsbruker

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Telefaks	+47 69382901
E-post	cathrine.lillestrand@solbergindustri.no
Hjemmeside	http://www.solbergindustri.no/
Kontaktperson	Cathrine Lillestrand
Utarbeidet av	Teknologisk Institutt as v/ Monica Rustad
Nødtelefon	Giftinformasjonen:22 59 13 00

2. Farlige egenskaper

Klassifisering	C; R34 Xi; R37
Farebeskrivelse	Helse: Etsende. Irriterer luftveiene. Brann og eksplosjon: Produktet er ikke klassifisert som brannfarlig. Miljø: Produktet regnes ikke som miljøskadelig.

3. Sammensetning /opplysning om innholdsstoffer

Komponentnavn	Identifikasjon	Merking/klassifisering	Innhold
saltsyre	EC-nr.: 231-595-7	C; R34, R37	25 - 35 %
vann	CAS-nr.: 7732-18-5 EC-nr.: 231-791-2		65 - 75 %

Kolonneforklaring	CAS-nr. = Chemical Abstracts Service; EU (Einecs- eller Elincsnummer) = European inventory of Existing Commercial Chemical Substances; Ingrediensnavn = Navn iflg. stoffliste (stoffer som ikke står i stofflisten må oversettes hvis mulig). Innhold oppgitt i; %, %vkt/vkt, %vol/vkt, %vol/vol, mg/m3, ppb, ppm, vekt%, vol%
Symbolforklaringer	T+ = Meget giftig, T = Giftig, C = Etsende, Xn = Helseskadelig, Xi = Irriterende, E = Eksplosiv, O = Oksiderende, F+ = Ekstremt brannfarlig, F = Meget brannfarlig, N = Miljøskadelig.
Komponentkommentarer	Se seksjon 16 for forklaring av risikosetninger.

4. Førstehjelpstiltak

Generelt	I tvilstilfelle bør lege kontaktes.
Innånding	Frisk luft, ro og varme. Kontakt lege hvis ikke alt ubehag gir seg.
Hudkontakt	Fjern tilsølt tøy. Vask straks huden med såpe og vann. Fortsett å skylle i minst 15 minutter. Etseskader skal behandles av lege.
Øyekontakt	Skyll straks med rikelige mengder vann i opp til 15 minutter. Fjern evt. kontaktlinser og åpne øyet godt opp. Ved fortsatt irritasjon fortsettes skylling under transport til sykehus. Ta med sikkerhetsdatabladet.
Svelging	Gi straks et par glass melk eller vann hvis den skadde er ved full bevissthet. Fremkall ikke brekninger. Kontakt lege.
Informasjon til helsepersonell	Behandles som etseskader/ brannskader.

5. Tiltak ved brannslukning

Passende brannslukningsmiddel	Velges i forhold til omgivende brann.
Uegnet brannslukningsmiddel	Bruk ikke full vannstråle. Ved bruk av bikarbonatholdige pulver kan det være fare for sprut pga. utvikling av karbondioksid.
Brann- og eksplosjonsfarer	Produktet er ikke klassifisert som brannfarlig. Kan utvikle meget giftige eller etsende damper ved oppvarming. Ved brann dannes: Klorforbindelser.
Personlig verneutstyr	Bruk friskluftmaske når produktet er involvert i brann. Ved rømning brukes godkjent rømningsmaske. Se forøvrig pkt 8.
Annen informasjon	Beholdere i nærheten av brann flyttes straks eller kjøles med vann.

6. Tiltak ved utilsiktet utslipp

Sikkerhetstiltak for å beskytte personell	Benytt personlig verneutstyr som angitt i pkt 8. Pass på! Produktet er etsende. Advar alle om de potensielle farene og evakuer om nødvendig.
Sikkerhetstiltak for å beskytte ytre miljø	Forhindre utslipp til kloakk, vassdrag eller grunn.
Metoder til opprydding og rengjøring	Spill tas opp med inert absorberende materiale. Spill samles opp i egnede beholdere og leveres som farlig avfall (se pkt. 13).

7. Håndtering og lagring

Håndtering	Hell aldri vann direkte i produktet, dette kan føre til en kraftig reaksjon/koking. Ved fortynning skal produktet alltid helles forsiktig i vann. Sørg for god ventilasjon. Unngå kontakt med huden og øynene.
Oppbevaring	Lagres tørt og i lukkede beholdere. Oppbevares i originalemballasjen. Oppbevares på et kjølig, godt ventilert sted. Lagres beskyttet mot varme og direkte sollys. Lagres adskilt fra: Sterkt alkaliske produkter.

8. Eksponeringskontroll / personlig verneutstyr

Administrative normer

Komponentnavn	Identifikasjon	enhet	Norm år
hydrogenklorid	CAS-nr.: 7647-01-0 EC-nr.: 231-595-7	8 t.: 7 mg/m³ T	2003

Eksponeringskontroll

Annen informasjon	Det oppgitte verneutstyr er veiledende. Risikovurderingen (Faktisk risiko) kan føre til andre krav.
Begrensning av eksponering på arbeidsplassen	Sørg for tilstrekkelig ventilasjon. Vask hendene etter hvert skift, og før spising, røyking eller bruk av toalett.
Åndedrettsvern	Ved utilstrekkelig ventilasjon: Bruk egnet åndedrettsvern med gassfilter, type B. eller type E.
Håndvern	Benytt hansker av motstandsdygtig materiale, f.eks.: Butylgummi. Neoprengummi. Nitrilgummi. viton. Gjennomtrengningstid > 8 timer.
Øyevern	Bruk godkjente vernebriller eller ansiktsskjerm.
Annet hudvern enn håndvern	Benytt hensiktsmessige verneklær for beskyttelse ved mulig hudkontakt.
Annen informasjon	Nøddusj og mulighet for øyeskylling må finnes på arbeidsplassen.

9. Fysiske og kjemiske egenskaper

Tilstandsform	Væske
Lukt	Stikkende lukt
Farge	Fargeløs til lysegul
Løselighet i vann	Løselig
Relativ tetthet	**Verdi:** 1,18 g/cm3
Smeltepunkt/smeltepunktsintervall	**Verdi:** -30 °C **Kommentarer:** (36%)
Kokepunkt/ kokepunktintervall	**Verdi:** 108 °C **Kommentarer:** (750 mmHg)
pH (handelsvare)	**Verdi:** 0
pH (bruksløsning)	**Verdi:** ~ 0
Damptrykk	**Verdi:** 105,5 mmHg **Kommentarer:** (36%, 20°C)
Damptetthet	**Verdi:** 1,26
Luktgrense	7mg/m3

10. Stabilitet og reaktivitet

Forhold som skal unngås	Hell aldri vann direkte i produktet - dette kan føre til kraftig reaksjon. Ved kontakt med metaller dannes hydrogengass som kan danne eksplosiv blanding med luft.
Materialer som skal unngås	Baser. Metall og metallforbindelser. Visse typer plast, lær, skinn og tekstiler kan nedbrytes.
Farlige spaltningsprodukter	Hydrogenklorid. Klorgass.
Stabilitet	Stabil under normale temperaturforhold og anbefalt bruk.

11. Toxikologisk information

Toksikologisk informasjon

Innåndingstoksisitet	**Verdi:** 4701 ppm **Forsøksdyreart:** Rotte **Eksponeringstid:** 30 min **Kommentarer:** Mus: 2644 ppm 30 min.
Andre toksikologiske data	LCL0 menneske: 1300 ppm 30 min.

Øvrige helsefareopplysninger

Generelt	Ved bruk representerer de etsende egenskaper den største faren.
Innånding	Irriterer luftveiene. Kan gi skader på slimhinner i nese, svelg, bronkier og lunger. Syredampene skader tennene.
Hudkontakt	Virker sterkt etsende. Kan forårsake alvorlige vevskader.
Øyekontakt	Etsende. Kan forårsake synsforstyrrelser og alvorlig øyeskade.
Svelging	Etsende ved svelging. Gir brennende smerter i munn, svelg og spiserør. Fare for store varige skader.
Kroniske effekter	Kortvarig kontakt kan gi varig vevskade.
Allergi	Allergifremkallende egenskaper er ikke kjent.
Kreft	Kreftfremkallende egenskaper er ikke kjent.
Fosterskadelige egenskaper	Effekter på fosterutvikling er ikke kjent.
Reproduksjonsskader	Reproduksjonsskadelige egenskaper er ikke kjent.
Arvestoffskader	Arvestoffskadende (mutagene) egenskaper er ikke kjent.

12. Miljøopplysninger

Toksikologisk informasjon

Akutt akvatisk, fisk	**Verdi:** 100-1000mg/l **Testmetode:** LC50 **Varighet:** 96h
Akutt akvatisk, alge	**Verdi:** 49 mg/l. **Testmetode:** EC 50. NOEC: 40 mg/l **Alge art:** Selenastrum capricornutum

Akvatisk kommentarer	Akutt akvatisk, bløtdyr: Crustaceous: LC50, 48 h:100-1000mg/l

Øvrige miljøopplysninger

Økotoksisitet	Produktet er ikke klassifisert som miljøskadelig.
Mobilitet	Løselig i vann.
Persistens og nedbrytbarhet	Produktet består utelukkende av uorganiske forbindelser som ikke er bionedbrytbare.
Bioakkumulasjonspotensial	Bioakkumulerer ikke.
Andre skadevirkninger / annen informasjon	Utslipp av produktet til vann kan lokalt gi lav pH med fare for fiskedød.

13. Fjerning av kjemikalieavfall

Avfallskode EAL	EAL: 06 01 02 saltsyre
NORSAS	7131 Syrer, uorganiske
Produktet er klassifisert som farlig avfall	Ja
Egnede metoder til fjerning av kjemikaliet	Leveres som farlig avfall til godkjent behandler eller innsamler. Koden for farlig avfall (EAL-kode) er veiledende. Bruker må selv angi riktig EAL-kode hvis bruksområdet avviker.

14.Transportinformasjon

Proper Shipping Name	HYDROCHLORIC ACID
Varenavn (nasjonalt)	SALTSYRE
Farlig gods ADR	**Status:** Ja **UN-nr.:** 1789 **Klasse:** 8 **Fare nr.:** 80 **Emballasjegruppe:** II
Farlig gods RID	**Status:** Ja **UN-nr.:** 1789 **Klasse:** 8 **Emballasjegruppe:** II
Farlig gods IMDG	**Status:** Ja **UN-nr.:** 1789 **Klasse:** 8 **Emballasjegruppe:** II **Marin forurensning:** N **EmS:** F-A, S-B
Farlig gods ICAO/IATA	**Status:** Ja **UN-nr.:** 1789 **Klasse:** 8 **Emballasjegruppe:** II
Fareseddel	8

15. Opplysninger om lover og forskrifter

Faresymbol

Sammensetning på merkeetiketten	saltsyre: 25 - 35 %
EC-nr.	231-595-7
R-setninger	R34 Etsende. R37 Irriterer luftveiene
S-setninger	S1/2 Oppbevares innelåst og utilgjengelig for barn. S26 Får man stoffet i øynene; skyll straks grundig med store mengder vann og kontakt lege. S36/37/39 Bruk egnede verneklær, vernehansker og vernebriller/ansiktsskjerm. S38 Ved utilstrekkelig ventilasjon, må det benyttes egnet åndedrettsvern.

	S45 Ved uhell eller illebefinnende er omgående legebehandling nødvendig; vis etiketten om mulig.
Referanser (Lover/Forskrifter)	Forskrift om klassifisering, merking m.v. av farlige kjemikalier, fastsatt av Miljøverndepartementet og Arbeids- og inkluderingsdepartementet, 16.juli 2002, med senere endringer, gjeldende fra 31. oktober 2005. FOR 1997-12-19 nr. 1323: Forskrift om utarbeidelse og distribusjon av helse-, miljø- og sikkerhetsdatablad for farlige kjemikalier. Sist endret 20-02-2004. Administrative normer for forurensning i arbeidsatmosfæren 2003, Direktoratet for Arbeidstilsynet (Best.nr. 361), med siste endringer mai 2007. Avfallsforskriften, FOR 2004-06-01 nr 930, fra Miljøverndepartementet. ADR/RID veg-/jernbanetransport av farlig gods 2007, Direktoratet for samfunnssikkerhet og beredskap. Databladet er utarbeidet med basis i opplysninger gitt av produsenten.

16. Andre opplysninger

Liste over relevante R-setninger (i seksjon 2 og 3).	R34 Etsende. R37 Irriterer luftveiene
Opplysninger som er nye, slettet eller revidert	Versjon: 1(02.11.2005). Punkter endret: 1-16. Ansvarlig: ST. Versjon: 2(19.10.2007). Punkter endret: 1-16. Ansvarlig: MR.
Leverandørens anmerkninger	Informasjonen i dette dokument skal gjøres tilgjengelig til alle som håndterer produktet.
Kvalitetssikring av informasjonen	Dette HMS-databladet er kvalitetssikret av Teknologisk Institutt as, som er sertifisert iht. NS-EN ISO 9001:2000.
Ansvarlig for HMS-datablad	SOLBERG INDUSTRI AS

Appendix F

Specifications on NaOH

SIKKERHETSDATABLAD
NATRONLUT 10-50%

1. Identifikasjon av stoffet / produktet og av selskapet / foretaket

Utgitt dato	19.04.2005
Revisjon	27.04.2009
Kjemikaliets navn	NATRONLUT 10-50%
Kjemisk navn	Natriumhydroksidløsning
Synonymer	Natronlut 10%. Natronlut 20%. Natronlut 25%. Natronlut 30%. Natronlut 32%. Natronlut 45-47%. Natronlut 50%.
Kjemikaliets bruksområde	Avfettingsmiddel Luting, metallbehandling.

Nedstrømsbruker

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Hjemmeside	http://www.solbergindustri.no/
Kontaktperson	Cathrine Lillestrand
Utarbeidet av	Teknologisk Institutt as v/ Monica Rustad
Nødtelefon	Giftinformasjonen:22 59 13 00

2. Farlige egenskaper

Klassifisering	C; R35
Farebeskrivelse	Helse: Sterkt etsende. Brann og eksplosjon: Produktet er ikke klassifisert som brannfarlig. Miljø: Produktet er ikke klassifisert som miljøskadelig.

3. Sammensetning /opplysning om innholdsstoffer

Komponentnavn	Identifikasjon	Merking/klassifisering	Innhold
Natriumhydroksid	CAS-nr.: 1310-73-2 EC-nr.: 215-185-5 Indeksnr.: 011-002-00-6	C; R35	10 - 50 %
vann	CAS-nr.: 7732-18-5 EC-nr.: 231-791-2		50 - 90 %

Kolonneforklaring	CAS-nr. = Chemical Abstracts Service; EU (Einecs- eller Elincsnummer) = European inventory of Existing Commercial Chemical Substances; Ingrediensnavn = Navn iflg. stoffliste (stoffer som ikke står i stofflisten må oversettes hvis mulig). Innhold oppgitt i; %, %vkt/vkt, %vol/vkt, %vol/vol, mg/m3, ppb, ppm, vekt%, vol%
FH/FB/FM	T+ = Meget giftig, T = Giftig, C = Etsende, Xn = Helseskadelig, Xi = Irriterende, E = Eksplosiv, O = Oksiderende, F+ = Ekstremt brannfarlig, F = Meget brannfarlig, N = Miljøskadelig.
Komponentkommentarer	Se seksjon 16 for forklaring av risikosetninger.

4. Førstehjelpstiltak

Generelt	I tvilstilfelle bør lege kontaktes.
Innånding	Frisk luft, ro og varme. Ved bevisstløshet, løs stramtsittende klær. Ved åndedrettsstans eller hjertestans, gi kunstig åndedrett eller hjertekompresjon. Kontakt lege.
Hudkontakt	Ta av tilsølte klær. Skyll med store mengder vann i minst 15 minutter. Ved utslett, sår eller andre hudplager: Kontakt lege, og ta med sikkerhetsdatabladet.
Øyekontakt	Skyll straks med rikelige mengder vann i opp til 15 minutter. Fjern evt. kontaktlinser og åpne øyet godt opp. Ved fortsatt irritasjon fortsettes skylling under transport til sykehus. Ta med sikkerhetsdatabladet. Ved lengre tids skylling, anvend lunkent vann for å unngå skade på øyet.
Svelging	Skyll munnen grundig. Drikk et par glass vann eller melk. Gi melk i stedet for vann hvis lett tilgjengelig. Fremkall ikke brekninger. Gi aldri noe via munnen hvis pasienten har nedsatt bevissthet. Kontakt lege øyeblikkelig!
Informasjon til helsepersonell	Behandles som lutskader/brannskader.

5. Tiltak ved brannslukning

Passende brannslukningsmiddel	Velges i forhold til omgivende brann.
Uegnet brannslukningsmiddel	Bruk ikke full vannstråle.
Brann- og eksplosjonsfarer	Produktet er ikke brennbart. Kan danne giftige eller eksplosive damper i kontakt med enkelte metaller.
Personlig verneutstyr	Bruk friskluftmaske når produktet er involvert i brann. Ved rømning brukes godkjent rømningsmaske. Se forøvrig pkt 8.
Annen informasjon	Beholdere i nærheten av brann flyttes straks eller kjøles med vann. Slokningsvannet kan være sterkt etsende.

6. Tiltak ved utilsiktet utslipp

Sikkerhetstiltak for å beskytte personell	Benytt personlig verneutstyr som angitt i pkt 8. Pass på! Produktet er etsende. Advar alle om de potensielle farene og evakuer om nødvendig.
Sikkerhetstiltak for å beskytte ytre miljø	Forhindre utslipp til kloakk, vassdrag eller grunn. Samle opp søl/spill i sand, jord eller annet egnet absorberende materiale.
Metoder til opprydding og rengjøring	Stopp lekkasje hvis mulig uten risiko. Spill tas opp med inert absorberende materiale. Spill samles opp i egnede beholdere og leveres som farlig avfall (se pkt. 13).

7. Håndtering og lagring

Håndtering	Hell aldri vann direkte i produktet, dette kan føre til en kraftig reaksjon/koking. Ved fortynning skal produktet alltid helles forsiktig i vann. Unngå enhver kontakt med produktet. Bruk anbefalt verneutstyr. Skift straks tilsølte klær.
Oppbevaring	Lagres tørt og i lukkede beholdere. Lagres adskilt fra: Syrer. Unngå metaller som sink og aluminium. Oppbevares i originalemballasjen. Bruk IKKE beholder av: Aluminium.

8. Eksponeringskontroll / personlig verneutstyr

Administrative normer

Komponentnavn	Identifikasjon	Verdi	Norm år
Natriumhydroksid	CAS-nr.: 1310-73-2 EC-nr.: 215-185-5 Indeksnr.: 011-002-00-6	8 t.: 2 mg/m3, T	2007

Eksponeringskontroll

Begrensning av eksponering på arbeidsplassen	Sørg for tilstrekkelig ventilasjon. Vask hendene etter hvert skift, og før spising, røyking eller bruk av toalett. Det må ikke spises, drikkes eller røykes under arbeidet. Personlig verneutstyr bør velges i henhold til CEN-standard og i samarbeid med leverandøren av personlig verneutstyr.
Åndedrettsvern	Ved utilstrekkelig ventilasjon: Bruk egnet åndedrettsvern med kombinasjonsfilter, type B2/P2.
Håndvern	Benytt hansker av motstandsdyktig materiale, f.eks.: Neoprengummi. Polyvinylklorid (PVC). Gjennomtrengningstid > 8 timer.
Øyevern	Bruk godkjente vernebriller.
Annet hudvern enn håndvern	Bruk egnede verneklær for å beskytte mot enhver mulighet for hudkontakt. Bruk ikke lærklær. Bruk støvler.
Annen informasjon	Nøddusj og mulighet for øyeskylling må finnes på arbeidsplassen. Det oppgitte verneutstyr er veiledende. Risikovurderingen (Faktisk risiko) kan føre til andre krav.

9. Fysiske og kjemiske egenskaper

Tilstandsform	Viskøs væske
Lukt	Svak. Karakteristisk
Farge	Vannklar
Løselighet i vann	Lett løselig i vann.
Relativ tetthet	**Verdi:** 1500 kg/m³
Smeltepunkt/smeltepunktsintervall	**Kommentarer:** 5°C (46%)
Kokepunkt/ kokepunktintervall	**Kommentarer:** ca.143 v/50%
pH (bruksløsning)	**Verdi:** > 14 **Kommentarer:** (20%)
Damptrykk	**Verdi:** 0.9 mmHg (20°C)

10. Stabilitet og reaktivitet

Forhold som skal unngås	Hell aldri vann direkte i produktet - dette kan føre til kraftig reaksjon. Det samme kan skje ved kontakt med syrer.
Materialer som skal unngås	Sterke syrer. Visse metallforbindelser. Aluminium. Ammoniumforbindelser. Visse typer plast, lær, skinn og tekstiler kan nedbrytes. Trikloretylen.
Farlige spaltningsprodukter	Reaksjon med metaller kan utvikle hydrogengass, som kan danne eksplosiv blanding med luft. Med ammoniumsalter dannes ammoniakk. Danner med Trikloretylen bl.a. Dikloracetylen som er giftig og selvantennende.
Stabilitet	Produktet er stabilt ved de angitte lagrings- og bruksbetingelsene.

11. Toksikologisk informasjon

Toksikologisk informasjon

LD50 oral	**Verdi:** 500 mg/kg **Forsøksdyreart:** LD20 Hare **Kommentarer:** LD50 Mus (intraperitoneal) 40 mg/kg
LD50 dermal	**Verdi:** 500 mg/kg **Forsøksdyreart:** Hare, Skinn **Varighet:** 24 h **Kommentarer:** Hare, øye: 0,4 mg= mild. Ape, øye 24 h: 1% alvorlig

Øvrige helsefareopplysninger

Generelt	Ved bruk representerer de etsende egenskaper den største faren. Sårene vil gro sent med betydelige arrdannelser.
Innånding	Damper virker etsende. I løpet av 24-36 timer kan den skadede utvikle

	alvorlig åndenød og lungeødem. Damper og sprøytetåke kan irritere luftveiene og forårsake halsirritasjon og hoste.
Hudkontakt	Sterkt etsende.
Øyekontakt	Virker sterkt etsende og fremkaller store smerter og alvorlige øyeskader. Øyeblikkelig førstehjelp er nødvendig. Damp eller sprut kan gi øyeskade, nedsatt syn eller synstap.
Svelging	Virker sterkt etsende. Selv små mengder kan være livsfarlig. Symptomer er voldsomme brennende smerter i munn, hals og mage.
Kroniske effekter	Varige vevsskader kan bli resultatet ved akutt påvirkning.
Allergi	Produktet er ikke kjent for å ha allergifremkallende egenskaper.
Kreft	Kreftfremkallende egenskaper er ikke kjent.
Fosterskadelige egenskaper	Arvestoffskadende (mutagene) egenskaper er ikke kjent.
Reproduksjonsskader	Reproduksjonsskadelige egenskaper er ikke kjent.
Arvestoffskader	Arvestoffskadende (mutagene) egenskaper er ikke kjent.

12. Miljøopplysninger

Toksikologisk informasjon

Akutt akvatisk, fisk	**Verdi:** 157-213 mg/l **Testmetode:** LC50 **Fiske art:** Leucisus idus melanotus **Varighet:** 48h
Akutt akvatisk, alge	**Verdi:** 78 mg/l **Testmetode:** EC50 **Alge art:** Selenastrum Capricornutum **Varighet:** 72h. NOEC < 30 mg/l
Akvatisk kommentarer	AKUTT TOKSISITET Bløtdyr LC50/48 h 100 - 1000 mg/l Crustaceans LC50/48h 33 - 100 mg/l Starfisk, saltvann LC50/96h 100 - 1000 mg/l Fisk

Øvrige miljøopplysninger

Økotoksisitet	Produktet er ikke klassifisert som miljøskadelig.
Mobilitet	Løselig i vann.
Persistens og nedbrytbarhet	Produktet består utelukkende av uorganiske forbindelser som ikke er bionedbrytbare.
Bioakkumulasjonspotensial	Forventes ikke å bioakkumulere.
Andre skadevirkninger / annen informasjon	Utslipp av produktet til vann kan lokalt gi høy pH med fare for fiskedød.

13. Fjerning av kjemikalieavfall

Avfallskode EAL	EAL: 06 02 04 natrium- og kaliumhydroksid
NORSAS	7132 Uorganiske baser
Produktet er klassifisert som farlig avfall	Ja
Egnede metoder til fjerning av kjemikaliet	Leveres som farlig avfall til godkjent behandler eller innsamler. Koden for farlig avfall (EAL-kode) er veiledende. Bruker må selv angi riktig EAL-kode hvis bruksområdet avviker.

14.Transportinformasjon

Varenavn (nasjonalt)	NATRIUMHYDROKSIDLØSNING
Farlig gods ADR	**Status:** Ja **UN-nr.:** 1824 **Klasse:** 8 **Fare nr.:** 80

	Emballasjegruppe: II **Varenavn:** NATRIUMHYDROKSIDLØSNING
Farlig gods RID	**Status:** Ja **UN-nr.:** 1824 **Klasse:** 8 **Emballasjegruppe:** II **Varenavn:** NATRIUMHYDROKSIDLØSNING
Farlig gods IMDG	**Status:** Ja **UN-nr.:** 1824 **Klasse:** 8 **Emballasjegruppe:** II **EmS:** F-A, S-B **Varenavn:** SODIUM HYDROXIDE SOLUTION
Farlig gods ICAO/IATA	**Status:** Ja **UN-nr.:** 1824 **Klasse:** 8 **Emballasjegruppe:** II **Varenavn:** SODIUM HYDROXIDE SOLUTION

15. Opplysninger om lover og forskrifter

Faresymbol

Etsende

Sammensetning på merkeetiketten	Natriumhydroksid: 10 - 50 %
R-setninger	R35 Sterkt etsende.
S-setninger	S1/2 Oppbevares innelåst og utilgjengelig for barn. S26 Får man stoffet i øynene; skyll straks grundig med store mengder vann og kontakt lege. S36/37/39 Bruk egnede verneklær, vernehansker og vernebriller/ansiktsskjerm. S45 Ved uhell eller illebefinnende er omgående legebehandling nødvendig; vis etiketten om mulig.
Referanser (Lover/Forskrifter)	Forskrift om klassifisering, merking m.v. av farlige kjemikalier, fastsatt av Miljøverndepartementet og Arbeids- og inkluderingsdepartementet, 16.juli 2002, med senere endringer, gjeldende fra 31. oktober 2005. Forskrift om registrering, vurdering, godkjenning og begrensning av kjemikalier (REACH) Vedlegg II: Sikkerhetsdatablad. Veiledning om administrative normer for forurensning i arbeidsatmosfære fra Direktoratet for Arbeidstilsynet, den til enhver tid gjeldende utgave. ADR/RID veg-/jernbanetransport av farlig gods 2007, Direktoratet for samfunnssikkerhet og beredskap. Avfallsforskriften, FOR 2004-06-01 nr 930, fra Miljøverndepartementet. Databladet er utarbeidet med basis i opplysninger gitt av produsenten.
Deklarasjonsnr.	20%: P-82529. 25 %: P-82530. 30%: P-82406. 32%: P-82531. 45-47%: P-33817. 50 %: P-82532

16. Andre opplysninger

YL-tall	0
Liste over relevante R-setninger (i seksjon 2 og 3).	R35 Sterkt etsende.
Opplysninger som er nye, slettet	Versjon: 1(19.04.2005). Punkter endret: 1-16. Ansvarlig: ST.

eller revidert	Versjon: 2(18.10.2007). Punkter endret: 1-16. Ansvarlig: MR. Versjon: 3(22.04.2009). Punkter endret: 1,3,4,8,14,15,16. Ansvarlig: MR. Versjon: 4(27.04.2009). Punkter endret: 1,3,16 (nytt navn lagt til) . Ansvarlig: MR.
Leverandørens anmerkninger	Informasjonen i dette dokument skal gjøres tilgjengelig til alle som håndterer produktet.
Kvalitetssikring av informasjonen	Dette sikkerhetsdatabladet er kvalitetssikret av Teknologisk Institutt as, som er sertifisert iht. NS-EN ISO 9001:2000.
Ansvarlig for Sikkerhetsdatablad	SOLBERG INDUSTRI AS

Appendix G

Specifications on 75% H_3PO_4

PRODUKTSPESIFIKASJON

FOSFORSYRE 75% **Teknisk** **H_3PO_4**	Cas.nr.: 7664-38-2 Ref.: 60297/219

KJEMISKE DATA :

	Spesifikasjon	Typiske analyser	enhet
Fosforsyre H_3PO_4.....	75 +/- 1		%
Fosforoksid P_2O_5.....	54 +/- 1		%
Uløselige substanser.....<	0,1		%
Alumium Al.....<	0,08		%
Klorid Cl.....<	50	10	ppm
Fluor F.....<	0,15	0,1	%
Magnesium Mg.....<	0,8		%
Jern Fe.....<	0,25		%
Silisium Si.....<	200		ppm
Sulfat SO_4.....<	0,4		%
Arsen As.....<	1,0	0,5	ppm
Kadmium (Cd), Kvikksølv (Hg), Bly (Pb).....<	2	1	ppm

FYSIKALSKE DATA :

Frysepunkt (75%) :	-20°C
Utseende :	Brunaktig, luktløs, noe tregtflytende væske.
Tetthet (15°C) :	1,610-1,650 g/cm^3

LEVERANSEFORM :

Bulk/IBC/fat/kanner

Appendix H

Specifications on micronutrients solution

APPENDIX H

Trace element solution

Nitriloacetic acid 1.5 g eller EDTA 0.5 g (Bruk EDTA viss tilgjengelig)

0.5 g $MnSO_4 \cdot 2H_2O$

3 g $MgSO_4 \cdot 7H_2O$

1 g NaCl

0.1 g $FeSO_4 \cdot 7H_2O$

0.1 g $CoCl_2 \cdot 6H_2O$

0.1 g $CaCl_2 \cdot 2H_2O$

0.1 g $ZnCl_2$

0.01 g $CuSO_4 \cdot 5H_2O$

0.02 g $NiCl_2 \cdot 6H_2O$

0.001 g Na_2SeO_3

0.01 g $AlK(SO_4)_2$

0.01 g H_3BO_3

0.01 g Na_2MoO_4

0.01 g $Na_2WO_4 \cdot 2H_2O$

All added in 1000 ml double distilled water