UNIVERSIDAD AUTÓNOMA DE BAJA CALIFORNIA

FACULTAD INGENIERÍA, ARQUITECTURA Y DISEÑO

PERFORMANCE EVALUATION OF TWO LAB-SCALE WASTEWATER PLANTS WITH THE ADDITION OF DIFFERENT ACTIVATED CARBON FORMS

T E S I S

QUE PARA OBTENER EL TÍTULO DE

BIOINGENIERO

PRESENTA

RICARDO ALBERTO MÉNDEZ FLORES

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Abstract

The performance of two lab-scale wastewater treatment plants (OECD1-2) using the wastewater coming directly from chemical company Merck KGaA (Darmstadt, Germany) was evaluated against the performance of ZABA®, their WW treatment plant. PAC and GAC were added as tertiary treatment, PAC for OECD 1 and GAC for OECD 2. The main parameter being evaluated was COD removal. Other parameters such as Q_d, temperature, O_2, MLSS, VSS, SV, F:M, R_s, HRT, BOD_5, NH_4-N, NO_3, o-PO_4-P and TP were evaluated as well.

With a COD removal of 97% for OECD 1 and 98% COD removal for OECD 2, the plants performed closely to ZABA®. The average F:M ratio for OECD 1 was 0.52 [g/g*d] and 0.48 [g/g*d] for OECD 2 accomplishing the target set at 0.5 [g/g*d] to achieve over 90% BOD_5 degradation. Levels of NH_4-N were monitored in the effluent and with 97% average nitrogen removal on both plants the overall performance was satisfactory.

Keywords: activated sludge, wastewater, activated carbon, COD, BOD_5.

Revisado por: ______________

Resumen

El desempeño de dos plantas piloto de tratamiento de aguas residuales (OECD 1-2) utilizando las aguas residuales procedentes directamente de la compañía química Merck KGaA (Darmstadt, Alemania) fueron evaluadas contra los parámetros de ZABA®, su planta de tratamiento de aguas residuales. PAC y GAC se agregaron como tratamiento terciario, PAC para OECD 1 y GAC para OECD 2. El parámetro principal a evaluar fue la eliminación de COD. Otros parámetros tales como Q_d, temperatura, O_2, MLSS, VSS, SV, F:M, R_s, HRT, BOD_5, NH_4-N, NO_3, o-PO_4-P y TP fueron también evaluados.

Con una eliminación de COD de 97% para OECD 1 y 98% de eliminación de COD para OECD 2, las plantas se desempeñaron de manera cercana a ZABA®. La proporción promedio F:M para OECD 1 fue de 0.52 [g/g*d] y 0.48 [g/g*d] para OECD 2 cumpliendo el objetivo fijado en 0.5 [g/g*d] para lograr más del 90% de degradación de BOD_5 . Los niveles de NH_4-N fueron monitoreados en el efluente y con una eliminación promedio de nitrógeno del 97% en ambas plantas, el rendimiento general fue satisfactorio.

Palabras clave: lodos activados, aguas residuales, carbón activado, COD, BOD_5.

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Table of Contents

List of abbreviations

α	alpha	
AC	active carbon	
AST	activated sludge tank	
ATP	adenosine triphosphate	
BOD_5	biological oxygen demand after five days	
c	concentration	
°C	degrees Celcius	
$C_6H_{12}O_6$	glucose	
CH_4	methane	
C:N:P	carbon nitrogen phosphorus ratio	
CO_2	carbon dioxide	
COD	chemical oxygen demand	[mg/L]
Cr	chromium	
d	day	
DIN	Deutsches Institut für Normung e.V. (German Institute Standardization)	
EN	Europäische Normung	
$FeClSO_4$	ferric chloride sulphate	
F:M	food to mass ratio	
g	gram	

GAC	granulated activated carbon
h	hours
H^+	cationic form of atomic hydrogen
H_2	hydrogen gas
H_2O	water
HCl	hydrogen chloride
HRT	hydraulic retention time
ISO	International Organization for Standardization
$K_2Cr_2O_7$	potassium dichromate
L	liter
m	meter
mm	millimeter
m^3	cubic meter
MLSS	mixed liquor suspended solids
N	nitrogen
N_2	nitrogen gas
NADP	nicotinamide adenine dinucleotide phosphate
NaOH	sodium hydroxide
NH_4-N	ammonium nitrogen
NH_4^+	ammonium
NO_2	nitrite
NO_3	nitrate

O_2	molecular oxygen	
OECD 1	lab-scale wastewater treatment plant #1	
OECD 2	lab-scale wastewater treatment plant #2	
o-PO4-P	ortho-Phosphat-Phosphor	[mg/L]
P	phosphorus	
PAC	powered activated carbon	
pH	potential of hydrogen	
Q	inflow	[L/d]
R_S	sludge age	
s	second	
SD	standard deviation	
SV	sludge volume	
TP	total phosphorus	
V	volume	
VSS	volatile suspended solids	
WS	waste sludge	
WWTP	wastewater treatment plant	
X_E	suspended solids in the effluent	
ZABA®	Zentrale Abwasserbehandlungsanlage	

List of figures

List of tables

1 Introduction

Nowadays, finding better, more efficient ways to treat wastewater produced by the industry, agriculture or the population are highly important for cities due to the contamination, toxicity and cost. Some companies have decided to build their own wastewater treatment plants due to company size, high production or the particular characteristics of the effluents. Special attention is taken from the companies to comply with federal and/or international regulations for industrial wastewater discharged to surface waters and municipal sewage treatment plants. Industrial wastewaters can be difficult and challenging to treat because of the significant variation in effluent characteristics of different industries. Specific treatment methods may be required for particular industrial effluents (Navamani et al., 2018).

The combination of activated sludge treatment and sedimentation tanks has been widely used to clean wastewater with satisfactory results (Alleman and Prakasam, 1983). Even then, experimentation with tertiary treatments, such as activated carbon and sand filters, are considered when toxic substances or pollutants that are not easily biodegradable are found in the inflow (Hamoda et al, 2004; Reungoat et al, 2010). Adsorption process by activated carbon is one of the best approaches in wastewater treatment; it has been used to successfully treat pesticides such as methoxychlor, methyl parathion and atrazine (Gupta et al, 2011). Its non-polar surface makes it a good adsorbent for hydrophobic substances such as aromatic compounds (Chowdhury, 2013).

The chemical company Merck KGaA has a large-scale wastewater treatment plant (WWTP) named ZABA® (Zentrale Abwasserbehandlungsanlage) currently running at Darmstadt, Germany (Figure 1).

Figure 1. Aerial view of the WWTP from Merck KGaA (Merck KGaA, 2014).

ZABA® is a WWTP running beside Merck's production plant with a high capacity to treat water. All the units (Table 1) are monitored online and physically.

Table 1. Description of ZABA® units (Merck KGaA, 2014).

Unit	**N°**	**Capacity (m^3)**	**Function**
Grills	1	N/A	Mechanical cleaning
Grift Chamber	2*	N/A	Primary sedimentation

NaOH tank	1	~ 100	Neutralization
HCl tank	1	~ 100	Neutralization
Balancing tank	1	10 000	Control the wastewater load
Bioreactor	3*	7 500	Activated sludge process
Sedimentation tank	3*	~ 500	Sedimentation process
Buffer tank	3*	~ 20 000	Water storage

*Not all running

The general operation of ZABA® it is presented in the Figure 2 and described afterwards.

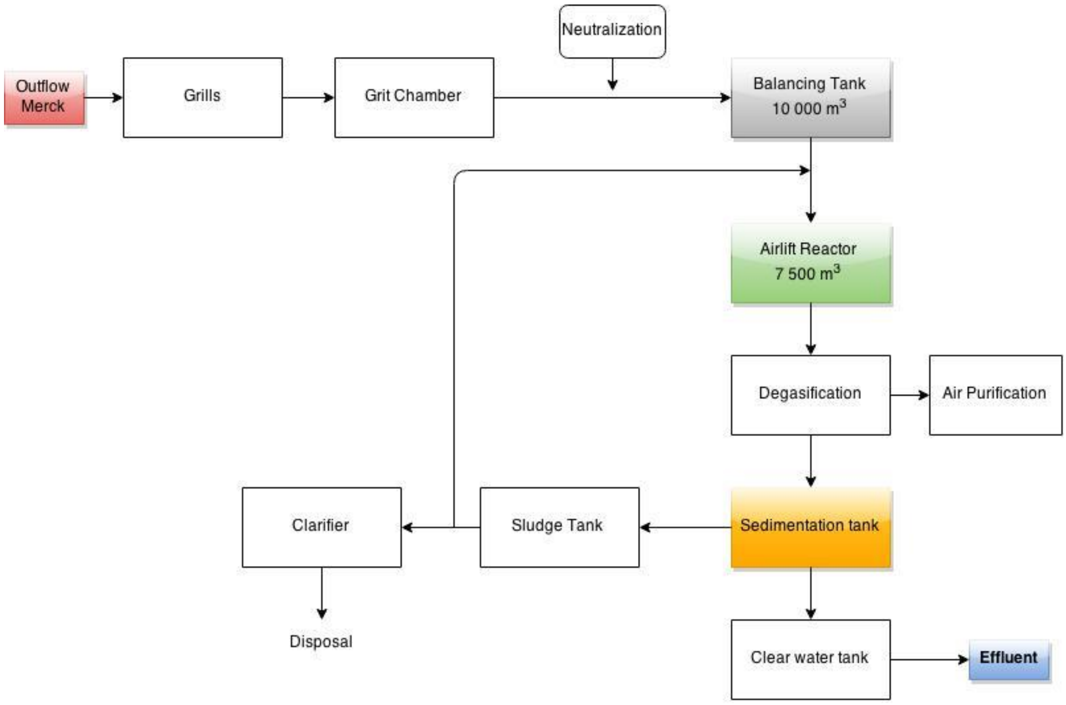

Figure 2. General process flow chart for the WWTP from Merck KGaA (ZABA®).

As shown in Figure 2, the outflow coming from the company goes into a mixed canal system containing water from production, research, office buildings and headquarters. The first purification step of the mixed wastewater is the mechanical cleaning which is characterized by grills and a grift chamber. This type of cleaning is used to protect subsequent steps against deposits resulting in a possible deterioration of some devices (e.g. pumps). In the non-aerated grift chamber, the horizontal velocity of the mixed effluent is reduced to 0.2 - 0.3 m/s, so that solids, like sand, with a diameter bigger than 0.2 mm are able to sediment.

Afterwards, a neutralization process occurs, which regulates the pH of the mixed effluent. The mixed wastewater will then be stored in a 10,000 m^3 balancing tank. This buffer tank is used to control the wastewater load to be introduced into the biological treatment. The biological treatment takes place in a 7,500 m^3 bioreactor where the inflow is purified by microorganisms through the activated sludge process.

After the biological treatment, the effluent goes to a sedimentation tank where clean water flows out from the top. In order to maintain the performance of the bioreactor at a high level, the bulk sludge is transported back into the bioreactor; the excess sludge is incinerated by an external company. The treated water goes in two directions; some goes to a buffer tank which serves as a clear water storage likely to be used by the fire department in an emergency case, while the rest of the water goes directly to Darmbach, a body of flowing water (Merck KGaA, 2014). The ZABA® WWTP uses high quality technology to treat the wastewater from Merck’s Darmstadt location, fulfilling all water quality standards set by the city (Regierungspräsidium Darsmtadt, 2014).

However, the search for profitable tertiary treatments has led the company to experiment with sand filters and activated carbon. The aim of this work is to evaluate the performance of two lab-scale wastewater treatment plants using wastewater coming directly from the company, imitating the operation parameters of ZABA® and adding a tertiary treatment to the process in the form of activated carbon. The experiment will run with two small wastewater treatment plants called OECD's. Both wastewater treatment plants are similar to ZABA® in terms of the main processes (activated sludge and sedimentation). Each OECD will use activated carbon in the process. One of the OECD's has a sand filter and an activated carbon unit attached. The other one received a daily dose of powder activated carbon in the aeration tank (Figure 3).

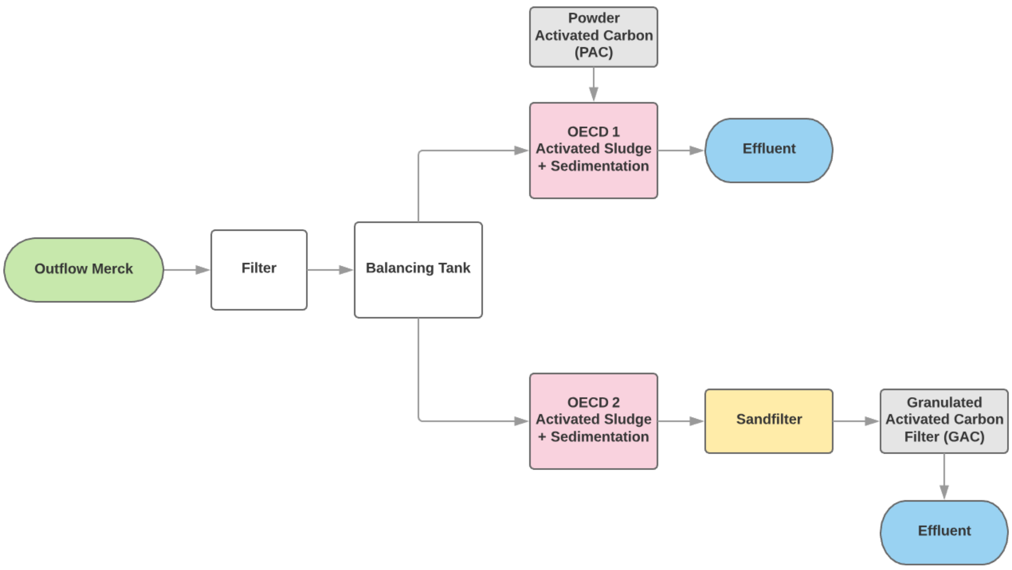

Figure 3. General scheme of the project. Two lab-scale wastewater plants (OECD) with the addition of different activated carbon forms, powder and granulated.

2 Theoretical framework

2.1 Basics of wastewater treatment

2.1.1 Wastewater

Human activity will result in different types of wastewater where the quantity and quality can be determined by many factors. In table 2, we describe the different types of wastewater (Water Environment Federation, 2008).

Table 2. Types of wastewater.

Type	**Description**
Domestic	Wastewater from kitchen, sink, toilet and similar facilities
Industrial	Wastewater from industry or commercial operation such as production, cleaning and cooling
Infiltration into sewers	Groundwater entering sanitary sewers through defective pipe joints and broken pipes
Storm water	Result of precipitation such as rain, hail and snow

The amount and composition of industrial wastewater will depend on the industry sector, the raw materials used, the processing method and the process itself. To be able to determine precisely the nature of the wastewater, identification data must be collected. Here we distinguish physical characteristics such as color, turbidity, odor, temperature, pH and conductivity. As well as chemical parameters that can be considered, such as the content of ammonium, phosphate, nitrate and heavy metals (Water Environment Federation, 2008). A huge number of different compounds are present in wastewater, impossible to determine individually. The concept of organic matter is important, which is an indicator of the combined concentration of all the organic compounds present in wastewater. This sum parameter can only show us the level of contamination but not the type of substances present in wastewater (Mudrack et al, 2003).

To estimate the concentration of organic matter, it is possible to use properties that all organic compounds have in common:

- They can be oxidized
- They contain organic carbon

In addition to the physical and chemical parameters, biological parameters can be determined such as the type and number of organisms occurring in wastewater.

An important parameter to describe sewage with precision is the biochemical oxygen demand after five days (BOD_5). This indicates how much oxygen is consumed through the microbial metabolic processes in the degradation of contaminants at 20 °C in 5 days. It is a measure of the degradable contaminants present in wastewater (Mudrack et al, 2003; Water Environment Federation, 2008).

2.1.2 General wastewater treatment

The basic cleaning steps in a WWTP are as follows: the first treatment step is through a mechanical process by separating solid undissolved components such as paper, sand and colloidal suspended solids. This is followed by biological treatment where the elimination of dissolved and colloidal remaining substances is carried out by microorganisms which incorporate the contaminants in their metabolism.

There are two different types of biological treatment. First, the trickling filters process, in which microorganisms are located on a fixed bed forming a layer (biofilm). The wastewater is sprayed over the fixed bed and cleaned by the adhering microorganisms. Second, the activated sludge process, in which the wastewater and microorganisms are mixed in a reactor. Here the microorganisms get together to form sludge flocs (activated sludge), but are also available as free bacteria within the mixture. The amount of activated sludge (mixed liquor suspended solids, MLSS) in a conventional activated sludge plant, depending on the required degradation performance, is about 3 to 6 grams per liter. The biological stage is followed by a separation of the suspended solids in a sedimentation tank. In the secondary clarifier, the suspended solids sediment and the result of the plant is a clear effluent. In the activated sludge treatment the settled sludge in the clarifier is partly recycled back into the biological stage. The sludge that is not recycled is removed as excess sludge from the system (Abwassertechnische Vereinigung, 1997). Figure 4 shows the schematic structure of a wastewater treatment plant with activated sludge process.

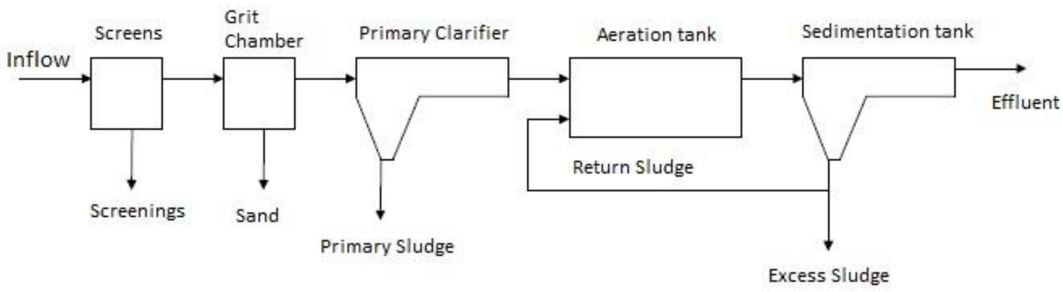

Figure 4. General schema of a biological WWTP. (Adapted from Abwassertechnische Vereinigung, 1997).

In order for the activated sludge process to operate properly there are two parameters that have to be considered: food to mass ratio and sludge age.

First, the food to mass ratio (F:M ratio) defines a balance between the food (BOD_5, COD) entering the biological system and the microorganisms (MLSS) in the bioreactor. To calculate the F:M ratio the following formula is used:

$$F{:}M\ ratio = \frac{C_{BOD5} * Q_d}{MLSS_{AST} * V_{AST}} \qquad [\frac{g}{g*d}] \quad \textbf{eq. (1)}$$

Where:

F:M ratio	=	food to mass ratio	[g / g*d]
C_{BOD5}	=	concentration of BOD_5	[g / L]
Q_d	=	daily inflow	[L / d]
$MLSS_{AST}$	=	mixed liquor suspended solids in the activated sludge tank	[g / L]
V_{AST}	=	volume of the activated sludge tank	[L]

The F:M ratio is considered as a limiting factor for the cleaning performance of the aeration tank. A value of 0.5 g/(g*d) may not be exceeded if the percentage of BOD_5 degradation is desired above 90% (Figure 5) (Abwassertechnische Vereinigung, 1997).

The other important parameter with a direct correlation to F:M ratio is the sludge age. This parameter indicates the average retention time of the sludge in the system and is defined as the ratio between the sludge mass present in the system and the daily sludge mass discharged from it (Ekama, 2010). To calculate the sludge age the following formula is used (Abwassertechnische Vereinigung, 1997):

$$R_s = \frac{V_{AST} * MLSS_{AST}}{Q_{WS} * MLSS_{WS} + Q_d * X_E} \qquad \textbf{eq. (2)}$$

Where:

R_S	=	sludge age	[d]
V_{AST}	=	volume of the activated sludge tank	[L]
$MLSS_{AST}$	=	mixed liquor suspended solids in the activated sludge tank	[g / L]
Q_{WS}	=	volume flow of waste sludge	[L / d]
$MLSS_{WS}$	=	mixed liquor suspended solids in the waste sludge	[g / L]
Q_d	=	daily outflow	[L / d]
X_E	=	suspended solids in the effluent	[g / L]

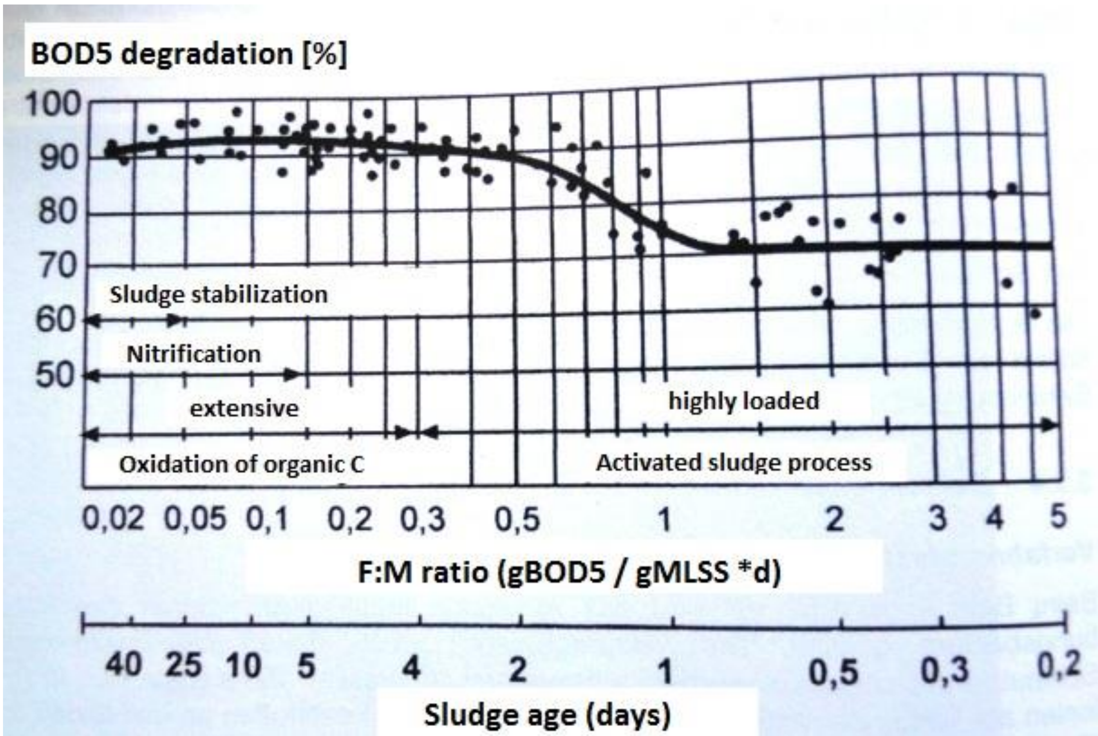

Figure 5. Percentage of BOD_5 degradation under different parameters. (Abwassertechnische Vereinigung, 1997).

2.1.3 Biological treatment

The principal objective of wastewater treatment is the elimination of organic compounds from the wastewater. Then, other secondary targets must be considered, such as the elimination of dissolved nitrogen compounds by the oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-), process called nitrification. As well as reducing nitrites and nitrates into gaseous nitrogen (N_2) in a process called denitrification. Another important criterion for wastewater treatment is the elimination of phosphorus. Every one of these biological purification processes is performed by different microorganisms. These microorganisms use the dissolved carbon, nitrogen and phosphorus compounds by integrating them as food into their metabolism. Thus, they are able to obtain energy and build new biomass.

Microorganisms present in wastewater need energy for their metabolisms. They receive this energy from organic and inorganic compounds. The transformation of high-energy molecules into low-energy molecules (catabolism) is generally energy free. The resulting energy will be transferred and stored in energy-transfer molecules like adenosine triphosphate (ATP) or nicotinamide adenine dinucleotide phosphate ($NADP^+$). Energy from these molecules is available when required, for example, in the building of endogenous components or new biomass (anabolism) (Mudrack et al, 2003).

Table 3. Classification of organisms regarding their energy source (Adapted from Abwassertechnische Vereinigung, 1997).

Organism	**Description**
Chemotrophs	Energy is extracted from chemical substances
Phototrophs	Use solar energy
Organotrophs	They get their protons from organic compounds. Regarding the carbon source: • Heterotrophic (from organic compounds) • Autotrophic (from CO_2)

For the maintenance of their metabolism, these bacteria require carbon and an energy source, as well as hydrogen (protons) or an electron donor to supply the cell with reducing equivalents. Table 3 gives a classification on organisms regarding their energy source. If the energy is extracted from chemical substances, the organisms are called chemotrophs. The chemotroph designation is in contrast to phototrophs, which use solar energy. The group of organisms using inorganic compounds as its hydrogen donors is regarded as litotroph. Organisms that get their protons from organic compounds are called organotrophs. We can make another distinction between organotrophs regarding the carbon source; these are either heterotrophic (from organic compounds) or autotrophic (from CO_2) (Abwassertechnische Vereinigung, 1997).

Furthermore, bacteria can be classified in terms of their relation to the presence of oxygen (Table 4).

Table 4. Classification of bacteria (Adapted from Abwassertechnische Vereinigung, 1997).

Bacteria	**Description**
Strict aerobes	Require oxygen for their metabolism
Strict anaerobes	Can only live in the absence of oxygen
Facultative aerobes	Can survive in the presence of oxygen but it is not necessary for their metabolism
Facultative anaerobes	Can switch to anaerobic metabolism in the absence of oxygen

In the metabolism of aerobic bacteria, the high molecular compounds will be oxidized into finished products such as CO_2 and H_2O. Since oxidation is generally electron free, they must be received again by another substance. These substances are known as terminal electron acceptors. These electron acceptors can be, for example, oxygen, nitrogen or sulfur. Anaerobic bacteria, however, does not oxidize organic substances but reduce them. The degradation is carried out only up to intermediates such as organic acids or alcohols. These intermediates are then implemented by various groups of bacteria into final products like CH_4 and CO_2 (Abwassertechnische Vereinigung, 1997; Mudrack et al, 2003).

Another classification can be done based on the morphological characteristics of the microorganisms. A brief description of the role of each group is given:

- Bacteria: Heterotrophic and autotrophic bacteria play the most important role in biological wastewater treatment processes, and they represent around 95% of the microorganisms present in the activated sludge. Some heterotrophic bacteria are responsible for the degradation of organic compounds, while some autotrophic bacteria oxidize ammonia and nitrite
- Protozoa: These heterotrophic organisms are, along with the bacteria, important for biological treatment and they represent about 5% of the activated sludge. They contribute to the elimination of pathogens, the clearing of the effluent and the flocculation of the biomass
- Fungi: Most fungi are aerobic, tolerate low pH values and require lower concentration of nitrogen than bacteria. They are not commonly found in activated sludge since they are not able to compete with bacteria
- Algae: They are not of interest in conventional wastewater treatment processes because of their autotrophic nature. They increase the

content of organic matter by synthesizing molecules using mineral sources of carbon as substrate (Ferrer and Seco, 2003)

2.1.3.1 Organic material removal

Most of the organic compounds present in wastewater are carbohydrates, fats and proteins. Carbohydrates generally exist as complex molecules such as cellulose; however, these are converted into glucose after some decomposition reactions. Glucose is aspired by the microorganisms in an aerobic environment into the end products CO_2 and H_2O.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad \textbf{eq. (3)}$$

Here of glucose 38 mol ATP are obtained per mole, which only 40% can be effectively used, the other 60% is lost as heat. By breaking down the C_6-compound (glucose), smaller carbon compounds are obtained which can be used as starting material for cell change.

The degradation steps of glucose are briefly explained next. First, the glucose is broken down to C_3-pyruvate, which is then converted by elimination of CO_2 in active acetic acid (acetyl-CoA). This active acetic acid enters the citric acid cycle (Figure 6). In the citric acid cycle, the acetic acid is oxidized to CO_2 and it will also deliver important initiators on the formation of new cell material. In these reactions, a total of 24 hydrogen atoms are split off. These transfer their electrons to the terminal electron acceptor oxygen to produce water (Mudrack et al, 2003).

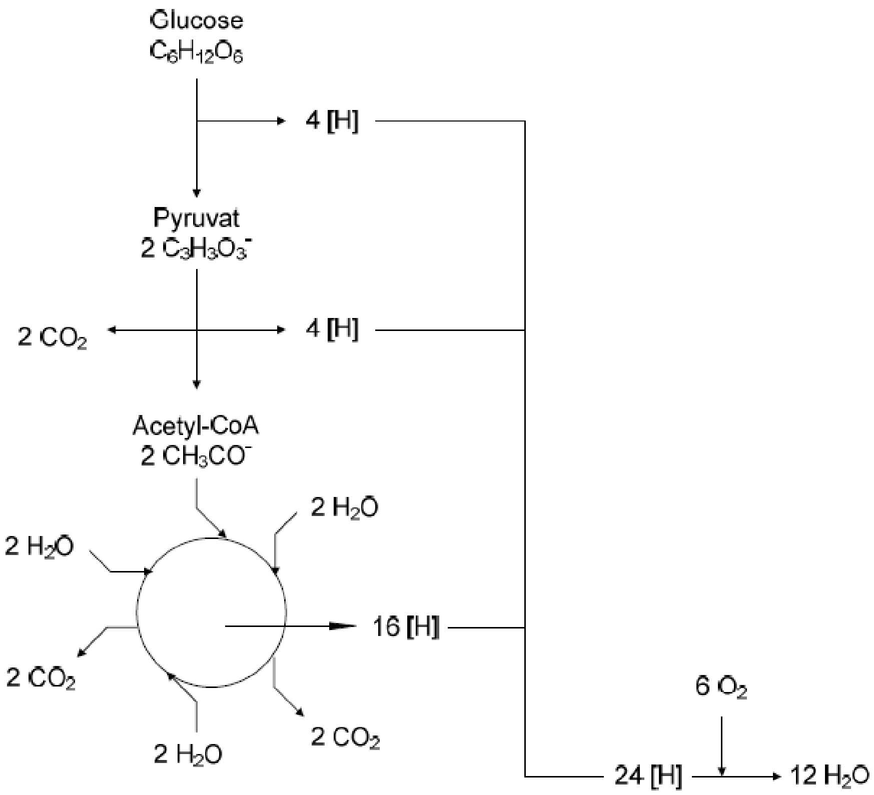

Figure 6. Aerobic degradation of glucose. (Adapted from Mudrack et al, 2003).

In the degradation of fats, hydrolysis of the fats leads to glycerol and the corresponding fatty acids. Glycerol, as glyceraldehyde, can be introduced directly into the pathway of glucose as an intermediate in the decomposition of glucose to pyruvate. The remaining fatty acids are relatively slowly removed through the elimination of C_2 via rupture, resulting in active acetic acid which is re-injected directly into the citric acid cycle. Through biodegradation, proteins are broken into amino acids that can then either be used by the cells to build their own proteins or are oxidized to produce energy. Here, substances that can again enter the citric acid cycle are formed (e.g. α-keto acid).

In anaerobic conditions polymer substrates (carbohydrates, proteins and fats) are mostly metabolized into methane. The first step is to hydrolyze bigger fragments and then, in the acidification phase, the formation of organic acids, acetic acid, alcohol, H_2, and CO_2. These substances are then converted in the acetogenic phase into acetic acid and finally into methane (Mudrack et al, 2003).

2.1.3.2 Nitrogen removal

The elimination of nitrogen from the wastewater is carried out via the oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-), through nitrification, and then by the following reduction of nitrite and nitrate into gaseous nitrogen (N_2). In addition, elimination is achieved by using nitrogen to build new biomass (proteins), which will be partially removed with the excess sludge. To obtain an optimal degradation rate, the ratio of BOD_5 to nitrogen should be approximately 100:5 in the inflow of the aeration tank (Slade et al, 2011).

Nitrogen is contained in the wastewater mainly as ammonium, urea or organic compounds (proteins). The organic nitrogen and urea is relatively quickly hydrolyzed into ammonium, usually before the aeration tank, but can also be taken up by the bacteria in a high molecular form (protein).Thus, nitrogen is available for the nitrogen-oxidizing bacteria (nitrification). These use the ammonium as a proton donor for their metabolism. Oxygen is used as an electron donor, and CO_2 serves as carbon source. Thus, since the bacteria do not require organic matter for their metabolism, they are classified as aerobic autotrophs. For the nitrification of ammonium to nitrate, two groups of bacteria are needed: ammonium oxidizers (e.g. *Nitrosomonas*) and nitrite oxidizing bacteria (e.g. *Nitrobacter*). In an aerobic environment, *Nitrosomonas* convert ammonium into nitrite, which is then further oxidized into nitrate by *Nitrobacter* (U.S. EPA, 1993; Abwassertechnische Vereinigung, 1997).

Nitrosomonas	$NH_4^+ + 1{,}5O_2 \rightarrow NO_2^- + H_2O + 2H^+$	**eq.(4)**
Nitrobacter	$NO_2^- + 0{,}5O_2 \rightarrow NO_3^-$	**eq.(5)**
Total	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	**eq.(6)**

With the entire reaction equation, the oxygen consumed for the oxidation of 1 g of ammonium-nitrogen (NH_4-N) can be calculated to be 4.6 g of O_2. It is therefore necessary to ensure that, when nitrification occurs, enough dissolved oxygen must be available (Water Environment Federation, 2008).

In anaerobic conditions the resulting nitrate and nitrite can be converted in to nitrogen gas (denitrification). Here, the nitrate ion is used as a terminal electron acceptor (U.S. EPA, 1993).

$$2\,NO_3^- + 12\,H^+ \rightarrow N_2 + 6\,H_2O \qquad \textbf{eq. (7)}$$

Denitrification occurs only in anaerobic conditions, since many denitrifying bacteria use it for their metabolism in the presence of dissolved oxygen. Only in the absence of dissolved oxygen do these bacteria use the fixed oxygen from nitrite and nitrate (Abwassertechnische Vereinigung, 1997; Mudrack et al, 2003).

2.1.3.3 Phosphorus removal

Like carbon and nitrogen, phosphorus is required for the microorganisms to build up specific cell components, e.g. nucleic acids or ATP. The optimum nutrient ratio of C:N:P in the inflow of an activated sludge plant should be around 100:5:1 (Slade et al, 2011). In wastewater with higher phosphorus content, this type of removal is usually not sufficient. When in an excessive phosphorus supply, many bacteria are able to store it in the form of polyphosphates, as a reserve (the stored phosphorus is then removed with the excess sludge). Another way to remove phosphorus from the wastewater is by precipitation using iron or aluminum salts. This precipitation can take place before, in, or after the aeration tank. The disadvantage of this method lies in the increased formation of sludge through the precipitated compounds (Mudrack et al, 2003).

2.2 Basics of adsorption technology

2.2.1 Activated carbon

Activated Carbon (AC) is a porous material in granulated or powder form with a large internal surface area. The source for activated carbon can vary according to the raw materials used, which can consist of nutshells, wood, coal, etc. Due to its high adsorption capacity, it is frequently used as an adsorbent in water treatment in addition to ion exchangers. It is used primarily for adsorption tasks and not for pure filtration tasks. It removes chlorine, residual ozone, odor and flavor, color, solvents, and other organic contaminants (Merkl, 2008).

Granulated activated carbon is used but not limited to the following activities (Merkl, 2008):

- Treatment of bank filtration and surface water up to drinking water quality
- Pre-treatment of river water for artificial groundwater enrichment
- Removal of anthropogenic contamination from groundwater with solvents and pesticides

Powdered activated carbon (PAC), however, is often used as a precaution. A main area of application is to solve flavor and odor problems. PAC can only be used once, with dosage amounts varying between 5 and 20 $g \cdot m^{-3}$. Re-use of activated carbon by reactivation is possible, whereby a thermal treatment at 800 °C, with the aid of steam at 750-800 °C, is used to eliminate the load of the carbon and to restore the adsorption capacity (Merkl, 2008).

2.2.2 Characterization of activated carbon

A significant measure of the total adsorption capacity is the inner surface. It is in the range of 800-1000 $m^2 \cdot g^{-1}$ for commercially activated carbon. However, the specific activity against sorptives is due to the pore system of the activated carbon. It is characterized by pore radius distribution as well as the pore volume (Grombach et al, 2000; Schrader, 2007).

According to the IUPAC (International Union of Pure and Applied Chemistry), three groups of pores are distinguished, according to the pore size:

- Macropores (> 50 nm diameter)

- Mesopores (2-50 nm diameter)
- Micropores (< 2 nm diameter)

Micropores generally contribute to the major part of the internal surface area. Macro and mesopores can generally be regarded as the highways into the carbon particle. All activated carbons contain micropores, mesopores and macropores within their structures but the proportions of each one varies considerably according to the raw material.

2.2.3 Adsorption of activated carbon

Adsorption is the process of accumulation of a substance on the surface of an adjacent phase. It is a physico-chemical separation process in which the substances to remove (adsorbate) are deposited on the surface of a solid (adsorbent). There is a thermodynamic equilibrium between adsorbate and adsorbent, when there is no longer any difference between the chemical potential of the adsorbate in the free solution and in adsorbed state. While the physical adsorption is considered a reversible process (binding of the activated carbon particles by van der Waals forces), chemical adsorption is usually an irreversible process due to the high binding energies (Bansal & Goyal, 2005).

The most important AC filtration factor is the physical attraction or adsorption of contaminants to the pore walls and is determined by their amount and distribution. AC is very effective in removing contaminants that have relatively large molecules, which includes a big part of organic chemicals. Optimal filtration is achieved when pores are barely large enough to admit the contaminant molecule (Figure 7).

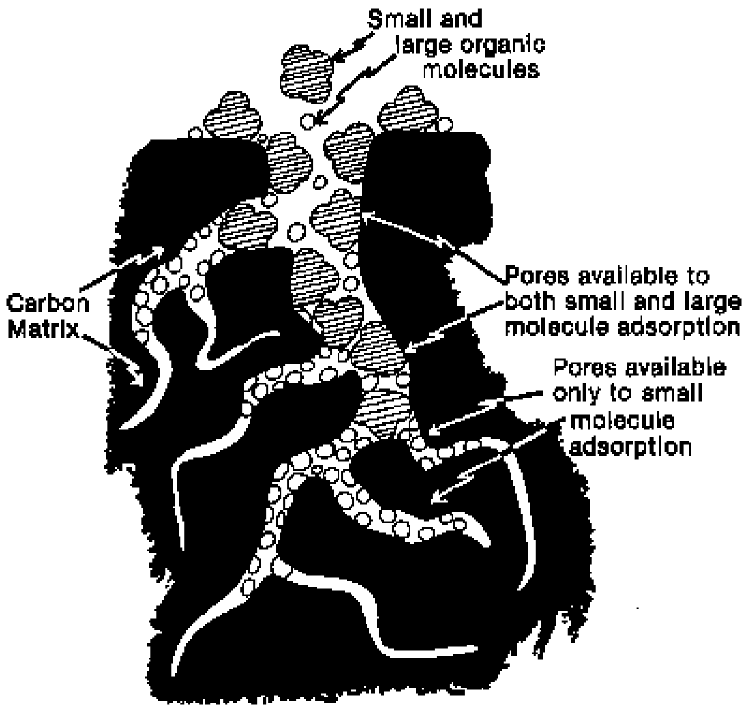

Figure 7. Activated carbon structure (Culp et al, 1978).

In general, organic chemicals tend to associate with the AC rather than staying dissolved in a dissimilar material like water. Then, the less soluble organic molecules are most strongly adsorbed. The concentration of organic contaminants can also affect the adsorption process. Activated carbon adsorption decreases with the increase in the solute polarity because the biggest part of the activated carbon surface is non-polar or hydrophobic. As a result, non-polar solutes are more rapidly and strongly adsorbed by activated carbon than polar solutes, in the case of polar solvents. The contact time between the contaminants and the AC has a direct relation with adsorption, meaning that higher exposure time result in higher amount of contaminants removed. Higher contact time is achieved by reducing the flow rate of water through the AC (Culp et al, 1978).

3 Material and methods

3.1 Experiments Methodology

Several objectives are set for the OECD plants:

1. Use the influent from ZABA® directly as feed to both plants
2. Stabilize the activated sludge process for reduction of organic matter and nitrification (BOD_5 degradation ≥ 90%)
3. Maintain mixed liquor suspended solids (MLSS) ≥ 2.0 g/L
4. Implement a different AC form for each plant (PAC and GAC)

The plants were inoculated with nitrifying seed sludge taken from a WWTP treatment plant located in the company (ZABA®). The content of ZABA® MLSS ranges are normally between 3 and 4 g/L for the activated sludge tank, while the return sludge ranges between 5 and 6 g/L. Afterwards, the activated sludge may be maintained in a concentration higher than 2.0 g/L.

The inflow, outflow and contents in the tanks are analyzed, as a routine monitoring of the plants, with a defined test and set frequency (Table 5). To evaluate the content of the ZABA® inflow, a sample is taken daily to analyze COD, NH_4-N and o-PO_4-P.

For both OECD tanks, the oxygen, temperature and pH are monitored daily. Concentration of MLSS, volatile suspended solids (VSS), and sludge volume is monitored twice a week. Determination of VSS percentage is measured to determine the organic fraction contained in the sludge. In addition, the settleability of the sludge is determined.

To evaluate the performance of the biological degradation of the plants, a filtered sample (0.45 μm filter) of each effluent is taken daily to analyze the COD, NH_4-N, NO_3, o-PO_4-P, and total P.

Table 5. Routine monitoring plan for feed tank, OECD 1 and OECD 2.

Plant	Sample	Test	Frequency
ZABA® Feed Tank	Inflow	COD, NH_4-N, o-PO_4-P, total P	*Daily*
OECD 1	Tank	O_2, T, pH	*Daily*
		MLSS, VSS, SV	*2x Week*
	Outflow	COD, NH_4-N, NO_3, o-PO_4-P, total P	*Daily*
OECD 2	Tank	O_2, T, pH	*Daily*
		MLSS, VSS, SV	*2x Week*
	Outflow	COD, NH_4-N, NO_3, o-PO_4-P, total P	*Daily*

3.2 Configuration of the pilot plants

The process flow for the pilot OECD plants is presented below.

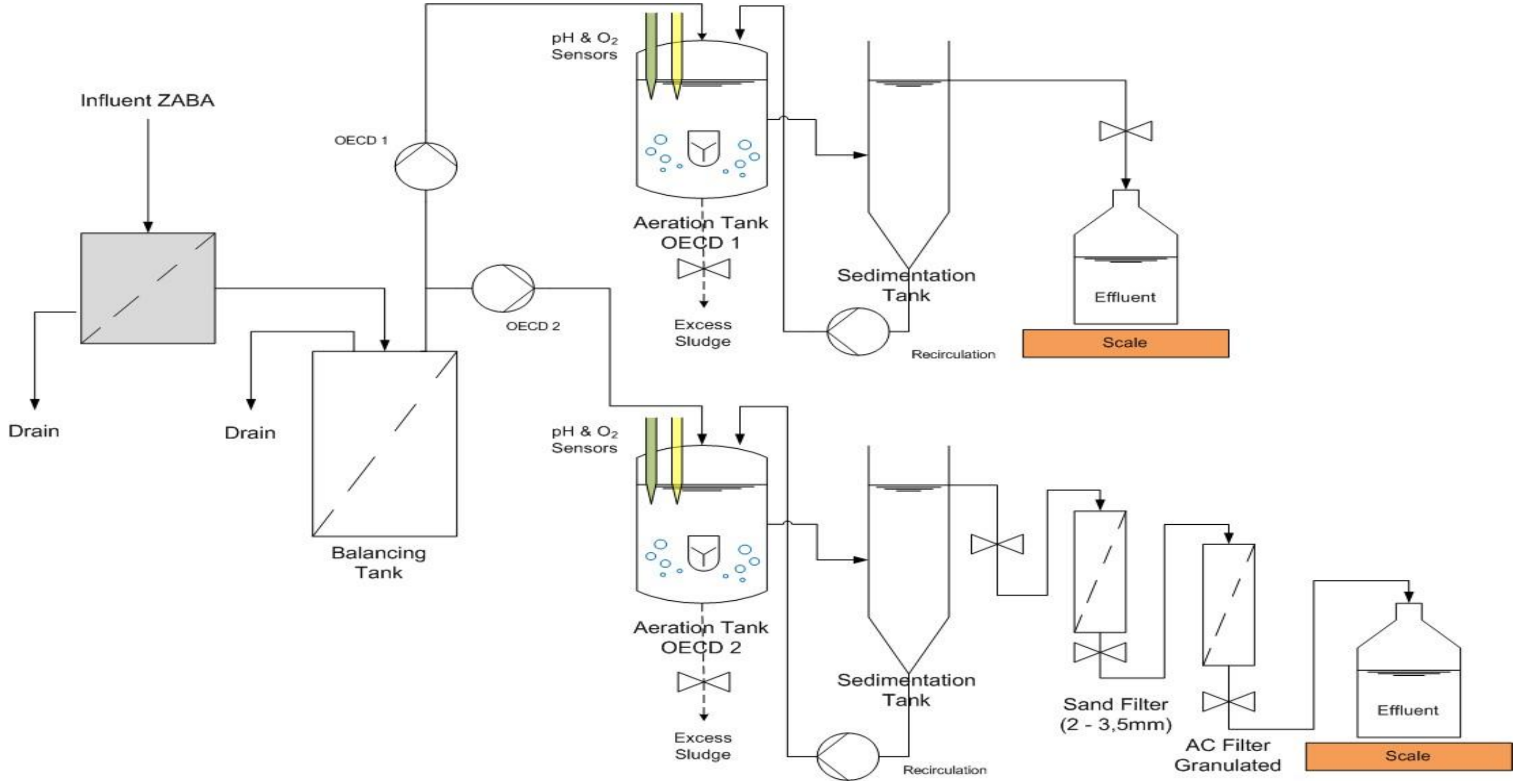

Figure 8. Process flow chart for OECD 1 & OECD 2.

The feed system (see Figure 9) consists of the following components:

- Pre-filter with drainage. A pipe system is installed to feed the pre-filter with ZABA® wastewater
- Balancing tank with drainage

Figure 9. Feed system for both OECD plants.

The OECD 1 plant (see Figure 10) consists of the following components:

- Bioreactor tank “OECD 1”
    - Feeding pump taking wastewater from the balancing tank
    - Sensor probes for oxygen, temperature and pH
    - Agitation system
    - Air stone
    - Recirculation system

- Sedimentation tank
- Powdered activated carbon. NORIT® SAE SUPER (Bulk Density: 0.3-0.4 g/cm^3; Dosage: 50 mg/d)
- Effluent reservoir + Weighing scale

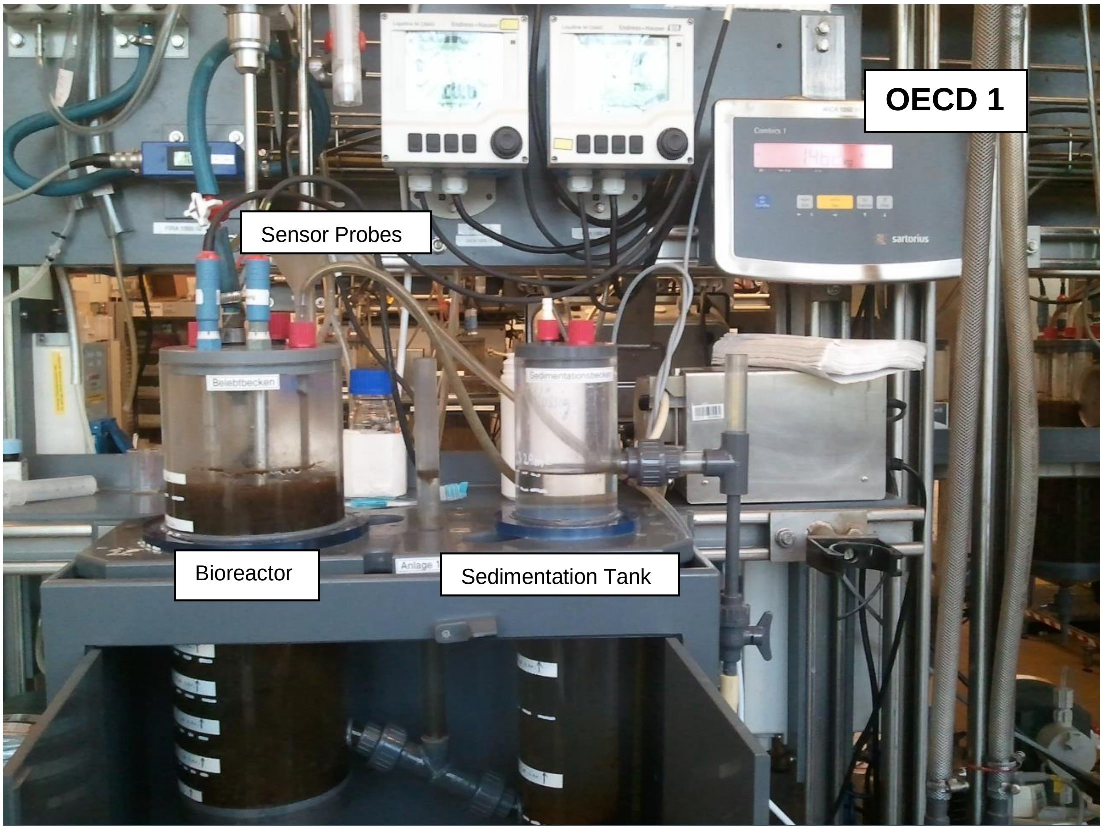

Figure 10. OECD 1 - Lab-scale WWTP #1.

The OECD 2 plant (see Figure 11) consists of the following components:

- Bioreactor tank “OECD 2”
    - Feeding pump taking wastewater from the balancing tank
    - Sensor probes for oxygen, temperature and pH
    - Agitation system

  - Air stone
  - Recirculation system
- Sedimentation tank
- Sand filter unit (2 – 3.5 mm diameter)
- Granulated activated carbon unit. NORIT® GAC 830R (Bulk Density: 0.45 – 0.54 g/cm^3)
- Effluent reservoir + weighing scale

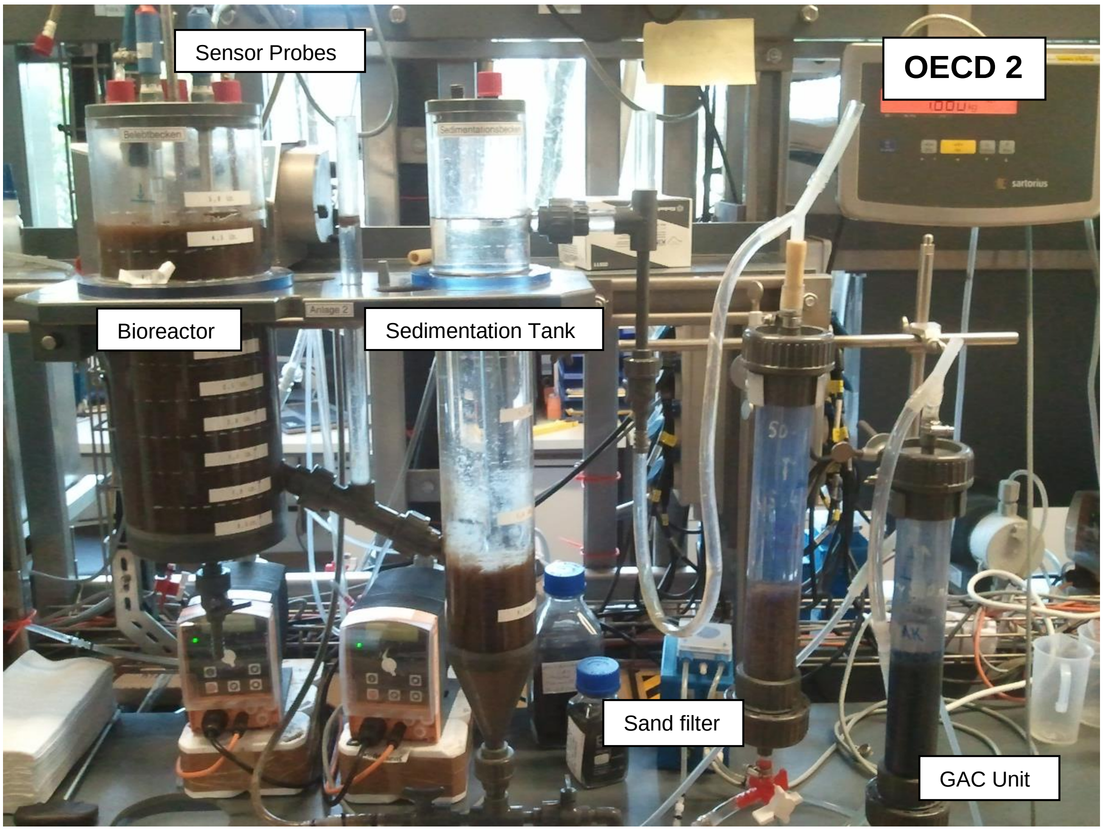

Figure 11. OECD 2 - Lab-scale WWTP #2.

3.3 Analysis

To control biological, physical, and chemical processes taking place in both OECD plants, as well as for evaluating its performance, several parameters can be measured in different points of the process. A brief description of each analytical method is given.

3.3.1 Determination of Chemical Oxygen Demand (COD)

For the analysis of COD, a cuvette test was used according to DIN ISO 15705 from Merck®. 5 mL samples (mixed with deionized water for a proper dilution) are heated for two hours at 148°C with a mixture of potassium dichromate ($K_2Cr_2O_7$) as an oxidizing agent, silver sulfate as a catalyst, and mercury (II) sulfate to help diminish the possible disturbances caused by the high concentrations of chloride. The potassium dichromate reacts with substances susceptible to oxidation present in the samples and green Cr (III) ions are formed. The concentration of these ions can later on be measured with a photometer. The uptake rate of one mole $K_2Cr_2O_7$ corresponds to an oxygen demand of 1.5 mole oxygen (O_2) which leads to the correlation between the released Cr (III) ions and the COD (Spectroquant®, 2013).

The cell tests from Merck® with article numbers 1.14541.0001, 1.14540.000 and 1.14560.0001 where used for the concentration ranges of 25-1500, 10-150 and 4-40 mg O_2/L respectively. The heating of the cell at 148 °C was done with the thermal reactor Spectroquant TR420/TR 320 and the measurement of the concentration with the photometer Spectroquant NOVA 60 (DIN ISO 15705, 2002).

3.3.2 Determination of Ammonium nitrogen

The determination of ammonium nitrogen (NH_4-N) was carried out according to an SOP from Merck KGaA analogous to DIN 38406-5. A filtered sample is added to a 50 mL volumetric flask, together with 4 mL of a salycilate-citrate solution and 4 mL of a sodium dichloroisocyanurate solution. The flask is filled with deionized water up to the 50 mL mark, and the solution is mixed and left to react for at least 70 minutes. The reaction product has a blue coloration which can be photometrically measured with a Hitachi U-1100 spectrophotometer at a wavelength of 655 nm. The concentration can be later on calculated using the factor of 0.20535, previously calibrated for the spectrophotometer available in the laboratory (DIN 38406-5, 1983).

3.3.3 Determination of Nitrate

To determine the nitrate nitrogen (NO_3-N), a cuvette test from Merck® with a concentration range of 0.5-25.0 mg/L NO_3-N (Article No:1.14563.0001) was used. In a closable test tube of 4 mL, a mixture of sulfuric and phosphoric acid, 0.5 mL of the sample and 0.5 mL of 2,6-dimethylphenol (DMP) are mixed. 4-nitro-2,6-dimethylphenol, the reaction product between the two last ones, can be photometrically determined after 20 minutes of reaction time at a wavelength of 340 nm (Spectroquant®, 2013). The factor for the concentration determination is 14.808 for this case.

3.3.4 Determination of Phosphate

The determination of the o-phosphate concentration can be made using an analog method to the DIN EN ISO 6878. The o-phosphate present in the sample reacts on an acid medium with a molybdate solution to form a blue colored heteropolymolybdate. The sample is added to a volumetric flask together with 1 mL sulfuric acid, 1 mL ascorbic acid, and 2 mL of the molybdate solution. The flask is then filled up with deionized water up to the 50 mL mark. After a reaction time of 20 minutes the extinction can be measured with the Hitachi U-1100 spectrophotometer at a wavelength of 880 nm, and finally the concentration can be found with the factor of 0.3503 (DIN EN ISO 6878, 2004).

3.3.5 Determination of Total Phosphorus

The TP (total phosphorus) is the content of all organic phosphorus compounds contained in the water. In determining the total phosphorus content, the molybdenum blue method was applied according to DIN EN ISO 6878 analogous to orthophosphate determination. The difference is that the total phosphorus is digested under heating into ortho-phosphate in an acidic medium with the aid of the oxidizing agent potassium peroxodisulfate. The digestion is carried out in round cuvettes with the addition of the sample, which is mixed with 1 mL of 2-molar sulfuric acid and 1.5 microliter of potassium peroxodisulfate. Subsequently, the sample is heated in the thermal reactor Spectroquant® TR 420 for 20 minutes at 120 ° C and digested into ortho-phosphate. After digestion, the sample was transferred to a 50 mL volumetric flask, and the method to determine o-phosphate is then followed (DIN EN ISO 6878, 2004).

3.3.6 Solids Content

3.3.6.1 Mixed liquor suspended solids (MLSS)

The MLSS content represents the portion of sludge that is left after a drying process. To determine this value, 50 mL of sludge are vacuum filtered and placed on a previously weighed aluminum recipient. The sludge is then dried at 105°C until it has a constant weight. The difference between the initial weight, the weight of the aluminum device, and the filter paper weight gives the MLSS content, which is expressed as g/L (DIN EN 12880, 2001).

3.3.6.2 Volatile suspended solids (VSS) content

This value represents the quantity of sludge that is composed of organic substances. It can be used as a measurement of how much bacteria is present in the sludge. The test carries on with the already dried sludge obtained in the determination of MLSS. This sludge is heated on a muffle at 520 °C for one hour, and after cooling it is weighed once again. The difference between this weight and that of just the aluminum device gives the VSS, which is also expressed in g/L (DIN EN 12879, 2001).

3.3.6.3 Sludge volume

This test shows how much volume is taken by the sludge in a determinate sample. To determine the sludge volume one litter measuring cylinder is filled with the sample and left undisturbed. After 30 minutes the volume of sediment sludge can be read and noted as mL-sludge/L. When the sludge volume is too high, a dilution of the sample is necessary: 250 mL of sludge are filled in the measuring cylinder, the rest of the volume is filled with deionized water, and the content is mixed; the result read on the cylinder is then multiplied by 4 to obtain the value of the sludge volume (DIN EN 14702-1, 2006).

4 Results and discussion

In this chapter, the main results are presented and discussed regarding the performance of the OECD WWTPs.

4.1 Characteristics of ZABA® inflow

It is highly important to characterize the composition of ZABA® inflow to run the plants correctly. Therefore, several parameters were monitored. The applied methods are briefly described in chapter 3.

Since Merck is a chemical company, it is expected to manage high COD concentration levels even going up to 2000 mg/L COD; concentrations reached at the beginning of 2015 (Figure 12). These variations are the result of multiple factors described in Table 6:

Table 6. Source of ZABA® inflow.

	Description
General	Wastewater coming from the buildings (e.g. headquarters, restaurants, museum, etc.) and the canal system
Production	Wastewater coming from general production (all departments)
Contiflex®	Wastewater coming from the liquid crystal production

The COD concentration of the ZABA® inflow is not constant. All types of wastewater vary depending on the time of the year. For example, the rain and snow seasons will bring high amounts of storm water into the system. Also, the company at some periods of the year increases the production in certain departments where the wastewater could have a higher COD concentration (e.g. liquid crystal production), a factor that must be considered.

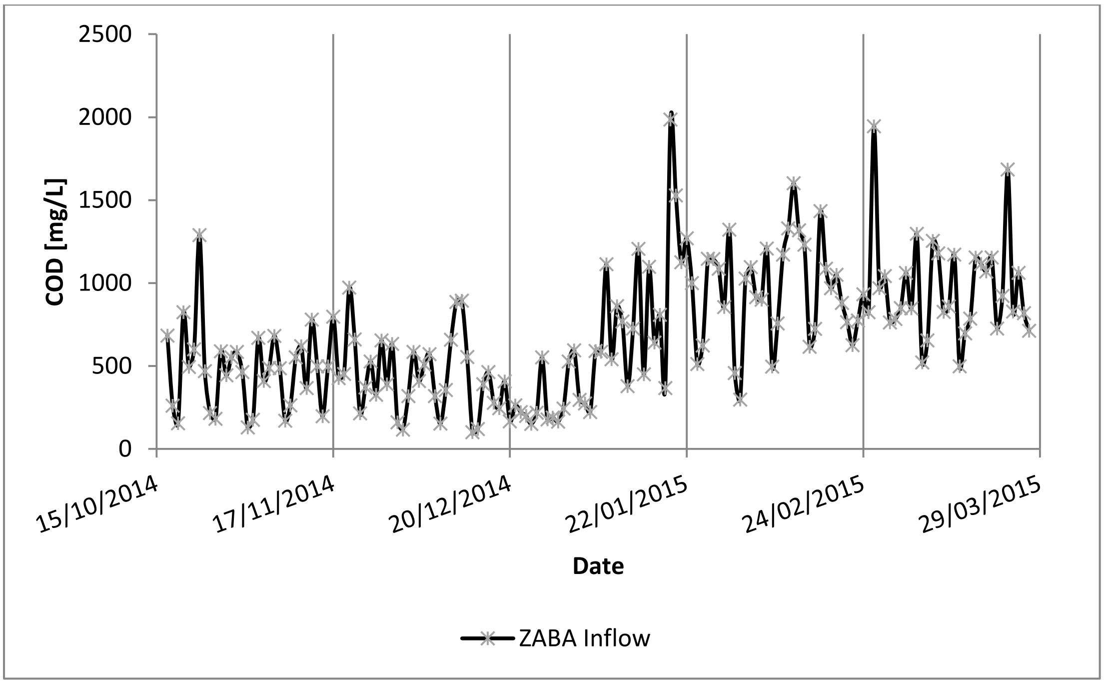

Figure 12. COD concentration in ZABA® inflow.

Figure 12 shows that the COD concentration before January (average 440 mg/L) was almost half of the concentration after that period (average 907 mg/L). This has a direct influence in the determination of other operational parameters such as F:M ratio and C:N:P ratio. ZABA®, and thus the OECD plants must be able to operate under no constant conditions.

The ZABA® inflow ammonium concentration (Figure 13) is not constant. Ammonium concentration showed a relative constant behavior during production days (Monday to Friday) but went down on the weekends due to a decrease in production. During the December break, the levels of ammonium went down to almost 0 mg/L. Not having been prepared for that event affected the sludge performance of the lab-plants. To counter the lack of ammonium in the inflow, a dosing station in the laboratory had to be implemented to compensate for the low concentration of ammonium. On the other hand, ZABA® was prepared against the lack of ammonium during that period, and any other variation that could affect the whole process, thanks to their automated control system.

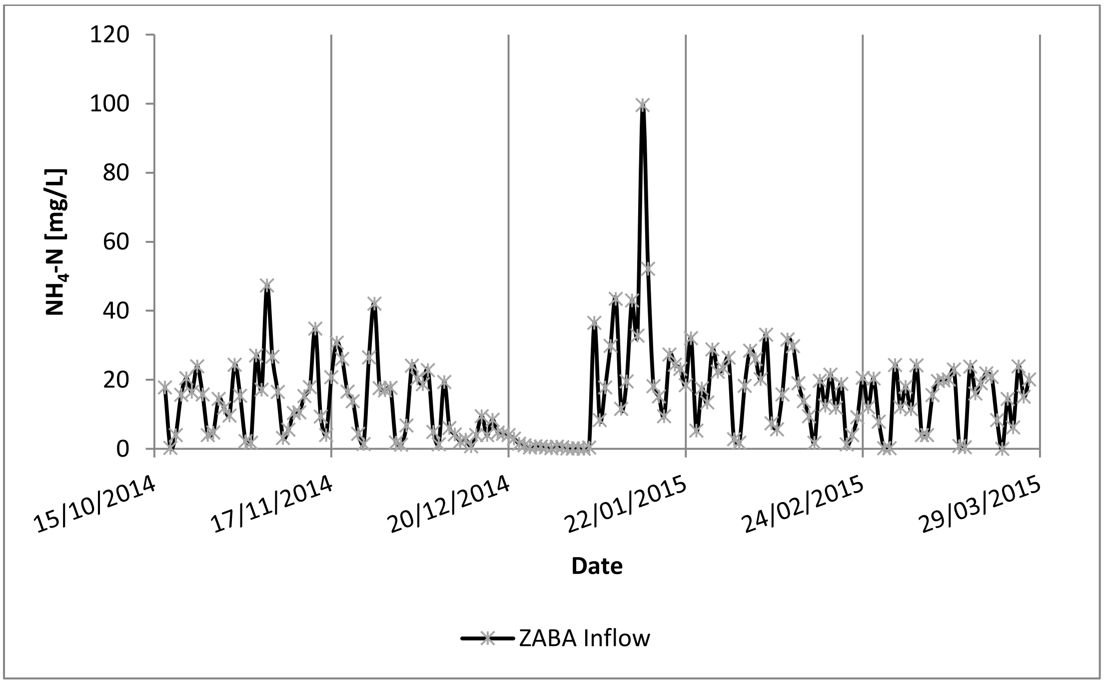

Figure 13. NH_4-N concentration in ZABA® inflow.

Every year, the wastewater department pipe system is cleaned, as a matter of maintenance, using ammonium and other chemicals. Subsequently, the levels of ammonium went up to even 100 mg/L on January 2015.

Orthophosphate was constantly present in ZABA® inflow with an average concentration of 3 mg/L. Thus, it was available for the microorganisms to take for their metabolism. The levels of orthophosphate in the effluent of the plants showed that an additional dose was not necessary (see section 4.5).

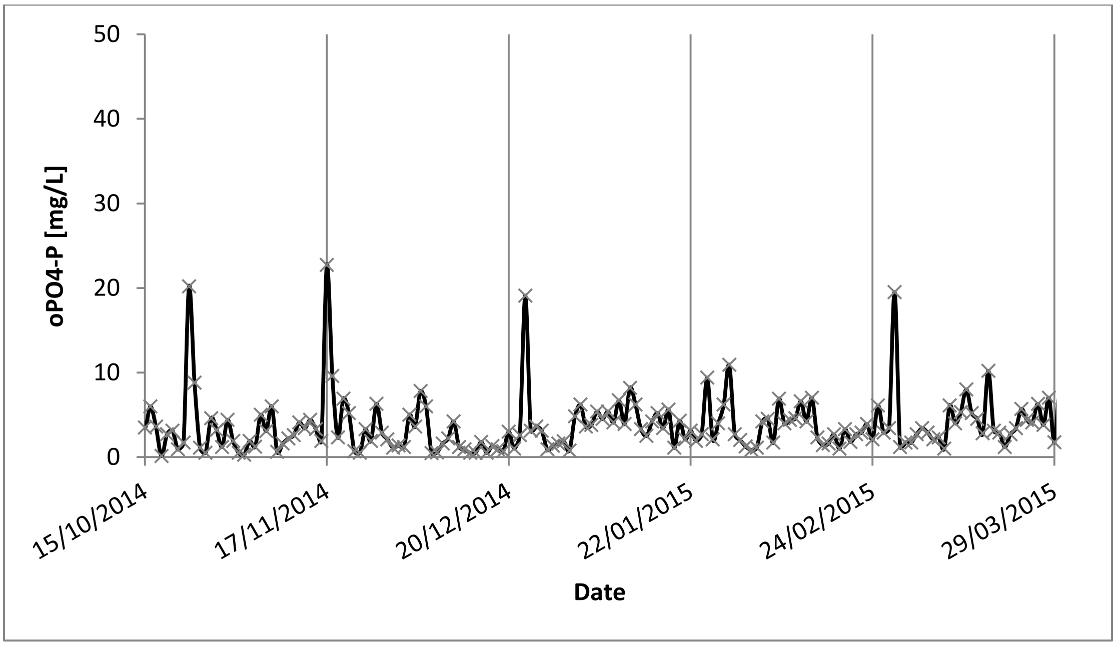

Figure 14. o-PO4-P concentration in ZABA® inflow.

4.2 Performance of OECD stations

4.2.1 Inflow

In order to run a plant capable to operate under no constant conditions, the wastewater pumped into each OECD plant is calculated taking in many factors into consideration.

F:M ratio was set to 0.4 g/g*d to reach a percentage of BOD degradation of above 90% (see section 2.1.2). Every activated sludge tank has a volume of 4.5 l and was filled with ZABA® wastewater with ~4 g/L of MLSS. After two weeks monitoring COD inflow, the concentration had an average of 450 mg/L (0.9 g/L BOD_5). To convert COD concentration to BOD_5, the COD/BOD relation for ZABA® was used:

$$\frac{COD}{BOD5} = 0.5 \qquad \textbf{eq. (8)}$$

The daily inflow (Q_d) was then calculated with the following equation (see section 2.1.2):

$$Qd = \frac{F{:}M * V_{AST} * MLSS_{AST}}{C_{BOD5}} = \mathbf{8.0}\,\frac{\boldsymbol{L}}{\boldsymbol{d}} \qquad \textbf{eq. (9)}$$

Where

- F:M ratio = 0.4 g/g*d
- V_{AST} = 4.5 L
- $MLSS_{AST}$ = 4 g/L
- C_{BOD5} = 0.9 g/L

The plants started working with approximately 8 L/d (Figure 15), meaning 3.6 g COD/d or 7.2 g BOD/d.

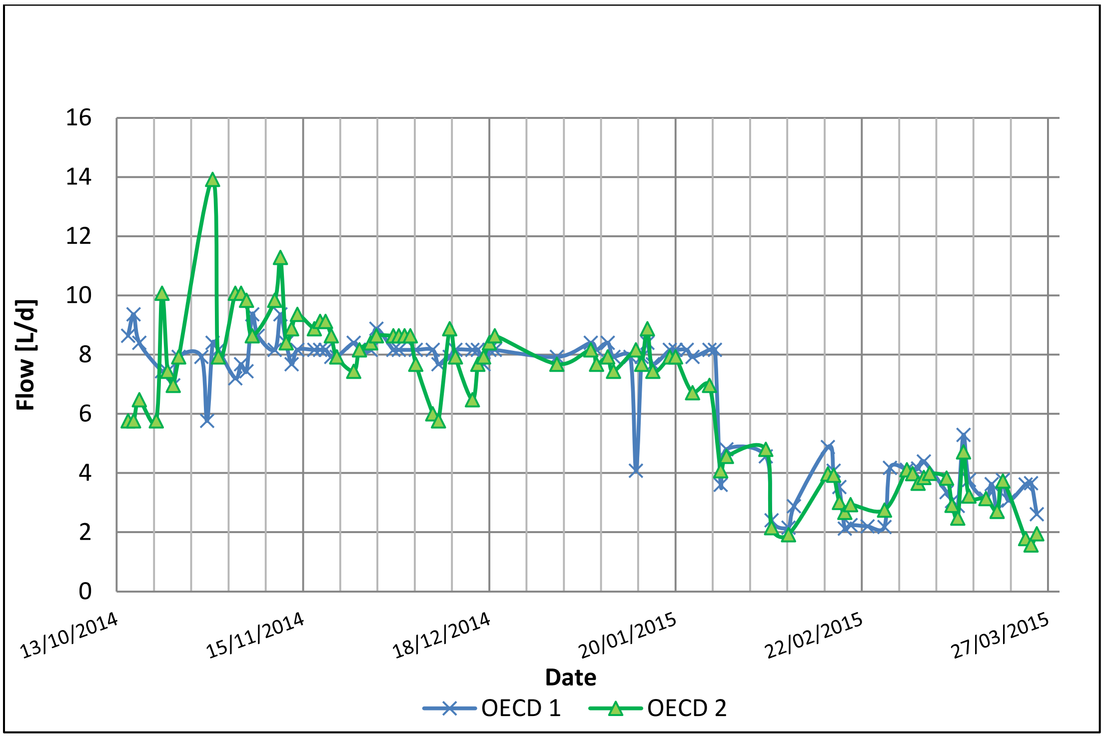

Figure 15. Inflow from ZABA® to OECD plants.

The C:N:P ratio was set in 100:8:1. The nitrogen and phosphorus ratio is flexible; for nitrogen around 6 – 8, and for phosphorus among 0.5 - 2. For a COD concentration of 3600 mg COD/d the corresponding NH_4-N and o-PO4-P concentration was approximately 288 mg/d and 36 mg/d, respectively. After two weeks of monitoring NH_4-N and o-PO4-P, the inflow concentration had an average concentration of 305 mg/L and 40 mg/L, respectively. At that moment, it was not considered to implement a dosing station since the N:P concentrations fulfilled the desired ratio. After experiencing sedimentation issues between December and January, the inflow was regulated to ~ 4 L/d

(Figure 15) due to an increase on the COD concentration. The levels of NH_4-N dropped down and a dosing station had to be implemented to compensate for the lack of ammonium in the system. After this, other parameters, not considered at the beginning of the operation such as sludge age, Hydraulic retention time (HRT), and return sludge rate, had to be considered to solve the sedimentation issue.

4.2.2 Temperature, pH and O_2 content

Temperature was monitored from the beginning of the project. The average temperature for OECD 1 was 21.12°C, and 21.35°C for OECD 2 (Table 7), being slightly higher on the first month of operation (Figure 16). Temperature has a direct effect on the F:M ratio and bacteria performance, and consequently in the operation of the plant. For this case, both OECD plants were operated under lab conditions, meaning it was not a factor disturbing the operation.

Table 7. Temperature and SD for OECD plants.

Plant	Temperature [°C]	SD
OECD 1	21.12	1.43
OECD 2	21.35	1.46

On the other hand, ZABA® has some warnings levels (Figure 16) for the bioreactor. In case any of them are reached or exceeded, the plant has to evaluate the process parameters and take a corrective action, if necessary. ZABA® is prepared for extreme weather, taking into consideration that the bioreactor is found outdoors and that Germany has hard winters. When running a wastewater treatment in a company facility or a city, temperature must be considered. The behavior presented in Figure 5 for BOD_5 degradation and the F:M ratio varies under different temperatures (Abwassertechnische Vereinigung, 1997).

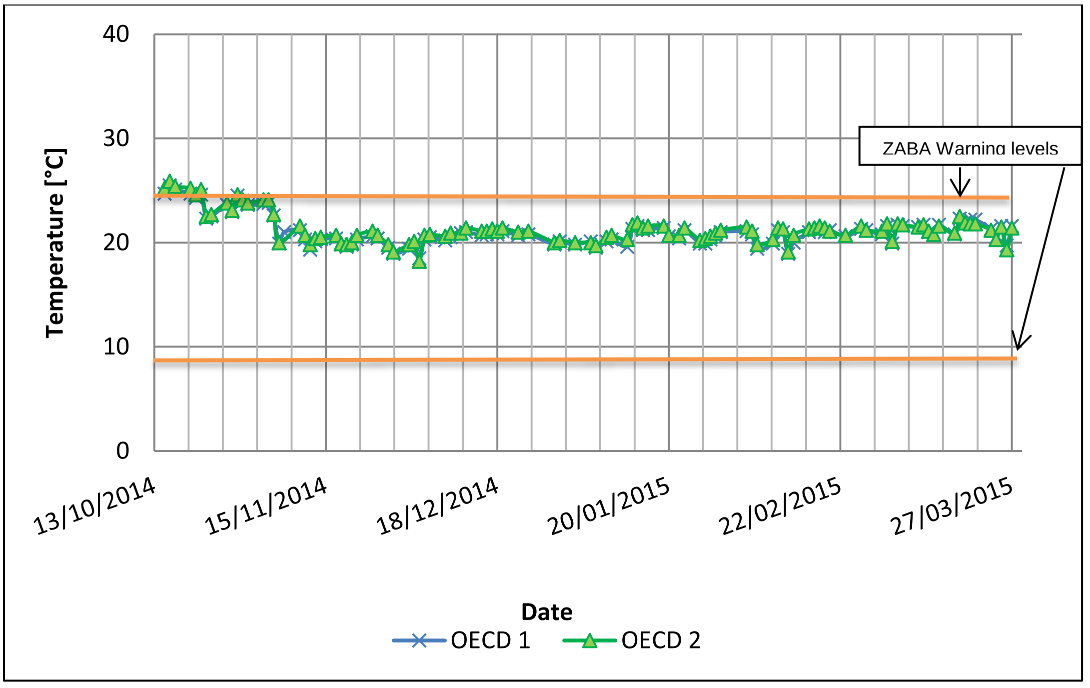

Figure 16. Temperature for OECD plants.

The pH was monitored from the beginning of the project (Figure 17). The average pH for OECD 1 was 7.86, and 8.06 for OECD 2 (Table 8).

Table 8. pH and SD for OECD plants.

Plant	pH	SD
OECD 1	7.86	0.26
OECD 2	8.06	0.26

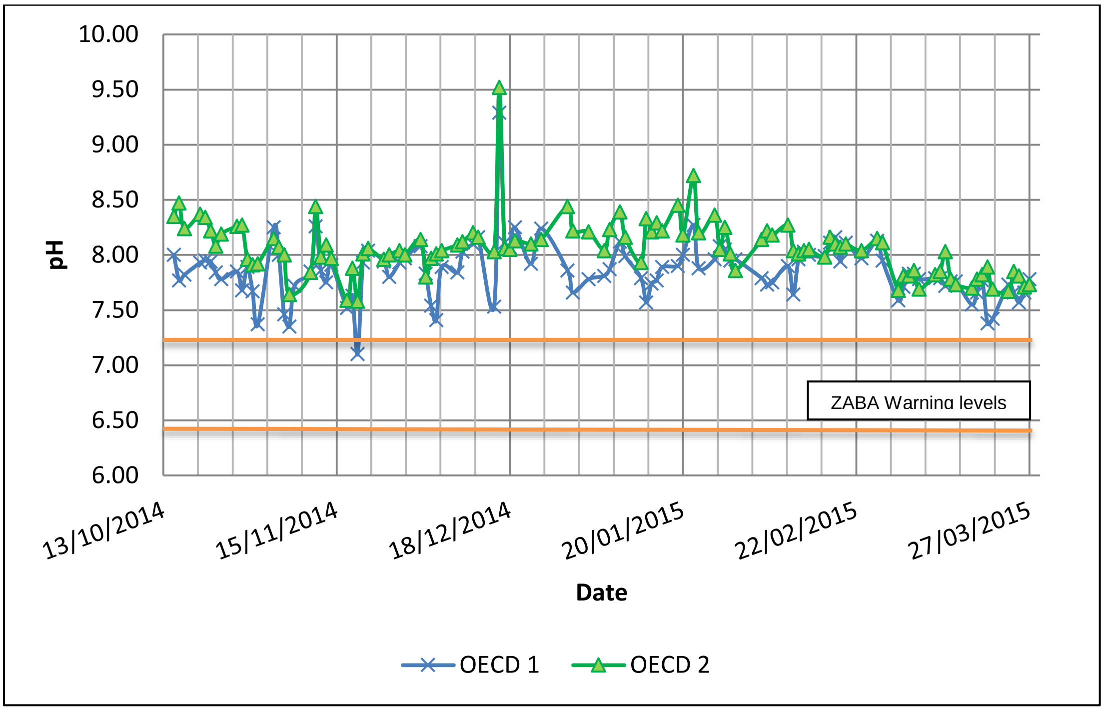

Figure 17. pH for OECD plants.

Most of the bacteria in the activated sludge are *Nitrobacter* and *Nitrosomonas*, and the optimum pH for nitrification is between 7.8 and 8.9 (Shammas, 1986). A drop in the pH can cause bacteria to die or lose its functionality. Even though warning levels for ZABA® are between 6.5 and 7.5, the wastewater department wanted to evaluate the bacterial behavior under a higher pH. As shown in Figure 17, the pH in the OECD plants was above the warning levels in which ZABA® operates. The natural tendency for the pH in the bioreactors is to go down due to nitrification (see section 2.1.3.2). Consequently, a solution of NaOH was pumped into both OECD plants to maintain the pH at the desired value. The performance of bacteria under higher pH showed no effect on COD removal (see section 4.3).

The O_2 was monitored from the beginning of the project (Figure 18). The average oxygen for OECD 1 was 3.39 mg/L, and 3.94 mg/L for OECD 2.

Table 9. O_2 and SD for OECD plants.

Plant	O2 [mg/L]	SD
OECD 1	3.39	1.06
OECD 2	3.94	1.50

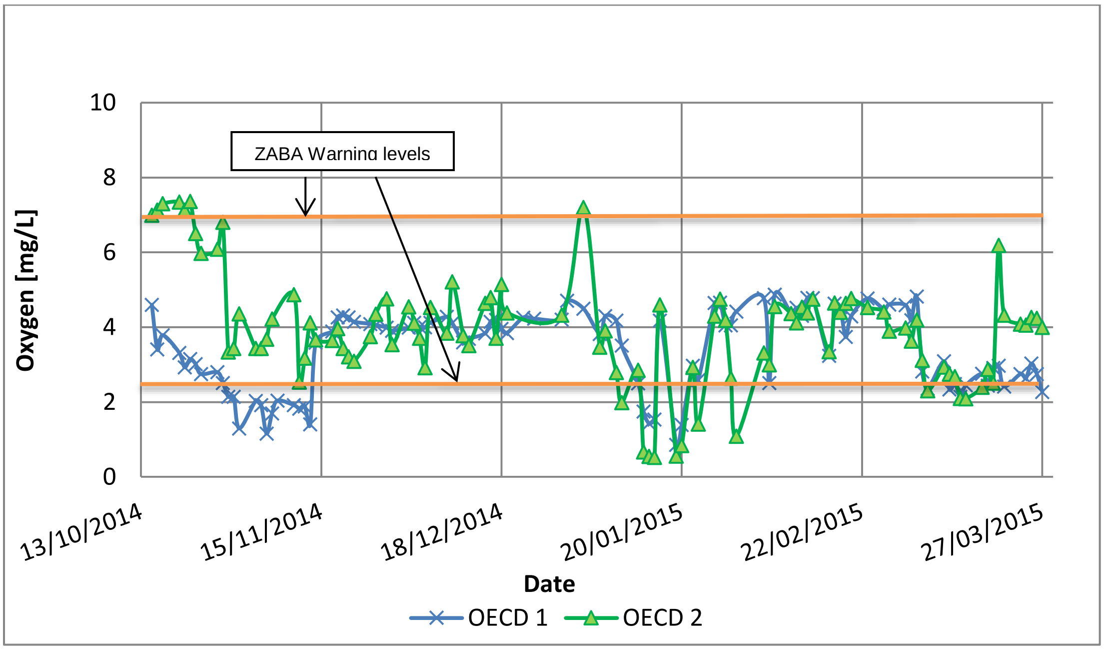

Figure 18. Oxygen for OECD plants.

Aerobic bacteria, like *Nitrobacter* and *Nitrosomonas,* are most predominant in activated sludge meaning that a constant presence of oxygen must be available. No anaerobic tanks were included in the experiment even though it is common to have a denitrification process on a WWTP. It is recommended to operate above 2.0 mg O_2/L (OECD, 2001). Going under the lower limit could cause the bacteria to die or to have sedimentation issues, like poor floc formation, or bulking among others (see Figure 19). Going over the upper limit can cause foaming, a typical problem in industrial WWTPs.

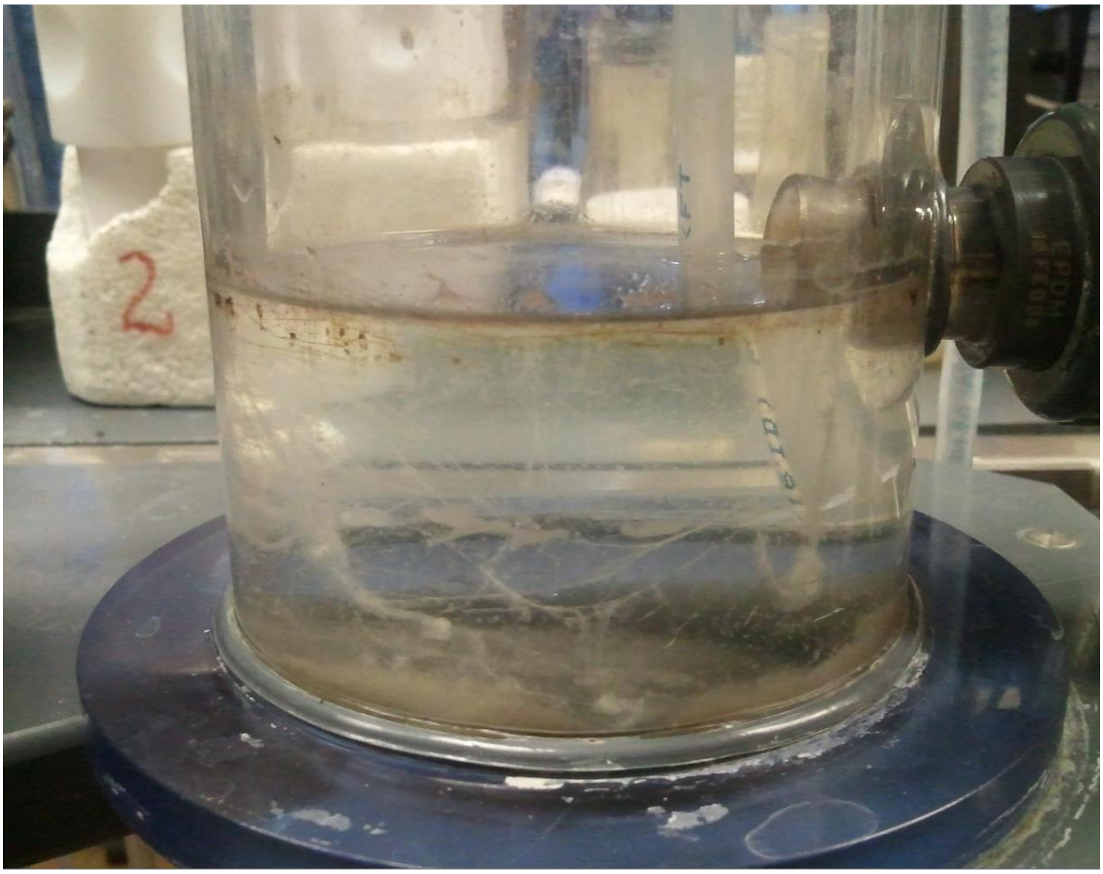

Figure 19. Sedimentation issues due to a poor oxygen control.

As shown in Figure 18, the oxygen concentration was not constant. This was mainly for two reasons:

1. Problems with the oxygen delivery system
2. Oxygen sensor

Maintenance and a continuous calibration of the oxygen sensors were implemented. Even though oxygen concentration showed a high variation, it did not affect the COD removal rate (see section 4.3) demonstrating a significant flexibility of the bacteria regarding O_2 intake.

4.2.3 Solids Content

4.2.3.1 Mixed liquor suspended solids (MLSS)

The concentration of MLSS was monitored twice a week from the beginning of the project (Figure 20). This parameter is used to describe the activated sludge as a hole: liquid, organic and inorganic matter. The average MLSS for OECD 1 was 4.14 g/L and 4.42 g/L for OECD 2. Average levels of MLSS were above the objective set in section 3.1 of 2.0 mg/L MLSS (OECD, 2001) for an optimum solids content.

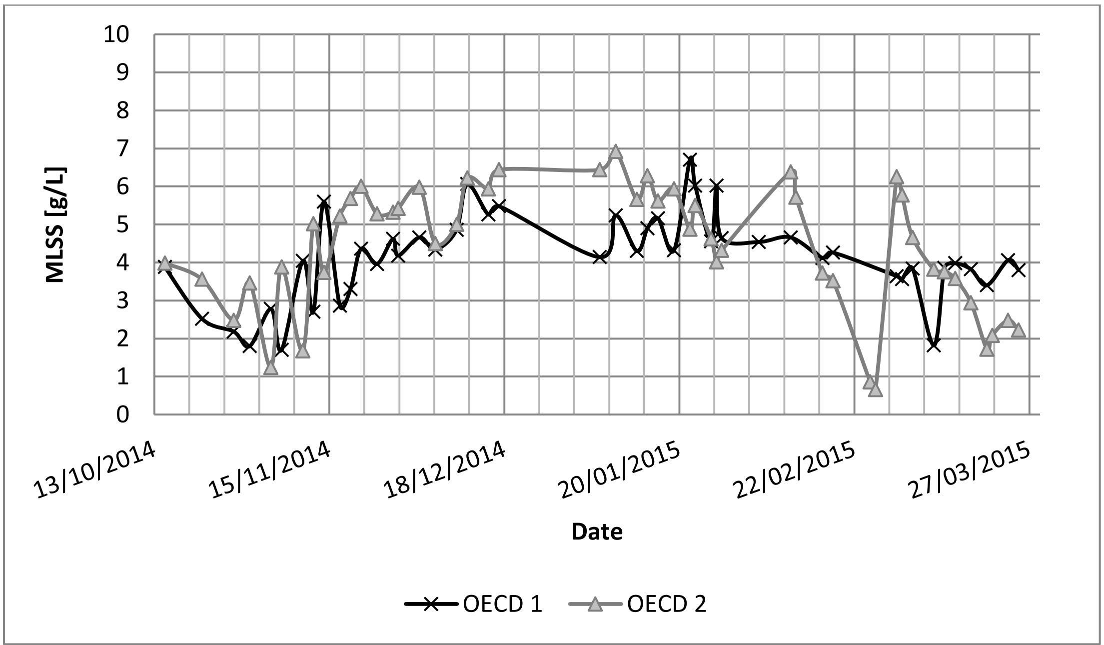

Figure 20. MLSS for OECD plants.

The bacterial population is susceptible to changes in temperature, pH, oxygen, and organic load, but there are other physical factors that may be considered while analyzing MLSS such as the recirculation system. A broken/clogged hose or any filtration in the recirculation system may cause an increase or decrease of MLSS. The recirculation rate plays an important role as well; pumping back more sludge than the inflow rate could affect MLSS and sedimentation as well.

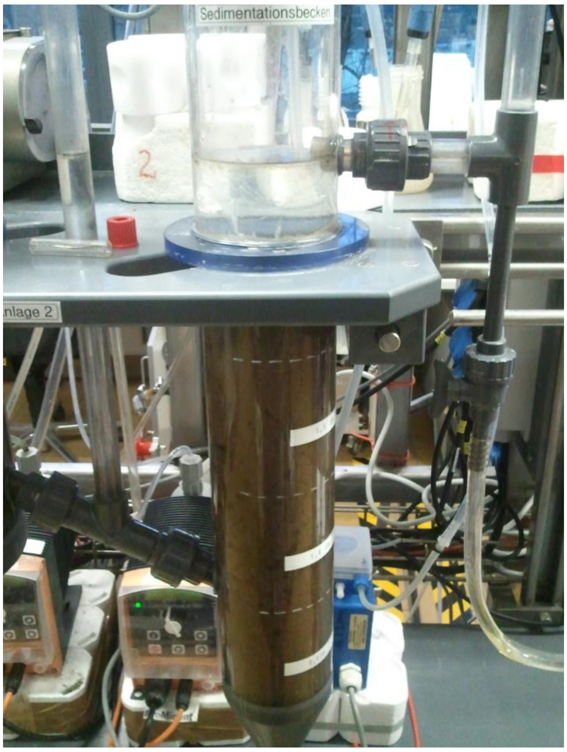

Figure 21. Sedimentation issue on OECD 2.

The first three months showed a similar behavior for both OECD plants operating above 2.0 mg/L MLSS but with a positive trend increasing the MLSS level even up to 5-6 mg/L (Figure 20). At the beginning of January, OECD 2 started to experiment some operational problems with the recirculation system causing sedimentation issues (Figure 21). The recirculation rate was one of the parameters to adjust after a root-cause analysis was performed. A complete verification and cleaning of the recirculation system and calibration of the recirculation pumps to fulfill the optimum rate was performed (~0.16 L/h). After this, OECD 2 started to gain stability during March with an average of 3.22 mg/L MLSS. Even when OECD 1 was more stable through time, it experienced a problem similar to OECD 2 at the beginning of March. The knowledge gained from the previous sedimentation problems with OECD 2 allowed the problem to be fixed quickly and for OECD 1 to stabilize by the end of the month. The role of the PAC in the stability of OECD 1 could be taken in consideration since sedimentation issues were absent. The positive role of hydrophobic interactions between the PAC and the activated sludge flocs, to help the flocs settle efficiently, may be considered (V. Urbain et al 1993).

4.2.3.2 Volatile suspended solids (VSS) content

The VSS content was monitored twice a week from the beginning of the project (Figure 22). The average VSS for OECD 1 was 80.66%, and 73.95% for OECD 2. The determination of this parameter is useful in plant operation because it offers an approximation of the amount of organic matter present in the wastewater. OECD 1 showed an increase over time of the bacteria population, almost going from 65% to 90% of organic matter. After having some operational problems between December and January, the OECD 2 plant experienced a decrease in bacteria population, going down to 50%, but once corrective actions were implemented it started to show signs of recovering and ended at 60%.

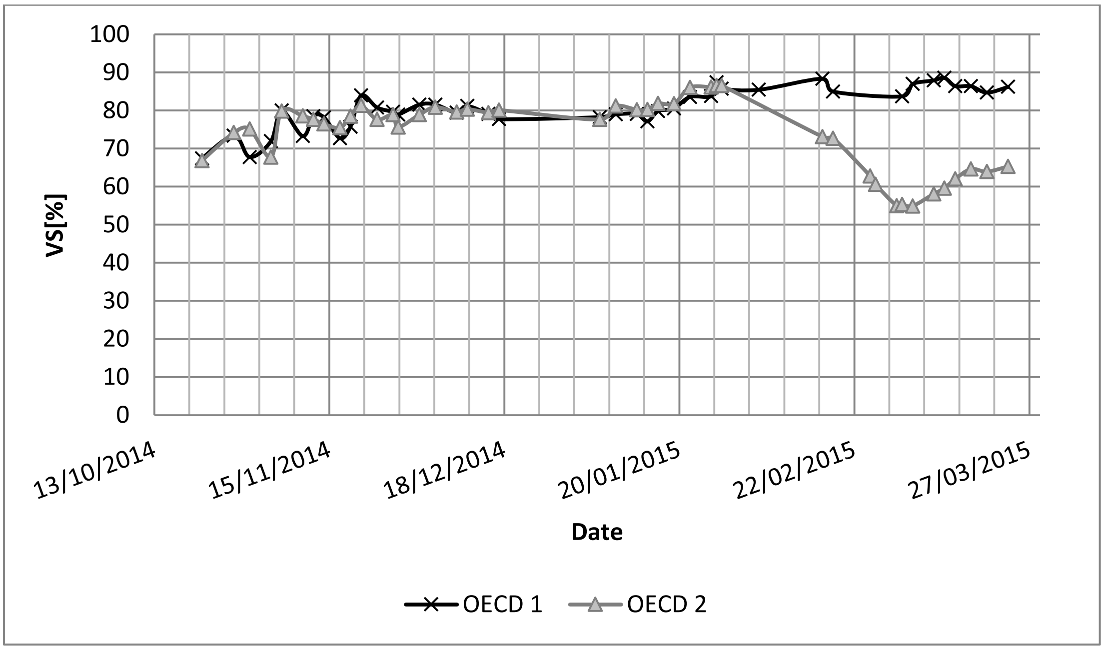

Figure 22. VSS content percentage for OECD plants.

4.2.3.3 Sludge Volume

The sludge volume was monitored twice a week from the beginning of the project (Figure 23). Sludge volume is a parameter that gives a reference on how fast the activated sludge sediments. The average sludge volume for OECD 1 was 772.63 mL/L, and 717.07 mL/L for OECD 2. Compared to ZABA®, with an average of ~400 mL/L, the OECD plants took almost twice the time to settle in the sedimentation tank without showing any constant behavior. ZABA® like other WWTPs, uses $FeClSO_4$ as coagulant for better and faster sedimentation (Zouboulis et al, 2007). Taking into consideration that $FeClSO_4$ was not used in the operation of the OECD plants, this behavior was expected.

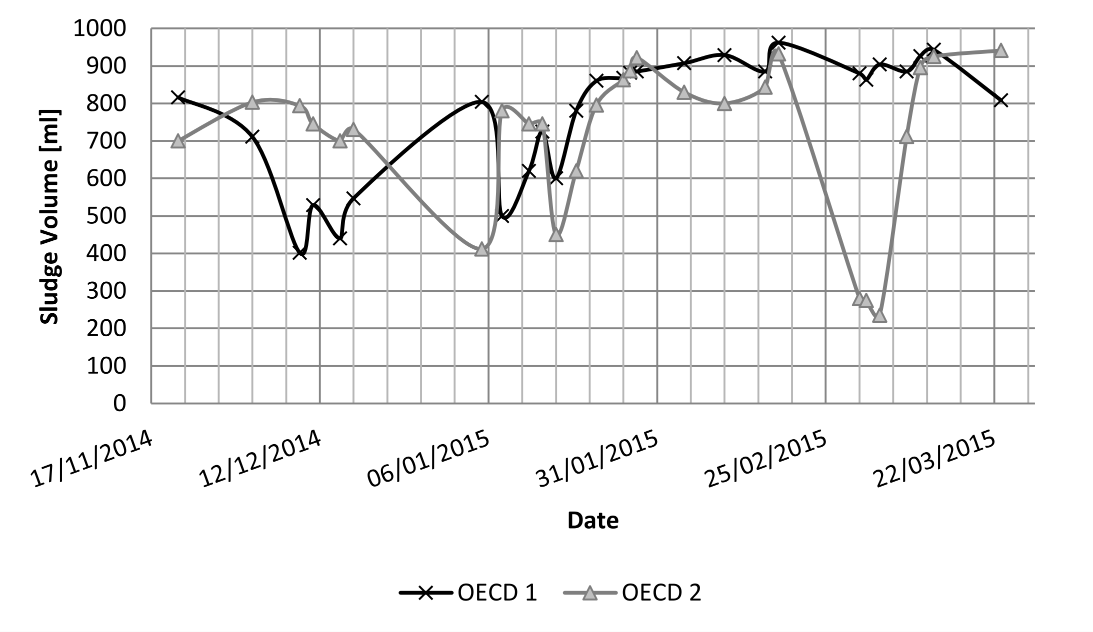

Figure 23. Sludge Volume for OECD plants.

4.2.4 F:M ratio

F:M ratio is one the most important parameters for a WWTP, which defines the balance between foods (BOD_5, COD) entering the biological system and the microorganisms (MLSS) in the bioreactor. The average F:M ratio for OECD 1 was 0.52 [g/g*d], and 0.48 [g/g*d] for OECD 2 (Table 10).

Table 10. F:M comparison between OECD plants vs Target.

Plant	F:M	SD	% Removal
OECD 1	0.52	0.28	97 %
OECD 2	0.48	0.51	96 %
Target (Section 2.1.2)	<0.5	N/A	> 90 %

It was desirable to have a F:M ratio below 0.5 to reach over 90% BOD degradation (see section 2.1.2). Overall, the plants performed really close to the target, even exceeding initial expectations. Theoretically, 90% removal was expected but both OECD plants performed over 96% in COD removal. Again, OECD 1 showed less variation and more stability with a lower standard deviation throughout time.

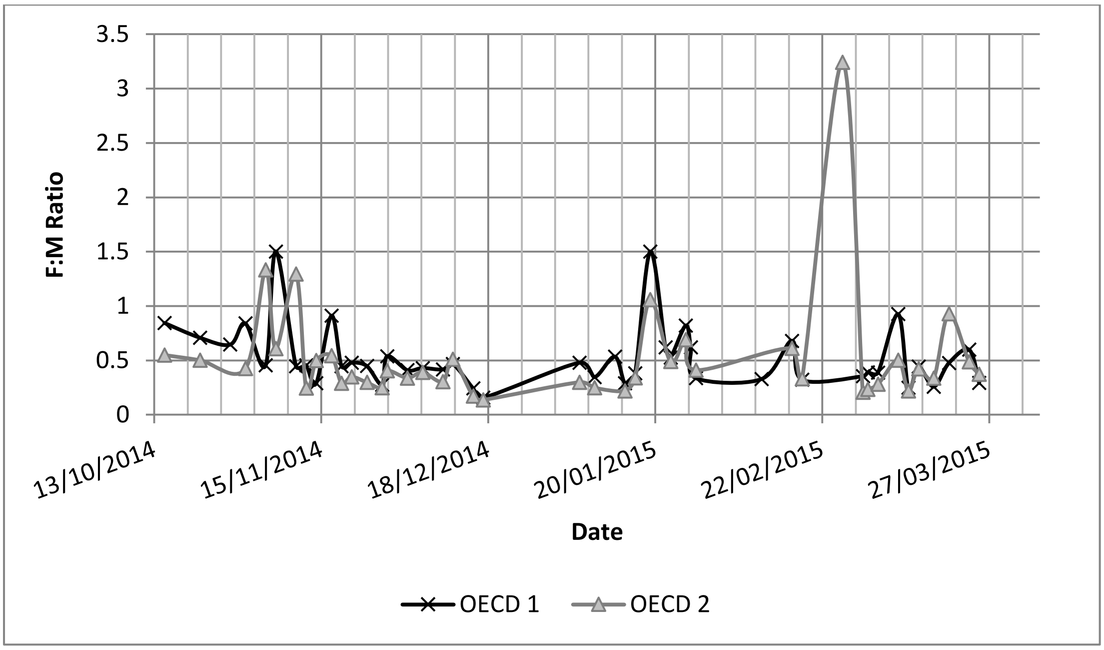

Figure 24. Food to Mass ratio for OECD plants.

Due to many factors and parameters are involved in the calculation of the F:M ratio, a constant variation was expected (Figure 24). For example, the daily inflow and BOD concentration has a direct impact on the F:M ratio. Any issues regarding the inflow pumps or a variation on the BOD concentration through the day may affect this parameter. Taking into consideration that the wastewater used for the operation came directly from the company, no constant concentration was present. Initially, an average BOD concentration was used as a reference to calculate Q_d (daily inflow) to maintain the desired F:M ratio (see section 4.2.1). After the COD concentration in the inflow went up in January and OECD 2 started to experience sedimentation issues, more attention was given into this parameter. As corrective action, COD concentration in the inflow had to be monitored weekly in order to calculate the daily inflow necessary to reach the optimum F:M ratio. Other parameters, like C:N:P ratio (see section 4.2.1), temperature (see section 4.2.2), sludge age (see section 4.2.5,) and HRT (see section 4.2.6), may impact the F:M ratio.

4.2.5 Sludge age

Sludge age was considered after sedimentation issues, and set at 18 days (see section 2.1.2). To calculate the daily volume flow of waste sludge discharged from the system, equation (2) was followed:

$$R_s = \frac{V_{AST} * MLSS_{AST}}{Q_{WS} * MLSS_{WS} + Q_d * X_E} \qquad \textbf{eq. (2)}$$

Since X_E=0 and $MLSS_{AST}$ =$MLSS_{WS}$, then:

$$Q_{WS} = \frac{V_{AST}}{R_s} = 0.\mathbf{25}\ \frac{L}{d} \qquad \textbf{eq. (10)}$$

Where:

Q_{WS} = 0.250 L/d

V_{AST} = 4.5 L

R_S = 18 days

4.2.6 HRT

HRT was considered after sedimentation issues. HRT gives an insight of how much time the feed stays in the system to, for example, degrade organic matter or perform nitrification. The average HRT for OECD 1 was 0.89 days, and 0.91 days for OECD 2 (Figure 25). To calculate the HRT the following equation was followed:

$$HRT = \frac{Vast}{Qd} \qquad \textbf{eq. (11)}$$

Where

HRT	=	Hydraulic retention time	[d]
V_{AST}	=	Volume in the activated sludge tank	[L]
Q_d	=	daily inflow	[L / d]

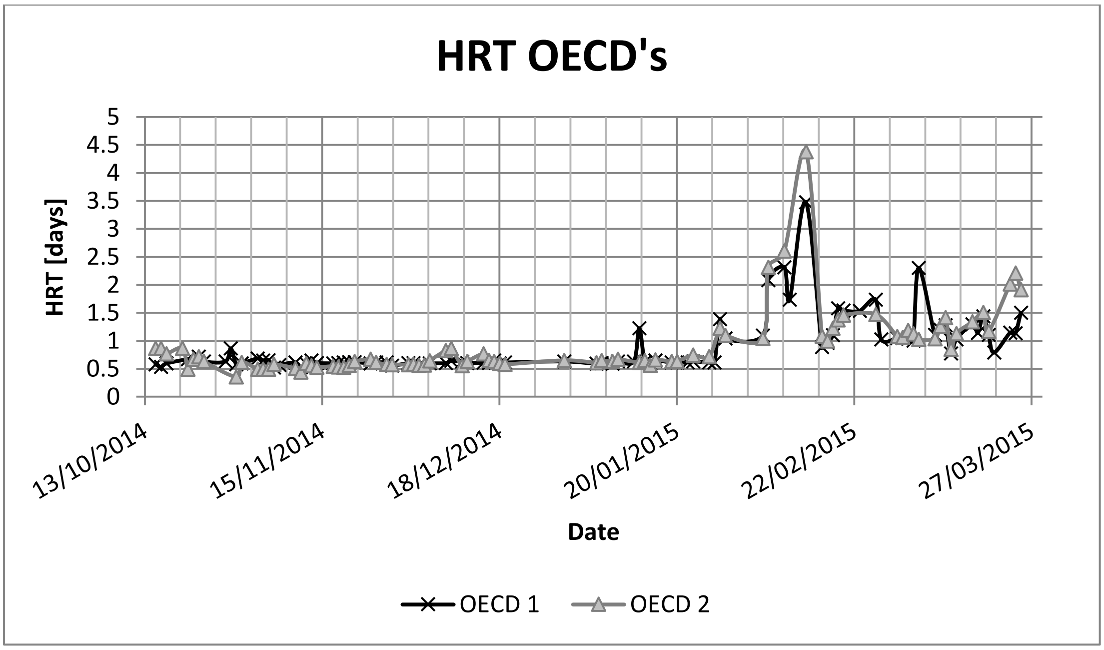

Figure 25. HRT for OECD plants.

At the beginning of the operation the activated sludge had just half day to process the organic matter since the HRT was ~ 0.5 days. The HRT was not considered at the beginning of the process but the bacteria managed to treat all the incoming water with more than 90% COD removal. After experiencing some sedimentation issues, due to a drastic change in the COD concentration, the HRT was increased above 1 day. The percentage of COD degradation was maintained (see section 4.3) and the levels of NO_3^- ions scale up showing a better nitrification and a stable COD degradation (Figure 32).

4.3 Removal of COD

The overall performance of the OECD plants was satisfactory and at some points over performing ZABA®, with more than 96% COD removal. Table 11 summarizes the average COD concentration in the effluent for each OECD, and the removal percentage compared to the initial COD concentration. There are three points to analyze:

- OECD1 with powder activated carbon
- OECD 2 with just the basic wastewater treatment
- OECD 2 after the granulated activated carbon unit

This distinction had to be made to see the performance of each type of system compared to ZABA®.

Table 11. COD concentration in the effluent and percentage of removal related to initial concentration.

Plant	COD [mg/L]	% Removal
OECD 1 (PAC)	21.53	97 %
OECD 2	30.33	96 %
OECD 2 (GAC)	14.67	98 %

A similar behavior between ZABA® and OECD 1 was expected since they have comparable configurations, where powder activated carbon is added to the system. The year before, ZABA® had an annual average COD concentration of 19.2 mg/L in the effluent with 98 % removal (Table 12). With an average

COD concentration of 21.53 mg/L and 97 % removal, OECD 1 performed closely to ZABA®.

Table 12. Annual results from ZABA®.

Results Zentrale Abwasserbehandlungsanlage – ZABA® MERCK KGaA Plant Darmstadt						
		2012		***2013***		
		Inflow	Outflow	Inflow	Outflow	
Wastewater Volume	*m^3*	1 985 569	2 146 205	2 118 499	2 165 598	
BOD5	*mg O_2/L**	542	2	476	3	
COD	*mg O_2/L**	774	**20.6**	735	**19.2**	
Ammonium Nitrogen	*mg N/L**	24.8	0.165	20.2	0.517	
Total Phosphor	*mg P/L**	6.98	0.37	7.1	0.42	
Temperature	*°C **	21.9	17.6	19.9	17.2	
pH	*	7.7	7.7	7.6	7.5	
Conductivity	*mS/cm**	1.4	0.42	1.8	1.17	
Cleaning performance/ Degradation rate		**98 %**		**98 %**		

Then it was necessary to compare if an external system, such as a granulated activated carbon unit like the one used in OECD 2, would significantly perform better than a system similar to ZABA® - OECD 1. Figure 26 compares the final outcome of each OECD. During the first period of the project, OECD 2 over performed OECD 1, with an average COD concentration of 8.20 mg/L and 98.33% removal. After that, the GAC unit gradually got saturated and eventually stopped filtering the inflow showing a performance similar to OECD 1. OECD 2 ended up with an average COD concentration of 14.67 mg/L and 98 % removal.

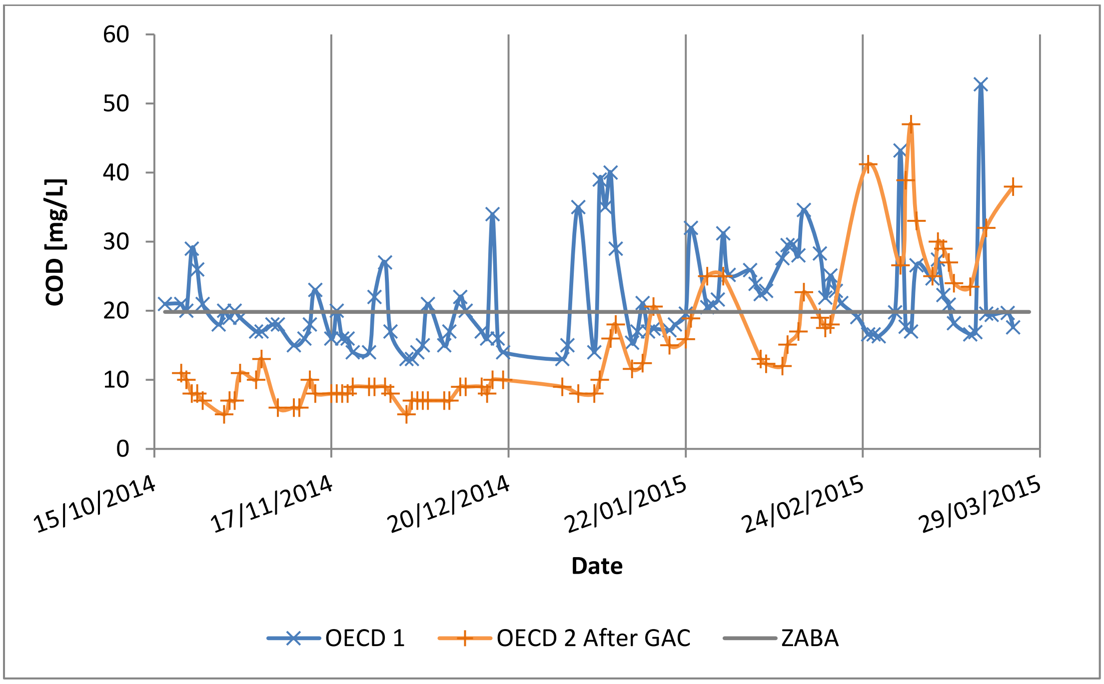

Figure 26. Effluent COD concentration of each OECD compared to ZABA® average performance.

With 1% difference between OECD 1 (PAC) and OECD 2 (GAC), there might not be a substantial difference when it comes to COD concentration levels reduction. The percentage of COD removal from both OECD plants showed a limited variation (Figure 27) and a similar performance to ZABA® (Figure 28). If the cost of implementing an external GAC unit to a WWTP like ZABA® it is higher than adding PAC to the bioreactor, the cost-benefit of the project would be irrelevant. An external GAC unit could be justifiable when a specific contaminant, not easily degradable, is present in the inflow. No estimates were calculated for this project.

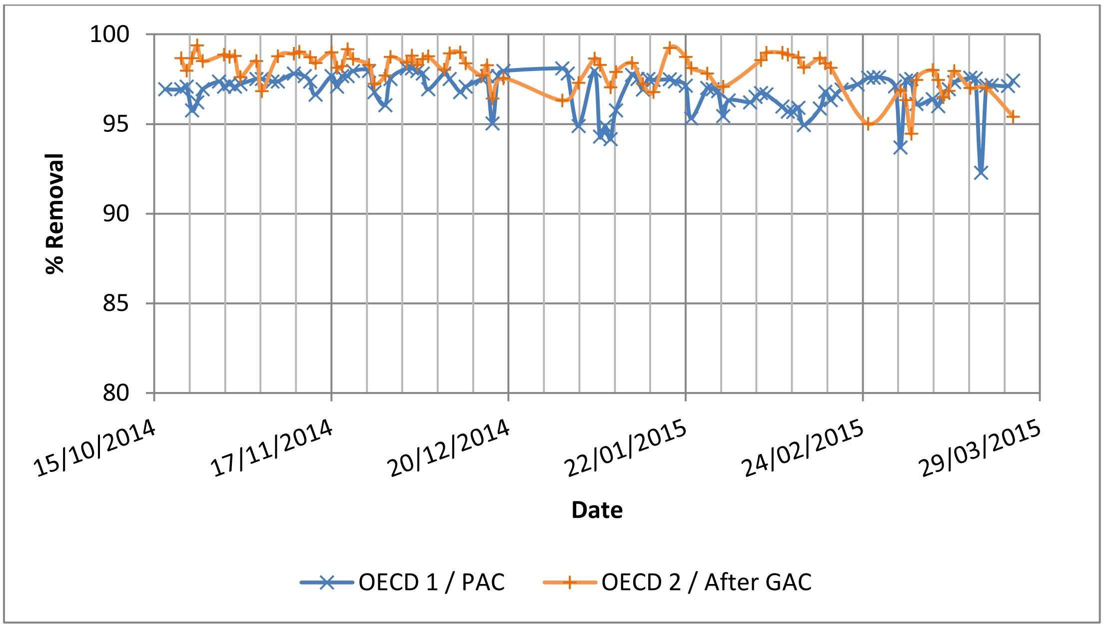

Figure 27. COD percentage removal of OECD 1/PAC vs OECD 2/after GAC.

To put this in perspective the level of COD removed by this type of WWTP, Figure 29 plots the initial COD concentration; ZABA® inflow versus the outcome of each plant showing how effective a WWTP can be even with high COD concentrations.

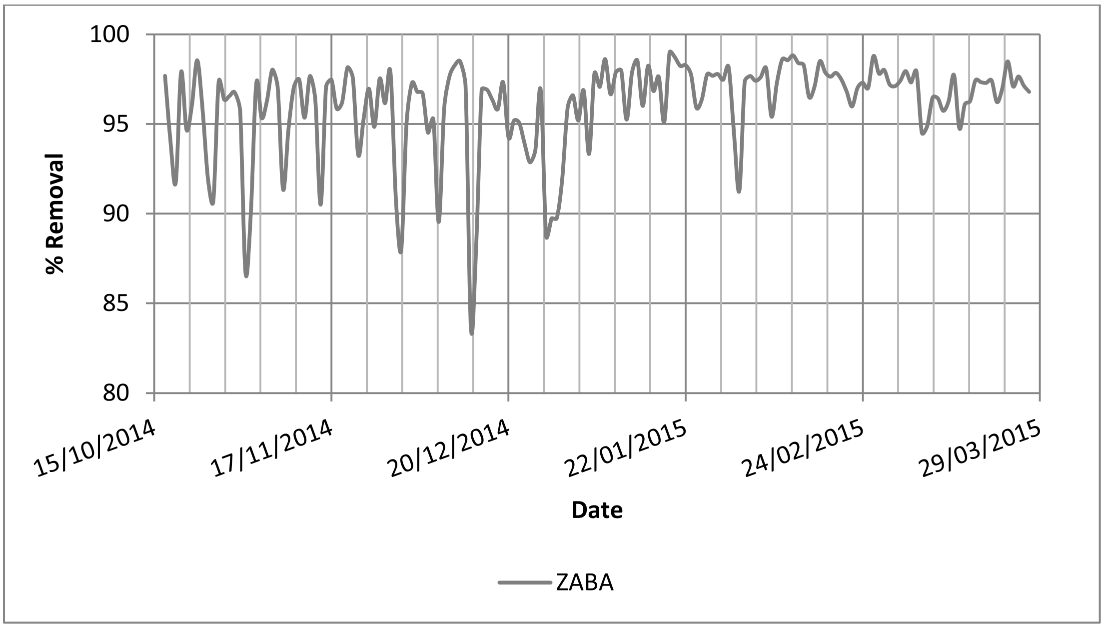

Figure 28. ZABA® COD percentage removal.

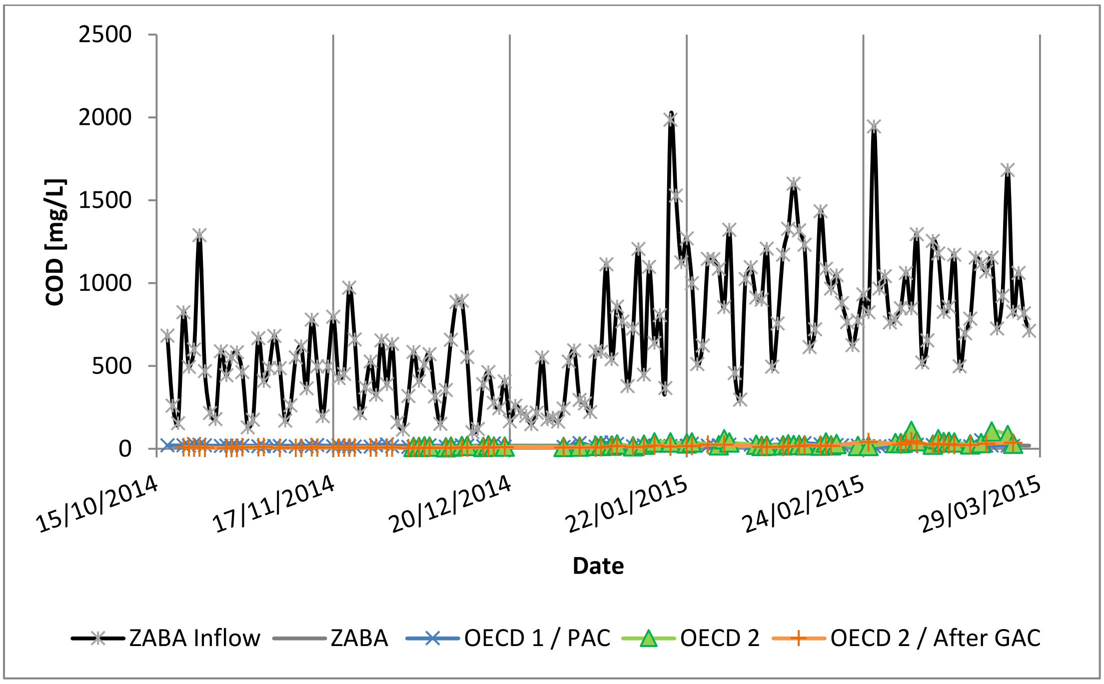

Figure 29. Initial COD concentration versus final outcome for each plant.

4.4 Removal of Nitrogen

Levels of NH_4-N were monitored in the effluent (Figure 30) and, with 97% average nitrogen removal on both plants (Figure 31), the overall performance was satisfactory. The average ammonium concentration was 0.87 mg/L for OECD 1, and 4.80 mg/L for OECD 2. An existing ammonium concentration in the effluent was an indicator of sufficient nitrogen available to the bacteria for nitrification. When the appropriate C:N:P ratio (see section 4.2.1) has been implemented, it is expected that all available ammonium is converted to NO_2^- or NO_3^- by bacteria through nitrification. It is important to note that, if not enough NH_4-N is reaching the system, all nitrogen available will be used by bacteria showing zero concentration in the effluent.

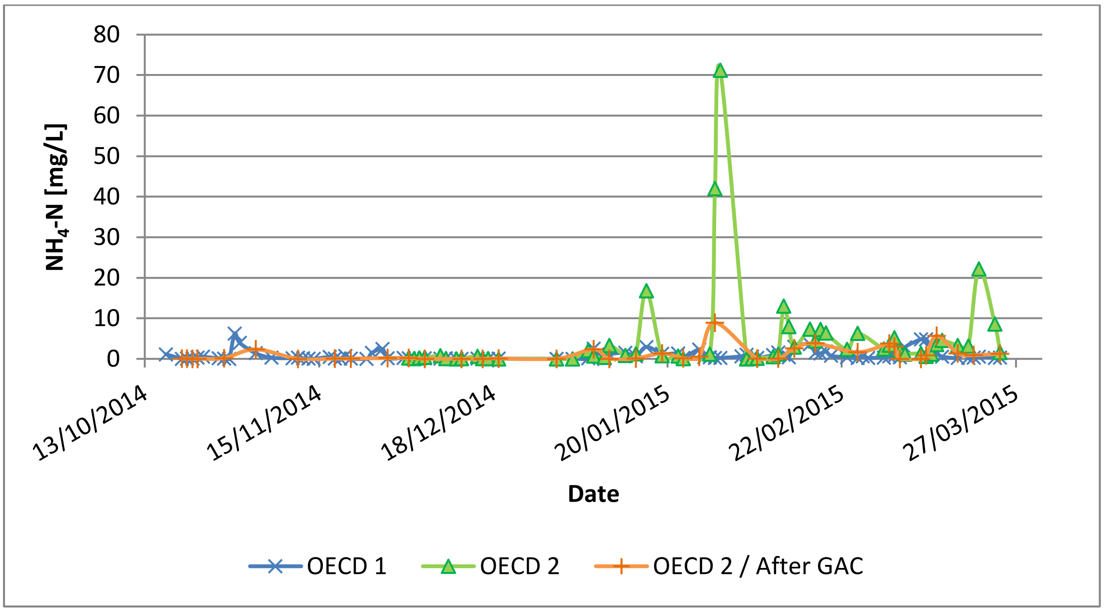

Figure 30. Effluent NH_4-N concentration for each OECD.

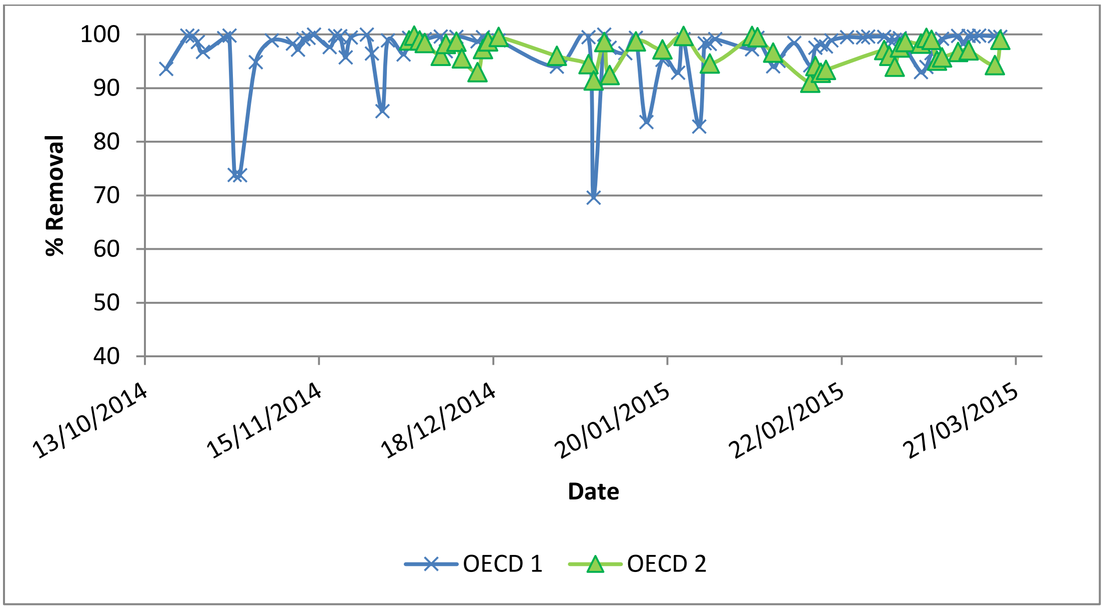

Figure 31. NH_4-N percentage removal.

The first period of the project showed almost zero ammonium concentration in the effluent (Figure 30), but the presence of nitrite and nitrate (Figure 32) showed that nitrogen was available to the bacteria for nitrification. During the December break, the levels of ammonium went down to almost 0 mg/L in the inflow (see section 4.1). Therefore, a dosing station in the laboratory had to be implemented to compensate for the changes in the inflow with a lower concentration of ammonium and a higher COD concentration changing the C:N:P ratio. Once the dosing station was implemented in February, the ammonium concentration incremented and nitrate levels rose, exhibiting an improved nitrification (Figure 32).

The average nitrate content was 22.19 mg/L for OECD 1, and 19.94 mg/L for OECD 2. Levels of nitrite (NO_2^-) were not estimated but physically monitored through sticks as a control indicator. A low concentration of nitrate could mean a high concentration of nitrite and vice versa. Lower nitrate levels in the first period of the project suggest a partially incomplete nitrification due to a short HRT in the system (see section 4.2.6). The HRT seems to play an important role for a full nitrification by giving enough time to the bacteria to perform full nitrification.

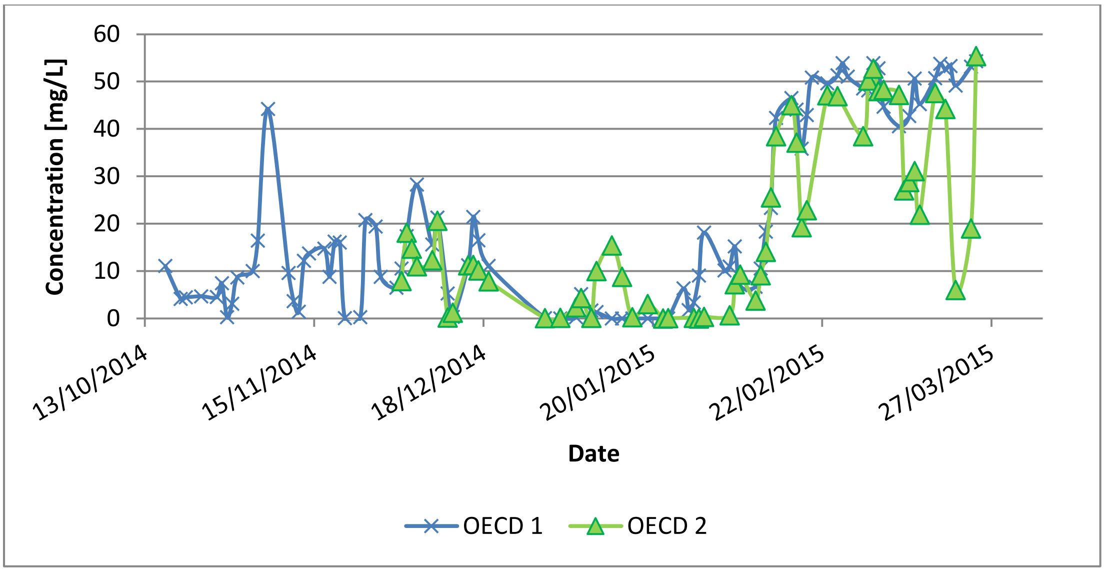

Figure 32. Effluent NO_3 concentration of each OECD.

4.5 Removal of Phosphorus

Levels of orthophosphate were monitored checking for its presence in the system. OECD 1 had an average orthophosphate concentration of 3.97 mg/L and 4.32 mg/L for total phosphor (Figure 33).

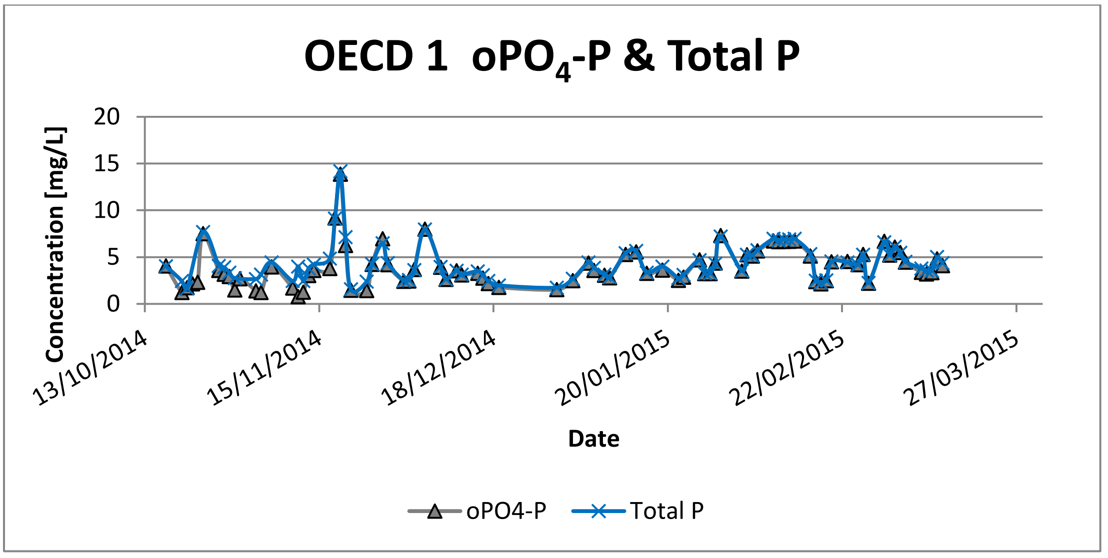

Figure 33. Effluent o-PO_4-P concentration for OECD 1.

OECD 2 had an average orthophosphate concentration of 4.24 mg/L and 4.42 mg/L for total phosphor (Figure 34).

The existence of orthophosphate in the effluent for both OECD plants was an indicator of sufficient concentration in the inflow and, consequently, sufficient phosphorus available for the bacteria to use when necessary. If the concentration in the effluent was zero it could mean that there is a lack of phosphate nutrients and a dosing station must be implemented in the system. No phosphate dosing station was necessary during the operation.

ZABA® like other WWTPs use $FeClSO_4$ as a coagulant to remove phosphorus from the effluent (Zouboulis et al, 2007). ZABA® had a total phosphor concentration in the effluent lower than 0.5 mg/L (Table 12) in the effluent by using this method. No $FeClSO_4$ was used during the project.

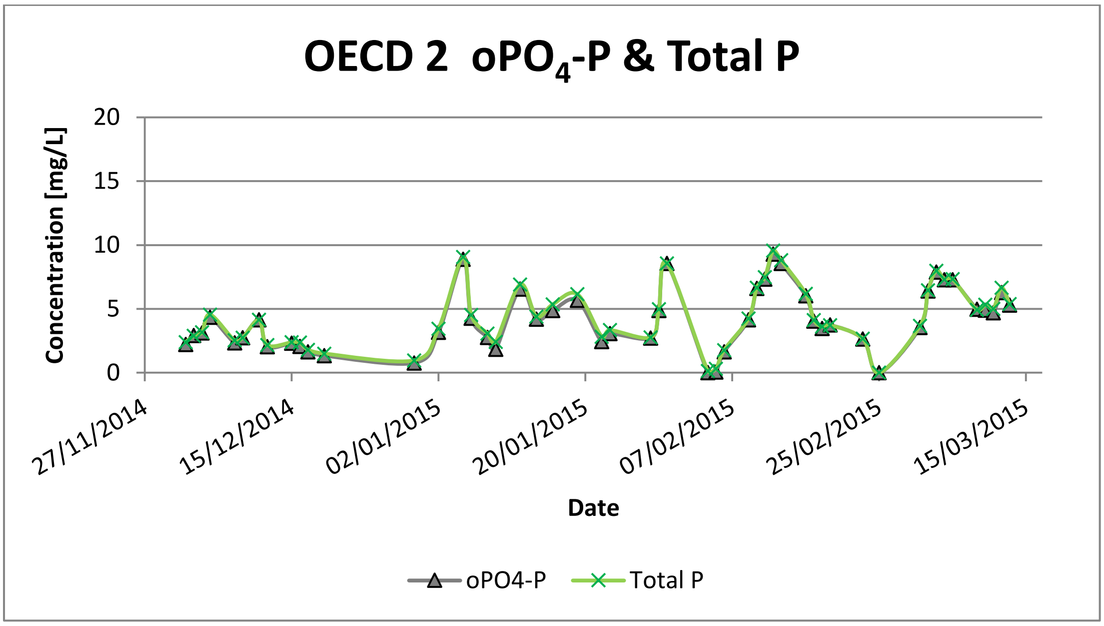

Figure 34. Effluent o-PO_4-P concentration for OECD 2.

5 Conclusion

The objectives presented in section 3.1 for the project were accomplished. For both plants, the average MLSS concentration was above 2.0 g/L while using ZABA® inflow at all times as a carbon resource. COD degradation was over the theoretically expected of 90% and even rivaled ZABA® performance with more than 97% of COD removal.

Bacteria proved to perform well under high pH conditions, variable oxygen levels and, more importantly, under different COD concentrations. Other operational parameters, such as F:M ratio, HRT, and C:N:P ratio, helped to control the performance of the plants. Sedimentation issues are common on WWTPs and were present in this operation but, with a full evaluation of chemical and physical parameters, it is possible to react in time and place some corrective and preventive actions.

OECD1 with PAC acted as a mirror of ZABA® regarding performance. PAC showed to have a positive role on stability for bacteria and even for sedimentation. If a coagulant would have been used in this plant, the sedimentation performance may have been similar, if not equal to ZABA®.

When evaluating performance for OECD 2, it was possible to differentiate the process with and without tertiary treatment. Compared to the effluent without tertiary treatment, water after the GAC unit had around 2-3% more COD removed. The GAC unit started to show signs of saturation and eventually stopped filtering the inflow, showing a performance similar to OECD 1. With approximately just 1% difference on COD removal between OECD 1 (PAC) and OECD 2 (GAC), there might not be a substantial difference when it comes to the reduction of COD concentration levels. The percentage of COD removal from both OECD plants showed a similar performance to ZABA®. If the cost of implementing an external GAC unit to a WWTP, like ZABA®, is higher than adding a PAC to the bioreactor, then the cost-benefit may be small. An external GAC unit could be justifiable when a specific contaminant not easily degradable contaminant is present in the inflow. Further studies implementing aromatic compounds in the inflow were considered by the company as a future perspective.

6 Conclusión (traducción al Español)

Los objetivos presentados en la sección 3.1 para el proyecto se cumplieron. Para ambas plantas, la concentración promedio de MLSS fue superior a 2.0 g/L utilizando el flujo de entrada de ZABA® en todo momento como fuente de carbono. La degradación de COD superó el teóricamente esperado 90% e incluso igualó el rendimiento de ZABA® con más del 97% de eliminación de COD.

Las bacterias probaron bien su funcionamiento bajo condiciones de pH alto, niveles variables de oxígeno y más importante, bajo diferentes concentraciones de COD. Otros parámetros operativos como la relación F:M, el HRT y la relación C:N:P ayudaron a controlar el rendimiento de las plantas. Los problemas de sedimentación son comunes en las plantas de tratamiento de aguas residuales y fueron parte de la operación, pero con una evaluación completa de los parámetros químicos y físicos es posible reaccionar a tiempo y poner algunas acciones correctivas y preventivas.

OECD 1 con PAC actuó como un espejo de ZABA® con respecto al rendimiento. El PAC demostró tener un rol positivo en la estabilidad de las bacterias e incluso en la sedimentación. Si se hubiera usado un coagulante en esta planta, el desempeño de la sedimentación puede ser similar al de ZABA® si no igual.

Al evaluar el desempeño del OECD 2 fue posible diferenciar el proceso con y sin tratamiento terciario. En comparación con el efluente sin tratamiento terciario, el agua después de la unidad de GAC tuvo alrededor de 2-3% más eliminación de COD. La unidad de GAC comenzó a mostrar signos de saturación y eventualmente dejó de filtrar el flujo de entrada mostrando un rendimiento similar al del OECD 1. Con aproximadamente solo 1% de diferencia en la eliminación de COD entre OECD 1 (PAC) y OECD 2 (GAC) podría no ser diferencia sustancial cuando se trata de reducir los niveles de concentración de COD. El porcentaje de eliminación de COD de ambas plantas OECD mostró un rendimiento similar al de ZABA®. Si el costo de implementar una unidad externa de GAC en una planta de tratamiento de aguas residuales como ZABA® es mayor que la adición de PAC al biorreactor, la relación costo-beneficio puede ser pequeña. Una unidad externa de GAC podría ser justificable cuando un contaminante específico no fácilmente degradable esté presente en el flujo de entrada. La compañía considera estudios adicionales implementando compuestos aromáticos en el flujo de entrada como una perspectiva futura.

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