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Study to increase the quality of treated water in the process of water reuse in vehicle washing systems

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Abstract

Wastewater generated from carwash is one of the wastewater resources, which contribute effectively in the increasing of environmental contamination due to the chemical characteristics of the vehicle wastes. The present work aims to evaluate and compare the efficiencies of removal of pollutants from vehicle washing wastewater in order to optimize the treatment plant operation in terms of energy and water. In the present work is conducted a case study on Transportes Gama station, located in Seixal. The station has a compact treatment plant, built by ECODEPUR®, with primary sedimentation, flotation, biological treatment, sand and activated carbon filtrations. The efficiency of each treatment operation and process was evaluated analyzing several parameters: pH, chemical oxygen demand (COD), total solids (TS), total suspended solids (TSS) and metals (Cu and Zn). To evaluate the enzyme effect in the efficiency removal of all parameters, two samplings and relative tests were made, the first with 30 L/week of enzymes and the second with halved amount added. The main results show that the COD and metals are within the limit of the national legislation for wastewater discharge in both tests. In the first assay the treatment plant presents a total removal efficiency around 96% the COD, 61% TS and around 80% Cu and 81.5% Zn. It was verified that the enzyme volume reduction had a small impact on total removal efficiency with 95.6, 58, almost 77 and almost 74% COD, TS, Cu and Zn respectively, of 3,900 €/year. Most of the treated wastewater is reuse in the vehicle washing, which represents a wastewater discharge near zero and a cost saving of 6,320 €/year, contributing also for sustainable use of water.

Keywords: vehicle washing, wastewater, wastewater treatment plant, water reuse

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Abbreviations list

Abbreviation	Description
BOD_5	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
EC	Electro Coagulation
EQS	Environmental Quality Standard
FCF	Flocculation Column Flotation
FF	Flocculation-Flotation
FFC	Flocculation Flotation Chlorination
FFO	Flocculation Flotation Ozonation
FSS	Fixed Suspended Solids
GHG	Greenhouse Gas
LC50	Letal Concentration 50
MBBR	Moving Bed Bioreactor
MBR	Membrane Bioreactor
PNEUA	Programa Nacional para o Uso Eficiente da Água
TFS	Total Fixed Solids
TS	Total Solids
TSS	Total Suspended Solids
TVS	Total Volatile Solids
UWWTD	Urban WasteWater Treatment Directive
VSS	Volatile Suspended Solids
WWTP	WasteWater Treatment Plant

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Chapter 1

1. Introduction

1.1. Framework

Vehicles washing wastewater is one the most heavily contaminated, because of the presence of many impurities such as oil and grease, suspended solids, sand, dust which come from their removal using detergent and surfactant. This mixture of water and pollutants can degrade the environment if discharged into sewers and surface water, therefore, it is necessary a purification treatment. It is reported that many technologies have been applied to solve this problem such as sedimentation, flotation and activated sludge process. However, most of them are not satisfactory enough, because do not reach the quality level to reuse the treated water in the main washing process.

Developments in washing technology provide better quality of wash but lead to higher water consumption and also to major loads of pollutant in the wastewater that can have a serious impact on the environment. Car wash generates high amount of wastewater according to the type of car wash system (Moazzem *et al*., 2018). Usually the water consumption is between 50 and 900 liters per washing (LifeMinAqua, 2016). Therefore, carwash station is regarded as an industrial installation (Boussu *et al*., 2007) that has high water consumption, because of this it needs water recycling in order to contribute for sustainable development (Janiek and Kupiec, 2007).

Sustainable car wash concerns conserving and recycling water. Water recycling provides a great method to conserve it, to reuse it for washing cars back in the facilities and to reduce wastewater in order to make the management of the station productive and to avoid waste of fresh water which is becoming increasingly scarce due to the growth in population, urbanization and climate changes (EarthTalk, 2019).

In some European countries water recycling in carwashes is already legislative (Janik and Kupiec, 2007). Despite of their advantages, water reclamation, reuse and recycling in car wash facilities are rather limited in particular in developing countries, where there are not strict rules about this issue. Indeed, in these countries water is not sufficient to suit the request and so car wash wastewater is often used to irrigate or even released without being treated (Almeida *et al.,* 2010). This phenomenon worsens with the public belief that this kind of wastewater is not very polluted compared with other industrial one (Lau, Ismail and Firdaus, 2012).

Sustainability in car washing facilities involves storing water above ground in order to keep water source clean, because when water is stored below ground the risk of ground water pollution is higher. Sustainable car wash encourages the use of green products, biodegradable and water-based cleaning product that accelerate the slow and long process of breaking down oil. It supports also energy saving using more efficient energy systems for water pumping, cleaning and drying to reduce the use of electricity (EarthTalk, 2019).

Water is an essential good to life that must be protected, spared and reused. There are several less noble urban uses of water supply, namely the washing of vehicles using manual and automatic systems. Vehicle washes can be performed with or without reuse of water. The efficient use of water in the urban sector promotes the recirculation of water in the washing operation of vehicles, using the appropriate treatment of the wastewater produced. This measure also allows the reduction of discharge of the waste washing water in the public drainage systems or in the water environment (Moazzem *et al*., 2018).

1.2. Objectives

In the present work is intended to evaluate and compare the efficiencies of removal of pollutants from the wastewater from vehicles washing, subjected to several treatments' levels, in order to reuse treated wastewater with the lowest possible costs. Thus, it is intended to collect and characterize the washing wastewater of a freight vehicle company, Transportes Gama station, in Seixal. This enterprise has a compact wastewater treatment plant with primary (decanting and flotation), secondary (biological) and tertiary (filtration and adsorption) treatments. Therefore, in the present study the removal efficiencies of pollutant several pollutants will be calculated, and optimization measures will be proposed to obtain a good quality of the treated water to be reused, with the lowest possible costs.

1.3. Work structure

This work consists of 8 main chapters in which the topic of interest is divided. Each of them faces issues related to different aspects, from the presentation of the problem, the environmental regulations, the description of the washing vehicles systems, waste water treatment plants up to the chemical analysis conducted on the samples, the discussion of the results and conclusions.

- Chapter 1 is the introduction in order to have a clear and immediate idea about the topic of this work and present the objectives;
- Chapter 2 defines and describes a vehicles washing station. It is defined as a non-domestic installation for external cleaning of vehicles. It is usually divided in four main steps, which are different from each other in terms of amount of water and chemical products used;
- Chapter 3 focuses on environmental legislation. Vehicles washing activity, regarded as an industrial one, must respect the limiting value of hazardous components before being released in surface water or sewers. National, regional and local legislations will have to be coherent with the specifications of EU Directives;
- Chapter 4 is the analytical part, where is reported the description of the laboratory analysis and the experiments conducted;
- Chapter 5 describes in detail the case study concerning with Transportes Gama washing wastewater treatment plant, consisting in primary, secondary and tertiary treatments;
- Chapter 6 reports the results of the analysis;
- Chapter 7 presents the conclusions of the work;
- Chapter 8 presents future studies.

The present work was present in Fórum de Engenharia Química e Biológica 2019, held at the ISEL from 8th to 10th May 2019. The abstract and poster are shown in Annex A.

This work will be also presented to the International Congress on Environmental Health, entitled New challenges for the future, which will be held in Lisbon from 27th to 29th September 2019. The abstract can be found in Annex A.

Chapter 2

2. Carwash process description

2.1. Carwash phases

Carwash process involves four main steps which are: pre-washing, washing, finishing and drying, according to Brown in the International Carwash Association (2002) and to Good Practices Guide for Carwash Installations by LifeMinAqua (2016).

During **pre-washing** (Figure 1 a), the vehicle is sprayed with descaling products. They are specially designed to start eliminating the most stuck dirt which, at a later stage, will be removed with the help of mechanical brushes and high-pressure cleaning water. Often a product for tires is applied. The aim is to leave the vehicle ready for the next phase (leave the surface wet and ready for the application of detergents).

In the **washing** step (Figure 1 b), the vehicle is sprayed with a mixture of water and detergents through sprinklers. Its function, in addition to cleaning, is to soften the surface of paint, to maximize the later mechanical action of the brushes and to prevent scratches. A detergent known as “active foam” is applied; its aim is to create a dense foam that completely covers the paint. The foam ensures the cleaning action, because it slowly removes the dirt remaining on the surface, which makes the later rinsing easier. The washing phase includes also arches with brushes. There are different types of brushes that require a different amount of water (nylon brushes provide a good wash, but they need a lot of water and on the other hand require a minimum of detergent; textile curtains absorb plenty of water and use high pressure water).

The **finishing** step includes a rinse with clean water, usually tap water, which depending on its hardness, is usually treated to soften it or demineralized it. It is usually water that has passed through an ion exchanger and/or reverse osmosis. After the previous stages the vehicle is in the best conditions to be subjected to drying thanks to turbo fans or by gravity and waxing which, with its hydrophobic nature, reduces the surface tension of the rinse water. The water layer is broken and forms large droplets which are easily removed.

The last stage of the washing process is **drying** (Figure 1 c) the vehicle. It is optional and it is mainly offered in the roll-over type. Generally, it is done with blowers or turbo fans dragging the remaining water droplets on the vehicle surface.

Figure 1: Carwash steps: a) Pre-washing; b) Washing; c) Drying

The little difference for a trucks wash is the absence of the drying step as is possible notice in Figure 2.

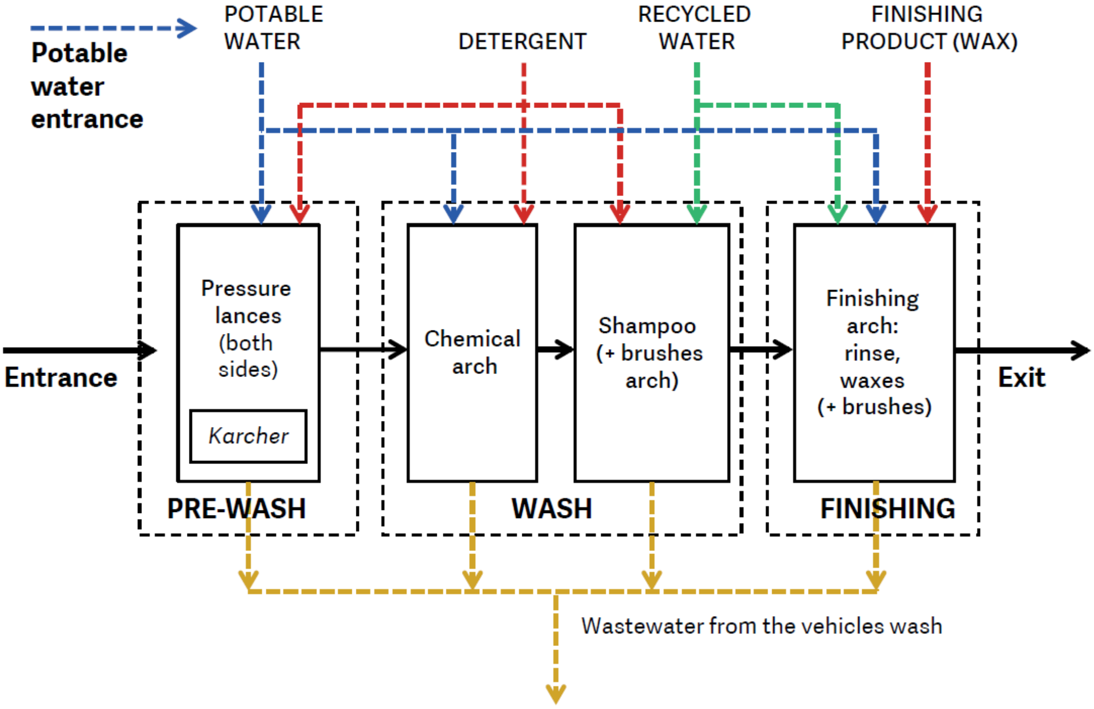


Figure 2: Flowchart of trucks cleaning phases (LifeMinAqua, 2016)

2.2. Cleaning system

According to the International Carwash Association - ICA (Brown, 2002), this industrial sector includes the automatic commercial services of car washing. ICA classifies them in three large groups: rollover, conveyor and self-service carwash, even if more systems exists like hand wash or lorries or trucks wash.

Rollover carwash system (Figure 3 a), it is a computer controlled washing system. During this process, the vehicle stays parked while the washing equipment moves back and forth on the rails, according to the program chosen. The washing uses brushes, textile curtains or frictionless washing with high-pressure sprayers. General stages of the washing process with detergents and finishing products are applied according to the program. It is the most used system for washing trucks, buses, etc. It is usually complemented with a manual prewash with pressure and hot water. The speed of a rollover car wash, depending on the programs and models, is usually about 8 to 12 vehicles per hour and 4 -5 trucks per hour.

Conveyor carwash system (Figure 3 b) is a computer-controlled system where the vehicle moves through a conveyor belt, whereas tunnel elements are fixed. There are three types of conveyor or in-bay automatic car wash: with nylon or PE brushes, with textile curtains and contactless or frictionless wash with high-pressure sprinklers. The entire washing process is usually carried out in cold water. A conveyor car wash may have capacity for 50-60 car/hour.

Self-service carwash system (Figure 3 c) equipment includes a compressor that propels water and equipped with two guns: one with a brush and the other sprays pressurized water. The car owner washes it using the machinery available. The owner can choose the washing cycle (several cycle are available at different prices), which will last more or less time: pre-washing, washing, rinsing and waxing. Unlike the rollover and conveyor car wash, the washing step usually expends warm water to ensure a good result. Self-service car wash machines do not dry, so this phase is outdoors. This system usually uses osmosis purified water for the rinsing stage to avoid lime stains from droplets. The washing capacity of a self-service car wash can vary and depends on the duration the customer's chooses, but usually the maximum capacity is 7 cars/hour (LifeMinAqua, 2016).

Figure 3: Carwash cleaning systems: a) Roll-over; b) Conveyor; c) Self-service

2.3. Environmental sustainability

2.3.1. Water consumption

The whole consumption of water in the vehicles wash industry mainly depends on the type of washing and on the vehicle (cars, trucks, lorries…). Table 1 shows water consumption according to type of car wash, expressed in liters per washing, it includes all washing stages. From Table 1 it is possible notice that a self-service system uses much less water and causes much more evaporation and losses per transport than a conveyor washing system. The range of values for the hand wash is due to how it is performed, with sponge, bucket, or a hose with adjustable outlet or if it is done with a hose and letting water flow throughout the process. Both the sources reported show the same value for the water consumption. Water consumption can vary a lot from one facility to another, especially in roll-over and conveyor car washes. The type of facility, the size of the vehicle and the program chosen by the customer (number of washing stages) affect it (Brown, 2002).

Table 1: Water consumption average for different types of car wash system

	Water consumption (L/washing)	
Washing type	**Huybrechts 2002; Janik, Kupiec, 2007**	**ECODEPUR® DEPURWASH, 2018**
Rollover carwash	100-350	250
Conveyor carwash	200-650	200
Self-service carwash	80-100	100
Lorry wash	350-900	800

Handwash	50-500	/

Many vehicle washing facilities are connected to the drinking water distribution network and make use of high quality water for all stages of the wash. The use of this water can be minimized using rainwater and recovered wastewater from washing to use it again in a new cycle. Drinking water is an increasingly scarce commodity, and every effort should be made to preserve the water reserves still available. Saving water means economic savings for today's generations (reducing drinking water consumption and wastewater disposal costs).

Nowadays the reuse of wastewater treated as a strategy to face growing water scarcity is one of the main challenges. In order to effectively contribute to the resolution of this problem, the modern technologies allow the treatment of the wastewater generated in the vehicle and machine wash operations, adapting the quality of the treated water to its reuse during the prewash and wash stages. Managing and optimizing water consumption has consequent reduction of the cost associated with the consumption of drinking water. The economic benefit achieved is based on the combination of several factors as reducing the number of cubic meters of water supply (less m^3 consumed), the tariff rating (consumption of less m^3 to a lower value of €/m^3 and also the value associated to the applied sanitation rate, since it is normally indexed to the amount of drinking water consumed (Zaneti *et al.*, 2012). Create a strategic water reserve, useful in periods of lack of water due to temporary interruption of supply (breaks, drought, ...) has technical advantages too. Reusing the treated wastewater has important implications also for the environment, because the level of pollutants released is reduced. Recycling water advantages and limitations are summarized in Table 2.

Table 2: Synthesis of implications of water recirculation in vehicle washing stations (LifeMinAqua, 2016)

Parameters	Description
Reduction potential	• The reduction potential of this measure is variable, reaching 50%
Benefits	• Reduction of public water consumption • Reduction of wastewater discharges
Limitations/ inconvenients	• Cost of acquisition, operation and maintenance of the water treatment equipment • Plus costs in consumables (detergents and other cleaning products),

	since their consumption is higher in stations with recirculation • Space requirement for installation of water treatment equipment • It is necessary to make at the municipal level an update of the regulation in order to establish the obligation of insulation of re-circulation in new stations and in the rehabilitation of existing units • Lack of municipal regulation that establishes the obligation, in periods of scarcity, to limit the operation of automatic washing stations that do not recycle

2.3.2. Chemical product

The car wash industry makes use of a wide range of products that can be grouped in three sets (LifeMinAqua, 2016): products to wash the vehicle (detergents) and finishing or polishing (waxes); products for maintenance and cleaning of the facility; products to treat wastewater and/or to control bad smells (if necessary).

Products to wash the outer part of the car can be divided in the following groups:

- Pre-washing product: intended for the most stuck dirt (gasoline residues, bird droppings, insects, etc.). These products are degreasing and descaling and are generally alkali in liquid (sodium hydroxide is the most common component in these formulations). Its concentration varies depending on the application (in tires, car bodyworks, trucks, etc.) and its application form (spray, high-pressure, manual sprays, etc.);
- Washing product: according to the Regulation EU No 259/2012, amending Regulation EC 648/2004 on detergents, detergents are defined as “any substance or mixture containing soap or other surfactants used in washing and cleaning processes. Detergents can be of any type (liquid, powder, paste, etc.)”. The active ingredients of detergents are surfactants, organic substances or mixtures used in detergents having certain properties such as: detergent (to detach the layer of dirt); foamy, with solubilization capacity; emulsifier (they surround fat particles, so they lose adhesion with the metal surface, allowing dirt to be easily removed); moisturizing and dispersing. Cleaning products tend to be pH neutral or slightly acidic. The type and concentration will also depend on the stage of the washing and how they are applied (shampoo arch,

active foam arch, brushes arch, high pressure sprinklers, etc.). Figure 4 shows the components in a detergent formulation, according to Sánchez (2007). Although surfactants are the fundamental ingredients of detergents, they are not enough. As shown in Figure 4, a wide range of other agents is required to help to improve the role of surfactants and a number of agents to complement them. These additives may be pollutants to water and the environment;

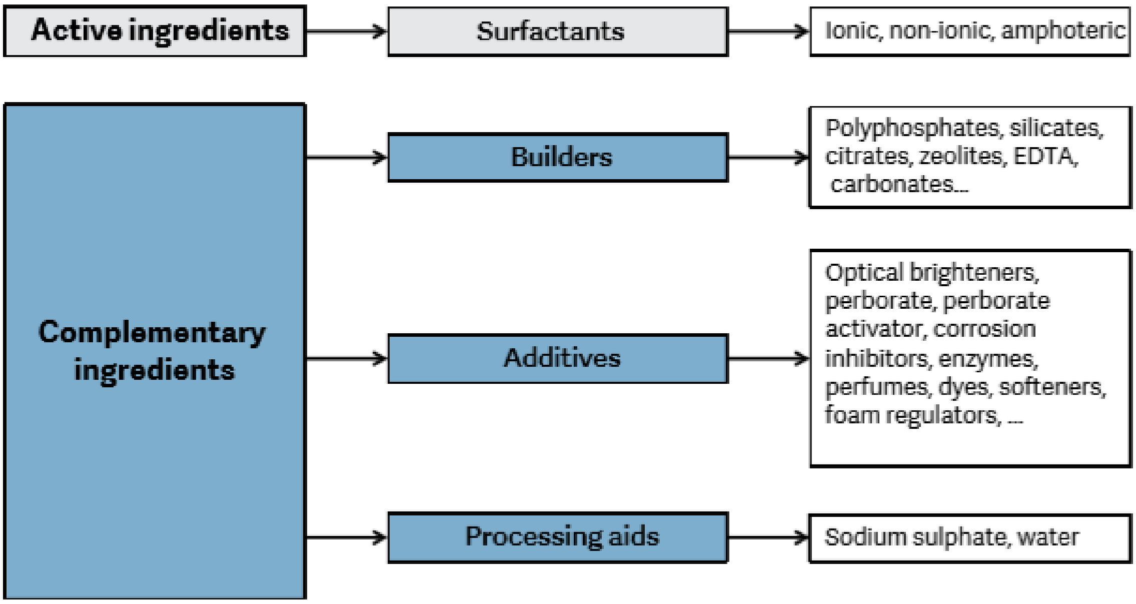


Figure 4: Detergent formulation components (Sánchez, 2007)

- Finishing or polishing products: they are applied to the vehicle, on its cleaned surface after the washing stage. To achieve a bright and long lasting finish, waxes or other polishing products are applied. After this step, waste is removed with a rinsing application which often employs osmosis-purified water. The finishing products can be formulated in the form of pastes, liquids or sprays and contain some of the following components (Company *et al*., 2007):
  - Waxes for the polishing of surfaces, they give strength and bright to paint, improve opacity and provide lubrication and durability. The most used waxes are paraffins, polyethylene, carnauba, microcrystalline and mixtures;
  - Abrasives to polish and remove traces of tar and other substances strongly adhered and for small imperfections on the bodywork. They usually contain tiny particles of clay or similar materials, soft calcium carbonate, silicone, aluminum silicates, etc;

- Emulsifiers, generally used to mix detergents together with dispersants, thickeners and preservatives. They include fatty alcohol ethoxylates, sorbitan esters, fatty acid soaps and polydimethyl siloxane ethoxylates, among other components;
- Silicones and derivatives improve the resistance and enhance the shine of the protective coating. They are mainly polydimethyl siloxanes;
- Solvents have a double function as a base for waxes, silicones and other components, and as a help in cleaning dirt and oils. Making use of them is important to avoiding damage to the paint and plastic elements. The water insoluble solvents, such as aliphatic hydrocarbons, are the most used ones;
- Thickeners are needed to keep abrasive materials in suspension in low viscosity formulation. Some of the most typical thickeners in polishes are cellulose ethers, magnesium aluminium silicate and carbopol resins.

Differences between the finishing and polishing products, which must ensure proper drying and brightness, are mainly in their durability and sustainability.

Products to clean the facility: all products used to clean the washing equipment and facilities (flooring, supports, toilets, etc.) will get into urban wastewater treatment, so they do not influence the pollution of the vehicle wash system.

Products to treat wastewater and/or control bad smells: in facilities where water is reused, additives or other products can be used in order to have the right quality. Depending on the technique used, these products can be (Company *et al*., 2007):

- Flocculants: It contains, among others, inorganic salts, polyelectrolytes and bentonite. This ensures that dirt particles join each other in flakes, they can quickly decant and be ready to be filtered (physicochemical treatment);
- pH regulators;
- Anti-foaming. This They reduce the formation of foam in the recycling system;
- Products to control odor in water recycling. These substances can be deodorants and, especially, antibacterial agents such as hydrogen peroxide or sodium hypochlorite. Applying the correct dose is very important.

All products mentioned are applied with water and will get into the sewage system and so into the aquatic environment. Some of the impacts these products may cause are (Sánchez, 1995):

- Surfactants are toxic substances which can accumulate in the aquatic environment. These substances are organic compounds, that can degrade in the environment with consume oxygen and cause anoxia. They can also inhibit biological and chemical oxidations, which produces, in highly contaminated water, low levels of Biological Oxygen Demand (BOD). This phenomenon is due to the fact that, in the presence of detergents, bacteria are surrounded by a layer of detergent that isolates them from the environment and prevents its activity. Beside surfactants, detergents have other components which may cause eutrophication;
- Formation of unwanted foams (depending on the kind of surfactants and additives). Generally, anionic surfactants produce a lot of foam, cationic surfactants produce it in limited quantities and nonionic surfactants produce just a bit. Foam is promoted, basically, to produce a visual effect to the client, but too much foam can be harmful for treatment plants and rivers. They have effects on coagulation and sedimentation and inhibit them in wastewater treatment plants. They also increase wastewater alkalinity and can reach pH over 12, caused by caustic soda or potash;
- Pollution of underground waters (not frequently); surfactants are usually absorbed in solids and are kept in the soil. These impacts may worsen in self-service car wash facilities where there is no permanent staff and the operator has little control over the quality of the generated wastewater.

In the ecological evaluation of surfactants for industrial use, the fact that aquatic biodegradation and toxicity are contradictory must be taken into account. Longer chain carbonate means higher toxicity instead the less branched suits better biodegradation (Sánchez, 1995). From an ecological point of view, it should be better select surfactants that degrade completely and as quickly as possible.

Nowadays, more and more manufacturers take into account biodegradation (since it must meet European regulations, Directive 73/404/EEC) and short term emulsifying action (important for the proper functioning of the hydrocarbon separator). It would be interesting that, for the proper functioning of any unit of water recycling, the finishing products are free of silicones, mineral oils and hydrocarbons (if they are not, waters must often be collected with finishing products, separately to the rest of the washing waters). It is noteworthy to know that in the Netherlands and in Scandinavia there is a specific Ecolabel for car washing products (Nordic Ecolabelling, 2000; Stichting Milieukeur, 2001).

2.3.3. Wastewater generation

A carwash plant produces effluents, mainly liquid and solids. One of the main effluent generated in car washing facilities is wastewater. Depending on the water consumed (as facility type and number of vehicles washed), a flow of wastewater of similar dimensions is generated. This flow will be slightly lower than water consumption in the washing facility, because of losses of about 10 liters in cars and 25-30 liters in trucks, for evaporation and dragging by washed vehicles (Huybrechts *et al*., 2002). If this effluent is not treated and reused, it is discharged from the facility through a sewage system or released into the environment. This type of activity requires prior discharge authorization, and in no case, it can be discharged without a proper pretreatment according to the type of permission of the facility. Generally, if the discharge is done into a municipal drainage system, the treatment includes solid sedimentation and hydrocarbon separator. If the discharge is done into the receiving environment, a higher treatment (usually biological) is needed to achieve the required discharge limits (LifeMinAcqua, 2016).

The composition of wastewater is different from one type of vehicle washing to another. The substances present in a wastewater can be classified according to their nature in four categories: floating, suspended, dissolved and biological. The floating substances are oils, fats, foams, in general the insoluble compounds lighter than water. These substances deteriorate the aesthetic characteristics of water, interfere with natural re-creation and prevent the penetration of solar radiation. The suspended substances are those insoluble with a density equal to or greater than that of water. These substances depress the purifying action of microorganisms. In low flow velocity these substances can settle on the bottom and if of an organic nature they go against putrefaction phenomena. Dissolved substances represent the largest category. There are organic and inorganic substances refractory to biological or chemical oxidation, salts (bicarbonates, sulphates, chlorides ...), cyanides and heavy metals, that seriously damage the aquatic ecosystem. Table 3 shows the average composition of domestic wastewater and vehicle washing wastewaters. As can be observed in Table 3 the vehicle washing wastewaters may have a higher pollutant concentration, for example Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD). These parameters resulting from a conveyor carwash can reach respectively 5400 mg/L and 1450 mgO_2/L for the TSS and the COD way more higher than the same parameters for a domestic wastewater, even if in some cases, as the one reported by LifeMinAqua case study can happen that the values are lower than the one for a domestic water according to the age and degree of grime of the vehicle.

Also, the vehicle washing wastewaters usually have more metals (Table 4) due to vehicles components wear (e.g. tyres and breaks). Heavy metal can be are very dangerous due to the toxicity. Several metal studies evaluate the threat and the health risks associated with it (Jaishankar et al., 2014).). Table 4 reports the concentration for several heavy metals that is possible found in wastewaters generated in different stations. For example copper concentration range is between 0.04 and almost 0.7 mg/L, while the zinc varies from 0.1 to 0.7 mg/L.

Table 3: Composition of domestic wastewater and vehicle wash wastewaters

Parameters	Units	Domestic wastewater (Tchobanoglous *et al*., 2003)	Conveyor carwash (Huybrechts *et al*., 2002)	Conveyor carwash (LifeMinAqua, 2016) mean values	Full Hand service carwash (Hashim and Zayadi, 2016)	Self-service carwash station, (Brown, 2002)
TSS	mg/L	120-400	310-5400	37.23	/	/
BOD_5	mg/L O_2	110-350	/	52.67	/	/
COD	mg/L O_2	250-800	20-1450	127.33	190	890
Sulphates	mg/L SO_4^{2-}	20-50	/	11.33	/	/
N tot	mg/L N	20-70	/	3.03	/	/
P tot	mg/L P	4-12	0.7-5.9	1.01	7.05	0.87
Nitrites	mg/L NO_3^-	0	/	0.05	0.13	/
Nitrates	mg/L NO_2^-	0	0.7-1.6	0.6	0.29	/
N – Kjeldahl	mg/L N	8-25	≤2-22	2.90	21.53	5.01
Fats and oils	mg/L	50-100	/	0.97	68	60
Escherichia coli	UFC/100 ml	10^3-10^8	/	10^3	/	/

Table 4: Results of metals in vehicle washing wastewaters

Parameter	Carwash Stubble, Mol[1] (mg/L)	Best carwash, Tienen[1] (mg/L)	Hasselt Carwash, Gent[1] (mg/L)	Texaco Carwash, Gent[1] (mg/L)	Phoenix sites[2] (mg/L)	Florida sites[2] (mg/L)	Boston sites[2] (mg/L)	LifeMin Acqua Pais Basc[4] (mg/L)
Arsenic	bdl	bdl	bdl	bdl	0.007	bdl	bdl	<0.05
Chromium	0.039	bdl	0.037	0.004	bdl	bdl	0.0688	/
Copper	0.450	0.043	0.657	0.127	0.119	0.235	0.1927	0.11
Mercury	bdl	bdl	bdl	bdl	bdl	bdl	bdl	<0.1
Nickel	bdl	bdl	0.01	bdl	bdl	0.03	0.0303	<0.02
Lead	0.057	bdl	0.113	0.006	0.016	bdl	0.061	<0.02
Zinc	0.71	0.123	0.807	0.304	0.31	0.308	0.6772	0.1

[1]Tchobanoglous (2003); [2]Brown (2002); [3]Smith *et al*. (2009); [4]LifeMinAqua (2016); bdl: below the technique's detection limit

2.3.4. Typical carwash wastewater treatment process

In general, the carwash wastewater treatment process includes the collection of the wastewater, a pre-treatment, a purification process and, finally, a disinfection or addition of clean water before being applied to a new car washing cycle; the water which does not enter into the recycling circuit can be discharged into the sewerage system or into the environment (if it is in the environment, it can be due to the lack of a bigger treatment of the water to discharge because the emission limit values for the discharge in the environment are more restrictive than the one in the sewage as will be explained in chapter 3) (Figure 5). The water which does not come into the recycling circuit can be discharged into the sewerage system or into the environment. From an engineering point of view, depuration of wastewater from carwashes depends largely by how the activity is managed and by their objectives: the minimization of energy through devices that allow to use the bare minimum of electricity; the use of biodegradable detergent products, which allow a biological treatment of the wastewater; minimization of sludge from the purification treatment and the reuse of purified water (Huybrechts *et al*., 2002).

The wastewater plant solutions usually involve the use of physical, chemical-physical and biological treatments, and of all the possible combinations capable of removing decantable materials, mineral greases, oils, non-emulsified hydrocarbons, detergents and metals.

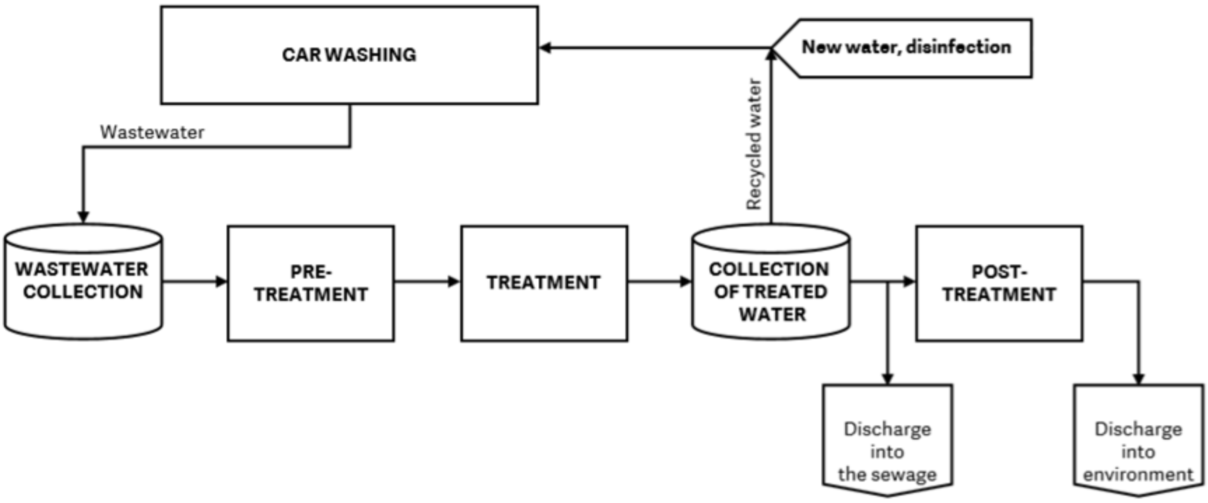


Figure 5: General circuit of wastewater treatments and recycling in carwash (Huybrechts *et al*., 2002)

One of the most applied physical treatment is **sedimentation**. Sedimentation treatment can consist of a series of sedimentation tanks, made in PVC, underground or not. In these tanks the wastewater follows a path through which solid fractions such as earth and sand are separated (grit removal). The particles settle at the bottom due to the gravity force, because particles density is superior to that of water (Metcalf and Eddy, 2003). Then the clarified water proceeds to the next treatment unit.

There are different settling basins and their volume has to be adequately scaled. In the car wash facilities, the settling tanks can be cylindrical or rectangular. In general, the decanters are connected in series, depending on the volume of wastewater generated.

It is a simple technology, without mechanical or electrical components and enforceable parts of settling solids, oils and fats, and COD (Huybrechts, 2002). Montfullà's carwash station, analyzed by LifeMinAqua (2016), has three decanters in series, thanks to which can reach elimination percentages were of 80% for suspended matter, 11% for oils and fats, and 45% for COD. This kind of unit has some limitations as the removal and treatment of the sludge require an authorized agent. It is unable to separate small particles. The efficiency is limited when it removes nutrients, detergents and heavy metals.

The settling basins, together with the oil and fat separators, are very spread technology in this field (gas station, car washing, etc.). In fact, it is the minimum technology necessary to be able to discharge into the sewer system (pretreatment). The investment cost will depend on the settling tank type and its capacity. The operation cost and maintenance increase due to the fact that the sludge accumulated has to be collected and treated (the cost is pretty high and it oscillates between 120 and 150 €/tone (transportation aside) (Tchobanoglous *et al.,* 2003; Balaguer *et al*. 2007; Al-Odwani *et al*. 2007).

Flotation is another solution widely used for the removal of oily substances, it is performed by hydrocarbon separator or flotator, coalescence de-oilers, in which the separation of the oily fraction takes place through a filter, (which it can be made of polypropylene, polyethylene, polyester, fiberglass, etc.) taking advantage of the differences of specific weight and coalescence, or the different surface tension of oils compared to water. The oily substances rise to the surface, while the clarified water below passes through the filter entering the outlet pipe. The separation is usually conducted statically: by sedimentation and flotation (Metcalf & Eddy, 2014).

The functionality is simple the influent arrives from the settling tank and due to the difference in density between oils and lipids, the lipids are separated by flotation and settling at the top. The clean water is evacuated through a siphon or a baffle and sent to further purification stages or to the sewer system. Generally, the conventional oil separator consists of a decantation part and another one in which the floating oil is captured. In gas stations, carwash stations, the coalescing hydrocarbon separators are majorly used. Flotators are distinguished for a great retaining capacity thanks to its active surface.

This technology is simple and does not have mechanic or electric components. Its weakness is that it produces waste that must be processed through an authorized consultant with consequent high cost. It is the minimal technology required for the pretreatment, so that everything can be dumped to the sewer system. This technology is required in any water pretreatment system for a carwash. It is important to make sure that they will be able to obtain the required emission limits that the legislation establishes both for the discharging system and the environment (LifeMinAqua, 2016, Al-Oldwani *et al*. 2007).

The treatment may include a **biological reator.** The biological treatment of wastewater is a process designed to eliminate the organic matter, both dissolved and suspended; oxygen is introduced into the wastewater, allowing the transformation of polluting organic substances and their degradation by a series of enzymes that feed on organic matter, creating at the base of the tank a deposit of sludge (activated sludge) which, favors the further proliferation of bacteria. The conditions to improve the microorganisms' growth are enhanced. These use organic wastewater as a substrate (aerobic treatment). In such a way the microorganisms grow and reproduce and generate sludge. A fraction of sludge has to be eliminated from the system when an undesired amount is reached. The biologic treatment can remove some of the nutrients (nitrogen and phosphorous which will have been used by the microorganisms), heavy metals and xenobiotics (Metcal & Eddy, 2014).

The biological treatment can be classified in suspended, fixed or hybrid system depending on where microorganisms grow. In order for the biological depurating process to take place, it is important to provide enough oxygen and, furthermore, ease the contact between the organic matter (substrate) and the microorganisms (biomass) in order to boost the reactivity, to give enough contact time and to avoid that there are inhibitor effects of the microbial metabolism due to the action of toxics which are present in excessive concentrations (Istoba and Rowafil, 2000).

The limitation of this technology is that it is necessary that the carwash facility uses biodegradable cleaning products, since the microorganisms are sensitive to toxic substances (LifeMinAcqua, 2016). It is necessary to provide additional energy consumption for the oxygen contribution provide by mechanical agitators or air injectors. The biological degrading velocity is influenced by the temperature. At low temperatures (< 12°C) there may be a decrease in the depurating efficiency. A high hydraulic retention time is required to assure the organic matter degradation.

Generally, the biological treatment is the most efficient and economical method to eliminate organic pollution of the effluents. Some applications of biological treatment have been developed for the carwash industry, which are compact and efficient (Van der Werf, 2000). It can be a required treatment technology if the discharge is into the receiving media. In order to reclaim wastewater from carwashes, further treatment can be required (Istobal and Rowafil, 2000). Moreover, a research regarding recycling carwash wastewater was carried out using a membrane bioreactor (MBR) and the result was very satisfactory as 99.2% COD was removed (Boluarte *et al*. 2016).

Finally, the **filtration** can be installed downstream of the treatment for the physical abatement of the residual polluting load of an already treated wastewater. Wastewater generally pass through a filtering mass of sand of different grain size for the removal of suspended solids. The filtration system consists of various sand layers with a determined granulometry. The particles that are bigger than the portions will be retained among the sand particles. Subsequently the wastewater goes to granular activated carbon filter for the filtration and absorption of the remaining traces of hydrocarbons or any solvents.. Usually, it is an automatic process.

In order to ensure a successful outcome or increase the performance, some coagulant - flocculants reagents can be used (previous dosage to the sand filtration) and chlorine (after the sand filtration in order to disinfect water and prevent bad odors). A pH between 6.8-7.8 it is required when using coagulants and flocculants reagents.

It is a simple physical process with a simple procedure. The maintenance cost is low. In conventional sand filter all the polluting substances are accumulated in the upper part, which limits the filtering capacity. It is important to configure the filter in order to: make the sand filter, avoid preferential paths, avoid obstructions. The color of this water is often gray, even retained a lot of particles (up to 25 µm) (LifeMinAqua, 2016). In carwash wastewater treatment plant the filtration stage is usually implemented after a pretreatment (Flocculation – flotation - sand filtration (Zaneti, Etchepare and Rubio, 2011)) or biological stage. Depending on the purifying water has to meet, after the sand filter, an active carbon filter, reverse osmosis or an ion exchange equipment can be added (this is more expensive, but necessary if more quality is required. It is always implemented after a previous sand filtration). It is a strong and frequently used method. It is highly recommended for facilities with high wash frequency or for large vehicles washing systems. It lets reuse up to 85% of the water from the wash. (Lenntech, Wasthec, 2016).

Nowadays more advanced kind of filters are used as membrane filters or reverse osmosis membranes. The reverse osmosis equipment consists of a semi-permeable membrane's unit through which the water flow that needs to be treated is introduced. Two effluents are generated: one presents a high salts concentration and it is called reject (or concentrate) stream, while the other one presents a low salts concentration and it is called ultra-filtrated or permeated. Currently, membranes are made of polyamides. In the market, the reverse osmosis devices are divided into units inside of which there are the membranes. In general, reverse osmosis is applied to the tap water that is used for the vehicle final rinse. If so, a sequence of operations should be conducted to provide proper functioning of the reverse osmosis. First tap water should be conditioned, to dechlorinate and decalcify. Then, the water goes through a micro filter in order to protect the membranes from suspended particles that are bigger than 5 µm (or bigger than the size required by the osmosis membranes). High quality water is obtained for the final rinse (more than one obtained by the ion exchange). The volume of the rejected stream will depend on the membrane type (between 40 and 70%). The investment and energy consumption costs are high.

The membrane system maintenance is complex. It is mainly used in conveyor and rollover car washes. It is also used in self-service car washes (Pedrol *et al*. 2010, Boussou *et al*. 2008). A study investigated the e performance of granular and membrane filtration systems with coagulation/flocculation and sedimentation in treating carwash wastewater for the purpose of reuse shows that the reduction of suspended solids from carwash wastewater was very high after coagulation and sand filtration treatment, 92% and 96% suspended solids were removed, respectively. After treating with ceramic ultrafiltration membrane and reverse osmosis, the removal percentage of suspended solids from car wash wastewater was almost 100%. Carwash wastewater contains different types of chemical substances from detergents, oils, grease and to tires contributing to its COD. Thus, the COD must be analyzed and reduced in order to reuse the treated car wash wastewater. It is observed that the COD of raw car wash wastewater was 295 mg/L, but sand filtration and ceramic membrane could not be able to reduce any significant COD. But after treating with reverse osmosis, 96% COD was removed. In this study, the initial concentration of copper and zinc in car wash wastewater was 1.2 and 0.53 mg/L, respectively. After sand filtration and ceramic ultrafiltration membrane there was not effect on the removal of heavy metals. However, after passing the pre-treated car wash wastewater through reverse osmosis, the copper and zinc were removed completely (Moazzem *et al*. 2017).

The ultrafiltration principle (UF) is based on the separation of dissolved particles through to a selectively permeable membrane. The ultrafiltration is used to separate suspended solids, colloidal particles, bacteria that measure between 1 and 100 nm. The UF is also used as a reverse osmosis pretreatment (it would be a treatment between the microfiltration and the reverse osmosis). It runs the same way as the reverse osmosis, but the membrane features are different. The ultrafiltration offers a great water treatment at a molecular scale. Depending on the size of the membrane pores, some detergents can go through them (20-30%) and they can get stuck at the permeate (in the water already purified). Therefore, they will be available for a new washing cycle. The process produces waste in a stream called concentrate (approximately, it is the 10% of the water volume that goes through the membranes). This concentrate contains all the polluted components that the membranes have retained and can be treated in a biological depuration system. There are some studies that have done some research in this field (Colen, 2002; Boussu *et al*. 2007). This kind of filtration system requires expert maintenance. The UF can be applied as a decalcification treatment, heavy metals removal and reduction of the salt content in wastewater. For the vehicle wash, it gives a higher quality than the majority of the processes in which the water is recycled (Boussou *et al*. 2007, Kiran *et al*. 2015, Lenntech b). In carwash wastewater, COD was mostly originated from the use of detergent and dirt from carwash, therefore, to promote best practice within carwash industry, it is recommended to minimize water used for each car washing and use only biodegradable cleaners. With respect to COD retention, UF membranes in literature study have within 90-95 of % rejection. It passes from 700 mg O2/L in the raw wastewater to 33.3 mgO2/L after the ultra-filtration system at 1 bar (Istirokhatun *et al*., 2015).

Downstream of the purification plant for car washes it is possible, usually is inserted a storage tank for collect the purified water and recirculate and reuse it. In Figure 6 is shown a typical carwash wastewater treatment plant (ECODEPUR®)

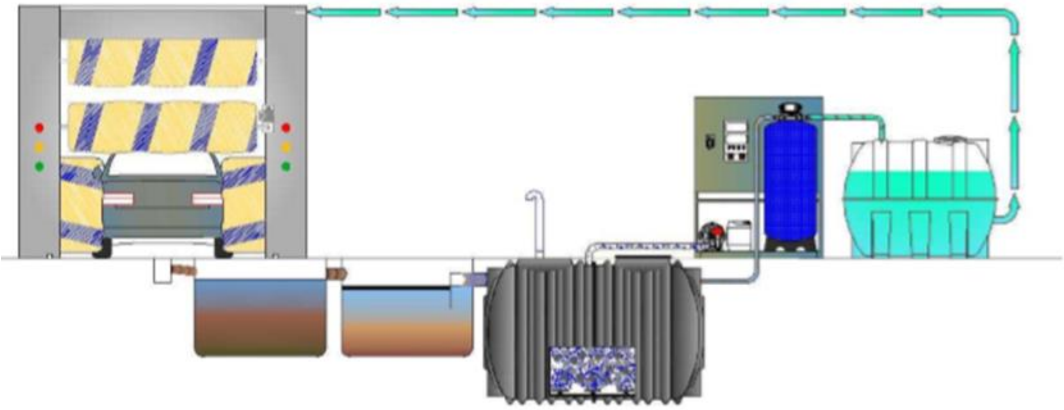


Figure 6: Carwash station treatment plant (ECODEPUR® DEPURWASH, 2018)

In Table 5 shows the COD of carwash wastewater after different treatments, as it can be observed the removal efficiency goes from 51 to 93%.

Table 6 presents the carwash wastewater characterization after treatment, with different technologies, in terms of pH, COD and TSS.

Table 5: COD of carwash wastewater after different treatments

Technology applied	COD Influent (mgO_2/l)	COD Effluent (mgO_2/l)	COD Removal efficiency %	References
Flocculation-flotation (FF)	683	332	51	Etcheparea *et al*., 2014
Flocculation-flotation-ozonation (FFO)	683	96	86	
Coagulation-flocculation-ozonation (CFO)	433	141	67	Boularte *et al*., 2016
Flocculation-column-flotation (FCF)-sand filtration (FCF-S)-chlorination (FCF-SC)	213	96	55	Zaneti *et al*., 2011
Aeration- coagulation (alum)-hydrogen peroxide (oxidant)	1019	80	93	Bhatti *et al*., 2011
Electro-coagulation (EC)	560	68	88	Gonder *et al*., 2017

Table 6: Characterization of treated carwash wastewater

Technology applied	pH	COD	TSS (mg/L)	References

		(mgO_2/L)		
FF	6.7-7	129-536	2-50	Etcheparea *et al*., 2014
FFO	6.9-8.2	12-167	0-49	
Oil-water separator	6-6.6	249-873	85-279	
EC process with Fe electrodes	8	68	230	Gonder *et al*., 2017
Flocculation using Moringa oleifera	5.5-9	100	50	Al-Gheethi *et al*., 2015

2.3.5. Sludge

The main solid waste generated in the vehicle washing is sludge. It mainly comes from, sedimentation tanks and hydrocarbon separators. If the facility has a water recycling plant, sludge will also accumulate at some points. The amount and composition of sludge depend on the type of cleaning products used, the degree of dirtiness of the washed vehicles and on the treatments applied to the wastewater. Sludge must be collected and treated by an authorized waste manager (Brown, 2002). In the present case study the amount of sludge produced is low and because of the youth of the ECODEPUR® treatment plant, after one year from the installation, the sludge has not yet been removed.

2.3.6. Energy

Generally, the energy cost represents 15 to 40% of the total cost of operation of the wastewater treatment plant (Soares *et al*., 2017). Energy cost in washing facilities is mainly attributed to three aspects (LifeMinAqua, 2016):

- Car washing equipment that includes brushes operation, the movement of the car thanks to the conveyor belt, pumps, blower, etc;
- Hot water production required for washing. Generally, conveyor car washes completely work with cold water, whereas rollover truck washes with pre-washing often

use hot water. As for the self-service car wash, pre-washing or washing phases usually use warm water;

- In automatic car washes, most of the energy is consumed in drying stage, as it uses blowers or turbofans.

With pumps, motors, and other equipment operating 24 hours a day, seven days a week, wastewater facilities can be among the largest consumers of energy in a community and thus among the largest contributors to the total GHG emissions (USEPA, 2013). The energetic consumption values for wastewater treatment plants using different technologies is presented in Table 7.

Table 7: Energetic consumption values for wastewater treatment plants using different technologies

Technology apllied	Energy cost (€/m^3)	Energy consumption (kWh/m^3)	References
FFO	0.64	8.97	Etchpare *et al.*, 2014
FFC	0.12	1.68	Etchpare *et al.*, 2014
FCF	0.37	5.19	Zaneti *et al*, 2011

These economic and environmental costs can be reduced by improving the energy efficiency of wastewater facilities equipment and operations, allowing the same work to be done exploiting less energy, and by promoting the efficient use of water, reducing demand for water turns into decreasing the energy consumption needed to treat and distribute water (USEPA, 2013).

For improving energy efficiency operators are focusing on three areas:

- Equipment upgrades: regards replacing items such as pumps and blowers with more efficient models;
- Operational modifications: involves decreasing the amount of energy required to perform specific functions. Typically, operational modifications result in higher savings than equipment upgrades, and may not require capital investments (USEPA, 2002)
- Modifications to facility buildings concerns with installing energy efficient lighting, windows, heating and cooling equipment, and with using renewable energy sources as solar and wind energy. Solar power in car washing includes one or more solar panels on the building's roof to heat the water for vehicle washing. It significantly reduces CO2 emissions and natural gas consumption (Janik and Kupiec, 2007).

Improving energy efficiency in wastewater facilities has environmental and economic benefits as reducing air pollution and GHG emissions by decreasing consumption of fossil fuel-based energy.

Chapter 3

3. Environmental legislation

3.1. European framework

Water is an essential element for human, animal and plant life, as well as for the economy. Protection and management of water resources go beyond national borders. The European Water Framework Directive establishes a legal framework to protect clean water and restore water quality in the EU, as well as to ensure its sustainable and long-term use. It is regulated by more specific rules, such as the Drinking Water Directive and the Bathing Water Directive, the Environmental Quality Standards Directive the Marine Strategy Framework Directive as well as international agreements.

The water framework directive, it requires the establishment of a list of priority substances that present a significant risk to the aquatic environment or from the aquatic environment itself at European level and a subset of priority hazardous substances. The directive on environmental quality standards has consequently set concentration limits for 33 priority substances and 8 other pollutants present in surface waters (Annex 10 of Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000). During a further review, 12 new substances were added to the existing list and the obligation for the Commission to establish an additional list of substances for which monitoring is required in all Member States (list of control) in order to facilitate future revisions of the list of priority substances.

Directive on Integrated Pollution Prevention and Control (Directive 96/61/EC), known as Directive IPPC has as goal the integrated treatment of industrial emissions of pollutants (air, water and soil) and their minimization according to the Best Available Techniques (BAT), which determine the emission limits of pollutants which is necessary to set to authorizations or to pertinent permissions of an industrial installation use. This Directive was integrated into the new Directive on industrial emissions (integrated pollution prevention and control), known as Directive IED (Directive 2010/75/UE). Regarding detergents and applied products is present the legislation Regulation 648/2004 of the European Parliament and of the Council of 31 March 2004. This regulation contains the aspects about the limitation based on the biodegradation of surfactants; limitations of the content of phosphates and other phosphorous compounds; surfactants tests and several annexes about that.

Directive 91/271/EEC – The Urban Wastewater Treatment Directive concerns the collection, treatment and discharge of urban and industrial wastewater and was altered by Directive 98/15/EC. The aim of the Urban Wastewater Treatment Directive (UWWTD) of 21 May 1991 is to protect the environment from the adverse effects of wastewater discharges. Urban wastewater is considered any domestic wastewater, mixture of domestic and industrial wastewater, and/or runoff or rainwater. The directive sets out guidelines and legislation on how urban wastewater is collected, treated and discharged. The directive requires that all European agglomerations with more than 2000 population equivalents are equipped with collecting and treatment systems for their wastewaters. According to Article 4 of UWWTD, the basic level of treatment is secondary treatment (i.e. removal of organic pollution) whereas in sensitive areas, a more stringent treatment is required (for instance, the removal of nutrients which are responsible for eutrophication). Article 5 concerns with the timetable for implementation of the directive, which depends on the sensitivity of the area into which wastewaters are discharged and the population equivalents served.

3.2. Portuguese framework

The Decree-Law no. 236/98, article 64, sets the discharge rules for each installation, by the territorially competent DRA (regional management of the environment or regional environmental directorates), taking into account the general discharge rules set out in Annex XVIII (Table 8). It regards also the short, medium and long-term environmental objectives established by the water resources plans and specific programs for each substance, group, family or category of substances in force for the receiving environment. It highlights the conditions contained in an agreement for environmental adaptation or promotion established and the sectorial standard of discharge applicable to them, for discharges from installations covered by this agreement. For the installations covered by the contracts provided for in Articles 68 and 78 of this Decree-Law, the standards contained in the respective contracts shall apply to the parameters in Annex XVIII.

Table 8: Emission limit values in surface water and sewage (Decree-Law no. 236/98, Annex XVIII)

Parameters	Units	Discharge in surface water	Discharge in sewer
Ph	Sorensen scale	6-9	
Temperature	°C	3°C more	
Color	mg/L Pt-Co scale	Non perceptible with dilution 1:20	Non perceptible with dilution 1:40
Odor		It must no cause harassment	It must no cause harassment
Coarse materials		Absent	Absent
TSS	mg/L	60	≤200
BOD_5	mg/LO_2	20	≤250
COD	mg/LO_2	150	≤500
Al	mg/L	10	≤2
As	mg/L	1	
Cd	mg/L	0.2	≤0.02
Cr tot	mg/L	2	≤4
Cr VI	mg/L	0.1	≤0.2
Fe	mg/L	2	≤4
Mn	mg/L	2	≤4
Hg	mg/L	0.05	≤0.005
Ni	mg/L	2	≤4
Pb	mg/L	1	≤0.3
Cu	mg/L	1	≤0.4
CN	mg/L	0.5	≤1
Active free Cl	mg/L	0.5	≤0.3
Sulfides	mg/L	1	≤2
Sulfites	mg/L	1	≤2
Sulphates	mg/L	2000	≤1000
Fluorides	mg/L	≤6	≤12
P tot	mg/L	10	≤10
NH4	mg/L	10	≤30
Nitrates	mg/L	50	≤0.6
N tot	mg/L	15	≤30
Animal/plant fats and oils	mg/L	15	≤40
Phenoli	mg/L	0.5	≤1
Aldehydes	mg/L	1	≤2
Mineral oils	mg/L	15	
Total surfactants	mg/L	2	≤4

Escherichia coli	UFC/100 mL	Known	-

The European UWWTD was implemented as Portuguese national law through Decree-Law no. 152/97 of 19 June, later altered by Decree-Laws no. 348/98, 149/2004 and 198/2008. Law no. 348/98 of 9 November corresponds to Directive 98/15/EC, which clarifies the rules relating to discharges from urban WWTPs in sensitive areas subject to eutrophication and defines the concentrations or the minimum percentage reduction for total phosphorus and total nitrogen. Table 9 reports the legal requirements for discharges of UWWTD in no sensitive areas. If the discharge is in sensitive area, the emission limit value are the one presented Table 10.

Table 9: Emission limit values of urban wastewater discharge (Decree-Law no. 152/97)

Parameters	Concentration	Minimal percentage of reduction
BOD_5	25 mgO_2/L	70-90%
COD	125 mgO_2/L	75%
TSS	35 mg/L	90%

Table 10: Emission limit values of urban wastewater discharge (Decree-Law no. 152/97)

Parameters	Concentration	Minimal percentage of reduction
Total P	2 mgP/L	80%
Total N	15 mgN/L	70-80%

Decree-Law no. 103/2010 of 24 September 2010 envisages water resources and, in particular, water quality as a priority area for environmental policy. Pollution of surface water poses a threat to the environment, human health and people's quality of life. This Decree-Law transposes Directive 2008/105 / EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy into the internal legal order.

Environmental quality standards (EQS) aim to control pollution by establishing maximum levels of concentration of certain substances in water, sediment and biota, which must not be exceeded for the protection of human health and the environment. This Decree-Law establishes environmental quality standards (EQS) for priority substances and other pollutants identified respectively in Annexes I and II of this Decree-Law, of which they form an integral part, with a view to ensuring the reduction pollution caused by priority substances and achieve good surface water status, in accordance with Article 46 of Decree-Law no. 58/2005 of 29 December, hereinafter referred to as the Water Law, and transposes into the legal system Directive 2008/105 / EC of the European Parliament and of the Council of 16 December on environmental quality standards in the field of water policy. This Decree-Law also lays down the technical specifications to be observed by laboratories with regard to quality assurance of analytical results and methods used for the analysis and control of priority substances and other pollutants in surface water, sediment and biota, partially transposing into national law Commission Directive 2009/90 / EC of 31 July laying down technical specifications for the chemical analysis and monitoring of water status.

The administrations of hydrographic regions (ARH) shall apply to the surface waters covered by this Decree-Law the EQS for the priority substances. The monitoring of the substances shall be carried out at least once a year, unless technical knowledge or expert analysis justifies another frequency. It is the responsibility of the Water Institute, IP, to define the methodology to be adopted in establishing the EQS and the criteria for verification of compliance, and the methodology and criteria should be published in River Basin Management Plans (PGBH). IP through its participation in the Committee referred to in Article 21 of Directive 2000/60 / EC of the European Parliament and of the Council of 23 October that the Commission European Union and the other Member States inform about the alternative EQS established for water, the data, the methodology used, the monitoring frequency established, the categories of water to which they apply, the reasons and grounds underlying the whole procedure.

The Portuguese Environment Agency, in accordance with its responsibilities as the National Water Authority, is responsible for complying with Decree-Law no. 103/2010, of September 24, amended by Decree-Law no. 83/2011 of 20 June, in particular with regard to the drawing up of inventories of emissions, discharges and losses of priority substances and other pollutants, the monitoring of surface waters, the assessment of their compliance with EQS, and the integration of such assessments in the river basin management plans, with a view to achieving the environmental objectives set. In addition, this decree-law also defines the environmental quality standard for total hydrocarbons, oil derivatives of C_{10} through C_{40}, to be applied to surface, transitional and coastal waters.

The National Program for the Efficient Use of Water (PNUEA) is a national policy instrument for the efficient use of water. Its main objective is to promote the efficient use of water in Portugal, especially in the urban, agricultural and industrial sectors, contributing to minimize the risks of water scarcity and to improve the environmental conditions in the water resources, without undermining the vital needs and the quality of life of the populations, as well as the socio-economic development of the country.

The program area "Measurement and reconversion of water use equipment" covers the implementation of a concrete set of measures to monitor losses and technological reconversion by water supply management entities and by industrial, agricultural, household, collective and individual consumers (actions planned for 2012-2020).

The actions envisaged in the other program areas are intended to sensitize, technically support and provide the normative and legislative framework necessary for the success of the implementation of the first program area and of the PNUEA as a whole. In the vehicle washing, the measures adopted in periods of normal water maintenance (measure 30, 31 and 32) are related to the recycling of treated water, to use adequate washing systems and to replace conventional devices for deliver water with pressurized ones. During period of water scarcity, it is forbidden using drinking water (APA, 2012).

3.3. Italian framework

Legislative decree 11 May 1999, no. 152 containing provisions on the protection of water from pollution and transposition of Directive 91/271 / EEC. According to the Legislative Decree no 152 of 2006 as regards the regulation of discharges and authorizations, the legislation is substantially unchanged from the Legislative Decree 152/99; the only difference is the definition of “discharged of waste water” (art. 74 letter f, Legislative Decree 152/06): “Any entry made exclusively through a stable collection system that seamlessly connects the wastewater production cycle with the surface water receptor body, on the ground, in the subsoil and in the sewer network, regardless of their polluting nature, also subjected to a preventive purification treatment. Water releases pursuant to art. 114" and the one about "industrial wastewater" (art. 74, letter h, Legislative Decree 152/06): "Any type of waste water discharged from buildings or installations where commercial activities or the production of goods are carried out, other than domestic waste water and run-off meteoric wastewater".

The Article 101 of Legislative Decree 152/06 establishes the principle according to which all discharges must be authorized and regulated according to the respect of the quality of the water bodies and must, in any case, respect the emission limit values indicated in Annex 5 to the third part of the Legislative Decree 152/06 (Table 11). It is allowable to discharge the waters deriving from treatments in surface waters or in sewers. With regard to surface water, discharges of urban and industrial water are permitted, in compliance with the emission limit values set in art. 101, paragraphs 1 and 2.

Article 124 of Legislative Decree 152/06 provides the general criteria for the discharge authorization which is issued to the owner of the activity that originates the discharge. The request for authorization is presented in the Province or to the Area Authority in the case of delivery to the sewer system. The authorization is valid four years from the time of issue and a year before the expiration must be requested for renewal. Discharge control is carried out by the competent authority which is the Regional Environmental Protection Agency (ARPA) for discharge into surface waters. The manager of the integrated water service organizes the control according to the methods provided in the management agreement for the discharge into the sewer. "Administrative sanctions are provided for those who carry out a discharge exceeding the emission values set in the tables of Annex 5, of Legislative Decree 152/06 or from the more restrictive ones provided by the regions from 3000 to 30,000 euros. […] For those who do not comply with the provisions indicated in the authorization provision from 1500 to 15,000 euros. The competence in the matter of ascertaining administrative offenses is in the region in whose territory the violation was committed. […] Criminal penalties are provided for anyone who carries out new industrial wastewater discharges without authorization or maintains discharges after the authorization has been suspended: arrest from 2 months to two years, plus a fine from 1500 to 10,000 euros" (Abram, 2011).

Table 11: Emission limit values in surface water and sewage (Legislative Decree 152/06, Part 3, Annex V, Table 3)

Parameters	Units	Discharge in surface water	Discharge in sewer
Ph	Sorensen scale	5.5-9.5	
Temperature	°C		
Color	mg/L Pt-Co scale	Non perceptible with dilution 1:20	Non perceptible with dilution 1:40
Odor		It must no cause harassment	It must no cause harassment
Coarse materials		Absent	Absent
Total suspended solids	mg/L	≤80	≤200
BOD_5	mg/L	≤40	≤250
COD	mg/L	≤160	≤500
Al	mg/L	≤1	≤2
As	mg/L	≤0.5	≤0.5
Ba	mg/L	≤20	-
B	mg/L	≤2	≤4
Cd	mg/L	≤0.02	≤0.02
Cr tot	mg/L	≤2	≤4
Cr VI	mg/L	≤0.2	≤0.2
Fe	mg/L	≤2	≤4
Mn	mg/L	≤2	≤4
Hg	mg/L	≤0.005	≤0.005
Ni	mg/L	≤2	≤4
Pb	mg/L	≤0.2	≤0.3
Cu	mg/L	≤0.2	≤0.4
Se	mg/L	≤0.03	≤0.03
Sn	mg/L	≤10	-
Zn	mg/L	≤0.5	≤1
CN	mg/L	≤0.5	≤1
Active free Cl	mg/L	≤0.2	≤0.3
Sulfides	mg/L	≤1	≤2
Sulfites	mg/L	≤1	≤2
Sulphates	mg/L	≤1000	≤1000
Chlorides	mg/L	≤1200	≤1200
Fluorides	mg/L	≤6	≤12
P tot	mg/L	≤10	≤10
NH4	mg/L	≤15	≤30

Nitrous nitrogen	mg/L	≤0.6	≤0.6
Nitric nitrogen	mg/L	≤20	≤30
Animal/plant fats and oils	mg/L	≤20	≤40
Total hydrocarbons	mg/L	≤5	≤10
Phenoli	mg/L	≤0.5	≤1
Aldehydes	mg/L	≤1	≤2
Organic aromatic solvents	mg/L	≤0.2	≤0.4
Nitrogen organic solvents	mg/L	≤0.1	≤0.2
Total surfactants	mg/L	≤2	≤4
Phosphorus pesticides	mg/L	≤0.1	≤0.1
Total pesticides	mg/L	≤0.05	≤0.05
-aldrin	mg/L	≤0.01	≤0.01
-dieldrin	mg/L	≤0.01	≤0.01
-endrin	mg/L	≤0.002	≤0.002
-isodrin	mg/L	≤0.002	≤0.002
Chlorinated solvents	mg/L	≤1	≤2
Escherichia coli	UFC/100 mL	Known	-

Chapter 4

4. Materials and method

4.1. Wastewater characterization

Given the considerable variety of compounds present in a wastewater, its characterization is practically impossible and expensive by determining the individual components. A water can be considered sufficiently characterized when some of its physical characteristics are known, the concentration of the main chemical compounds (organic and inorganic) present in solution, the type and concentration of some microorganisms. The characterization of a water is based on the determination of a series of physical, chemical and biological parameters. The main polluting parameters that characterize the wastewater are listed in Table 12 (Metcalf & Eddy, 2014).

Table 12: Main parameters characterizing wastewater

Parameters	**Description**
Physical parameters	• Temperature • Electric conductibility • Solids • Color • Odor
Chemical parameters	• pH • BOD • COD • TOD • TOC • Alkalinity • Nitrogen • Oils and grease • Minerals oils • Surfactants • Dissolved oxygen • Toxic substances
Biological parameters	• Total coliforms • Fecal coliforms

In the present work total solids, suspended solid, volatile and fixed solids, metals, pH, temperature and COD are analyzed.

4.2. Sampling

The sampling of a wastewater is a fundamental operation for the purposes of a correct characterization. This operation involves choosing the sampling point and the sampling technique. In this work the samples were taken manually from six points of the carwash plant, two samples were taken after each treatment unit as shown in Figures 7 and 8 (influent, after sedimentation, after flotation, after biological treatment, after filtration system, after storage tank), two times over two months.

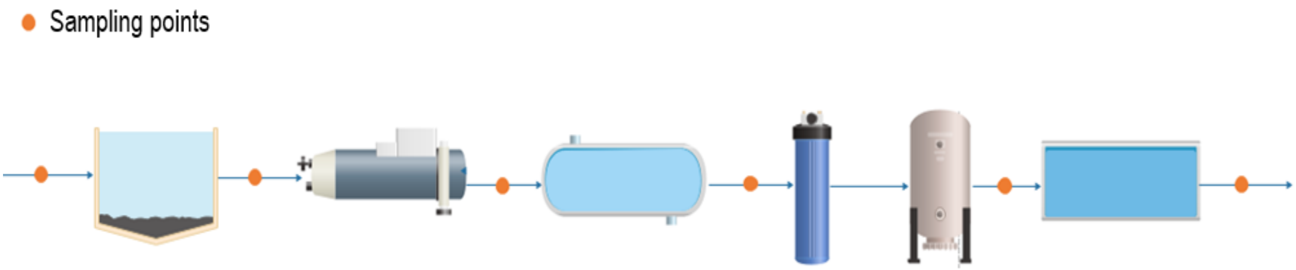


Figure 7: Scheme of sampling points (made with EdrawMax)

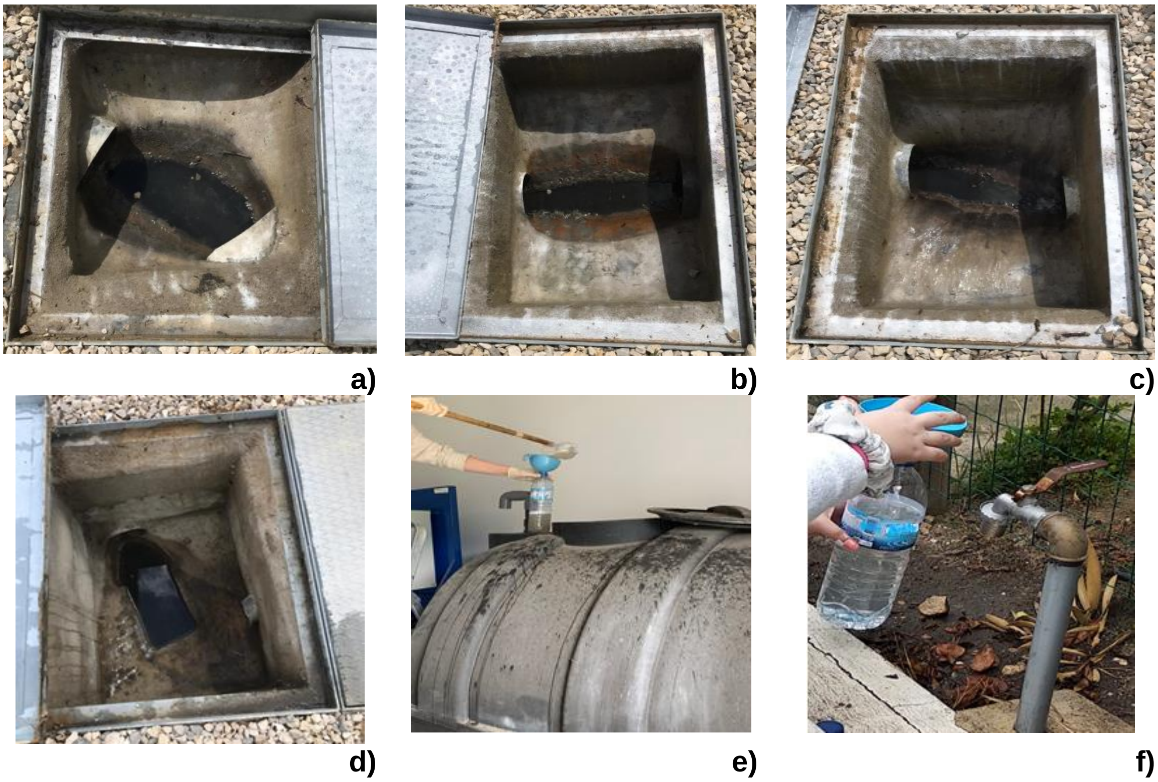


Figure 8: Sampling boxes for the treatments: a) Influent; b) Sedimentation outlet; c) Flotator outlet; d) Biological reactor outlet; e) Filtration collection storage; f) Final treated water collection

In Figure 9 an overview of the wastewater treatment plant is presented.

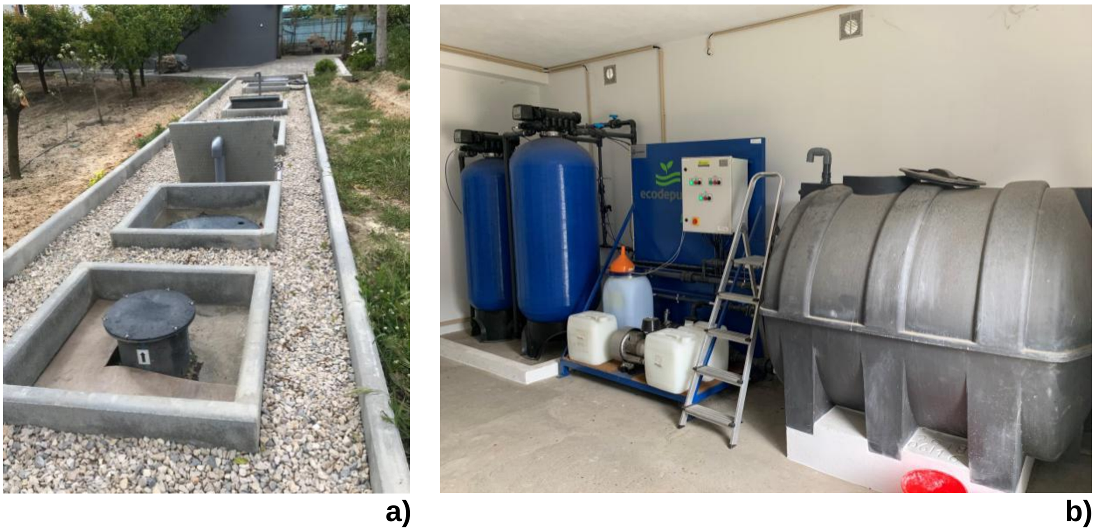


Figure 9: Overview of the treatment plant: a) Primary and secondary treatments; b) Tertiary treatment

During the second collection, samples were picked from two more collection points, which were from the inside of the biological reactor and after the sand filter. The first collection was on 8/4/2019 at 14:30 pm and second was performed on 20/5/2019 at 14:30 pm at Transportes Gama truck’s wash station, in Seixal. The sampling point must be that in which the turbulence of the liquid stream to be sampled is sufficient to guarantee the homogeneity of composition. During the collection in fact the station was in operation, so fresh samples from the washing trucks were collected. Once the water samples have been taken, they must be stored until the time of analysis in conditions that prevent significant changes in wastewater quality. During storage some phenomena can occur such as oxidation, precipitation and complexation of chemical species, biological degradation of organic substances that alter the quality of the water (Paolini, 1988). The conservation techniques are intended to delay these phenomena and consist of various interventions such as refrigeration and the addition of chemical reagents. The samples in this work were collected in PET containers (Figure 10) to provide that the material in suspension does not adhere to container walls. Samples were refrigerated at 4°C up to the time of analysis to minimize microbiological decomposition.

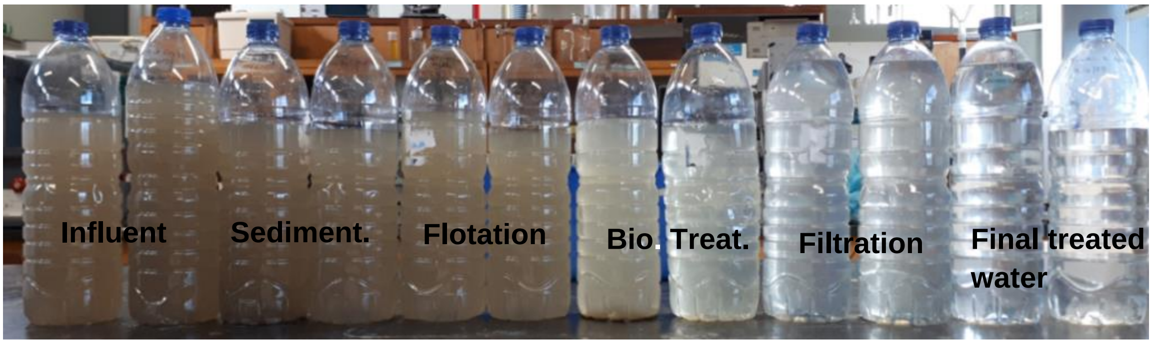


Figure 10: Samples collected

The amount of enzymes present in the MBBR has been halved, it is changed from 30 L/week, for the first sampling to 15 L/week, for the second one. The same samples has been collected from the same points, with the addition of two new collection points, one from the inside of the biological reactor and the other after the sand filter. The same experiments have been conducted to look if the final value of the treated wastewater are adequate to definitely decrease the amount of the enzymes in order to reduce the cost of the biological reactor and optimize the plant costs.

4.3. Temperature and pH measure

The temperature is normally expressed in degrees Celsius and is measured with thermometers. Temperature is a parameter that greatly influences both the life of aquatic organisms and the efficiency of purification plants. Abrupt temperature variations can alter the regularity of the aquatic ecosystem. Therefore, an accurate temperature control is necessary to avoid thermal pollution of the receiving water bodies. Due to an increase in temperature of a water body there is a reduction in solubility and oxygen transfer rate, thus making the re-creation of the body more difficult. Moreover, in the presence of biodegradable substances, there is also a greater speed of oxygen consumption due to the acceleration of microbial activity, which together with the reduction of oxygenation speed, can lead to oxygen deficiency in the water body (Marecos do Monte *et al.,* 2016). In wastewater treatment plants a temperature increase within certain limits causes an increase in the efficiency of the treatments. The temperature effect is generally described by a Van't Hoff-Arrhenius relation (Equation 1).

$$K_T = K_{20}{\theta_K}^{(T-20)} \qquad (1)$$

The pH is one of the main chemical parameter used to characterize wastewaters. The pH is the decimal cologarithm of the hydrogen ion activity a_{H^+} (Equation 2).

$$pH = -\log_{10} a_{H^+} \qquad (2)$$

The activity of the hydrogen ions is linked to that of the ions oxidize them (a_{OH^-}) from the ionic product of water (Equation 3).

$$K_w = (a_{H^+}) \times (a_{OH^-}) \qquad (3)$$

For pure water at 25 °C, K_w is equal to 10^{-14} so pH and pOH can be represented by equation 4.

$$\mathrm{pH} + \mathrm{pOH} = 14 \qquad (4)$$

At this temperature, the water is neutral when the pH is equal to 7, it is acidic for pH lower than 7 and basic for pH greater than 7.

The pH of the wastewater is measured with the pH meter Orion 720A (Figure 11 a). To use the pH meter it was necessary to calibrate it every day (Figure 11 c), using two or three solutions with known pH, pH 4, 7 and pH 10 (Figure 11 b). The pH control is not only important to avoid alterations of aquatic ecosystems, but its control is also fundamental for the satisfactory functioning of the purification plants. For example, the microorganisms of biological processes, responsible for the demolition of biodegradable substances, cannot tolerate pH values below 4 and above 9.5.

a) **b)** **c)**

Figure 11: pH a) meter Orion 720A; b) standard solutions 7 and 10; c) calibration

4.4. Solids Measure

Solids refer to matter suspended or dissolved in water or wastewater. Solids are one of the main physical parameters to characterize a wastewater. Solids may affect water or effluent quality adversely in several ways. Waters with high dissolved solids generally are of inferior palatability. Solids analyses are important in the control of biological and physical wastewater treatments and for assessing compliance with legal wastewater effluent limitations.

4.4.1. Parameters definition

The **total solids** (TS) amount of a water is defined as the residue obtained by evaporation at 103-105 ° C (dry residue). Therefore, from the analytical point of view, the substances that are released during the water evaporation phase are not included in the total solids.

The total solids content is expressed in mg/L or in ppm. Total solids can be divided into filterable and suspended (Paolini, 1988).

The **total suspended solids** (TSS) are those which are retained in the filter during the filtration operation conducted using a filter with a porosity of 0.45 µm (Marecos do Monte *et al.*, 2016). They comprise also a part of colloidal solids. Suspended solids can be distinguished into sedimentable and non-sedimentable (Metcalf and Eddy, 2003).

The various classes of solids (total, filterable, suspended) can be also divided into **fixed and volatile solids**. Solids that do not volatilize at a temperature of 550 ± 50 °C are fixed, volatile those that are lost at this temperature. The volatile solids are mainly composed of organic substances, those fixed by inorganic substances (minerals). Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts (Marecos do Monte *et al.*, 2016).

The **sedimentable solids** are those that are deposited on the bottom of a one-liter Imhoff cone after a sedimentation time of 2 hours. The solids that are separated in surface during the Imhoff cone sediment are called freely floating (Paolini, 1988).

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Each sample requires close attention to desiccation after drying. Try to minimize opening desiccator because moist air enters. Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water.

4.4.2. Equipment

The equipment applied to the wastewater characterization parameters was according to the Standard Methods for the Examination of Water and Wastewater (Rice *et al*., 2017) the following:

Total solids

- Evaporating dishes: porcelain dishes;
- Drying oven Horo;
- Muffle furnace Heraeus®;
- Desiccator provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator;
- Analytical balance, capable of weighing to 0.1 mg.

Total suspended solids

- All the apparatus for total solids;
- Glass-fiber filter disks (0.45 µm);
- Filtration apparatus: Filtration apparatus with reservoir and coarse fritted disk as filter support;
- Suction flask, of sufficient capacity for sample size selected.

Fixed and volatile solids

- All the previous apparatus.

4.4.3. Procedure

In order to measure the different kind of solids, the method 2540 from Standard Methods for the Examination of Water and Wastewater (Rice *et al*. 2017) are used:

Total solids

- Preparation of evaporating dishes: Put the ceramic dishes in the furnace at 550 ± 50 °C per 1h and then store and cool them in the desiccator per 1h. This operation is repeated until constant weight is reached (difference between the two weight is lower than 4%);
- All the samples were analyzed in duplicate according to the following procedure:
    - Homogenize the samples;
    - Pipet 20 mL of each sample to a pre-weighed dish;
    - Let evaporating all the water in a steam bath (Figure 12 a).

- Dry the evaporated samples for at least 1 h in an oven at 103-105 °C (Figure 12 b);
- Cool the dishes in the desiccator until room temperature (at least 1h) (Figure 12 c), and weigh.
- Repeat this cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained.

Figure 12: Steps for TS procedure: a) Evaporation, b) Solids in the oven at 103-105°C, c) Solids in the desiccator

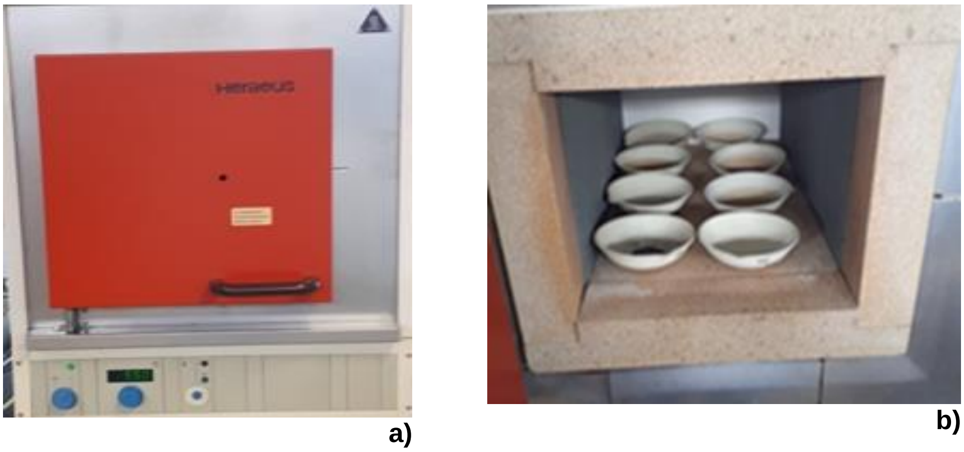
Total suspended solids

- Preparation of glass-fiber filter disk (Figure 13 a): Insert disk with wrinkled side up in filtration apparatus. Apply vacuum and wash disk with 20 mL portions of reagent-grade water. Continue suction to remove all traces of water, turn vacuum off, and discard washings. Remove filter from filtration apparatus (Figure 13 b) and transfer to an inert weighing dish;
- Sample analysis:
  - Dry the samples in an oven at 103-105°C for 1 h;
  - Cool in desiccator to balance temperature and weigh;
  - Repeat cycle of drying, cooling, cooling, and weighing until a constant weight is obtained.

Figure 13: Equipment for TSS measure**:** a) Capsule with filter; b) Filtration apparatus

Fixed and volatile solids

- Samples analysis: Ignited in a oven at 550 ± 50 °C the dry residue (Figure 14).



a) b)

Figure 14: Oven a) HERAUS; b) with capsule

4.4.4. Calculation

Total solids are calculated with Equation 5.

$$mg\ total\ solids/L = \frac{(A - B) \times 1000}{Sample\ volume\ (mL)} \tag{5}$$

where:

A = weight of dried residue + dish (mg);

B = weight of dish (mg).

Total suspended solids are calculated with Equation 6.

$$mg\ total\ suspended\ solids/L = \frac{(A - B) \times 1000}{Sample\ volume\ (mL)} \tag{6}$$

where:

A = weight of filter + dried residue (mg);

B = weight of filter (mg).

Fixed and volatile solids are calculated with Equations 7 and 8:

$$mg\ fixed\ solids/L = \frac{(A - B) \times 1000}{Sample\ volume\ (mL)} \tag{7}$$

$$mg\ volatile\ solids/L = mg\ total\ or\ suspended\ solids/L - mg\ fixed\ solids/L \quad (8)$$

where:

A = weight of residue + dish or filter after ignition (mg);

B = weight of dish or dish with filter (mg).

4.5. Chemical oxygen demand measure

4.5.1. Chemical oxygen demand definition

The COD is one of the main chemical parameters used to characterize wastewaters in terms of organic matter. The COD indicates the amount of oxygen required to chemically oxidize the oxidizable substances (organic and inorganic) present in a waste water. The COD is determined with the potassium dichromate test and is expressed in terms of mg/L of equivalent oxygen consumed. This test oxidizes both organic substances that are refractory to biological oxidation. However, there are some organic substances such as benzene, toluene, pyridine which are not oxidized by dichromate and others such as certain alcohols, amino acids, which are only partially oxidized. Furthermore, the COD does not provide any indication on the oxygen demand due to free ammonia and nitrogen bound to the organic substance (organic nitrogen) since the oxidation of these compounds is not possible chemically. The advantages of COD measurement are that it is fast (the test has a total duration of about three hours, two of which are dedicated to ebullition); it is a much more reproducible measure and allows to evaluate the content of organic substances even in the presence of toxic compounds without the need for a preliminary dilution of the samples. The COD, being a chemical test, however, has the disadvantage of not distinguishing between biodegradable and non-biodegradable substances (Di Palma, 2017).

4.5.2. Equipment

To execute the experiments the following equipment was used:

- Reflux apparatus: DK 20 Heating Digester (Velp Scientifica);
- Becker;
- Blender,
- Pipets: 50 mL and 25 mL;
- Flasks: 100 mL and 250 mL;
- Tubes with plug and closing cap;
- Glass spheres;
- Funnel;
- Erlenmeyer;
- Burette: 25 mL, graduate 0.05 mL.

4.5.3. Reagents

To execute the experiment the following reagents were used:

- **Mercury sulphate,$HgSO_4$,** powder 0.5 g. It is used to avoid the interferences made by chlorides.
- **Standard potassium dichromate solution, 0.04167M**: Dissolve 6.1295 g $K_2Cr_2O_7$, previously dried at 150°C for 2 h, in distilled water and dilute to 500 mL. This reagent undergoes a six-electron reduction reaction; the equivalent concentration is 0.25 N;

b)

a)

Figure 15: Standard potassium dicromate reagent: a) $K_2Cr_2O_7$ powder; b) $K_2Cr_2O_7$ solution

- **Sulfuric acid reagent**: Add Ag_2SO_4 powder, to conc. H_2SO_4 at the rate of 5.5 g Ag_2SO_4/kg H_2SO_4. Sulfuric acid density is 1.84 kg/L. So dissolve 5.5090 g Ag_2SO_4 to 543.48 mL conc. H_2SO_4. Let stand 1 to 2 d to dissolve.;


a) **b)**

Figure 16: Sulfuric acid with catalyst reagent: a) Sulfuric acid conc. and Ag_2SO_4; b) Ag_2SO_4 + H_2SO_4 solution

- **Ferroin indicator solution**: Dissolve 0.3712 g 1,10-phenanthroline monohydrate and 0.1737 g $FeSO_4$ x $7H_2O$ in distilled water and dilute to 25 mL;
- **Standard ferrous ammonium sulfate (FAS) titrant, 0.25M:** Dissolve 98 g $Fe(NH_4)_2(SO_4)_2$ x $6H_2O$ in distilled water. Add 20 mL conc. H_2SO_4, cool, and dilute to 1000 mL.

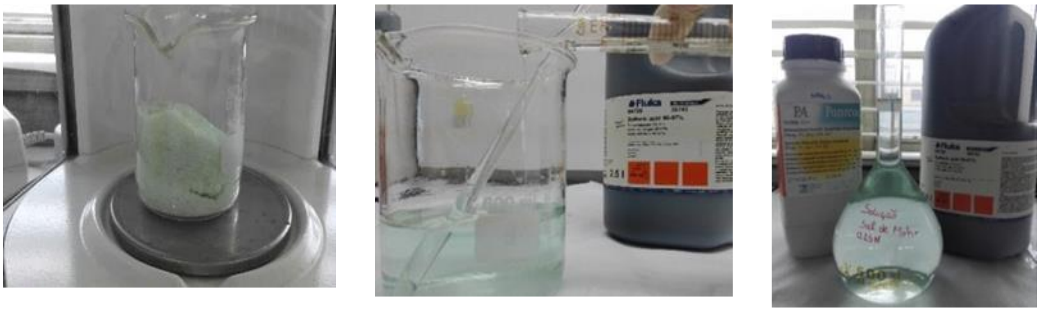

a) **b)** **c)**

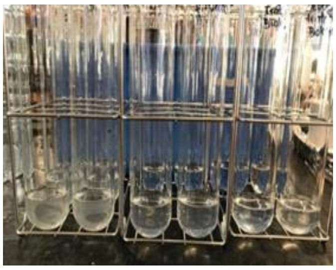
Figure 17: FAS preparation: a) Weighed $Fe(NH_4)_2(SO_4)_2$; b) Addition of sulfuric acid conc.; c) FAS solution

4.5.4. Procedure

The method 5220 – COD Open Reflux from Standard Methods for the Examination of Water and Wastewater (Rice *et al*. 2017) are used for COD measure.

The process consists in an open reflux boiling for 2 hours of the water samples under examination with concentrated sulfuric acid and a known dichromate excess by means of a standard solution of ferrous ammonium sulfate in the presence of a ferroin indicator. As a catalyst, silver sulfate is used and chloride interference (they do not cause oxygen consumption in natural waters but would be oxidized by dichromate) is eliminated by the addition of mercuric sulphate. The samples collected from the sedimentator, the flotator and the biological reactor were diluted with distilled water (1:4). The execution of the experiment follows the next procedure:

- Take 25 ml of each samples and put it in the digestor tube (Figure 18 a);
- Add 0.5 g of $HgSO_4$ (Figure 18 b);
- Add 2.5 ml of sulfuric acid reagent while mixing and cooling down (operation performed under the hood) (Figure 18 c);
- Add 12.5 ml of $K_2Cr_2O_7$ with the pipette (it becomes orange) (Figure 18 d);
- Add 35 mL of sulfuric acid reagent while cooling down;
- Put 4 glass spheres inside the tubes and close with the plug and the closing cap,
- Start the open reflux digestion for 2 h (Figure 18 e);
- Cool the tubes to room temperature;
- Wash the plug from the condensate (Figure 18 f);
- Pour the sample in the flask and dilute to 250 mL with distilled water (Figure 18 g);
- Take 50 ml from the flask and place it in the erlenmeyer;
- Add 3 drops of ferroin indicator (Figure 18 h) and do the titration until the first shade of reddish-brown appears (the color will change from orange to green to blue till reddish-brown (Figure 18 i).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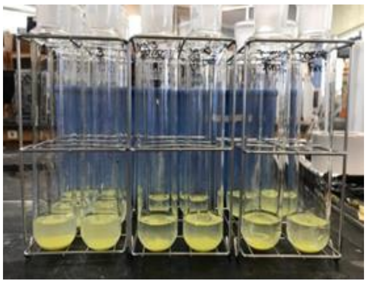
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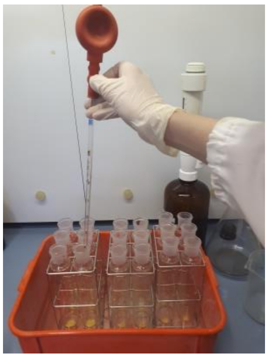
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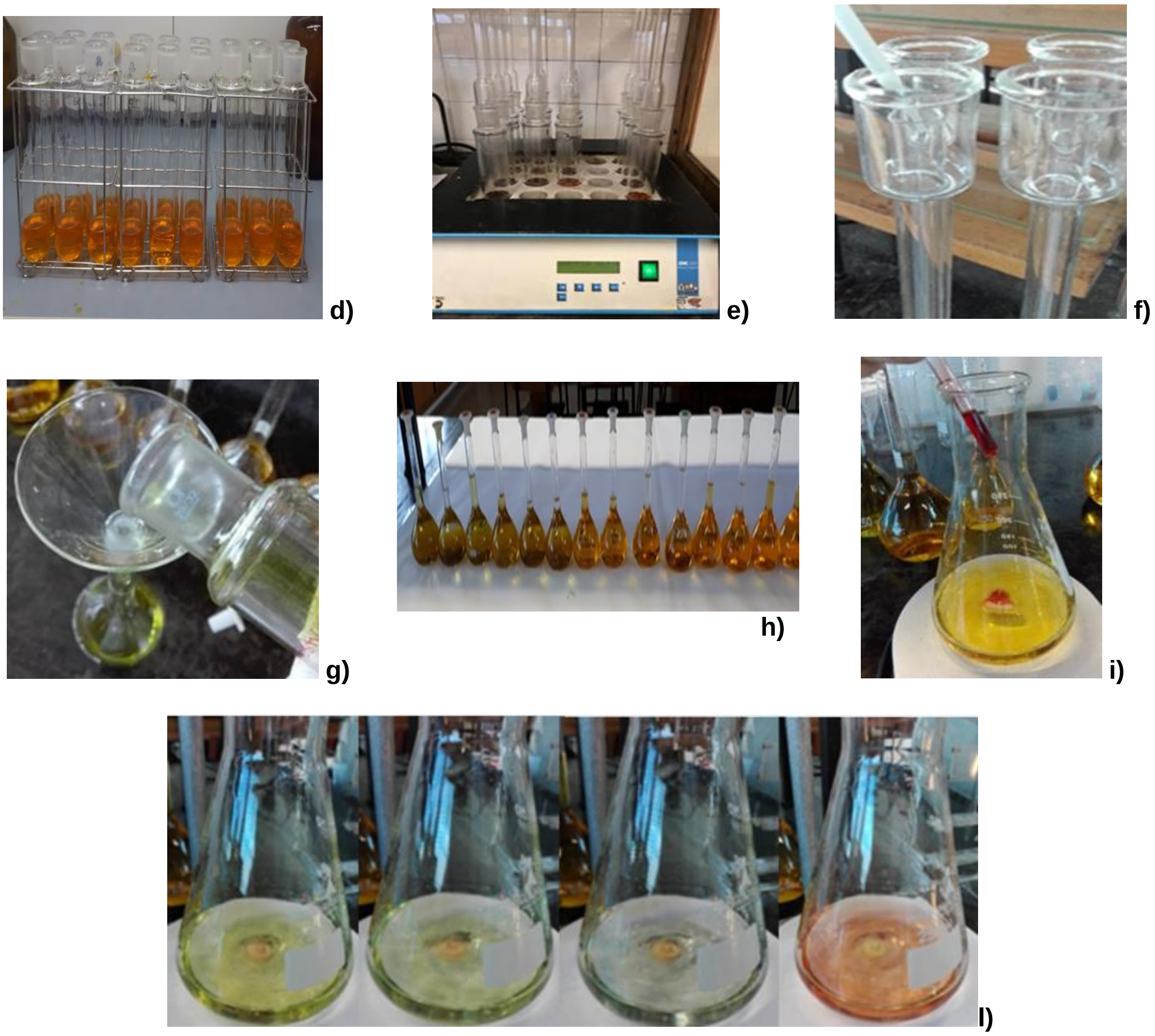


Figure 18: COD: a) Samples in digestor tubes; b) Addition of $HgSO_4$; c) Addition of 2.5 mL of Sulfuric acid with catalyst; d) Addition of $K_2Cr_2O_7$; e) Open reflux digestion; f) Condensate washing; g) Transfer of samples; h) Diluted samples after digestion; i) Addition of ferroin indicator; l) Toned color during titration

4.5.5. Calculation

In COD, before starting the titration of the samples, the FAS molarity should be checked by the following procedure:

- Prepare two erlenmeyers;
- Fill them with 12.5 mL of $K_2Cr_2O_7$, 50 mL of distilled water and 15 mL of sulfuric acid concentrated;
- Add 3 drops of ferroin indicator;
- Titrate with the Mohr Salt solution until the indicator turns from blue to dark red;
- Calculate its molarity (Equation 11).

$$\text{FAS molarity} = \frac{\text{Volume } 0.04167\text{M } K_2Cr_2O_7 \text{ solution titrated}}{\text{Volume FAS used in titration, mL}} \times 0.25 \tag{11}$$

To calculate the eq/L O_2 as firsts calculate the total equivalent of $K_2Cr_2O_7$ in the reactor (Equation 12).

$$eq\ K_2Cr_2O_7\ tot = \frac{0.25 \times 25}{1000} \tag{12}$$

Then calculate the equivalent present in each erlenmeyer (Equation 13).

$$eq\ K_2Cr_2O_7\ in\ erlenmeyer\ volume\ (50\ mL) = \frac{M_{FAS}\ \times Average\ V_{FAS}\ used}{1000} \tag{13}$$

Then correct this measure relating it to the flask volume used (Equation 14).

$$eq\ K_2Cr_2O_7\ in\ flask\ volume\ (250\ mL) = \frac{M_{FAS}\ \times Average\ V_{FAS}\ used}{1000} \times 5 \tag{14}$$

Calculate the difference between the total equivalents of potassium dichromate and the equivalents in the flask to find the potassium dichromate reacted, this calculation is possible because 1 eq of $K_2Cr_2O_7$ is equal to 1 eq of FAS (Equation 15).

$$eq\ K_2Cr_2O_7\ \ reacted =\ \ eq\ K_2Cr_2O_7\ tot - eq\ K_2Cr_2O_7\ in\ flask\ volume\ (250\ mL) \tag{15}$$

Then calculate the eq/L (Equation 16).

$$\frac{eq}{L} = \frac{eq\ K_2Cr_2O_7\ \ reacted\ \times\ 1000}{Sample\ volume\ in\ the\ tube\ (25\ mL)} \tag{16}$$

In the end to obtain the mg O_2/L multiply the eq/L per 8000 mg/eq which is the weight of equivalent oxygen (Equation 17).

$$mg\frac{O_2}{L} = \frac{eq}{L} \times 8000 \tag{17}$$

All the calculations of CQO are reported in Annex C.

4.6. Metals Measure

4.6.1. Copper and Zinc

Copper (Cu) and Zinc (Zn) are the most abundant of the heavy metals in carwash wastewater, derived mainly from tyres, brake drums, engine block, intake manifold, and paintings (Oknich, 2002). While metals occur naturally in most freshwater systems and are important to biological processes, elevated concentrations are detrimental to aquatic ecosystems (Waters, 2011). Waters (2011) also reported acute toxicities (LC50) of 0.0025-0.755 mg/l of Cu against fish after 48 h of exposure and 0.0096-0.9 mg/l against fish after 96 h of exposure while for Zn; the reported LC50 was 0.068-3.290 mg/l against Daphnia magna and 0.238-2.66 mg/l against fish after 48 h and 96 h of exposure respectively.

4.6.2. Equipment

In order to perform the experiment to evaluate the metals concentration the following equipment is used:

Copper

- DK 20 Heating Digester (Velp Scientifica) (Figure 19 a);
- Spectronic® 20 Genesys™, spectrophotometer at 540 nm (Figure 19 b);
- Graduated cylinders, 25 mL, with ground-glass stoppers;
- Plastic cells, 2mL (Figure 19 c).

a) **b)** **c)**

Figure 19: Equipment for metals analysis: a) Digestion for metals evaluation; b) Spectronic® 20 Genesys™; c) Cell with CuVer1 reagent powder

Zinc

- DK 20 Heating Digester (Velp Scientifica) (Figure 19 a);
- Spectronic® 20 Genesys™, spectrophotometer at 620 nm (Figure 19 b);
- Graduated cylinders, 50 mL and 25 mL, with ground-glass stoppers;
- Plastic cells, 2 mL.

4.6.3. Reagents

In order to perform the experiment to evaluate the metals concentration the following reagents are used:

Copper

- CuVer 1 reagent powder, HACH;
- Standard copper solution 1000 mg/L Cu, HACH;
- Distillated water: use water for rinsing apparatus and preparing solutions and dilutions.

Zinc

- Distillated water: use water for rinsing apparatus and preparing solutions and dilutions;
- Zinc standard solution 1000 mg/L Zn, HACH;
- ZincoVer 5 reagent powder pillow, HACH;
- Cyclohexanone, HACH.

4.6.4. Procedure

This determination of metals concentration requires the following common procedure:

- Take 250 mL of the sample;
- Add 2.5 mL of concentrated nitric acid (HNO_3);
- While stirring, pipet 100 mL of the acidified sample into the digestion tubes;
- Add 2.5 mL of hydrochloric acid (HCl), diluted 50% with distillated water;
- Place the tubes in the digestion apparatus at a temperature of 128 °C until the volume of the solution in the tube was reduced to 20 ml (monitored in order to avoid boiling) (Figure 19 a);
- Cool down the sample to room temperature;
- Check the pH, must be around pH=4, using 5N and 0.02N sodium hydroxide solutions (NaOH);
- Transfer the samples to a 100 ml volumetric flask and checked with distilled water.

Copper measurement proceeds with the following steps:

- Pipet 25 ml of sample and add CuVer1 reagent powder;
- Wait 2 minutes that the reaction starts;
- Put the sample in the cell (Figure 19 c);
- Put the cell in the spectrometer and the absorbance was read;
- Calculate the Cu concentration thanks to the equation of the calibration curve (Equation 9) (the procedure to build the calibration curve is reported in Annex E):

$$y = 0.1383x + 0.0747 \qquad (9)$$

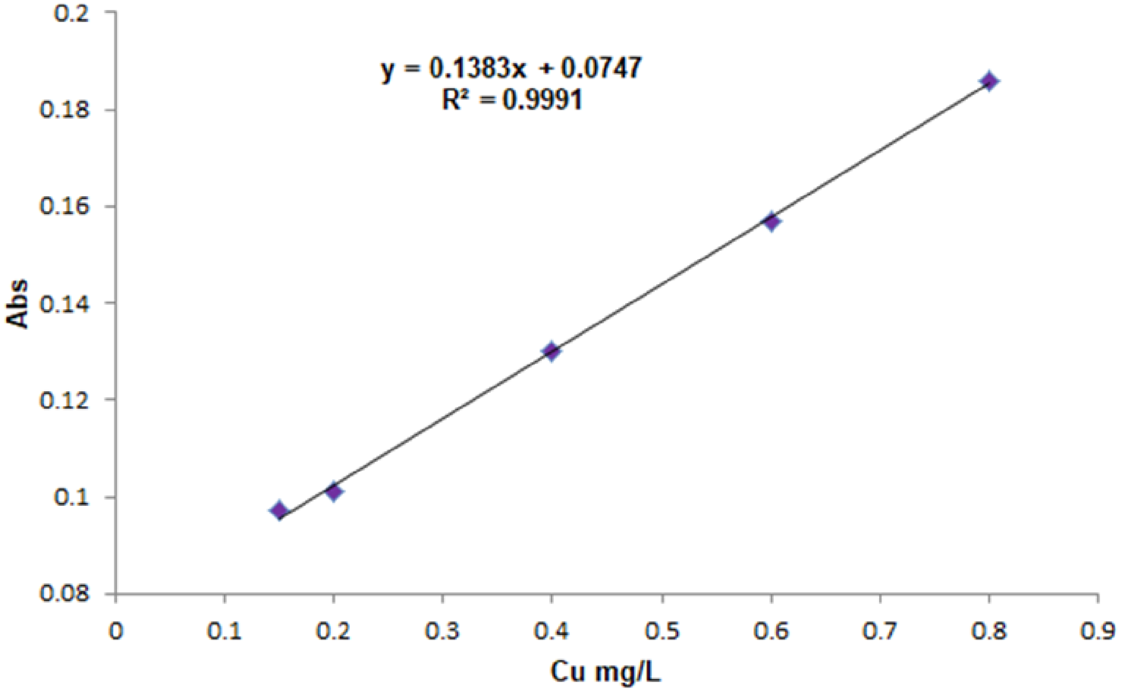


Figure 20: Cu calibration curve

Zinc measurement proceeds with following steps:

- Pipet 50 ml of sample and add ZnVer5 reagent powder (Figure 22 a);
- Take 25 mL of the samples in which has been added the reagent powder and add 1 mL of cyclohexanone;
- Shake for 30 seconds;
- Wait 3 minutes that the reaction starts;
- Put the sample in the cell (Figure 22 b);
- Put the cell in the spectrometer and the absorbance was read;

- Calculate the Zn concentration thanks to the equation of the calibration curve (Equation 10) (the procedure to build the calibration curve is reported in Annex E):

$$y = 0.2857x + 0.1476 \tag{10}$$

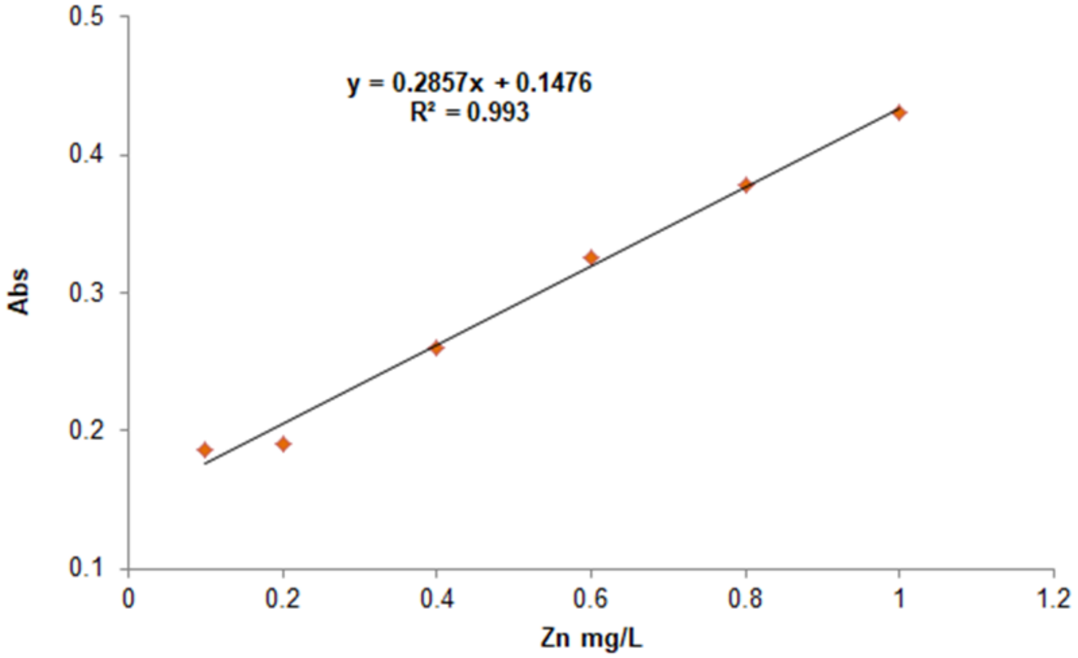


Figure 21: Zn calibration curve

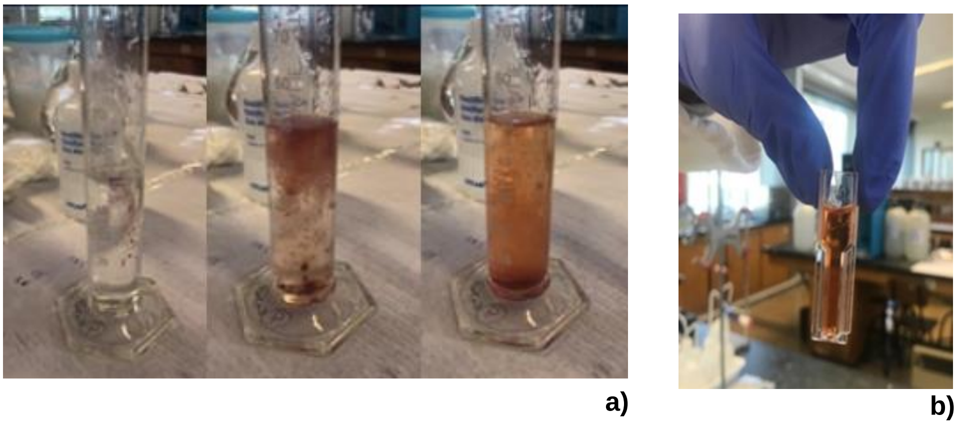


Figure 22: Procedure for Zn measure: a) Addition of ZincVer5 reagent powder; b) Cell full of reacted sample

Chapter 5

5 Case study

5.1. Transportes Gama enterprise and wastewater treatment plant

Transportes Gama is a big enterprise that offers to its clients a variety of means of transport (200 vehicles). Transportes Gama station is located in Seixal, in Rua Ferreira de Castro, Paio Pires (Figure 23).

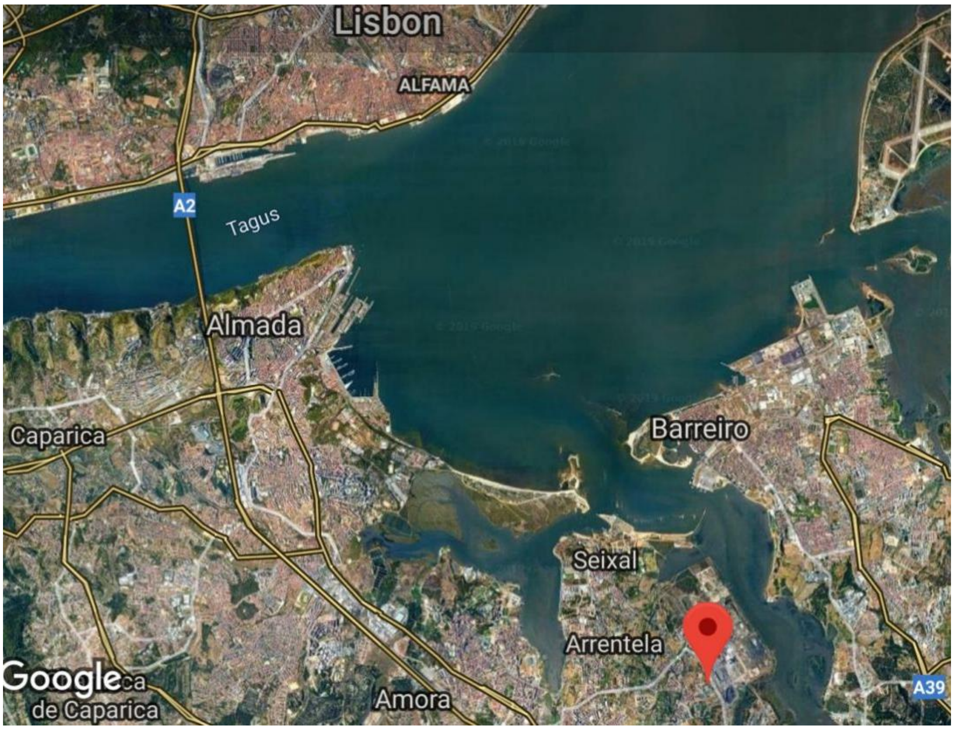


Figure 23: Location of Trasportes Gama station in Seixal, Rua Ferreira de Castro, Paio Pires

Transportes Gama trucks wash station (Figure 24), can wash 8-10 trucks per day. The washing procedure consists in manually pre-washing with pressurized water, followed by washing step with a conveyor system (Figures 24 a and b) and then the finishing step takes place, the drying step is absent. The washing collected wastewater flows to the wastewater treatment plant (Figure 24 c). Transportes Gama trucks wash station includes a full line of vehicle wash wastewater treatment plant. The wastewater treatment plant consists of a set of unitary operations and process, placed in series: sedimentation, flotator, biological treatment and filtration. In Figure 25 is reported the wastewater treatment flow scheme including the volume of the equipment and their residential time (data given by ECODEPUR®). The detailed process flow scheme is in Annex F. The plant can treat a maximum flow rate of 15 m^3 /day. This treatment plant aims to achieve the predefined treatment objectives and to maximize water treatment and reuse. This treatment plant allows to achieve a total reuse of treated water, 99.9%, except for the one lost by vaporization, but also due to water drops that remain on trucks surface.


a) b) c)

Figure 24: Transportes Gama station: a) Truck washing system; b) Inside washing truck; c) Connection of the discharge to the treatment plant

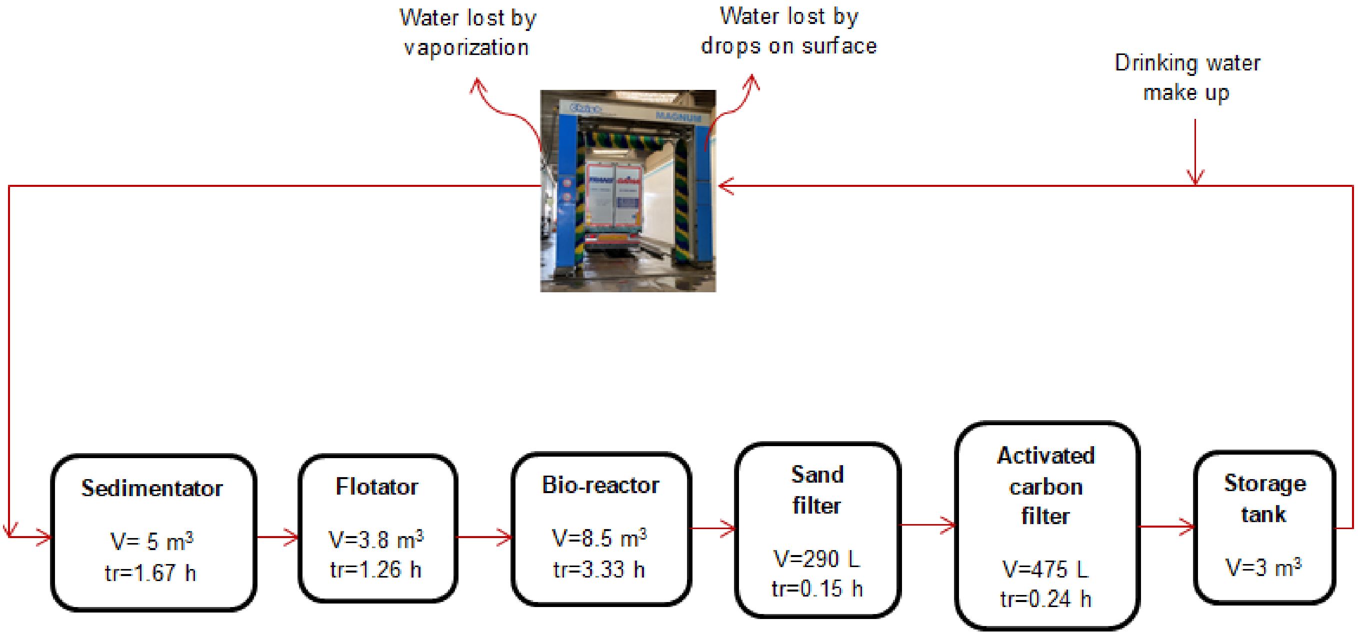


Figure 25: Wastewater treatment flow scheme

Transportes Gama wastewater treatment plant was provided by ECODEPUR®. ECODEPUR®, a portuguese leader in the design and construction of treatment systems and reuse of wastewater, ECODEPUR® follows the market trends, focusing on overcoming and constant innovation as the basis of their growth and development. The investment, both in technology and in terms of production capacity, has resulted in the improvement, renewal and optimization of processes. The wastewater treatment plant was built on June 2018 and covers primary secondary and tertiary treatments:

- ECODEPUR® DS - 5000: Primary decantation are containers for the separation of the sands and sludge that are washed away by the contaminated effluent before being sent to the hydrocarbon separator. The decanters of solids work by gravity, resulting in the decantation of the affluent solids (ECODEPUR® DEPURWASH Sistema de Tratamento e Reciclagem de Águas de Lavagem);
- ECODEPUR® DEPUROIL NS8 PL (CE EN858 Class 1): Separation of "Mineral Oils", CE EN858 -1, Class 1 (<5,0 mg / l), with pre - decantation, double coalescing system, automatic safety shut - off system (anti - de - calibration) and cast iron cover B125 with designation "SEPARATOR" according to CE EN 858 – 1 (Separador de hidrocarbonetos ECODEPUR® gama DEPUROIL);
- ECODEPUR® DEPURWASH: Treatment, Storage and Re-pressurization of the treated effluent in order to be reused by the washing system without potential danger to the equipment, people and environment.

ECODEPUR® treatment plant can treat a maximum flow rate of 15 m^3/day, which are responsible for a global energetic consumption of 0.9 kWh/m^3, lower than the energetic consumption required by a carwash wastewater treatment plant constituted of FFO or FFC as reported in Table 7. Filtration system spends 3.6 kWh/day, the aeration for the biological reactor 5.6 kWh/day and the re-pressurizing pump 4.2 kWh/day.

During a whole working day, the variation in flow rate and its composition depend on the working time schedule of the washing station and on the vehicle washed and its relative degree of dirtiness. All these variables can affect more or less significantly the characteristics of the wastewater and its consequent treatment.

5.2. Primary treatments

5.2.1. Sedimentation

In the case study wastewater treatment plant the first step is a sedimentation of type II, flocculant particles. In this type of sedimentation, the particles do not maintain their individuality, but tend to agglomerate, the mass of the particles thus increases over time and therefore the efficiency of removal of solids is a function of residence time and overflow rate. Given the complexity of the model, there is still no mathematical model to describe this phenomenon. An experimental relationship can be obtained by means of column sedimentation test (M. L. Davis, 2010).

ECODEPUR® DS 5000 (Figure 27) Type Solid Decanters are containers for the separation of the sands and sludges that are entrained by the contaminated effluent before being sent to the hydrocarbon separator. It is made of linear polyethylene anti-UV additives, by roto modeling system, which translates into high mechanical resistance and insensitivity to corrosion. This type of sedimentator is a circular one with up lateral entrance and exit of the stream (Figure 26) (ECODEPUR, 2018 b). Sedimentator characteristics are shown in Table 13.

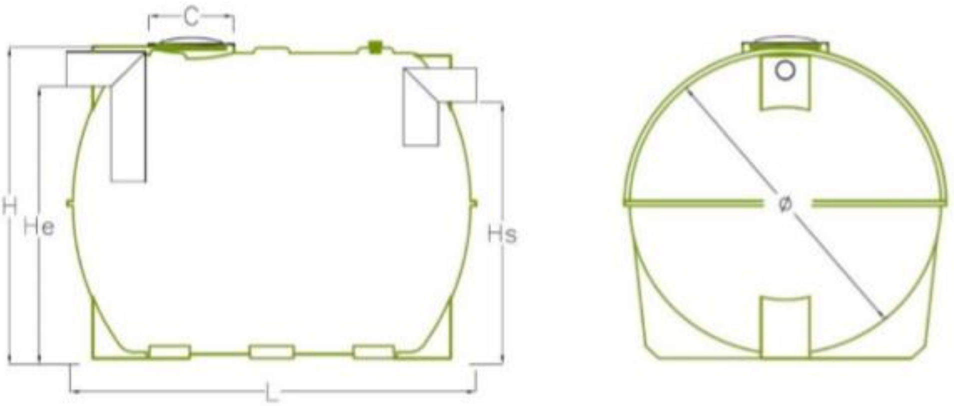


Figure 26: Sedimentator plant

Table 13: Sedimentator characteristics

Type	**Total volume (L)**	**L (mm)**	**D (mm)**	**H (mm)**	**He (mm)**	**Hs (mm)**	**C (mm)**	**Tube D (mm)**	**Retention time (h)**
DS-5000	5000	2360	1800	1870	1570	1470	400	200	1.67

It has some benefits:

- High mechanical resistance and insensitivity to corrosion;
- Total water tightness;
- Easy installation and maintenance;
- No energy consumption;
- Low cost;
- Built-in breathing.

Figure 27: Sedimentator

5.2.2. Flotation

Flotation is the second step in the case study wastewater treatment. The ECODEPUR®, DEPUROIL® (Figure 29) range, is an oil separator for use in the separation of hydrocarbons from oily wastewater, double coalescing filter and safety shut-off valve. The DEPUROIL® Range is CE marked in accordance with the legal requirement that comes from the entry into force of Regulation (EU) No. 305/2011 of the European Parliament for Construction Products, fulfilling all the requirements of the European Standard EN 858-1. ECODEPUR® hydrocarbon separators, DEPUROIL® Range are Class 1 according to EN858, featuring a dual coalescing filter and safety shut-off valve. This allow to obtain a final effluent with hydrocarbon concentration of less than 5 mg/L, under the standard test conditions, thus complying with the discharge requirements established in current legislation (Decree-Law no. 236/98). The hydrocarbon separators are made of linear polyethylene, high mechanical resistance and insensitivity to corrosion and duly tested by an independent entity (National Civil Engineering Laboratory - LNEC). The production of the equipment under controlled conditions, the use of quality raw materials and the inspection of the finished product, guarantee the quality of the final product.

The hydrocarbon separators have several advantages:

- High levels of treatment (double filtration system);
- Built - in automatic safety shut - off system (solid anti - de - calibration system);
- Built-in sampling device;
- Protective cap to internal components in PE;
- Possibility of incorporating by-pass and acoustic and luminous alarm probe directly into the equipment structure;
- High storage capacity of separate products;
- High mechanical resistance and insensitivity to corrosion;
- Easy installation and maintenance;
- Total water tightness;
- No energy consumption;
- Low cost.

The hydrocarbon separator admits on entry non-emulsified oily waters chemically containing hydrocarbons having densities related to the water one between 0.85 and 0.95. The heaviest materials (sludge, sand, etc.) sediment pre - decanting zone and are retained there. This compartment also retains hydrocarbons which are in easily floatable forms. For the separation zone only, water and substances lighter than water are passed, in particular the hydrocarbons that are to be separated. The separators are equipped with a coalescing filter, which allows the aggregation of the smaller oil particles into larger particles. The aggregation of the particles allows the increase of sufficient lift force to be released from the main flow lines towards the surface. In this chamber, the hydrocarbons build up on the surface, at the same time as the treated water, leaves the bottom of the equipment. The hydrocarbon separator is fitted with an automatic shut - off valve (solid anti - de - calibration system), which prevents the outflow of hydrocarbons once the maximum retention capacity of the equipment is reached, thus preventing contamination of the receiving medium. The flotator compartments and equipment are represented in Figure 28, it’s characteristic in Table 14. The operation of the hydrocarbon separators does not require energy consumption, based on the gravitational separation of materials with different density of water, assisted by the presence of a coalescent cell of oleophilic nature.

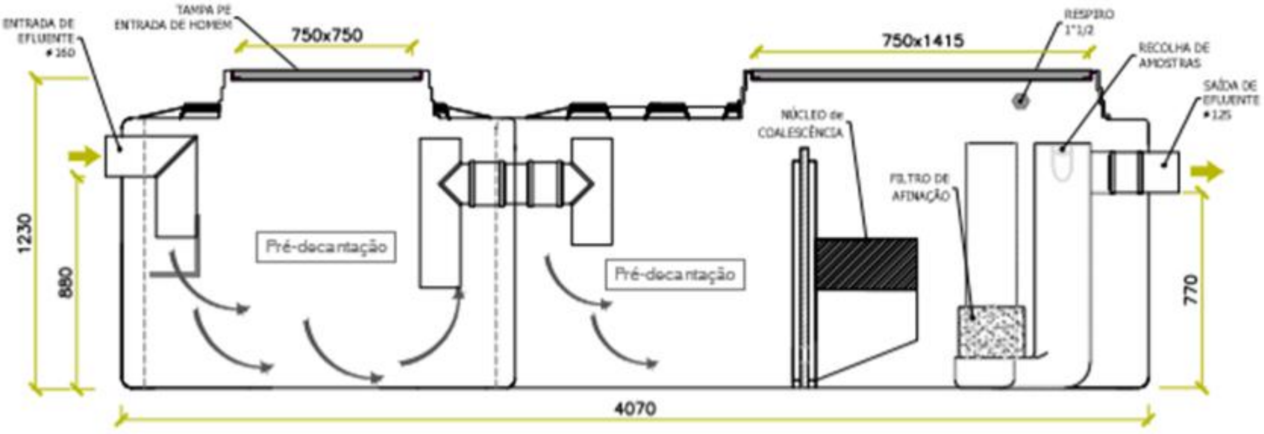


Figure 28: Flotator plant

Table 14: Flotator characteristics

Type	Flow rate (m^3/h)	Total V (L)	V Predecant (L)	V hydrocarb. collect. (L)	L (mm)	I (mm)	H (mm)	He (mm)	Hs (mm)	Tube D (mm)	Weight (kg)
Depuroil NS 8	3	3770	1030	2500	4070	960	1230	880	770	160	250

Figure 29: Flotator

5.3. Secondary treatment

5.3.1. Biological reactor

The effluent from the hydrocarbon separator is sent to a biological reactor in order to promote the removal of dissolved organic matter from the emulsion of detergents, chemicals and the dirt removed from the vehicles themselves. The biological batch reactor uses the MBBR (Moving Bed Bio-Reactor) (Figure 30 and 31 a) technology which is based on the development of biomass in plastic support media (spheres) (Figure 31 c) that float free in mixed liquor (Figure 31 b). The polypropylene (PP) spheres, that being much lighter, allow reactors of greater height and the application of hydraulic and organic loads also high (0.88 kg BOD_5/m^3 day). The plastic spheres must fulfill the following characteristics: high specific area, for allow greater contact area of the biofilm with the water to be treated, high porosity to minimize clogging and maximize ventilation and low cost (Table 17). The use of synthetic carrier means allows the growth of a biomass concentration per unit volume higher than conventional systems. This effect makes the reactor less sensitive to variations in concentration and flow. Toxic events or hydraulic shocks have a much lower effect on treatment effectiveness as they do not affect the total biofilm population and ensure a faster recovery. The MBBR characteristics are reported in Table 15.

To ensure complete treatment, the system also incorporates the addition of specific extremely active biological product, ECOZIMEX, based on cultures of microorganisms aerobic and facultative anaerobic, enzymes and supplements in trace elements and growth factors, for the liquefaction and digestion of fats, fatty substances, proteins, starch and cellulose. Enzymes have immediate and enhanced action thanks to the combined presence of bacteria, enzymes and nutrients. It is completely safe and harmless to people and the environment and it is completely biodegradable. It improves the efficiency of treatment systems either by competition with undesirable microorganisms or by increasing the rates of degradation of organic matter preventing and avoiding clogs and blockages of the system. It promotes the formation of biofilms on contact surfaces that prevent subsequent accumulation of fat, significantly reducing odors problems, improving the removal of BOD (chemical oxygen demand) and COD (chemical oxygen demand), while at the same time sedimentation of sludge. ECODEPURE® used 30 L/week (150 €/week) until 10th of May 2019 and then 15 L/week (75 €/week).

In the realization of an MBBR the most onerous phase is the start-up; by introducing the virgin filling bodies foams can be formed for the secretion of surface-active substances by the bacteria that begin to adhere to the supports; the foams disappear in a few days. Biomass rooting on virgin supports takes 3–5 weeks, with longer times during the winter. Once the biofilm has taken root, the mobile bed reactors suffer less from the negative effects of low temperatures than the activated sludge. The decrease in temperature negatively affects the speed of removal of pollutants, but positively influences the solubility of oxygen in water; the two effects compensate in an interval of a few degrees Celsius.

In an MBBR the global kinetics of removal of pollutants in MBBRs are mainly controlled by the diffusion of oxygen rather than by bacterial metabolisms alone. In mobile bed systems the ventilation serves three fundamental purposes: mixing, aeration and cleaning. Good mixing of water, nutrients and bio-elements is the fundamental idea of this technology. By providing the optimal conditions for mixing inside the reactor, all the bacteria anchored to the bio-elements are continuously exposed to the same type of environment. This allows the bio-reactor to operate at maximum capacity and fully utilize the specific surface available.

Aeration also provides part of the oxygen required for biological processes and during start-up of the bio-reactor it should be more delicate to allow the bio-film to take root permanently. As this biological film ages and loses its effectiveness, it detaches from the support, is discharged with filtered water and replaced by new, more active microorganisms. This continuous natural renewal action puts the water to be filtered in contact with a biofilm always at maximum efficiency and guarantees a biological treatment process that regulates itself and responds to load fluctuations (Metcalf and Eddy, 2014). The risk of clogging is very small, backwashes are not necessary to remove the excess biomass, the turbulence of the reactor causes the detachment of the external part of the biofilm, which can be separated from the water through a sedimentation action, mainly of the third type (zone sedimentation), but also second and fourth one are present, which takes place directly in the reactor itself, regulating the activity of the fan and the pump connected to the filters (Table 16). No cleaning or washing of the supports is necessary. High specific activity of the biomass, age of the mud independent of the hydraulic retention time: the same polluting loads can be treated in reactors of smaller volume than the equivalent active sludge tanks (Moazzem *at al*., 2012).

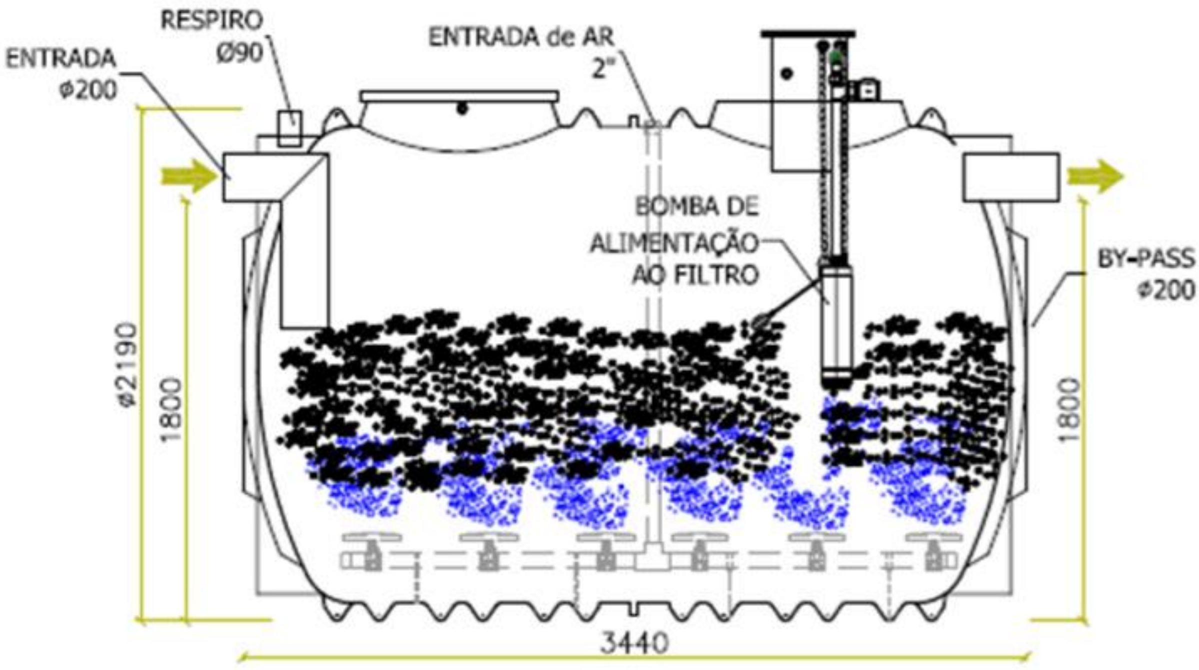
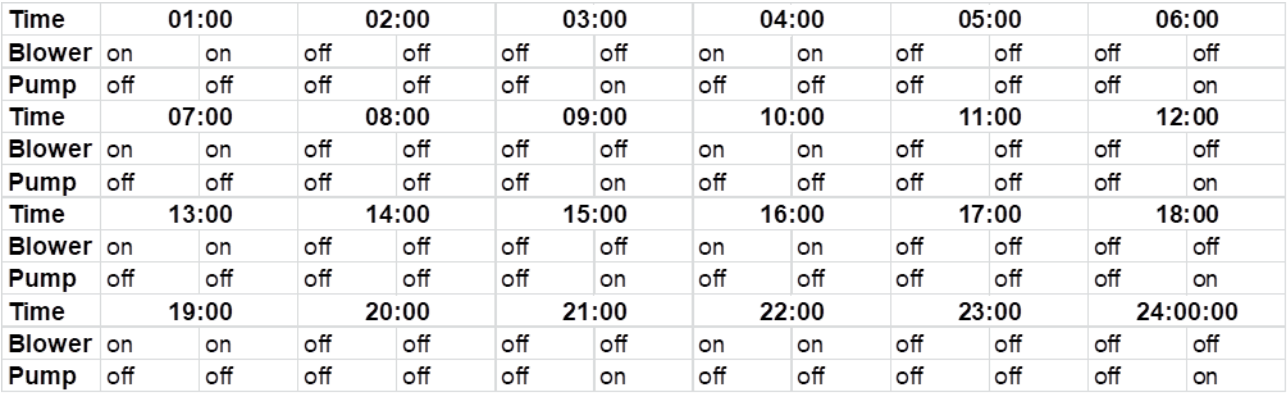


Figure 30: MBBR plant

Table 15: MBBR characteristics

Equipment	**Material**	**Volume (m^3)**	**Diameter (mm)**	**Length (mm)**	**Height (mm)**	**Flowrate (m^3/h)**	**N° spheres**
DEPURWASH 3.0	PE	10	2190	3.440	2.265	3	412500

Table 16: Biological reactor working schedule



Time	**01:00**		**02:00**		**03:00**		**04:00**		**05:00**		**06:00**	
Blower	on	on	off	off	off	off	on	on	off	off	off	off
Pump	off	off	off	off	off	on	off	off	off	off	off	on
Time	**07:00**		**08:00**		**09:00**		**10:00**		**11:00**		**12:00**	
Blower	on	on	off	off	off	off	on	on	off	off	off	off
Pump	off	off	off	off	off	on	off	off	off	off	off	on
Time	**13:00**		**14:00**		**15:00**		**16:00**		**17:00**		**18:00**	
Blower	on	on	off	off	off	off	on	on	off	off	off	off
Pump	off	off	off	off	off	on	off	off	off	off	off	on
Time	**19:00**		**20:00**		**21:00**		**22:00**		**23:00**		**24:00:00**	
Blower	on	on	off	off	off	off	on	on	off	off	off	off
Pump	off	off	off	off	off	on	off	off	off	off	off	on

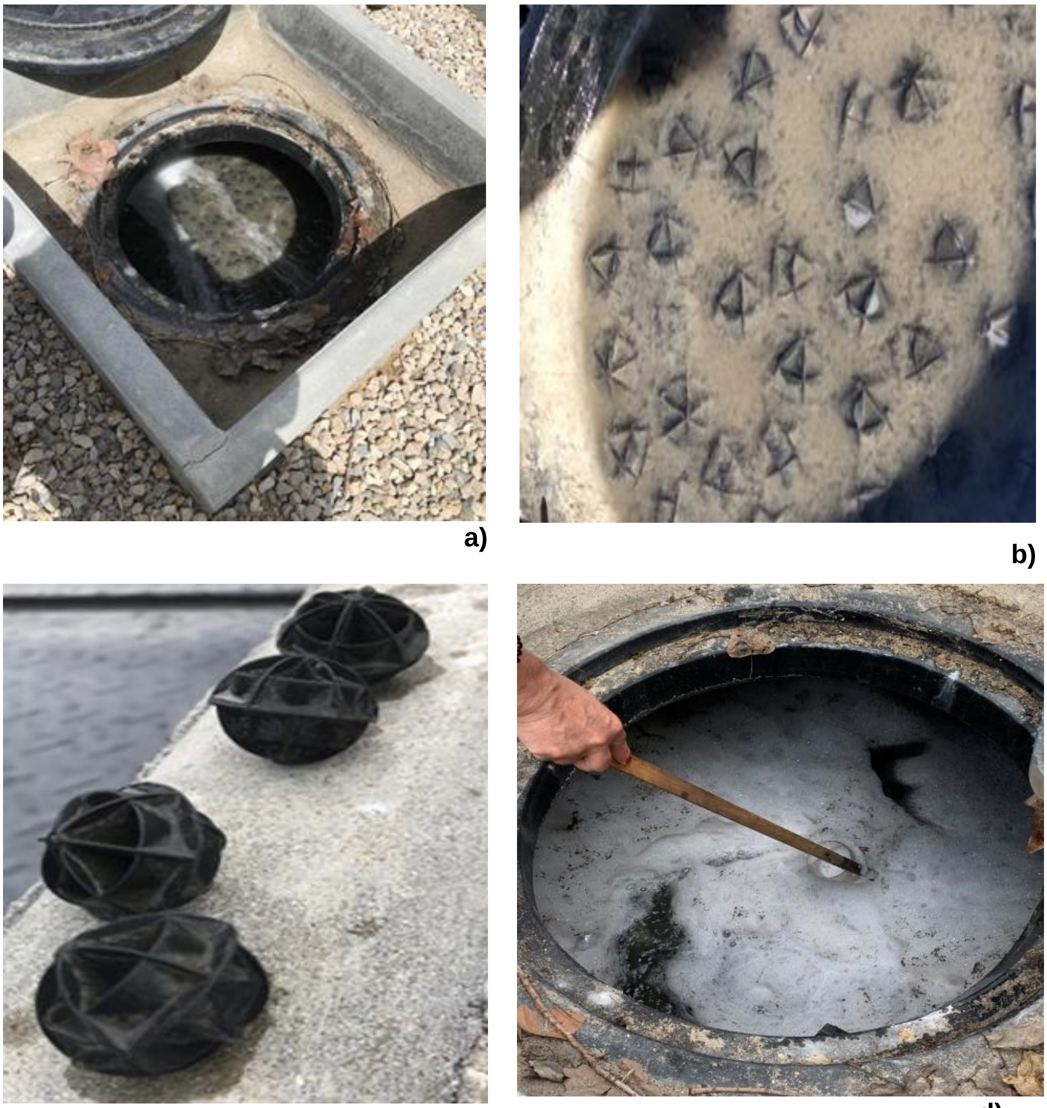
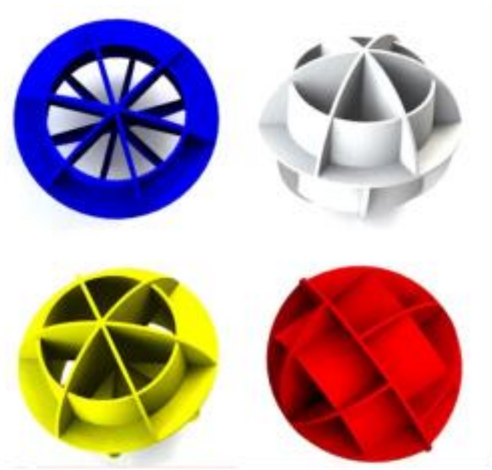

a) b) c) d)

Figure 31: Overview of the biological treatment**:** a) Biological reactor; b) Suspended biomass and fixed biomass on sphere; c) Sphere support; d) Bioreactor with halved amount of enzymes

Table 17: Support spheres characteristics

Parameters	**Value**
Specific surface	470 m^2/m^3
Shape	Spherical
Thickness	0,6 mm
Diameter	28 mm
Height	25 mm
Nº spheres per m^3	75.000 Un.
Empty index	90% aprox.



Material	PP
Density	0,905 ~ 0,985 gr/cm^3
Weight per sphere	1,6 gr
Weight per m^3	135 kg/m^3
Collocation	Random

5.3.2. Command and tuning module

The control and tuning module is supplied in a metal structure, where the blower, the enzyme dosing system, the electric panel and the re-use pump are installed, guaranteeing a simplified installation and minimizing working time. This has the electrical and hydraulic connections of the constituent equipment. This module has the following dimensional characteristics:

- **Enzyme Dosing System:** to ensure complete treatment, the system also incorporates the addition of specific aerobic enzymes for the degradation of contaminated hydrocarbon effluents. This addition is carried out by means of a peristaltic dosing pump of an extremely active biological solution, based on cultures of microorganisms, enzymes and supplements in trace elements and growth factors, for the liquefaction and digestion of fats, fatty substances, proteins, starch and cellulose. Peristaltic pumps are great for dosing liquids and have a flow setting of 0-100%. The peristaltic movement is originated by an automatic propulsion circuit inside a tube, which effects the compression followed by a recovery of the original form, leading to the suction of the liquid. The flow is controlled by adjusting the motor speed by means of a potentiometer placed on the front panel. This system is mounted on the metal structure and fed electrically (Figure 32). It is responsible for using 2 kW-h/m^3. It's characteristics are in Table 18.

Table 18: Enzymes dosing system characteristics

Type	Flowrate (L/h)	Pmax (bar)	Weight (kg)	Height (mm)	Width (mm)	Thickness (mm)	Rotation (rpm)	Power (W)	Phase
1-3	3	3	0.7	137	90	109	25	6	Mono

Figure 32: Enzymes dosing system

- **Blower:** the blower will supply air to the biological reactor and has the characteristics reported in Table 19.

Table 19: Blower characteristics

Type	Phase	Power (kW)	(V)	(Hz)	(A)	Insulation class	Protection	Weight (kg)	Working time per day (h)	Energy wasted per day (kW/d)
SC302SG 0.71	Three-phase	0.7	240	50	3.8	F	IP55	14	8	5.6

- **Filter lift pump:** after the settling period that follows the aeration / reaction time, the effluent is pumped under pressure to a multimedia filter followed by an activated carbon filter. The elevation to the filters is processed through submersible pumps installed inside the reservoir and has the following characteristics shown in Table 20.

Table 20: Filter lift pump characteristics

Type	Power (kW)	Exit D (mm)	Flowrate min (m^3/h)	P (bar)	Weight (kg)	Phase	Ampere	Working time per day (h)	Energy wasted per day (kW/d)
SCUBA SC409	0.9	1”1/4	6	3.5	18	Mono	5.28	4	3.6

5.4. Tertiary treatment

5.4.1. Filtration

The filtration is a physical treatment. Various chemical and physical phenomena follow in order to remove suspended particles (which are retained in the calibrated sand bed) and refractory organic matter (which is adsorbed by the contact surface of the activated carbon granules). Media filters and activated carbon are supplied already installed (and with the filtering charge inside) on the metal frame (Figure 33). After a predetermined period of time, and to avoid that the pressure loss increases excessively, the filters are rinsed counter-current and the filtration drain is returned to the biological reactor. The counter wash cycle of the filter is performed by means of a timer clock. The tip flow is calculated taking into account a traverse velocity of 10 m/h. Pressure filters are used to handle not excessive volumes of water (because otherwise they would be too expensive) and have the disadvantage of being closed, which does not allow the periodic control of the filter bed.

Figure 33: Pressure filtration system

5.4.1.1. Sand filter

Filtration on a granular medium is an operation used to remove suspended solids residues from an effluent previously subjected to primary and secondary treatment. The filter consists of a column partially filled with more inert materials of suitable granulometry which make up the filtering bed. Three sixths of the volume are occupied by anthracite with particles size of 2-3 mm, two sixths of fine sand of 0.8-1.2 mm and a sixth by coarse sand of 2-4 mm particles. The waste water is made to flow under pressure (5.5 bar) through the bed that holds the solids still present. The continuous deposition of the solids causes a progressive increase in the load loss so that when it reaches the allowed limit up to 5 bar when the filter is clogged (head loss of 0.5 bar when the filter is clean) the filtration operation is interrupted and the backwashing starts. The efficiency of the filtration depends on the characteristics of the filter medium and the solids to be removed and on the operating conditions. The main features of the filter media are: shape, dimensional distribution, density and resistance to abrasion, especially important in the backwashing operation. The size and shape of the granules determine the size of the inter granular voids (Marecos do Monte *et al.,*2016). The average size of the granules of the filter medium is calculated based on their size distribution. The filter medium is characterized by several parameters, for example the effective particle size and uniformity coefficient (gives an idea of the size distribution of the granules of the filter medium). In the case study wastewater the sand filter characteristic are in Table 21.

Table 21: Sand filter characteristics

Type	Flowrate (m^3/h)	P (bar)	V bed (L)	Weight bed (kg)	H (mm)	D (mm)	Retention time (h)	Phase	Potenza (kW)
ECO-FM 24T	1.5	5.5	290	358	2170	610	0.15	Mono	0.008

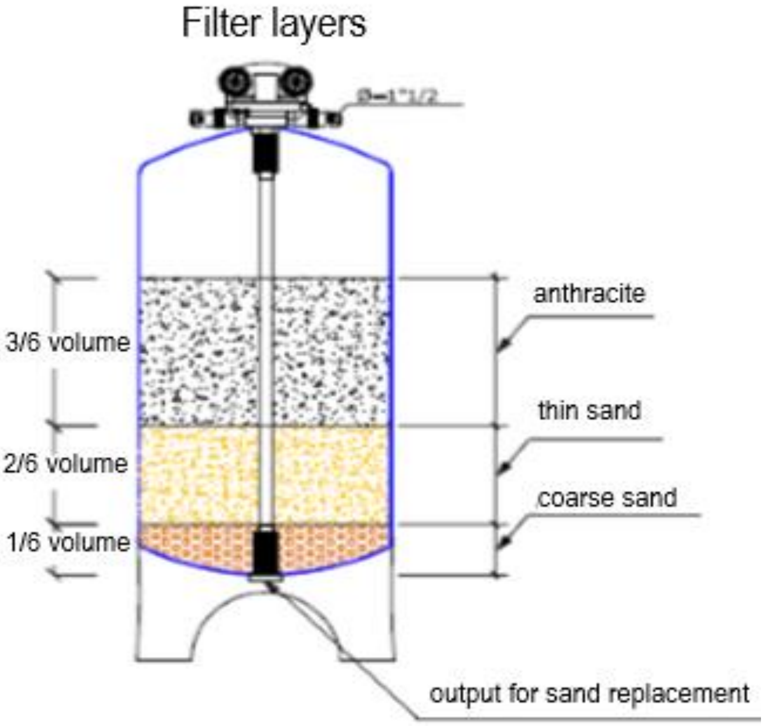


Figure 34: Sand filter

Backwashing is performed by sending treated water from the storage tank upwards. Since the filter has a descending flow with two different filtering media, the density of the two materials is so different to allow a hydraulic reclassification, consequent to the backwashing operation (Figure 35), which will lead to a filtering bed constituted in the upper part by the material with greater granulometry and density minor (anthracite) and in the lower part from the finest to higher density (sand). In the intermediate area of the bed there will be a mixing between the two materials. The drainage system consists of coarse sand . The filter is out of service for 8 minutes every 2 hours.

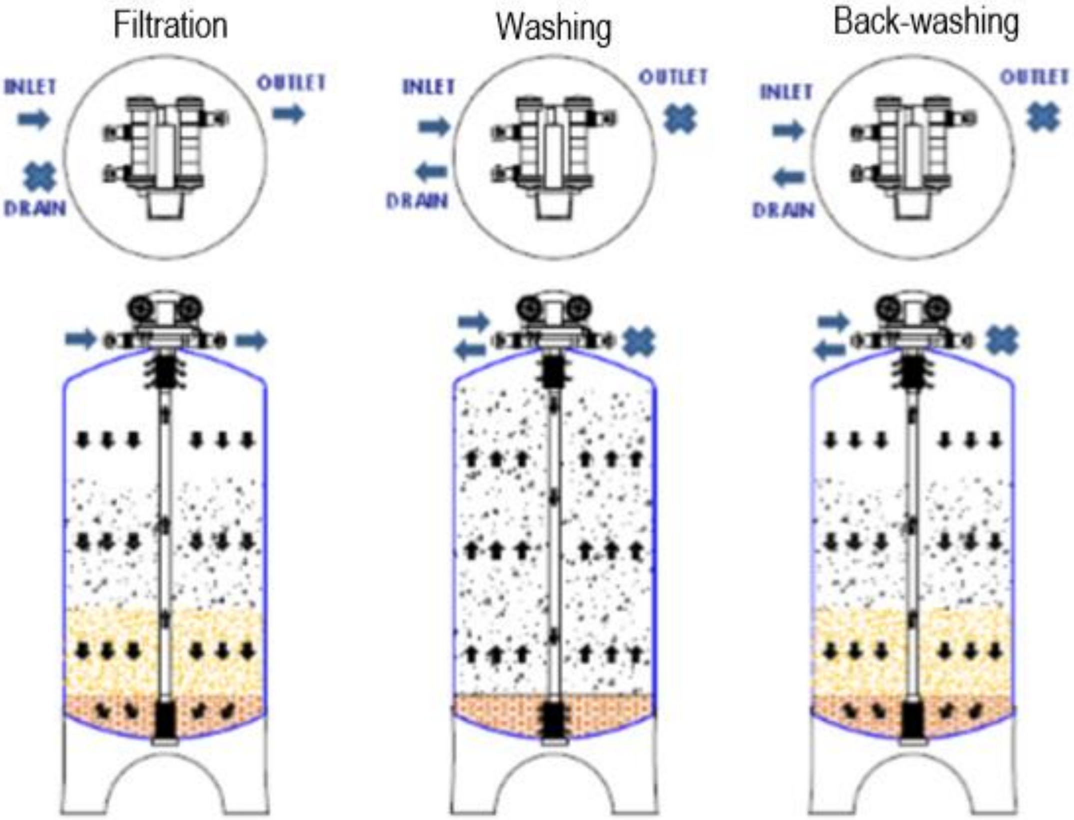


Figure 35: Filters operation

5.4.1.2. Activated carbon filter

The filtration using activate carbon is a chemical-physical treatment. Even after sedimentation, secondary treatment and sand filtration, soluble organic materials that are resistant to biological breakdown will persist in the effluent. The persistent materials are often refractory organics. The most practical available method for removing refractory organic compounds is by adsorbing them on activated carbon (U.S. EPA, 1979). This filter is a fixed pressurized bed (4 bar) made of granular activated carbon (GAC). Downflow columns are favored because of the advantage of achieving both adsorption and filtration in one step. Backwashing, which occurs every 2 hours for 8 minutes, is provided to limit the head loss (up to 5 bar when the filter is clogged and 0.5 bar when it is clean) two to build up of particulate matter in the column. It has a carbon screen and support grid installed in the bottom where one sixth of the filter volume is occupied by coarse sand particles of 2-4 mm, in the remaining five sixths of the volume activated carbon is present, its size is 0.6-2.4 mm (Figure 36). Other issues to consider are resistance to abrasion, ash content, and particular size which is particularly relevant to column design. Hydraulic loading rates between 5 to 12 m/h are used for down flow columns. The activated carbon filter characteristics are shown in Table 22.

Table 22: Activated carbon filter characteristics

Type	Flowrate (L/h)	V bed (L)	Weight bed (kg)	Retention time (h)	H (mm)	D (mm)	Phase	Power (kW)
ECO-FCA 30 T	4.5	475	330	0.24	2248	770	Mono	0.008

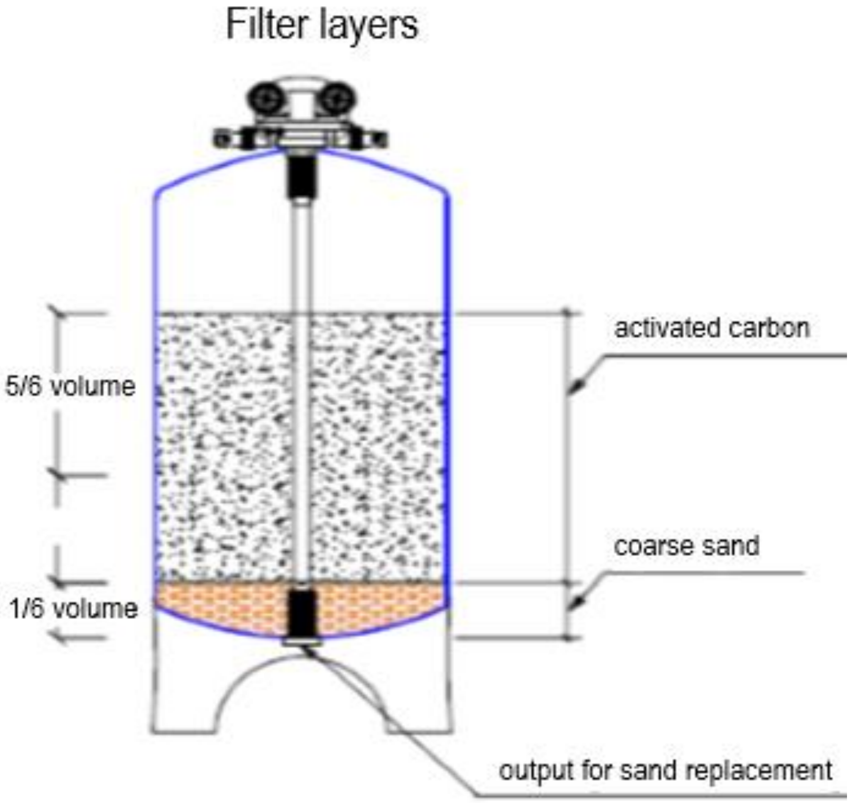


Figure 36: Activated carbon filter

For typical mesh sizes, backwash rates vary from 20 to 50 m / h. While the carbon bed depth is in the range 3 to 12 m, the column shell must be deep enough to allow for expansion during the backwash of 10 to 50 percent (U.S. EPA, 1973). After the adsorption capacity of the carbon has been exhausted, it can be restored by heating it in a furnace at a temperature sufficiently high to drive off the adsorbed organic matter. Keeping oxygen at very low levels in the furnace prevents carbon from burning. The organic matter is passed through an afterburner to prevent air pollution. In small plants where the cost of an onsite regeneration furnace cannot be justified, the spent carbon is shipped to central regeneration facility for processing. There is a loss of about 5 to 10 percent during each regeneration cycle. Carbon regeneration is a major consideration in the selection and design of GAC facilities.

5.5. Storage tank

The treated and clarified effluent is conveyed to an accumulation reservoir (Figure 38), constituting a water reserve ready for reuse. The reservoir has UV protection and is totally black opaque in order to avoid the development of algae and other microorganisms during the storage period and has the characteristics presented in Table 23 and summarized in Figure 37.

Table 23: Storage tank characteristics

Material	**V (m^3)**	**D (mm)**	**Cover (mm)**	**H (mm)**
PE	3	1500	1910	1540

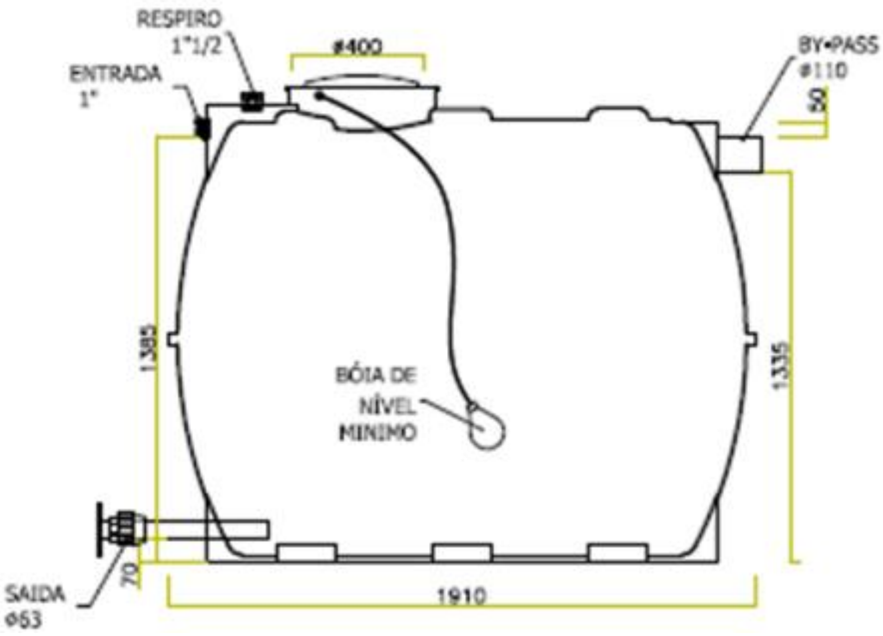


Figure 37: Storage tank diagram

Figure 38: Storage tank

5.6. Pressurizing pump to the washing system

Hydropressor group that will supply the washer system with treated water. A minimum level probe located in the accumulation tank will protect the pressure pump from dry running in the event of water shortage. In order to guarantee a high functional safety to the reuse line, the ECODEPUR® DEPURWASH system is equipped with by-pass to evacuate excess effluents (use of treated water less than the production capacity) and water inlet system in case lack of treated water in the system (use of treated water in excess of production capacity). This pump is supplied already mounted on the metal frame and has the characteristics presented in Table 24.

Table 24: Pressurizing pump characteristics

Type	**Power (kW)**	**Exit D (mm)**	**Flowrate min (m^3/h)**	**P (Bar)**	**Weight (kg)**	**Phase**	**(A)**
GENYOSYSTEM 5HM06P	1.1	1”	2.5	4	14	mono	6.84

Chapter 6

6 Results and discussion

6.1. Sedimentation and flotation

The values of the wastewater characterization parameters and the removal efficiency in sedimentation are reported in Table 25. From the results it is possible highlighting that this operation, because its physical nature has not a great influence on the removal of COD (6% and around 4%), even if, according to Metcalf & Eddy (2014) it is expected to remove around 20% of COD.

The reduction of TS in sedimentation is low (2.5% and 5%) because it affects most of all the reduction of the suspended particles with shape and weight enough to sediment, and usually is expected a removal of 30-50% (Huybrechts *et al*. 2002). The sedimentation acts according to Stoke's law on the particles with the right size. For fixed and volatile total solids is possible observe that while the amount of TFS decreases, TVS increase. This variation is due probably to a loss in weight of solid that must be added to that due to organic substances, because of phenomena that occur at 550 °C.

The removal for copper is almost the same for both the samplings and good enough considering a physical operation. This metals reduction occurs because the metals stays trapped in the particles that are subjected to Stokes' law as happen for the organic particulate (Smythe *et al*. 2007) The differences between the removal efficiencies for the first and second sampling are due to the variation of the influent flow rate, its temperature, because cold or warm water cause the formation of density currents that move along the bottom of the basin (Metcalf & Eddy, 2014). For the present work the collection have been realized at the same hour, while trucks were being washed in order to have more or less the same conditions.

The parameters analyzed and the removal efficiency in flotation, are reported in Table 26. From them it is possible noticing that this operation, even if it is physical has an influence on the removal of COD, because grease and oils, containing organic matters, are removed (around 25% and 14%) but these values of removal efficiency obtained are lower than ones reached applying different flotation technologies which are between 50-80% as reported in Table 5. Typical COD values are between 249-873 mgO_2/L (Etcheparea *et al*.,

2014) higher than the one for the first and second sampling, because it depends on the type of vehicle washed (a car or a truck as in this case study), its relative degree of dirtiness and on the washing substances.

On the TS the removal efficiency is very low for both samplings (0.5% and around 6%) because the flotation aims to remove oil and grease and not solids particles. It is significant that for the first sampling the removal efficiency is almost zero, so there is no flotation impact on it. Probably such a difference could be due to the uncertainty of the measures The removal efficiencies for copper and zinc are almost the same for both the samplings respectively around 20% for copper and 13% for zinc, their reduction occur because metals particles are trapped in grease and oils (Paolini, 1998).

Table 25: Sedimentation parameters analyzed (mean values) and removal efficiencies

Sampling number	**COD (mgO_2/L)**			**TS (mg/L)**			**TFS (mg/L)**			**TVS (mg/L)**			**[Cu] (mgCu/L)**		
	In	Out	*Ef.* %	In	Out	*Ef.* %	In	Out	*Ef.* %	*In*	*Out*	*Ef. %*	*In*	*Out*	*Ef. %*
1	1479	1382	6.6	1003	978	2.5	515	462	10.3	488	520	-	0.49	0.41	16.3
2	1663	1603	3.6	1145	1085	5.2	597	520	12.9	548	565	-	0.51	0.43	15.6

Table 26: Flotation parameters analyzed (mean values) and removal efficiencies

Sampling number	**COD (mgO_2/L)**			**TS (mg/L)**			**TFS (mg/L)**			**TVS (mg/L)**			**[Cu] (mgCu/L)**			**[Zn] (mgZn/L)**		
	In	***Out***	**Ef. %**	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef.%***
1	1382	1304	25.2	978	973	0.5	462	453	1.9	520	516	0.7	0.41	0.33	19.5	0.65	0.57	12.3
2	1603	1386	13.6	1085	1022	5.7	520	472	9.1	565	550	2.6	0.43	0.35	18.6	0.69	0.60	13.0

6.2. Biological treatment

The values of the wastewater characterization parameters and the removal efficiency for biological treatment, are presented in Table 27. From them it is possible highlighting that this chemical process has an impact on the COD of almost 42% when 30 L/week of enzymes are used to almost 33% of removal when halved of the amount of the enzymes is used. These values are very low if compared with a membrane bioreactor (MBR) which has a COD removal efficiency of 99.2% (Boluarte *et al*. 2016), this probably because in a MBBR, the secondary sedimentation happens inside it, so the organic matters present is not reduced to the maximum. However, in comparison with a conventional biological treatment, MBBR can remove up to 120 kg COD/m^3 against the 18 kg COD/m^3 (Ecologyx, 2018). The impact on the TS is of 11% and 10% for respectively the first and second sampling. The effect on the zinc removal is almost the same for both of the samplings, even if the enzymes in the second sampling are halved, almost 39% and 35%, but the removal efficiencies for the copper are quite different, around 45% for the first sampling and around 15% for the second. This difference can be charged to the different amount and kind of microorganism, but because the amount of TVS, 460 mg/L for the first sampling and 588 mg/L for the second sampling, said that the quantity of microorganism is not the cause, probably copper reduction difference is due to the different wastewater composition related to the kind of vehicle washed. Copper comes from washing tyres and brakes, so if the vehicle is more or less old the amount of metals present can vary, it is commonly found in paints and rubber products such as brake pads (Brown, 2002).

Table 27: Biological treatment parameters analyzed (mean values) and removal efficiencies

Sampling number	Parameters																	
	COD (mgO_2/L)			**TS (mg/L)**			**TFS (mg/L)**			**TVS (mg/L)**			**[Cu] (mgCu/L)**			**[Zn] (mgZn/L)**		
	In	***Out***	**Ef. %**	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef.%***
1	1304	758	41.8	973	865	11.0	453	405	10.6	516	460	10.8	0.33	0.18	45.4	0.57	0.35	38.6
2	1386	930	32.8	1022	920	10.0	472	332	29.6	570	588	-	0.26	0.22	15.4	0.60	0.39	35.0

6.3. Filtration and storage tank

The filtration values of the parameters analyzed and the removal efficiency are reported in Table 28. From them it is possible observing that this operation has the greatest influence on the reduction of all the parameters, compared to the removal efficiencies of the other units operation and process. It is been calculated the removal efficiency after the sand filtration for the COD, TS and Cu, which are respectively: 7%, around 13% and around 14%, against the 89%, 27% and 23% obtained after the activated carbon filter. Therefore, the sand filter impact on the total filtration system is less significant and it is possible affirm that most of the removal is done by the activated carbon filter, which combine the effect of filtration with adsorption. It is due to this operation that COD, TSS and Cu values are below the legal limit.

The final treated water storage in the tank, then flows through the distribution net to be reused in the washing station. Sometimes happens that the amount of water required to wash trucks is higher than the one provided by the recycle of water. In this case an addition of drinking water is made occurs a dilution of the treated water, so it possible explain why after the storage tank the values of the parameters analyzed are lower than the effluent from the filtration system (Table 29).

Table 28: Filtration parameters analyzed (mean values) and removal efficiencies

Sampling number	**COD (mgO_2/L)**			**TS (mg/L)**			**TFS (mg/L)**			**TSS (mg/L)**			**FSS (mg/L)**			**[Cu] (mgCu/L)**		
	In	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef. %***	***In***	***Out***	***Ef.%***	***In***	***Out***	***Ef.%***
1	758	97	87.1	865	488	43.6	405	232	42.7	225	125	44.4	20	15	25	0.18	0.10	44.4
2	930	103	88.8	920	672	26.9	333	252	24.2	285	190	33.3	85	30	64.7	0.22	0.17	22.7

Table 29: Storage parameters analyzed (mean values) and dilution

Sampling number	**COD (mgO_2/L)**			**TS (mg/L)**			**TSS (mg/L)**			**[Cu] (mgCu/L)**			**[Zn] (mgZn/L)**		
	In	***Out***	***Di. %***	***In***	***Out***	***Di. %***	***In***	***Out***	***Di. %***	***In***	***Out***	***Di.%***	***In***	***Out***	***Di.%***
1	97	53	45.0	488	390	20.0	125	85	32.0	0.10	0.096	4.0	0.35	0.12	65.7
2	103	74	28.6	672	480	28.6	190	153	19.5	0.17	0.12	29.4	0.40	0.19	52.5

6.4. Wastewater treatment plant

pH and temperature results

Table 30 presents the results of pH and temperature in wastewater from Transportes Gama service station for the first and second sampling. The pH varies a lot throughout the treatment system.

Table 30: pH and T determinations

Samples	1st sampling		2nd sampling	
	pH	**T (°C)**	**pH**	**T (°C)**
Wastewater	/	/	6.1	23.3
Influent	4.9	19.0	4.8	22.9
Sedimentation	4.7	18.9	4.6	22.8
Flotation	4.8	19.0	4.5	22.7
Inside MBBR	/	/	6.7	22.9
After MBBR	7.5	21.0	6.2	23.0
Sand filtration	/	/	6.3	22.8
Filtration system	7.0	18.5	6.1	22.9
After storage tank	7.1	18.0	6.3	22.6

The highest temperature of the residual water sample from the biological treatment is due to the reactions developed by the predominantly aerobic microorganism. Before the biological reaction takes place, the pH of the previous units of operation are acid because of the substances used during the washing step. After the biological treatment the pH is around 7 in all the next units due to the enzymes that neutralize the wastewater.

Solids results

Several weighing's were carried out to determine solids. The weighing carried out for TS and TSS are given in Annex B. Figures 39 and 40 are a representation of the reduction of TS and TSS along all the wastewater treatment plant. Tables 31 and 32 show the values obtained for the TS, TFS, TVS, TSS, FSS and VSS together with their relative removal efficiencies. The final value of the TSS is below the limit of law, while the final values of TS is not a truthful parameter because of the many variations that can affect this result since the sampling step.

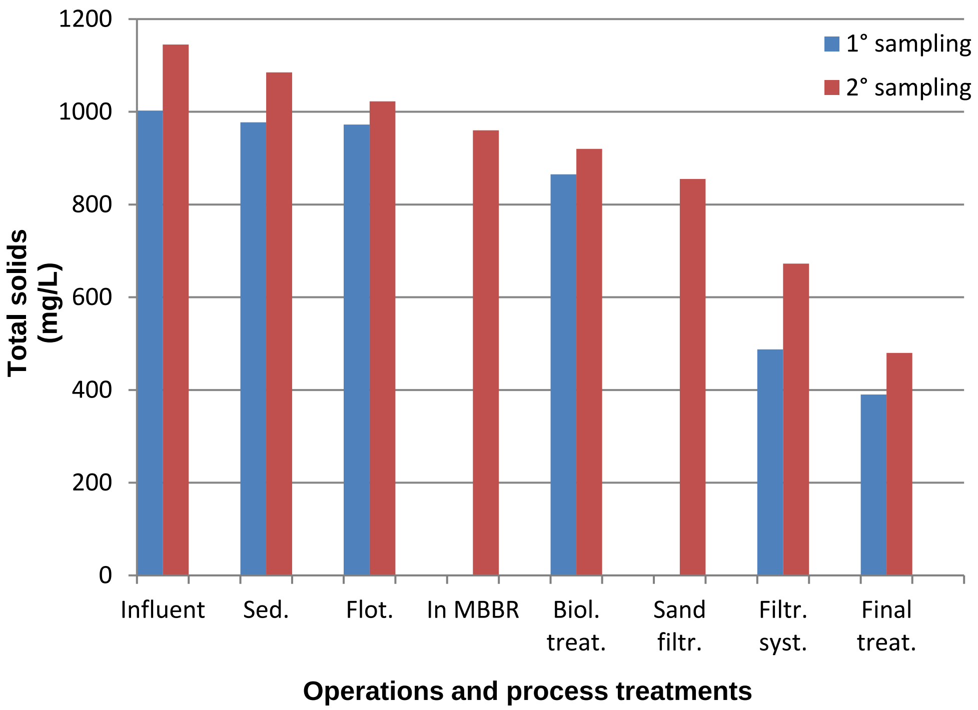


Figure 39: TS in the wastewater treatment plant

Table 31: Total solids and removal efficiency

Items	1° Sampling			2° Sampling		
	TS (mg/L)	**TFS (mg/L)**	**TVS (mg/L)**	**TS (mg/L)**	**TFS (mg/L)**	**TVS (mg/L)**
Influent	1003	515	488	1145	597.5	547.5
Final treatment	390	173	217	480	137.5	342.5
Total removal efficiency (%)	61.1	66.4	55.5	58.0	77.0	37.4

According to the values of wastewater treatment plant, it can be observed that the sample from the biological treatment contains a reduced content of TS in comparison to the previous units operations. The final sample, after the whole treatment process, presents, in comparison with the initial values, a significant reduction in TS content (58-61.1%).

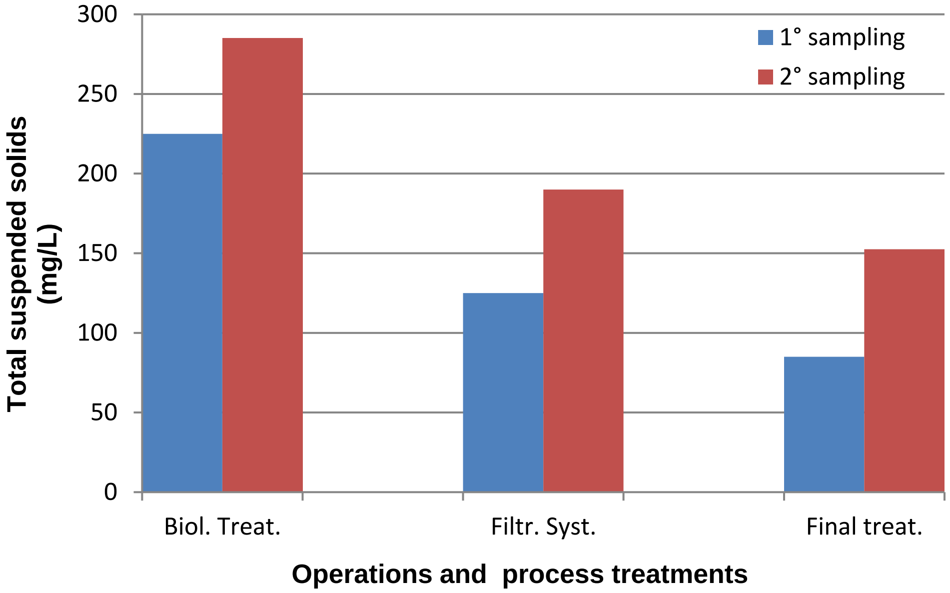


Figure 40: TSS in the wastewater treatment plant

Table 32: Suspended solids Total removal efficiency

	1° Sampling			**2° Sampling**		
Items	**TSS (mg/L)**	**FSS (mg/L)**	**VSS (mg/L)**	**TSS (mg/L)**	**FSS (mg/L)**	**VSS (mg/L)**
Biological treatment	225	20	205	285	85	200
Final treatment	85	5	80	153	17.5	135
Total removal efficiency (%)	62.2	75	60.9	46.3	79.4	32.5

COD results

The calculations of the COD are presented in Annex C. Figure 41 shows the values obtained from the COD of the wastewater from the service stations for the first and second sampling. As is possible see wastewater from the Gama Transport station, in general, contains a greater amount of organic matter. The influent value of COD is very high, but it is not unusual as reported also in Table 3. Table 33 reports the total removal efficiencies from which is possible observe that are the almost the same for both the samplings: 96.4% against 95.5%, so is possible affirm that the reduction of the enzymes has not a negative impact on the biological treatment. The impact of the filtration system on the dejection

(87% for the first sampling and around 90% for the second one) is higher than the one of the biological reactor (around 42% for the first sampling and 33% for the second one), these values are expected because of the characteristics of the biological reactor, which is a MBBR that means that the secondary sedimentation occurs inside it and not outside, so the organic matters is still present in the effluent from the bio-reactor. COD limit of law is respected thanks to the action of the filtration system.

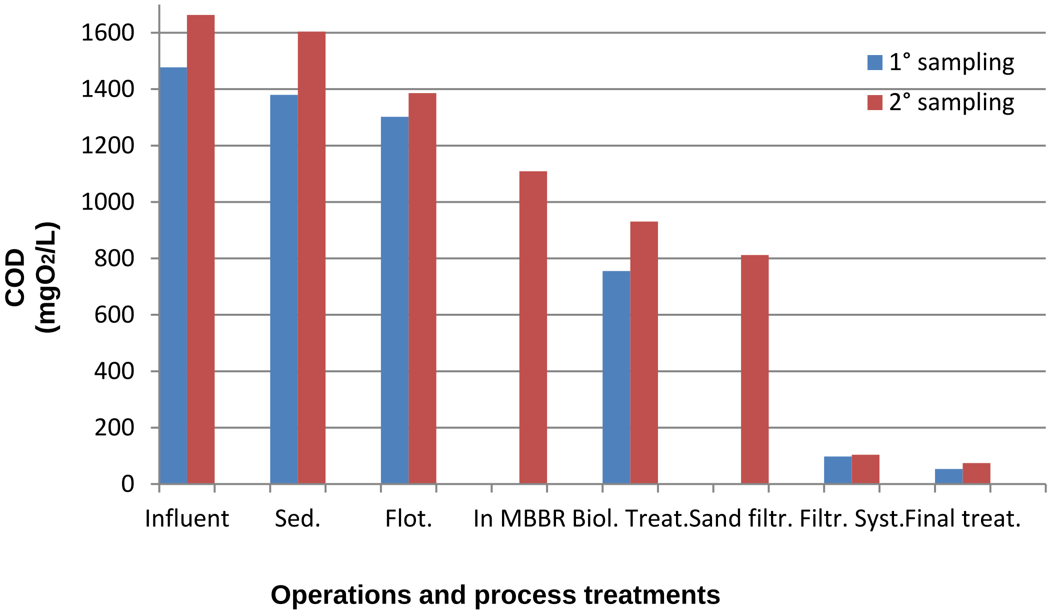


Figure 41: COD in the wastewater treatment plant

Table 33: COD total removal efficiency

Items	**1° Sampling** **COD (mgO$_2$/L)**	**2° Sampling** **COD (mg O$_2$/L)**
Influent	1479	1663.3
Final treatment	53.6	74.2
Total removal efficiency (%)	96.4	95.5

Metals results

Figure 42 and 43 show the amount of copper and zinc in the wastewater along all the treatment plant. Table 34 shows the values obtained in the determination of metals, copper and zinc, from the wastewater from the service station. Thanks to the calibration curves obtained in Chapter 4, it was possible, with the same procedure, determine metals concentrations which calculation are reported in Annex D.

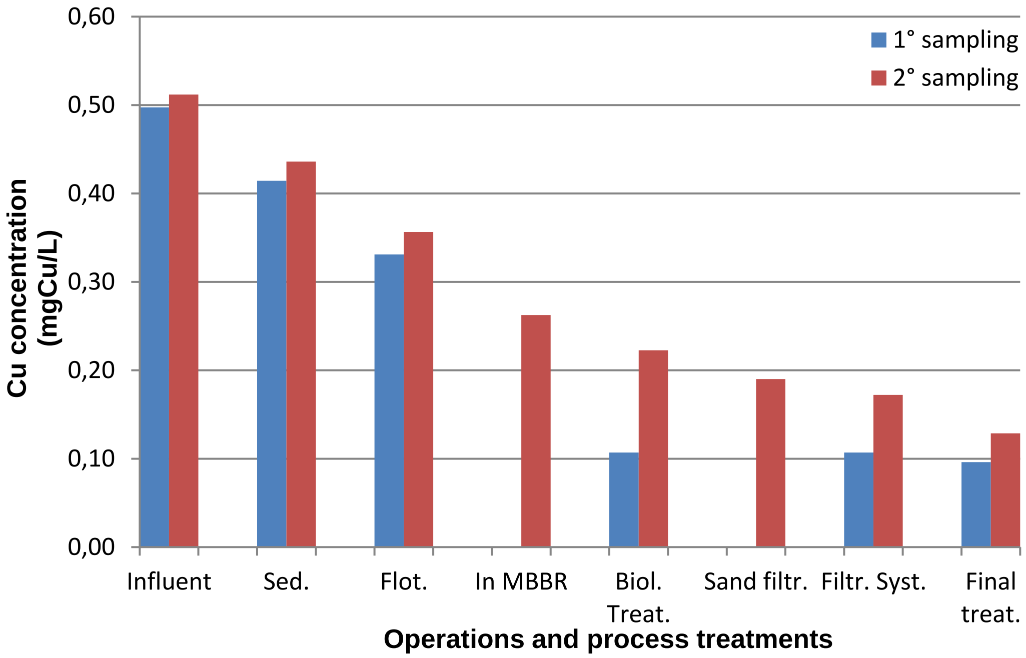


Figure 42: Cu in the wastewater treatment plant

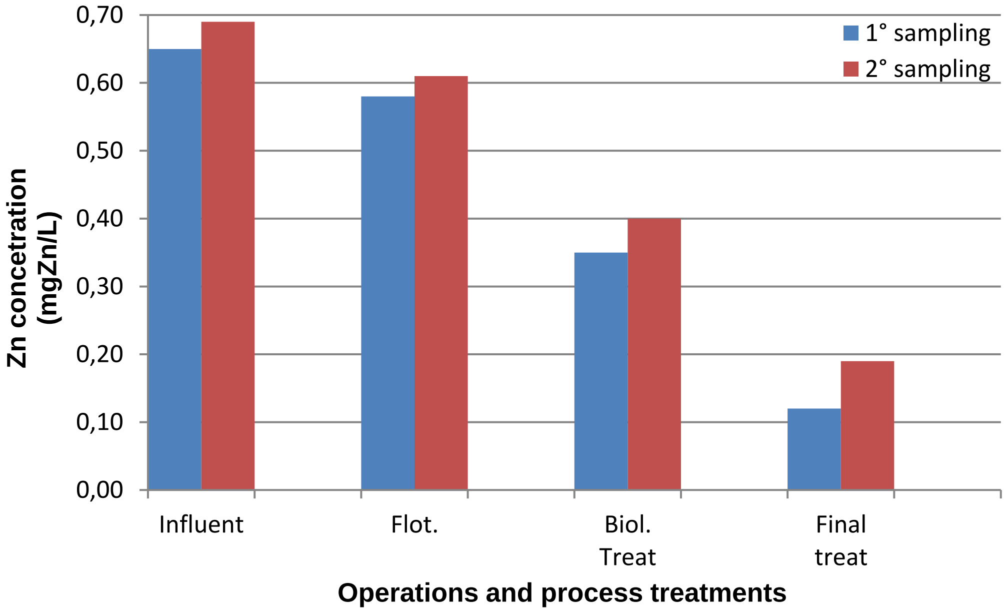


Figure 43: Zn in the wastewater treatment plant

Table 34: Metals total removal efficiency

Items	1° Sampling		2° Sampling	
	Cu (mg/L)	Zn (mg/L)	Cu (mg/L)	Zn (mg/L)
Influent	0.49	0.65	0.51	0.69
Final treatment	0.096	0.12	0.12	0.18
Total removal efficiency (%)	80.4	81.5	76.4	73.9

The total Cu and Zn removal efficiencies for the first collection are around respectively 80% and 81%. For the second collection the Cu and Zn removal efficiencies are around respectively 77% and 74%. Also, for the metals as for the COD the halved amount of enzymes has not influenced them negatively, in fact both of them are still below the limit of law.

Total Results

The different amount of enzymes used in the biological treatment has not a negative impact on the performance of the total wastewater treatment plant. The parameters analyzed of the final treated water for the second sampling are below the limit of law, so the amount of enzymes used per week can be halved leading to cost saving for 3,900 € per year.

Recycling the 99.9% of wastewater represents a water saves of 2,628 m^3 per year, assuming that Transportes Gama station washes 9 trucks per day for which is used an average of 800 L/washing. That in terms of financial cost means 6,318 € per year saved; this calculation was carried out considering a water cost of 24.04 €/month comprehensive of all the taxes as reported for the 2017 in ERSAR (Portuguese regulatory entity of services of water and waste) taking into account a monthly consumption of 10 m^3/month, which means 2.404 €/m^3, for the location of Seixal.

Chapter 7

7. Conclusions

With this work the optimization and the quality of the reuse of the wastewater after treatment were verified, in accordance with European and National water saving measures, in order to contribute to sustainable development.

On the present work, the following conclusions were drawn:

- The enzymes amount can be halved, leading to cost saving for 3,900 € per year;
- Recycling water saves 2,628 m^3 of water equal to save almost 6,320 € per year.

Implementation of a water recycling system into a vehicle wash leads to higher water quality reused in the washing operation, lower fresh water consumption and lower sewer discharges fees, which in turn reduces the burden on sewage treatment plants, which protects the environment from pollution.

Water conservation should go together with energy conservation in order to make the car wash business efficient from the operator’s and environmental points of view.

Based on the present work it is possible affirm that Transportes Gama truck wash station, thanks to ECODEPUR® technologies, reach the goal of optimizing the quality and the reuse of treated water.

Chapter 8

8. Future studies

In light of this work future possible challenges in the case study wastewater treatment plant can be:

- optimize the sedimentation and flotation units in order to improve the removal efficiencies;
- try to reduce more the enzymes amount, to decrease the consequent operative costs or try use other kind of microorganisms in order to pursue the same goal.
- other possible step is to change the vehicle wash structure by a dry cleaning system that has spread especially in recent years thanks to the creation of specific products, called "savewater", that is, that do not need to be rinsed, protecting the environment all focused on reducing energy and water consumption. For example Edo s.r.l. company, operating in the carwash sector, after years of intense research and experimentation of innovative systems for motor vehicle detergency, has designed LIMPO completely environmentally friendly dry and steam car washing system.

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Annexes

Annex A

Abstract for the Fórum de Engenharia Química e Biológica, 2019

Water reuse in vehicle washing systems: a case study to optimize treatment plant operations

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Wastewater generated from carwash contributes effectively to environmental contamination due to the presence of many impurities as oil and grease, suspended solids, sand, metals and surfactants. Car wash generates a high amount of wastewater according to the type of car wash system [1]. The quantity of used water is between 150 and 350 liters per day [2]. Water recycling provides a great method to manage the station's productivity and to minimize the water consume. The present work aims to evaluate the efficiency of pollutants removal from the wastewater obtained from vehicles washing, in order to reuse this treated wastewater in the first rinse of the vehicles. This work presents a case study of a carwash station located in Seixal, Transportes Gama station, that has a compact treatment plant with the following operations: primary sedimentation, flotation, biological treatment, secondary sedimentation, sand and activated carbon filtrations and adsorption on activated carbon (Figure 1) [3]. The efficiency of each operation was evaluated by several parameters, namely pH, temperature, chemical oxygen demand (COD), suspended solids and metals (Zn and Cu). The early results show that the COD and suspended solids are within the limits of the national legislation for wastewater discharge and the total efficiency removal of these pollutants in the treatment plant is higher than 75%. The ultimate objective of this work will be to optimize treatment plant operation for pollutant removal, savings of energy and added reagents. This practice of water reuse is in line with the European Water Savings Objectives (EU Water Framework Directive) by reusing water in industry whenever possible.

Figure 1. Wastewater treatment plant for Carwash
(left: overview of the treatment plant, right: pressure filters)

The authors thank to ECODEPUR and Transportes Gama, Seixal

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[1] Moazzem, S.; Wills, J.; Fan, L.; Roddick, F.; Jegatheesan, V. *Environmental Science and Pollution Research*. **2018**, 25, 8654–8668.

[2] Grup Fundació Ramon Noguera, Consorci Life MinAqua, Glam Comunicació. Good practices guide for car wash installations. September **2016**, 1, 13.

[3] ECODEPUR® DEPURWASH Sistema de Tratamento e Reciclagem de Águas de Lavagem.

Poster for the Fórum de Engenharia Química e Biológica, 2019

Water reuse in vehicle washing systems: a case study to optimize treatment plant operations

Rabagliati, B.[1*], Matos, M.[1], Santos, M.T.[1]

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Abstract

Wastewater generated from carwash contributes effectively to environmental contamination due to the presence of many impurities as oil and grease, suspended solids, sand, metals and surfactants. Car wash generates a high amount of wastewater according to the type of car wash system [1]. The quantity of used water is between 150 and 350 liters per day [2].

Water recycling provides a great method to manage the station's productivity and to minimize the water consume. The present work aims to evaluate the efficiency of pollutants removal from the wastewater obtained from vehicles washing, in order to reuse the treated wastewater in the first washing step of the vehicles.

Figure 1. Tracks

Figure 2. Wastewater treatment plant for Carwash- overview of the treatment plant

Figure 3. Flotator

Figure 4. MBBR

Figure 5. Pressure filters

Methodology

This work presents a case study of a carwash station located in Seixal, Transportes Gama station, that has a compact treatment plant (Figure 2) with the following operations: primary sedimentation, flotation (Figure 3), biological treatment (Figure 4), secondary sedimentation, sand and activated carbon filtrations and adsorption on activated carbon (Figure 5) [3]. The efficiency of each operation was evaluated by several parameters, namely pH, temperature, chemical oxygen demand (COD), suspended solids (Figure 7 and 8) and metals (Zn and Cu). The sampling of a water is a fundamental operation for the purposes of a correct characterization. This operation involves choosing the sampling point and the sampling technique. In this work the samples were taken manually from six different points of the carwash plant, two samples were taken after each treatment unit as shown in Figure 6 (wastewater, after sedimentation, after flotation, after biological treatment, after filtration system, after storage tank), three times over three months The collection was the 8/4/2019 at 15:00 pm at Transportes Gama track's wash station, in Seixal (Figure 1). The sampling point must be that in which the turbulence of the liquid stream to be sampled is sufficient to guarantee the homogeneity of composition. During the collection infact the station was in operation, so fresh samples from the washing tracks were collected. Once the water samples have been taken, they must be stored until the time of analysis in conditions that prevent significant changes in water quality. The samples in this work were collected in PET (Figure 3) containers and refrigerated at 4°C. Then the experiments started.

● Collection point

Figure 6. Wastewater treatment scheme from car washing - collection points

Results

From the early analysis of the waste water after several kind of treatments the results are represented in the following Table 1.

Table 1. Treated water characteristics

Parameter	Wastewater	Sedimentation	Flottation	Biological treat.	Filtration	Final treat.
pH	4.93	4.75	4.84	7.51	7.01	7.13
TºC	19	18.9	19	21	18	18.5
COD (mg/g)	1343.1	1490	1382.1	758.3	97.5	53.6
ST (mg/g)	1003	978	973	865	488	390
SV (mg/g)	488	516	520	460	256	217
SF (mg/g)	515	462	453	405	232	173

Figure 7. Evaporation

Figure 8. Solids at 103°C-105°C

Conclusion

The early results show that the COD and suspended solids are within the limits of the national legislation for wastewater discharge and the total efficiency removal of these pollutants in the treatment plant is higher than 75%.

References

[1] Moazzem, S.; Wills, J.; Fan, L.; Roddick, F.; Jegatheesan, V. *Environmental Science and Pollution Research*. **2018**, 25, 8654–8668.
[2] Grup Fundació Ramon Noguera, Consorci Life MinAqua (Universitat de Barcelona, IQS, Aqualogy and GUREAK), Glam Comunicació. Good practices guide for car wash installations. September 2016, 1, 13.
[3] ECODEPUR® DEPURWASH Sistema de Tratamento e Reciclagem de Águas de Lavagem.

Abstract for the ICEH, 2019

ICEH
LISBON 2019
Lisbon, 25-27 September 2019
"NEW" CHALLENGES FOR THE FUTURE

Title:

Total water reuse in vehicle washing systems – a step to a sustainable use of water

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Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 500 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Wastewater generated from carwash contributes effectively to environmental pollution due to the presence of oil and grease, suspended solids, metals and surfactants. Carwash generates a high amount of wastewater according to the type of car wash system[1]. The quantity of water used in washing is very high between 50 and 900 L/vehicle[2]. Water recycling provides a great method to manage the station's environmental friendly to minimize the drinking water consume by wastewater reuse.

The present work aims to evaluate the efficiency of pollutants removal from vehicles washing wastewater in a case study, Transportes Gama station, located in Seixal. The station has a compact treatment plant, built by Ecodepur[3], with: primary sedimentation, flotation, biological treatment, secondary sedimentation, sand and activated carbon filtrations (Figure 1).

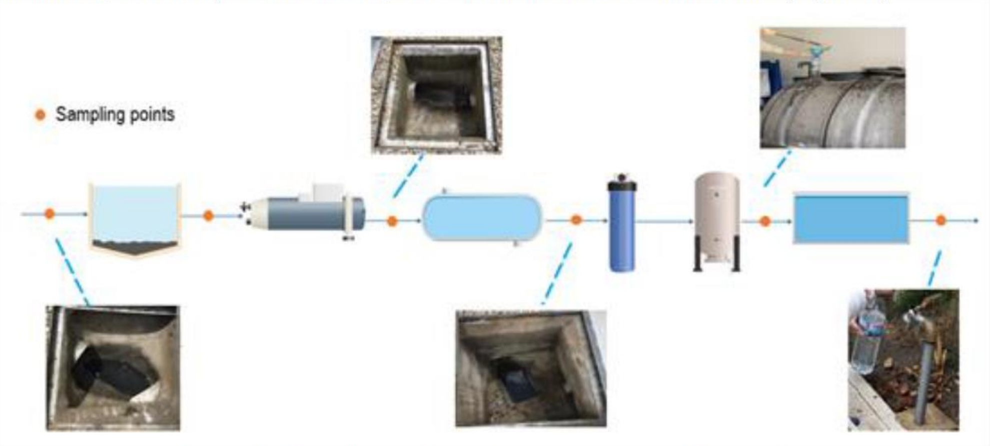


Figure 1. Sampling points in the wastewater treatment plant

The ultimate objective of this work is to optimize treatment plant operation for pollutant removal, savings of energy and added reagents. This practice of water reuse is in line with the European Water Savings Objectives (EU Water Framework Directive) by reusing water in industry whenever possible.

The efficiency of each operation and process was evaluated by several parameters: pH, temperature, chemical oxygen demand (COD), total solids (TS), total suspended solids and metals (Zn and Cu). To evaluate the enzyme effect in the efficiency removal of all parameters two arrays we done, the first with 30 L/week and a second with half of enzyme volume

added. The results show that the COD and metals are within the limits of the national legislation for wastewater discharge in both tests. The main costs of wastewater treatment plant are energy and enzyme addition for biological treatment process. In the first assay the treatment plant presents a total efficiency removal of 96.3% for COD, 61.1 for TS, 80.4 for Cu and 81.5 % for Zn. It was verified that the enzyme volume reduction had a small effect in the total removal efficiency with 95.6, 58.1, 76.5 and 73.9% for COD; TS, Cu and Zn respectively, but represents a saving of 3,900 €/year.

Most of the treated wastewater is reuse in the vehicles washing, which represents a wastewater discharge near zero, in this way it possible to contribute for sustainable use of water.

The authors thank to ECODEPUR and Transportes Gama, Seixal

References

[1] Moazzem, S.; Wills, J.; Fan, L.; Roddick, F.; Jegatheesan, V. Environmental Science and Pollution Research. 2018, 25, 8654–8668.
[2] Grup Fundació Ramon Noguera, Consorci Life MinAqua (Universitat de Barcelona, IQS, Aqualogy and GUREAK), Glam Comunicació. Good practices guide for car wash installations. September 2016, 1, 13.
[3] ECODEPUR® DEPURWASH Sistema de Tratamento e Reciclagem de Águas de Lavagem.

Annex B

Table 35: Weighing for TS, TFS and TVS (1st sampling)

				Capsule+Residue (Oven) 103-105ºC (g)			Capsule+Residue (Furnace) 550ºC (g)				TS [mg/L]	TS [mg/L] average	TFS [mg/L]	TFS [mg/L] average	TVS [mg/L]	TVS [mg/L] average
Sample	**Capsule**	**Weight**	**Sample volume (L)**	**1ª**	**2ª**	**3ª**	**1ª**	**2ª**	**3ª**	**4ª**						
1ª Caixa Visit	1 Caixa	37.615	0.02	37.636	37.635	37.6349	37.626	37.625	\	\	1005	1003	515	515	490	487.5
	1. Caixa	32.168	0.02	32.188	32.188	32.1876	32.18	32.178	32.178	\	1000		515		485	
2ª Caixa Visit	2 Caixa	40.375	0.02	40.395	40.395	40.3943	40.384	40.384	\	\	985	978	465	462	520	515
	2. Caixa	39.823	0.02	39.845	39.843	39.8425	39.834	39.833	39.832	\	970		460		510	
3ª Caixa Visit	3 Caixa	43.468	0.02	43.489	43.488	43.4879	43.48	43.478	43.477	\	990	973	455	453	535	520
	3. Caixa	32.843	0.02	32.862	32.862	\	32.852	32.852	\	\	955		450		505	
Aft.Bio.Treat.	1- Dps Bio.	39.262	0.02	39.281	39.28	\	39.274	39.271	39.271	\	900	865	410	405	490	460
	2- Dps Bio.	30.351	0.02	30.367	30.367	\	30.359	30.359	\	\	830		400		430	
Aft.Filtr.	1- Dps Fil.	39.116	0.02	39.125	39.125	\	39.121	39.12	39.12	\	475	488	235	232	240	255
	2- Dps Fil.	37.408	0.02	37.418	37.418	\	37.414	37.413	\	\	500		230		270	
Final Treat.	1 Final	39.111	0.02	39.119	39.119	\	39.116	39.115	39.115	\	385	390	175	173	210	217.5
	2 Final	41.345	0.02	41.353	41.353	\	41.351	41.348	41.349	\	395		170		225	

Table 36: Weighing for TSS, FSS and VSS (1st sampling)

				Caps.+residue+filter(oven)		Caps.+residue+filter(furnace)							
Sample	**Capsule**	**Weight**	**Samples volume (**	**1º**	**2º**	**1º**	**2º**	**TSS [mg/L]**	**Average TSS**	**FSS [mg/L]**	**Average FSS**	**VSS [mg/L]**	**Average VSS**
Aft.Bio.Treat	100	42.525	0.02	42.53	42.5293	42.53	42.5252	225	225	20	20	205	205
	101	47.213	0.02	47.218	47.2174	47.21	47.2133	225		20		205	
Aft.Filtr.	102	51.812	0.02	51.815	51.8144	51.81	51.8122	125	125	15	15	110	110
	103	38.326	0.02	38.329	38.3288	38.33	38.3266	125		15		110	
Final Treat.	104	36.316	0.02	36.317	36.3172	36.32	36.3156	85	85	5	5	80	80
	105	51.353	0.02	51.355	51.3543	51.35	51.3528	80		5		75	

Table 37: Weighing for TS, TFS and TVS (2nd sampling)

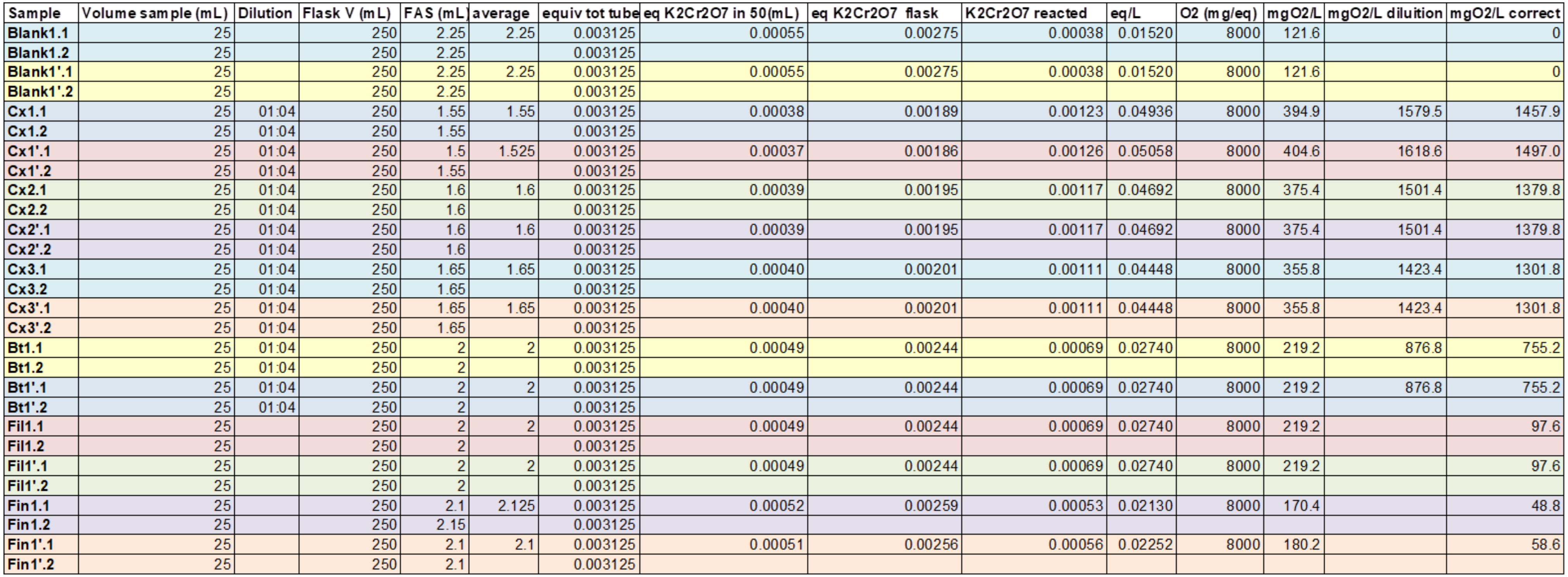
				Capsule+Residue (Oven) 103-105ºC (g)					Capsule+Residue (Furnace) 550ºC (g)					TS [mg/L]	TS [mg/L] average	TFS [mg/L]	TFS [mg/L] average	TVS [mg/L]	TVS [mg/L] average
Sample	**Capsule**	**Weight**	**Sample volume (L)**	**1ª**	**2ª**	**3ª**	**4°**	**5°**	**1ª**	**2ª**	**3ª**	**4ª**	**5°**						
1ª Caixa Visita	2A	45.7717	0.02	45.7960	45.795	45.7949	/	/	45.782	45.784	45.7830	45.7834		1160	1145	585	597.5	575	547.5
	3A	45.469	0.02	45.4943	45.493	45.4936	45.4916	45.4915	45.4810	45.4823	45.481	/	/	1130		610		520	
2ª Caixa Visita	5A	36.197	0.02	36.219	36.219	36.2191	/	/	36.207	36.208	36.209	36.2076	/	1090	1085	515	520	575	565
	7A	47.756	0.02	47.7788	47.777	47.7778	47.7774	/	47.766	47.767	47.767	47.7663	/	1080		525		555	
3ª Caixa Visita	8A	45.52	0.02	45.5399	45.5396	/	/	/	45.53	45.53	/	/	/	995	1022.5	510	472.5	485	550
	9A	65.4916	0.02	65.513	65.512	65.5126	65.5126	/	65.501	65.503	65.5	/		1050		435		615	
Inside Bio. Trea	6	32.999	0.02	33.019	33.018	33.0188	/	/	33.006	33.007	/	/	/	985	960	380	390	605	570
	110	39.119	0.02	39.137	39.138	39.1378	/	/	39.126	39.127	39.127	/	/	935		400		535	
Aft.Bio.Treat.	10A	79.699	0.02	79.719	79.718	79.7174	/	/	79.706	79.706	/	/	/	925	920	350	357.5	575	562.5
	11A	79.17	0.02	79.188	79.189	79.1866	79.1884	/	79.1770	79.178	79.176	79.1774		915		365		550	
Aft. Sand filtr.	115	43.474	0.02	43.492	43.491	43.4901	43.4907	/	43.48	43.481	/	/	/	830	855	325	320	505	535
	13A	61.958	0.02	61.9770	61.974	61.9758	61.9754	/	61.964	61.964	/	/	/	880		315		565	
Aft.Filtr.	12A	65.027	0.02	65.04	65.0397	/	/	/	65.0330	65.032	65.031	65.0324	65.0313	660	672.5	240	252.5	420	420
	A16	38.98	0.02	38.9940	38.993	38.9926	38.9934	/	38.985	38.9850	/	/	/	685		265		420	
Final Treat.	A32	82.379	0.02	82.389	82.389	82.3881	82.3890	/	82.381	82.384	82.381	/	/	490	480	105	137.5	385	342.5
	1B	44.037	0.02	44.046	44.0460	/	/	/	44.041	44.04	44.041	44.0400	/	470		170		300	

Table 38: Weighing for TSS, FSS and VSS (2nd sampling)

				Caps.+residue+filter(oven)		Caps.+residue+filter(furnace)								
Sample	**Capsule**	**Weight**	**Samples**	**1º**	**2º**	**1º**	**2º**	**3º**	**TSS [mg/L]**	**Average TSS**	**FSS [mg/L]**	**Average FSS**	**VSS [mg/L]**	**Average VSS**
Aft.Bio.Treat	2B	37.7119	0.02	37.718	37.7175	37.715	37.7132	37.7136	280	285	85	85	195	200
	3B	39.2052	0.02	39.211	39.2110	39.207	39.2069	/	290		85		205	
Aft.Filtr.	D	36.4773	0.02	36.481	36.4813	36.478	36.4780	/	200	190	35	30	165	160
	118	42.5276	0.02	42.532	42.5312	42.528	42.5281	/	180		25		155	
Final Treat.	120	51.3539	0.02	51.357	51.3567	51.354	51.3542	/	140	152.5	15	17.5	125	135
	123	38.3253	0.02	38.329	38.3286	38.327	38.3259	38.3257	165		20		145	

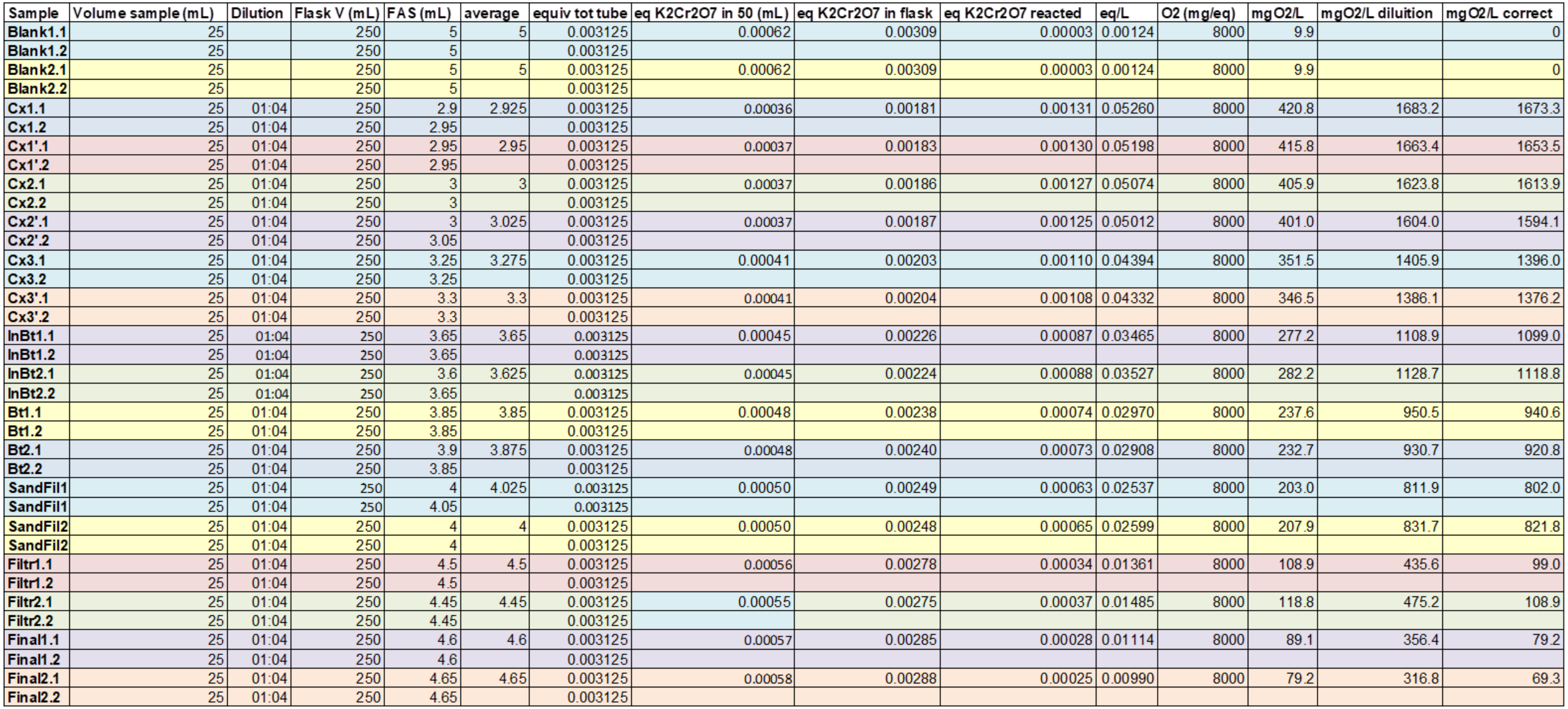
Annex C

Table 39: COD calculation (1st sampling)



Sample	Volume sample (mL)	Dilution	Flask V (mL)	FAS (mL)	average	equiv tot tube	eq K2Cr2O7 in 50(mL)	eq K2Cr2O7 flask	K2Cr2O7 reacted	eq/L	O2 (mg/eq)	mgO2/L	mgO2/L diluition	mgO2/L correct
Blank1.1	25		250	2.25	2.25	0.003125	0.00055	0.00275	0.00038	0.01520	8000	121.6		0
Blank1.2	25		250	2.25		0.003125								
Blank1'.1	25		250	2.25	2.25	0.003125	0.00055	0.00275	0.00038	0.01520	8000	121.6		0
Blank1'.2	25		250	2.25		0.003125								
Cx1.1	25	01:04	250	1.55	1.55	0.003125	0.00038	0.00189	0.00123	0.04936	8000	394.9	1579.5	1457.9
Cx1.2	25	01:04	250	1.55		0.003125								
Cx1'.1	25	01:04	250	1.5	1.525	0.003125	0.00037	0.00186	0.00126	0.05058	8000	404.6	1618.6	1497.0
Cx1'.2	25	01:04	250	1.55		0.003125								
Cx2.1	25	01:04	250	1.6	1.6	0.003125	0.00039	0.00195	0.00117	0.04692	8000	375.4	1501.4	1379.8
Cx2.2	25	01:04	250	1.6		0.003125								
Cx2'.1	25	01:04	250	1.6	1.6	0.003125	0.00039	0.00195	0.00117	0.04692	8000	375.4	1501.4	1379.8
Cx2'.2	25	01:04	250	1.6		0.003125								
Cx3.1	25	01:04	250	1.65	1.65	0.003125	0.00040	0.00201	0.00111	0.04448	8000	355.8	1423.4	1301.8
Cx3.2	25	01:04	250	1.65		0.003125								
Cx3'.1	25	01:04	250	1.65	1.65	0.003125	0.00040	0.00201	0.00111	0.04448	8000	355.8	1423.4	1301.8
Cx3'.2	25	01:04	250	1.65		0.003125								
Bt1.1	25	01:04	250	2	2	0.003125	0.00049	0.00244	0.00069	0.02740	8000	219.2	876.8	755.2
Bt1.2	25	01:04	250	2		0.003125								
Bt1'.1	25	01:04	250	2	2	0.003125	0.00049	0.00244	0.00069	0.02740	8000	219.2	876.8	755.2
Bt1'.2	25	01:04	250	2		0.003125								
Fil1.1	25		250	2	2	0.003125	0.00049	0.00244	0.00069	0.02740	8000	219.2		97.6
Fil1.2	25		250	2		0.003125								
Fil1'.1	25		250	2	2	0.003125	0.00049	0.00244	0.00069	0.02740	8000	219.2		97.6
Fil1'.2	25		250	2		0.003125								
Fin1.1	25		250	2.1	2.125	0.003125	0.00052	0.00259	0.00053	0.02130	8000	170.4		48.8
Fin1.2	25		250	2.15		0.003125								
Fin1'.1	25		250	2.1	2.1	0.003125	0.00051	0.00256	0.00056	0.02252	8000	180.2		58.6
Fin1'.2	25		250	2.1		0.003125								

Table 40: COD calculation (2nd sampling)



Sample	Volume sample (mL)	Dilution	Flask V (mL)	FAS (mL)	average	equiv tot tube	eq K2Cr2O7 in 50 (mL)	eq K2Cr2O7 in flask	eq K2Cr2O7 reacted	eq/L	O2 (mg/eq)	mgO2/L	mgO2/L diluition	mgO2/L correct
Blank1.1	25		250	5	5	0.003125	0.00062	0.00309	0.00003	0.00124	8000	9.9		0
Blank1.2	25		250	5		0.003125								
Blank2.1	25		250	5	5	0.003125	0.00062	0.00309	0.00003	0.00124	8000	9.9		0
Blank2.2	25		250	5		0.003125								
Cx1.1	25	01:04	250	2.9	2.925	0.003125	0.00036	0.00181	0.00131	0.05260	8000	420.8	1683.2	1673.3
Cx1.2	25	01:04	250	2.95		0.003125								
Cx1'.1	25	01:04	250	2.95	2.95	0.003125	0.00037	0.00183	0.00130	0.05198	8000	415.8	1663.4	1653.5
Cx1'.2	25	01:04	250	2.95		0.003125								
Cx2.1	25	01:04	250	3	3	0.003125	0.00037	0.00186	0.00127	0.05074	8000	405.9	1623.8	1613.9
Cx2.2	25	01:04	250	3		0.003125								
Cx2'.1	25	01:04	250	3	3.025	0.003125	0.00037	0.00187	0.00125	0.05012	8000	401.0	1604.0	1594.1
Cx2'.2	25	01:04	250	3.05		0.003125								
Cx3.1	25	01:04	250	3.25	3.275	0.003125	0.00041	0.00203	0.00110	0.04394	8000	351.5	1405.9	1396.0
Cx3.2	25	01:04	250	3.25		0.003125								
Cx3'.1	25	01:04	250	3.3	3.3	0.003125	0.00041	0.00204	0.00108	0.04332	8000	346.5	1386.1	1376.2
Cx3'.2	25	01:04	250	3.3		0.003125								
InBt1.1	25	01:04	250	3.65	3.65	0.003125	0.00045	0.00226	0.00087	0.03465	8000	277.2	1108.9	1099.0
InBt1.2	25	01:04	250	3.65		0.003125								
InBt2.1	25	01:04	250	3.6	3.625	0.003125	0.00045	0.00224	0.00088	0.03527	8000	282.2	1128.7	1118.8
InBt2.2	25	01:04	250	3.65		0.003125								
Bt1.1	25	01:04	250	3.85	3.85	0.003125	0.00048	0.00238	0.00074	0.02970	8000	237.6	950.5	940.6
Bt1.2	25	01:04	250	3.85		0.003125								
Bt2.1	25	01:04	250	3.9	3.875	0.003125	0.00048	0.00240	0.00073	0.02908	8000	232.7	930.7	920.8
Bt2.2	25	01:04	250	3.85		0.003125								
SandFil1	25	01:04	250	4	4.025	0.003125	0.00050	0.00249	0.00063	0.02537	8000	203.0	811.9	802.0
SandFil1	25	01:04	250	4.05		0.003125								
SandFil2	25	01:04	250	4	4	0.003125	0.00050	0.00248	0.00065	0.02599	8000	207.9	831.7	821.8
SandFil2	25	01:04	250	4		0.003125								
Filtr1.1	25	01:04	250	4.5	4.5	0.003125	0.00056	0.00278	0.00034	0.01361	8000	108.9	435.6	99.0
Filtr1.2	25	01:04	250	4.5		0.003125								
Filtr2.1	25	01:04	250	4.45	4.45	0.003125	0.00055	0.00275	0.00037	0.01485	8000	118.8	475.2	108.9
Filtr2.2	25	01:04	250	4.45		0.003125								
Final1.1	25	01:04	250	4.6	4.6	0.003125	0.00057	0.00285	0.00028	0.01114	8000	89.1	356.4	79.2
Final1.2	25	01:04	250	4.6		0.003125								
Final2.1	25	01:04	250	4.65	4.65	0.003125	0.00058	0.00288	0.00025	0.00990	8000	79.2	316.8	69.3
Final2.2	25	01:04	250	4.65		0.003125								

Annex D

Table 41: Absorbance and Cu concentration values (1st sampling)

Samples	Blank	ABS	Time (min)	Cu [mg/L]	average Cu [mg/L]
1.1	0.126	0.143	02:00:24	0.494	0.497
1.2	0.126	0.144	02:00:18	0.501	
2.1	0.111	0.132	02:00:15	0.414	0.414
2.2	0.111	0.132	02:00:11	0.414	
3.1	0.101	0.121	02:00:02	0.335	0.331
3.2	0.102	0.120	02:00:28	0.328	
deps Bio	0.981	0.100	02:00:10	0.183	0.179
deps Bio.	0.981	0.099	02:00:30	0.176	
deps. Fil	0.061	0.090	02:00:17	0.111	0.107
deps Fil.	0.064	0.089	02:00:36	0.103	
Final	0.058	0.088	02:00:46	0.096	0.096
Final.	0.060	0.088	02:00:05	0.096	

Table 42: Absorbance and Cu concentration values (2nd sampling)

Samples	Blank	ABS	Time (min)	Cu [mg/L]	average Cu [mg/L]
1.1	0.127	0.147	02:00:26	0.523	0.512
1.2	0.124	0.144	02:00:38	0.501	
2.1	0.111	0.133	02:00:41	0.422	0.436
2.2	0.113	0.137	02:00:28	0.450	
3.1	0.106	0.125	02:00:08	0.364	0.356
3.2	0.105	0.123	02:01:01	0.349	
IN Bio	0.101	0.110	02:00:16	0.255	0.262
IN Bio2	0.999	0.112	02:00:36	0.270	
Aft. Bio	0.102	0.106	02:00:22	0.226	0.223
Aft. Bio2	0.998	0.105	02:00:10	0.219	
Sand fil.	0.993	0.101	02:00:17	0.190	0.190
Sand fil2	0.992	0.101	02:00:09	0.190	
Aft. Fil.	0.976	0.098	02:00:28	0.168	0.172
Aft. Fil2	0.978	0.099	02:00:23	0.176	
Final	0.071	0.093	02:00:28	0.132	0.129
Final2	0.069	0.092	02:00:20	0.125	

Table 43: Absorbance and Zn concentration values (1st sampling)

Samples	Blank	ABS	Time (min)	Zn [mg/L]
1.1	0.115	0.334	03:00:40	0.652
1.2				
2.1				
2.2				
3.1	0.106	0.312	03:00:17	0.575
3.2				
deps Bio	0.103	0.248	03:00:34	0.351
deps Bio.				
deps Fil				
deps Fil2				
Final	0.102	0.182	03:00:31	0.120
Final2				

Table 44: Absorbance and Zn concentration values (2nd sampling)

Samples	Blank	ABS	Time (min)	Zn [mg/L]
1.1	0.118	0.345	03:00:36	0.691
1.2				
2.1				
2.2				
3.1	0.109	0.321	03:00:15	0.607
3.2				
IN Bio				
IN Bio2				
Aft. Bio	0.104	0.261	03:00:21	0.397
Aft. Bio2				
Sand fil.				
Sand fil2				
Aft. Fil.				
Aft. Fil2				
Final	0.101	0.201	03:00:39	0.187
Final2				

Annex E

Cu Calibration curve

Shake the sample, possibly filter it if there are solids in suspension, and pour 2 mL into a tube, using a pipet. Add the CuVer1 powder and shake to dissolve the powder, the sample will change color to violet, if any copper is present. Pour the blank sample into a cell and place it in the cell holder, then do the same with the reacted sample. In the spectrometer is read the absorbance value (Abs). Thanks to this procedure is possible make the calibration curve reporting on the ordinate axis the absorbance value measured for six solutions containing 0.15 mg / L and 0.2 mg / L diluted with distillated water to 1L flask and 0.4, 0.6 and 0.8 and mg / L diluted to 250 mL flask (Table 45). The concentration of Cu is reported on the abscissa axis.

Table 45: Absorbance values for building Cu calibration curve

	Cu (mg/L)	**Dilution volume (mL)**	**Wave lenght (nm)**	**Blank**	**ABS**	**Volume (mL)**	**Time (min)**
A	0.15	1000	560	0.074	0.097	2	02:00:29
B	0.2	1000	560	0.067	0.101	2	02:00:21
C	0.4	250	560	0.068	0.130	2	02:00:18
D	0.6	250	560	0.068	0.157	2	02:00:11
E	0.8	250	560	0.071	0.186	2	02:00:33

Method 8506

COPPER (0 to 5.00 mg/L)

For water, wastewater and seawater **

Bicinchoninate Method* (Powder Pillows or AccuVac Ampuls);
USEPA approved for reporting wastewater analysis* – (digestion required; *See Section I*)**

USING POWDER PILLOWS

1. Enter the stored program number for copper (Cu), bicinchoninate–powder pillows

Press: **1 3 5 READ/ENTER**

The display will show:
DIAL nm TO 560

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

2. Rotate the wavelength dial until the small display shows:
560 nm

Note: *Determination of total copper needs a prior digestion (see* Digestion *in* Section I *for digestion procedures).*

Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *following these steps. Adjust pH of stored samples before analysis.*

3. Press: **READ/ENTER**

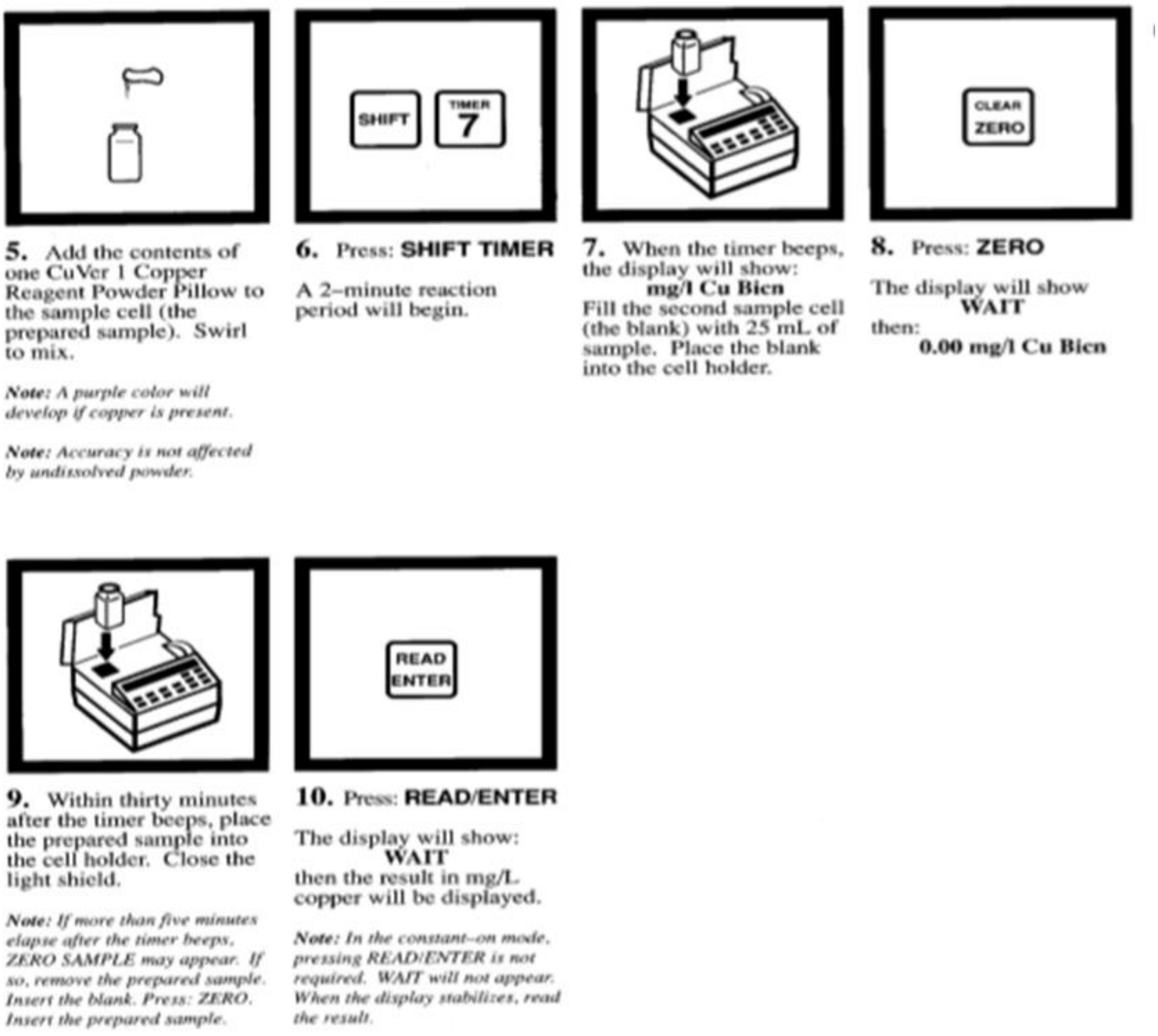
The display will show:
mg/l Cu Bicn

4. Fill a sample cell with 25 mL of sample.

Note: *The Pour–Thru Cell can be used with this procedure.*

Note: *For proof of accuracy, use a 1.00 mg/L copper standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

Note: *Determine a reagent blank for each new lot of reagent. Repeat Steps 4 to 10, using demineralized water as the sample. Subtract this value from each result obtained with this lot of reagent.*



5. Add the contents of one CuVer 1 Copper Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

Note: A purple color will develop if copper is present.

Note: Accuracy is not affected by undissolved powder.

6. Press: **SHIFT TIMER**

A 2–minute reaction period will begin.

7. When the timer beeps, the display will show:
mg/l Cu Bicn
Fill the second sample cell (the blank) with 25 mL of sample. Place the blank into the cell holder.

8. Press: **ZERO**

The display will show
WAIT
then:
0.00 mg/l Cu Bicn

9. Within thirty minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.

Note: If more than five minutes elapse after the timer beeps, ZERO SAMPLE may appear. If so, remove the prepared sample. Insert the blank. Press: ZERO. Insert the prepared sample.

10. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L copper will be displayed.

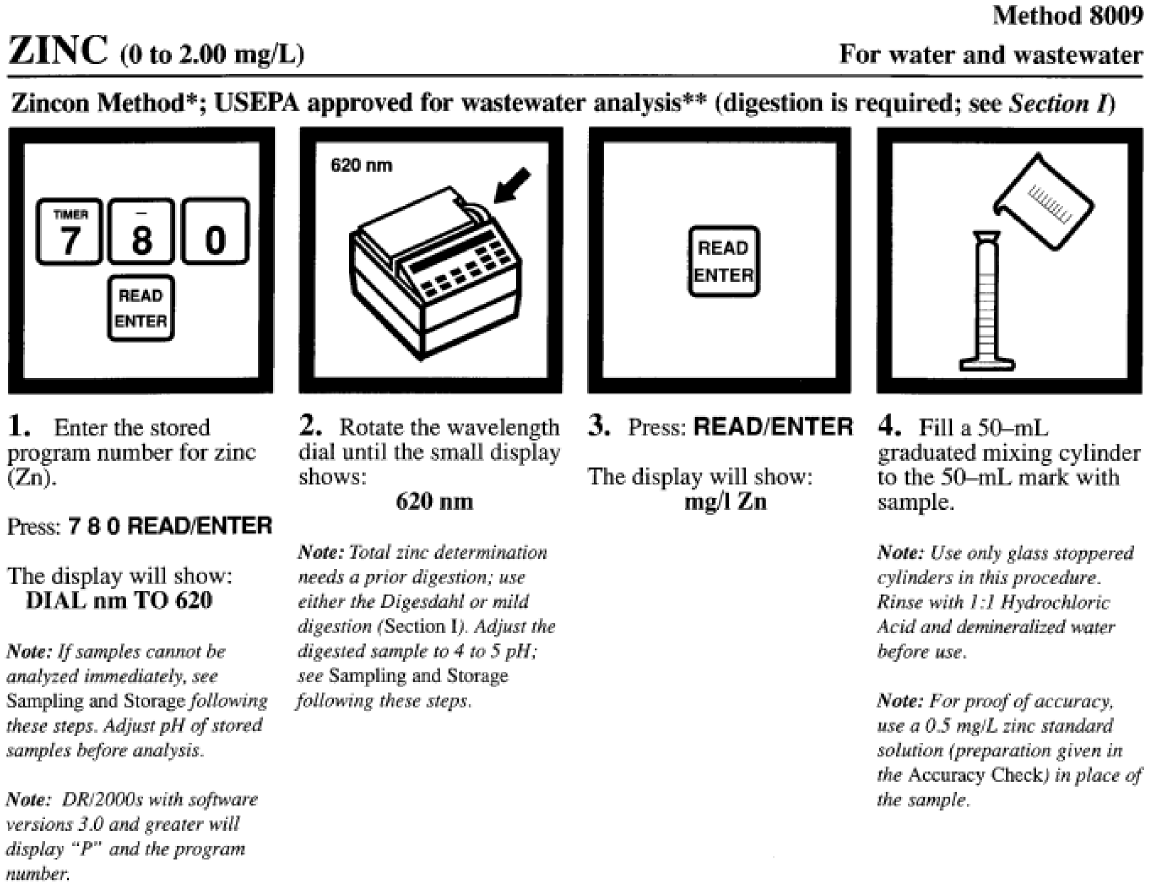
Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

Zn Calibration curve

Shake the sample, possibly filter it if there are solids in suspension, and pour 50 mL into a graduated cylinder. Add the ZincVer5 powder and shake energetically to dissolve the powder, the sample will change color to orange. Take 25 mL of the sample in a graduated cylinder and add 1 mL of cyclohexanone, shake for 30 seconds and then wait 3 minutes for the reaction to start, the sample will become brownish. Pour the blank sample into a sample cell and place it in the cell holder, then do the same with the reacted sample. In the spectrometer is read the absorbance value (Abs). Thanks to this procedure is possible make the calibration curve reporting on the ordinate axis the absorbance value measured for six solutions containing from 0.1 mg / L to 0.2 mg / L diluted with distilled water to 1L flask and 0.4, 0.6, 0.8 and 1 mg / L diluted to 250 mL flask (Table 46). The concentration of Zn is reported on the abscissa axis.

Table 46: Absorbance values for building Zn calibration curve

	Zn **(mg/L)**	**Dilution volume** **(mL)**	**Wave lenght** **(nm)**	**Blank**	**ABS**	**Volume** **(mL)**	**Time** **(min)**
A	0.1	1000	620	0.102	0.186	25	03:04
B	0.2	1000	620	0.105	0.191	25	03:05
C	0.4	250	620	0.105	0.26	25	03:26
D	0.6	250	620	0.109	0.326	25	03:21
E	0.8	250	620	0.114	0.378	25	03:14
F	1	250	620	0.117	0.430	25	03:30



Method 8009

ZINC (0 to 2.00 mg/L)

For water and wastewater

Zincon Method*; USEPA approved for wastewater analysis (digestion is required; see *Section I*)**

1. Enter the stored program number for zinc (Zn).

Press: **7 8 0 READ/ENTER**

The display will show:
DIAL nm TO 620

Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *following these steps. Adjust pH of stored samples before analysis.*

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

2. Rotate the wavelength dial until the small display shows:
620 nm

Note: *Total zinc determination needs a prior digestion; use either the Digesdahl or mild digestion (*Section I*). Adjust the digested sample to 4 to 5 pH; see* Sampling and Storage *following these steps.*

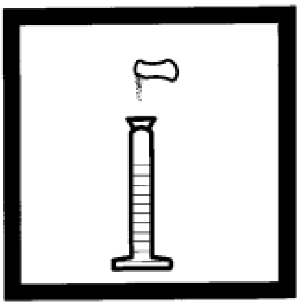
3. Press: **READ/ENTER**

The display will show:
mg/l Zn

4. Fill a 50–mL graduated mixing cylinder to the 50–mL mark with sample.

Note: *Use only glass stoppered cylinders in this procedure. Rinse with 1:1 Hydrochloric Acid and demineralized water before use.*

Note: *For proof of accuracy, use a 0.5 mg/L zinc standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



5. Add the contents of one ZincoVer 5 Reagent Powder Pillow. Stopper. Invert several times to completely dissolve powder.

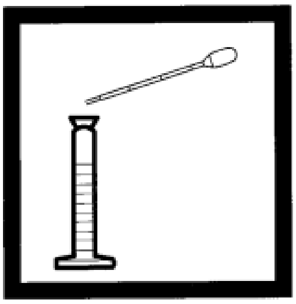
Note: *Inconsistent readings may result for low zinc concentrations if all the particles are not dissolved.*

Note: *At this point the sample color should be orange. If the color is brown or blue, dilute the sample and repeat the test. Either the zinc concentration is too high, or an interfering metal is present.*

Caution: This reagent contains cyanide and is very poisonous if taken internally or inhaled. Do not add to an acidic sample. Store away from water and acids.

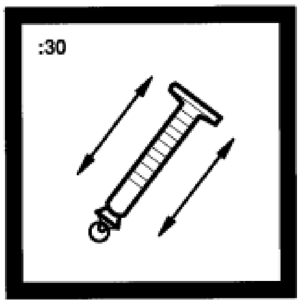
6. Measure 25 mL of the solution into a sample cell (the blank).

Note: *The Pour–Thru Cell cannot be used with this procedure.*



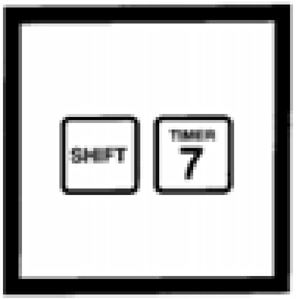
7. Add 1.0 mL of cyclohexanone to the remaining solution in the cylinder.

Note: *Use a plastic dropper, as rubber bulbs may contaminate the cyclohexanone.*



8. Stopper the cylinder (the prepared sample). Shake for 30 seconds.

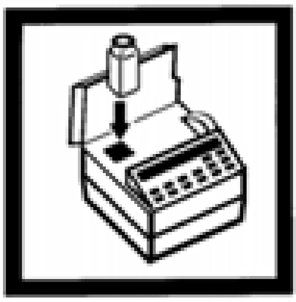
Note: *The sample color will be reddish–orange, brown or blue, depending on the zinc concentration.*



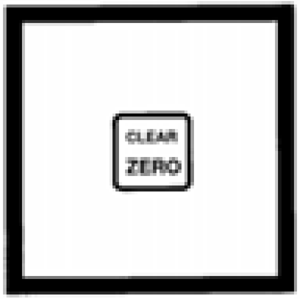
9. Press: **SHIFT TIMER**

A 3–minute reaction period will begin.

10. Pour the solution from the cylinder into a sample cell.

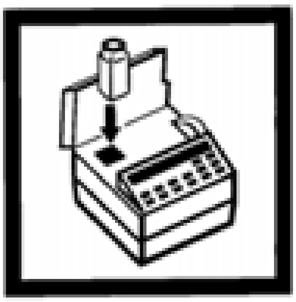


11. When the timer beeps, place the blank into the cell holder. Close the light shield.

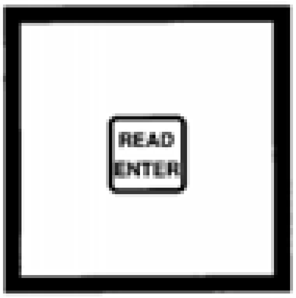


12. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l Zn



13. Within ten minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L zinc will be displayed.

Annex F

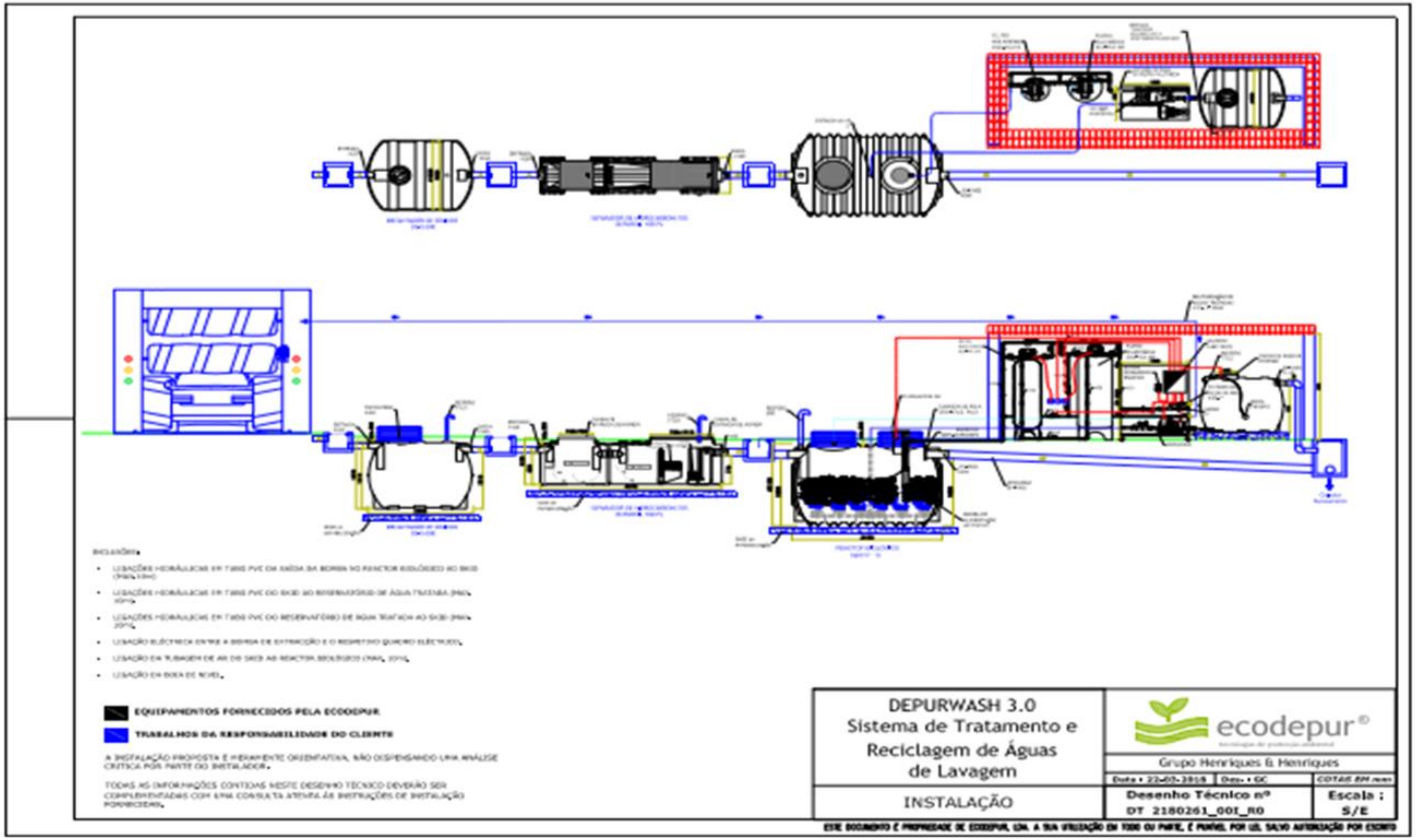


Figure 44: Wastewater treatment plant from Transportes Gama