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KAHRAMANMARAŞ SÜTÇÜ İMAM UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE USE OF EXTENDED ACTIVATED SLUDGE PROCESSES FOR BIODEGRADATION OF SOME PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPS) IN THE WASTEWATER TREATMENT PLANTS

MOSSTFA MAAN TAHER MAAROOF

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MOSSTFA MAAN TAHER MAAROOF

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M.Sc. thesis entitled “The Use of Activated Sludge Processes for Biodegradation of Some Pharmaceuticals and Personal Care Products (PPCPs) in the Wastewater Treatment Plants ” and prepared by MOSTAFA MAAN TAHIR MARROF, who is a student at Bioengineering and Sciences Department, Graduate School of Natural and Applied Sciences, Kahramanmaraş Sütçü İmam University, At 10/10/2014 was certified by all the/majority jury members, whose signatures are given below.

Assoc. Prof. Dr. Yağmur UYSAL (Supervisor) ……

Department of Environmental Engineering
Kahramanmaraş Sütçü Imam University

Assoc. Prof. Dr. Mustafa DOLAZ (Member) ……

Department of Environmental Engineering
Kahramanmaraş Sütçü Imam University

Assoc. Prof. Dr. Mehmet ÜNSAL (Member)

Department of Civil Engineering ……
Kahramanmaraş Sütçü İmam University

I approve that the above signatures related to the members.

Prof. Dr. M. Hakkı ALMA

Director of Graduate School

……

DECLARATION

I declare and guarantee that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. Based on these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

MOSSTFA MAAN TAHER MAAROOF

ATIKSULARDAN BAZI İLAÇ VE KİŞİSEL BAKIM ÜRÜNLERİ KALINTILARININ UZAKLAŞTIRILMASINDA AKTİF ÇAMUR PROSESİNİN KULLANILMASI

(YÜKSEK LİSANS TEZİ)

MOSSTFA MAAN TAHIR MAAROOF

ÖZET

Kişisel bakim ürünleri kısacası kozmetikler tüm dünyada yoğun olarak üretilen ve insanlar tarafından yaygın olarak kullanılan kimyasallardır. Bu kimyasalların kalıntıları kullanılmaları sonucunda insan atıkları vasıtası ile en son olarak atıksulara karışmaktadır. Atıksular arıtıldıktan sonar alıcı ortamlara deşarj edilirler. Eser miktarlarda alıcı ortamlara ulaşan bu kimyasal ilaç kalıntıları, ulaştıkları içme suyu kaynakları için bir tehdit unsuru oluştururlar. Bu çalışmada, insanlar tarafından yoğun olarak kullanılan ilaç ve kozmetik ham maddeleri seçilerek, bu kimyasalların atıksularda değişen konsantrasyonlarda bulunduklarında biyolojij olarak arıtılabilirlikleri incelenmiştir. Bu amaçla, aerobic olarak işletilen 5 farklı biyoreaktör kullanılmış ve çalışma koşulları optimize edilmiştir. Çalışmada kullanılan çamur Gaziantep Atıksu Arıtma Tesisi havalandırma havuzu çıkışından alınmıştır ve reaktörler sentetik olarak hazırlanan evsel etıksu ile beslenmiştir. Besleme suyuna değişen konsantrasyonlarda kimyasal ilaç kalıntıları eklenmiş ve farklı alıkonma sürelerinde giderim verimlilikleri araştırılmıştır. İlaç kalıntısı analizlerinde Yüksek Basınçlı Sıvı Kromatografisi (HPLC) kullanılmış, HPLC ölçümleri öncesinde örneklere Katı Faz Ekstraksiyonu (SPE) ön saflaştırma işlemi uygulanmıştır. Kimyasal Oksijen İhtiyacı (KOİ) giderim değerleri açısından Triclosan, Ibuprofen ve Parasetamol için maksimum giderim verimleri sırası ile %92,5; % 95,4; % 99,1 olarak elde edilmiştir.

Anahtar Kelimeler: Aktif çamur, Atıksu arıtımı, Biyodegradation, İlaç kalıntıları, KOİ, Kişisel bakım ürünleri, HPLC, Ibuprofen, Triclosan, Parasetamol

Kahramanmaraş Sütçü Imam University

Fen Bilimleri Enstitüsü

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Danışman: Doç. Dr. Yağmur UYSAL
Sayfa sayısı: 103

THE USE OF EXTENDED ACTIVATED SLUDGE PROCESSES FOR BIODEGRADATION OF SOME PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPS) IN THE WASTEWATER TREATMENT PLANTS

(M.Sc. THESIS)

MOSSTFA MAAN TAHIR MAAROOF

ABSTRACT

Pharmaceuticals and personal care products (PPCPs) compounds have the potential to affect the efficiency of the biological wastewater treatment plants, it is critical to screen these pharmaceuticals for toxicity towards the activated sludge, PPCPs are chemicals that are manufactured and are used worldwide on a large scale. It is end up in the wastewater system as a result to disposal or human wastes. Wastewater is sent back to the river after being treated. Trace amounts of these chemicals are found in source water, which contaminate drinking water, this study presented a useful treatment method for PPCPs using selected PPCPs as tracers to investigate the effects of wastewater discharge on the waterways and to estimate the occurrence of PPCPs. The work was carried out as a laboratory experiment with five aerobic bioreactors, Sludge from the Gaziantep WWTP was used to start the reactors which The COD removal efficiency was 88.5%, the bioreactor were worked at different HRT .The removal of PPCPs was investigated in extended activated sludge process; the analytical method based on solid-phase extraction (SPE) was followed by High Performance Liquid Chromatography (HPLC) method that developed and validated for determination PPCPs in extended activated sludge effluent. The efficiency ratio of Removal by using this method were 92.5 %, 95.4%, 99.1% of the triclosan, Ibuprofen and paracetamol, respectively.

Key words: pharmaceuticals and personal care products, Biodegradation, wastewater treatment, activated sludge process, HPLC, Triclosan, Ibuprofen, Paracetamol, Removal efficiency, COD

Kahramanmaraş Sütçü Imam University
Graduate School of Natural and Applied Sciences
Department of Bioengineering and Sciences, October/ 2014

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October-2014

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ABBREVIATIONS

API : Active Pharmaceutical Ingredients
AOP : Advanced Oxidation Process
AS : Activated Sludge
ATC : Anatomical Therapeutic Chemical
BNR : Biological Nutrient Removal
BOD : Biological Oxygen Demand
CASP : Conventional Activated Sludge Plant
CD : Carbon dioxide
COD : Chemical Oxygen Demand
DO : Dissolved Oxygen
EC : Effective Concentration
EPA : Environmental Protection Agency
GC : Gas Chromatography
HRT : Hydraulic Retention Time
HPLC : High Performance Liquid Chromatography
MB : Membrane Bioreactor
MLSS : Mixed Liquor Suspended Solids
MLVSS : Mixed Liquor Volatile Suspended Solids
OECD : Organization for Economic Co-operation and Development
OTC : Over-The-Counter
OUR : Oxygen Uptake Rate
PAC : Pharmaceutically Active Compounds
PHC : Potentially Harmful Compound
PPCPs : Pharmaceuticals and Personal Care Products
RAS : Returned Activated Sludge
RE : Removal Efficiency
RO : Reverse Osmosis
SBR : Sequencing Batch Reactor
SRT : Sludge Retention Time

SOUR : Specific Oxygen Uptake Rate

STP : Sewage Treatment Plant

SPE : Solid phase extraction

SVI : Sludge Volume Index

UF : Ultra Filtration

VOC : Volatile Organic Compounds

VSS : Volatile Suspended Solids

USGS : United States Geological Survey

WTP : Wastewater treatment plant

Explanation	Definition
Ka Dissociation constant	Describes the ability to ionize or dissociate to aquatic phase
Kbiol Biodegradation rate constant	Describes the sorption potential l/gSS/d
kd Sorption coefficient	Describes the sorption potential
kow Octanol-water-partition coefficient	Describes lipophilicity of a compound l/kg

1. INTRODUCTION

One of the key issues in wastewater treatment management is the re-use of wastewater for drinking water supply or for industrial or agriculture purposes because of the limited of freshwaters (Fig. 1.1). In the past, all attention in wastewater treatment plants was mainly given to reduce amounts of nutrients such as phosphors and nitrogen and organic matter mainly found in wastewater. In the last decades, more attention has been also directed to remove other substances presented in wastewater together with common pollutants in trace concentrations namely pharmaceuticals and personal care products (PPCPs) (Lehmonen, 2012).

In many parts of the world, there are several reports indicate that a wide variety of pharmaceuticals and PPCPs have been detected in different water samples like river water, ground water, wastewater and drinking water e.g. anti- inflammatory drugs, lipid regulators, antibiotics, paracetamol, contraceptives, beta blockers and tranquilizers, estrone, ibuprofen, triclosan, diclofenac, and clofibric acid. This growing list of household and personal care products are advertised as "antibacterial" because they contain a chemical matter like triclosan. It is accepted that this product protects human from harmful bacteria (European Commission, 2012), and this chemical has been used all over the world with increasing amount. Thus, with increasing consumption of pharmaceuticals in human life and with developing of various analytical instruments and methods that have very low detection limits, researchers encouraged their studies to determine these trace compounds in various environmental matrices (Helcom, 2010).

The exposure to these chemical compounds has become very common that it has shown up in the blood, urine and breast milk of people across the globe, as for people who use these chemicals like triclosan daily their test results have shown higher levels of these chemicals in their bodies, and it has been proven that even those who do not use triclosan on their skin are exposed to it through food, water, and household dust and it also enter the environment through subsequent excretion in faces and urine of humans and animals as a result of consuming drugs (Joss et al., 2008; Davis , 2010). Via wastewater treatment plants (WWTP) effluents or application of (animal) manure on fields pharmaceuticals end up in aquatic systems because WWTPs are not able to remove these compounds efficiently in

their current configuration. A continuous input of pharmaceuticals to the environment, although in low concentrations, can and does yield effects on the environment (Lahti, 2012).

The use of pharmaceuticals is likely to increase and therefore it is important to analyze and optimize their biological removal in treatment plants or to introduce new measures such as for instance source separated sanitation concepts nowadays. There is a big variety of different chemical compounds, which people use in their everyday life. In the end, some of those chemicals and their compounds can enter into the wastewater (Helcom 2007). Currently, municipal sewage treatment plants are not engineered specifically for PPCP removal as most were built before PPCP became part of the equation.

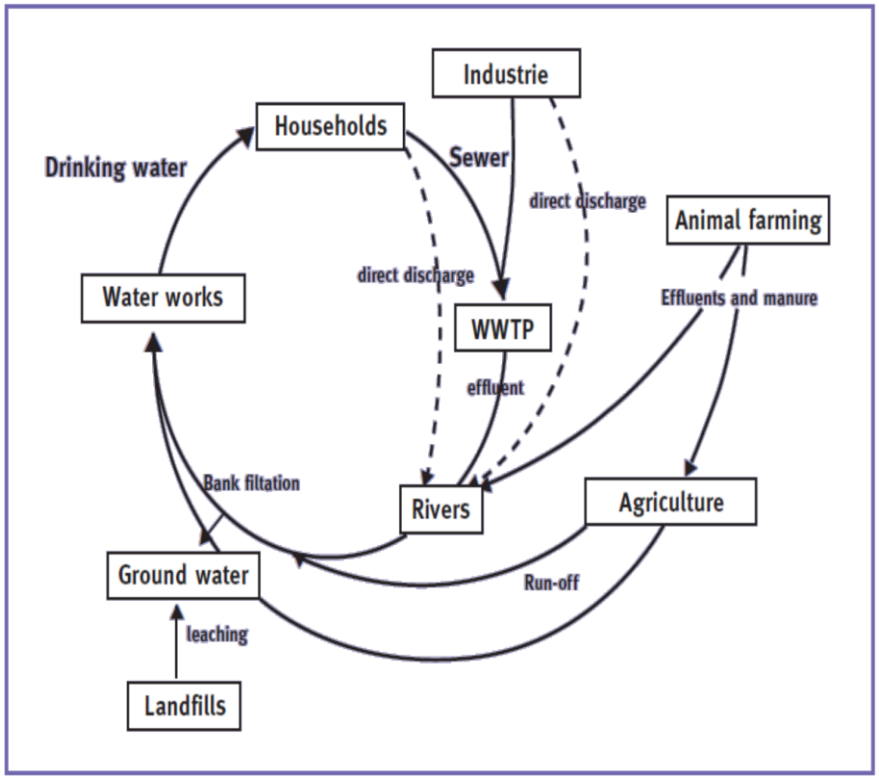


Figure 1.1: The role of WWTP in the water cycle (WHO, 2012).

Removal efficiencies from treatment plants vary from chemical to chemical and among individual sewage treatment facilities. Sewage treatment plants are designed to reduce nitrates, phosphates, dissolved organic carbon, and pathogens, which have been the major pollutants of concern in domestic waste. Some PPCPs are not affected by sewage treatment

processes, others may be degraded, and still others may be converted to "daughter" compounds (Davis, 2010). For example, an activated sludge process can only remove part of the contaminants. In this process the contaminants absorb to sludge, degrade biologically, evaporate or remain in the treated water. Sewage overflows and sewer leakages cause the entry of some wastewater into the environment already before wastewater has been led to the treatment plant. About 5- 20% of wastewater leaks into the environment due to overflows or sewer leakages. It means that some harmful chemicals can also enter into the environment with overflows and sewer leakages, to prevent that kind of emissions; wastewater should be treated before it is discharged into the sewer (Joss et al. 2008).

The chemical compounds, which enter into the water with the effluent, can be harmful or even hazardous to the aquatic environment. The concentrations of the chemicals are usually low in the water, but the low concentrations can also be harmful or hazardous. These chemical compounds can be persistent and in the waters, they can accumulate in the sediments or the organisms and the food chains and also reach people through food or drinking water. The major sources of wastewater are human sewage and industrial effluents. Untreated wastewater, if discharged directly to the receiving water bodies in the environment can cause water borne diseases. (Davis, 2005). So the biological wastewater treatment method which was established in the early years of twentieth century and has been applied worldwide, involves high concentration of bacteria in the tanks removing small organic carbon molecules by eating them. Consequently, as the bacteria grow more, the water will be cleansed and discharged to receiving water bodies such as river or the sea (Hardman et al., 2001; Williams, 2005; Merck, 2006). Still different chemical compounds which are toxic can produce a toxic shock that kills the bacteria in the wastewater treatment plant. As a result, plant may pass untreated effluent directly to the environment (Daughton, and Ternes, 1999; Metcalf and Eddy 2003). These drugs which are untreated in water treatment remain in the discharged water. This led to increase concern about the influence of these drugs on aquatic organisms and humans because of the formation of different tolerant pathogenic bacteria to anti-microbial drugs (Takeshi, et al., 2006).

Thus, we need to begin to consider pharmaceuticals and personal care products as a source of water pollution. More research is necessary in order to understand what happens to PPCPs when we use them and how their presence in water systems may be affecting human health and aquatic populations. Regulation is necessary to limit the concentrations of these harmful compounds in effluents from wastewater treatment plants; regulations are required to be updated as more harmful constituent compounds are identified.

1.1. Objective and scope of study

The main objective of this study is to use the extended activated sludge process and to explore the ability and effect of some pharmaceuticals and personal care products PPCPs to the efficiency of microorganisms as well as to determine the biodegradations towards these chemicals compounds. Such processes would help to reduce chemical emissions from effluents,

The other aims of this study is to lessen the amount of PPCPs that reach the biological processing unit by controlling disposal process of those products.

2. LITERATURE REVIEW

2.1. Wastewater Treatment Plants

2.1.1. Scientific history

Before the late 1800s, the general means of disposing human excrement was the outdoor privy while the major proportion of the population used to go for open defecation. Sewage treatment systems were introduced in cities after Louis Pasteur and other scientists who showed that sewage borne bacteria were responsible for many infectious diseases. The early attempts, in the1900s, at treating sewage usually consisted of acquiring large farms and spreading the sewage over the land (Ardern and Lockett 1914a; Davis, 2010), where it decayed under the action of microorganisms. It was soon found that the land became diseased. Later attempts included the discharge of wastewater directly into the water bodies, but it resulted in significant deterioration of the water quality of such bodies. These attempts relied heavily on the self-cleansing capacities of land and water bodies and it was soon realized that nature couldn't act as an indefinite sink. In general from about 1900 to the early 1970s treatment objectives were concerned that removal of suspended and floatable material from wastewater also, Treatment of biodegradable organics (BOD removal) and elimination of disease-causing pathogenic micro-organisms (Ardern and Lockett, 1914b; Ardern and Lockett 1915; Gerardi, 2006; Metcalf and Eddy 2003; Boersema, and Reijnders, 2009).

3.1.2. The wastewater treatment plants WWTPs

The wastewater treatment plant receives used water from household sinks, showers, toilets, washing machines, and dishwashers; these include human waste, food scraps, oil, soaps, and chemicals (Perlman, 2013).business and industrial manufactures also dispose chemicals and other by-products. The role of wastewater treatment is to remove suspended solids and disinfect pathogens before being discharged to the environment (Weinar and Matthews, 2003; Davis, 2010).

Each treatment plant has a National Pollutant Discharge Elimination System (NPDES) permit listing allowable levels of BOD5, suspended solids, coliform bacteria, and other pollutants that can be discharged to the environment (Alshouli, 2012).Wastewater

treatment was originally developed to control pollution within the United States (EPA 1998). Through a combination of physical and biological processes, wastewater treatment was designed to remove organic material from the solutions that are brought into WWTPs. In the U.S., wastewaters are collected from homes, businesses, and industries, and delivered to WWTPs through a large array of collection sewers and pumping stations (EPA 1998; Weiner and Matthews, 2003; Gerardi, 2006). By providing a buffer between concentrated wastewater and the natural environment in many urban areas, treatment plans release water in a controlled manner. If it weren't for WWTPs, wastewater would degrade water quality, land resources, and the air in which multiple forms of life depend on it (Management and Support Systems 1996; Cheremisinoff, 2002; Han, 2012). The wastewater treatment process is very complex and can be broken down a number of ways, but many ways consist of a very similar process overall. The most processes of a WWTP consist of preliminary, primary, secondary, and finally tertiary treatment. The first step once the water has reached the wastewater treatment facility through the multiple water transfer structures is preliminary treatment. During preliminary treatment, the waste passes through screens or bar racks which help to remove larger debris that may later hinder downstream processes. Some of the larger debris that may be removed consists of wood, cardboard, rags, and other plastic or paper products (Hammer, 2012; Management and Support Systems 1996; Metcalf and Eddy. 2003). Next, the water travels to a grit tank where the water flow is slowed down and in some instances chlorine is added to control odor and aid in the settling of solids like sand, rocks, and other solids that passed through the preliminary screens (Metcalf and Eddy, 2003; Whitacre, 2013). The solids that have collected within the bar screens and grit tanks are then removed, washed, and taken to the local landfill (Hammer, 2012; EPA, 2013). After preliminary treatment, the next step in the wastewater treatment process is primary treatment. During this stage, suspended and floating materials are removed from the water (Corbitt, 2004; Gaur, 2008). The water is sent to a sedimentation tank where the water flow is stopped and suspended solids sink to the bottom of the tank and floatable material migrates to the surface of the water. The solids that settle to bottom form a mass known as sludge. Other materials, such as oil and grease, which float to the surface, are removed by rotating skimmers in the sedimentation tanks (EPA 1998; Metcalf and Eddy, 2003; Turovskiy, and Mathai, 2006). Other bio solids that do not form sludge are removed

by pumps and may later be used as fertilizers, removed and sent to landfills, or incinerated (Wisconsin Department of Natural Resources Wastewater Operator Certification, 2010; Davis, 2010).

The third step in wastewater treatment is secondary treatment. Secondary treatment helps to reduce the concentration of dissolved and colloidal organic substances and suspended matter remaining in the wastewater (Management and Support Systems 1996; Turovskiy, and Mathai, 2006; Han, 2012).The majority of secondary treatment involves biological treatment of the wastewater. During this phase, water is mixed with oxygen which starts a process known as aeration which takes place in aeration tanks. Activated sludge, which is bacteria that has become activated due to the presence of oxygen, begins feeding on waste solids and incoming organic matter, thus clarifying the water even further by converting the organic matter into useless by-products (Carlsen, 1997; Ren, 2004; EPA 2013). When activated sludge isn't used in certain wastewater treatment plants, another approach which consists of trickling filters is employed (fig.2.1) Trickling filters usually consist of a bed of stones between three and six feet deep in which the wastewater is passed through. Bacteria grow on these stones and removes organic matter within the wastewater as it passes through, similar to activated sludge (Grady, et al., 1980). After the trickling filter or activated sludge stage, the water is then sent to a clarifying or settling tank. Here the water is allowed to sit and the excess bacteria and activated sludge microorganisms are removed. When plants use activated sludge, the excess that is removed in the sedimentation tanks is often recirculated back to the aeration tanks to keep the biological process going (Cheremisinoff, 2002; Bitton, 2005; Swedish Environmental Protection Agency, 2008).

The final step in the wastewater treatment process before the water is expelled into the receiving watercourse is tertiary or advanced treatment. During this step, the water that has been expelled from secondary treatment is treated with chlorine or run under high intensity ultraviolet light in order to kill harmful bacteria, viruses, different forms of microorganisms, and amoebic cysts that have been able to make it safe through the previous treatments (Henze, et al., 2002; Metcalf and Eddy. 2003). When chlorine is applied as a disinfectant, the water in many units must also go through a Dechlorination

phase in order to remove the water of the added chlorine before it is released into the environment (Shaar, et al., 2010).Ozonation has also been used in advanced treatment to help remove bacterium and other harmful substances similar to chlorine's effect (Kimm, and Platt, 2007). Tertiary treatment also helps to remove nitrogen and phosphorus within the wastewater before it is expelled because these two elements increase algae growth and may deplete oxygen levels in effluents (Mara, and Horan, 2003; Wiley, and Pesce, 2007).

Once the wastewater has went through the complete cycle of treatment, which may take anywhere between eight and sixteen hours, according to The system of the wastewater treatment after that it is often expelled into a receiving body of water (Hammer, 2012; Weiner and Matthews, 2003). Wastewater effluents can be used for industrial, agricultural, recreational purposes or even as drinking water sources after another advanced form of water treatment (Liberti, and Notarnicola, 1999; Wisconsin Department of Natural Resources Wastewater Operator Certification, 2010). The discharge of effluent wastewater is a significant part of the wastewater treatment program and it can be beneficially used in more than one way such as irrigation or hydroelectric power (Cheremisinoff, 2002; Kitis, 2004).

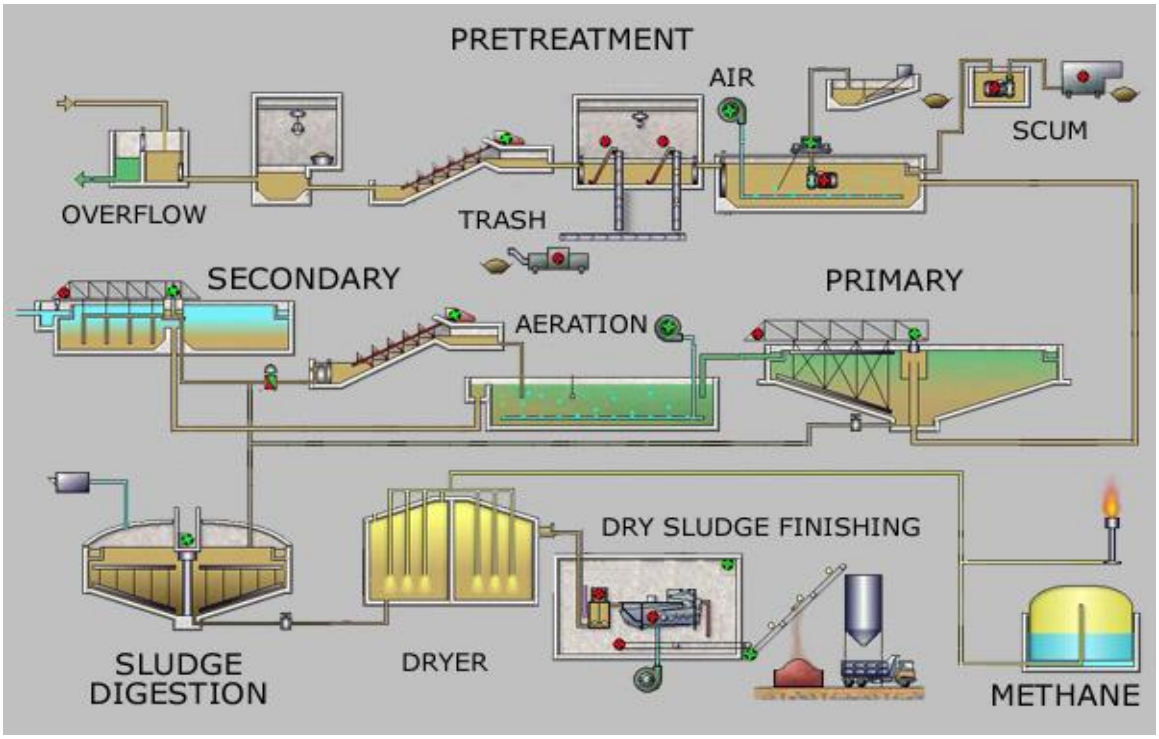


Figure 2.1: The Operation unite of WWTP. (Drinan, and Whiting, 2001)

2.2. The Biological treatment

In a municipal WWTP the objective of biological treatment is to biodegrade constituents into acceptable end products, capture solids into biological floc or biofilm and to remove nutrients and other organic particulates, Microorganisms in the biological treatment oxidize organics into more simple constituents. The microorganisms are also used to remove nitrogen through nitrification and denitrification. Biological treatment can be divided into aerobic, anaerobic and/or anoxic sections. (Metcalf and Eddy, 2003; Davis, 2010).

2.2.1. The Activated sludge as an operation

Activated sludge is a suspended growth secondary treatment process that primarily removes dissolved organic solids as well as settleable and non-settleable suspended solids. The activated sludge consists of a concentration of microorganisms and sludge particles that are naturally found in raw or settled wastewater. These organisms are cultivated in aeration tanks, where they are provided with dissolved oxygen and food from the wastewater. The term "activated" comes from the fact that the particles are teeming with bacteria, fungi, and protozoa (Drinan, and Whiting, 2001; Shaar, et al., 2010; Einschlag, and Carlos, 2013). As shown in (fig.2.2).

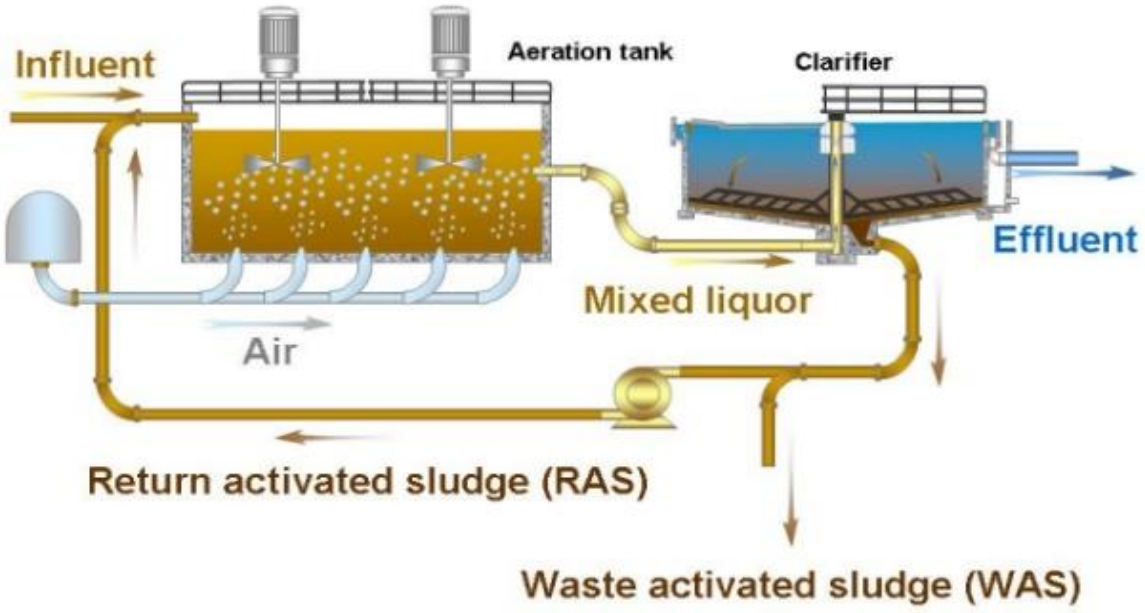


Figure 2.2: The operation of activated sludge processes

2.2.2. Activated sludge processes

The activated sludge treatment process can be operated in a variety of different modes. Each of the variations utilizes the basic process of suspended growth in an aeration tank, but new methods of operation are routinely being added to the industry. The three basin modes of operation for the activated sludge process are:

- Conventional Activated Sludge
- Extended Aeration Activated Sludge
- Contact Stabilization Activated Sludge

They all accomplish the biochemical reduction of organics using aeration basins and return and waste sludge systems. The detention times, MLSS, and F: M loadings are different in each case. The one control parameter that they all share is the dissolved oxygen requirement of 2.0-4.0 mg/L. The fact that aerobic conditions exist in the aeration basin means that the mixed liquor should have a light earthy odor that is not objectionable. Dissolved oxygen levels are maintained by aeration equipment using blowers and diffusers or mechanical aerators (Bitton, 2005; Shaar, et al., 2010).

The primary difference between these three modes of operations has to do with the length of time that the microorganisms reside in the treatment system. This concept is expressed as the system's solids retention time, or SRT. A system's SRT is calculated as the pounds of MLSS in the system divided by the pounds of suspended solids that enter the system every day (Cheremisinoff, 2002; Metcalf and Eddy. 2003 Mara, and Horan, 2003; Ravi, 2007).

2.2.3. Conventional activated sludge processes

Conventional activated sludge has an aeration basin detention time of 4-6 hours. During this time the microorganisms will completely stabilize the BOD before the mixed liquor leaves the basins. The MLSS concentrations usually run from 2000-3500 mg/L. F:M ratios should be between 0.2-0.5. MCRT or sludge age varies from 5-15 days (Metcalf and Eddy. 2003). As shown in (fig.2.3).

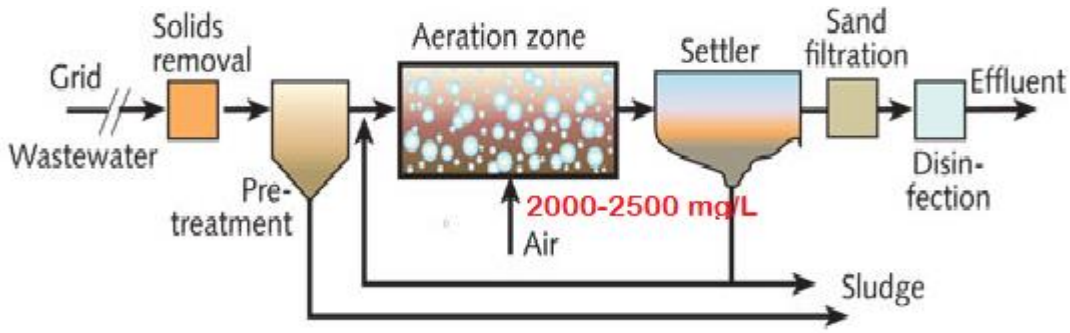


Figure 2.3: The conventional activated sludge operation

2.2.4. Contact stabilization processes

Contact stabilization uses two separate aeration processes. The primary effluent enters the contact chamber where the bugs begin to break down the BOD and increase the overall settle ability of the organics that are not yet oxidized (Bitton, 2005).The raw organics and MLSS settle out in the clarifier just like conventional activated sludge. But instead of returning the RAS to the contact basin, it is pumped to another aeration basin called a stabilization basin. Here the RAS is aerated until the organics have been eaten or stabilized by the bugs. The effluent from the stabilization basin is returned to the contact basin, to maintain the MLSS there, and the process begins again. (Wiley, and Pesce, 2007; Wisconsin Department of Natural Resources Wastewater Operator Certification, 2010).The main advantage of the contact stabilization process is that most of the solids and BOD reduction happens off-line from the main flow. This prevents massive solids loss during hydraulic shocks on the system and reduces recovery time since the bulk of the biomass is kept in the stabilization basin (Metcalf and Eddy. 2003; Vaigan, et al. 2009).The detention time in the stabilization basin is from 4-8 hours, The MLSS concentrations is 4,000-6,000 mg/L in the stabilization chamber (Drinan, and Whiting, 2001; Chen, and Lo, 2006). As shown in (fig.2.4).

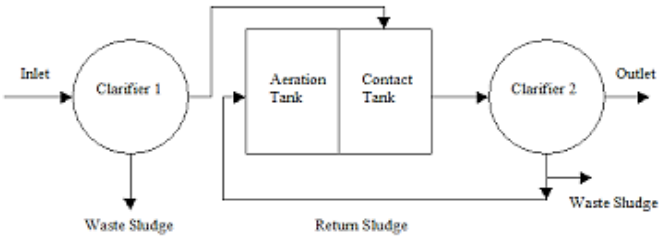


Figure 2.4: The contact stabilization unit (Metcalf and Eddy. 2003)

2.2.5. The Extended aeration processes

Extended aeration systems are designed to completely stabilize all of the organic materials in the aeration basins. The detention times range from 16-24 hours and MLSS ranges run from 3000-5000 mg/L. They have the lowest F: M ratios of any of the activated sludge processes, usually 0.05-0.2. The only solids that remain are in the form of inert ash. Extended aeration plants normally have pretreatment but not primary clarifiers. RAS is returned to the head works and waste sludge is sent to an aerobic digester, Owing to these characters, it was devised in this work. (Wiley, and Pesce, 2007; Wisconsin Department of Natural Resources Wastewater Operator Certification, 2010; Drinan and Whiting 2001).as shown in (fig.2.5)

The scientific progress as well as the advancement of health and environmental levels pose more stringent and strict legislation of ecology. Hence, capacity of sludge treatment station should be increased to reach high performance levels as well as improved their efficiencies. Also, measure should be applied to lessen expectable shocks to these station and to improve their whole capacity to obtain well-treated effluent in which the quality in accordance with the current environmental laws

1. The ability to withstand light organic load shocks since it can accommodate huge variations in afferent organic load entering the system.
2. The ability to overcome sludge production problems, since the formed sludge is little in average of 0.03-0.1 Kg sludge/Kg BOD. Day.
3. The operation requires light consumption O_2 which reach 1.25 time the subjected BOD ratio.
4. High occurrence of nitrification process (Grady, et al, 1980).
5. The ability of accommodate toxic shocks due to high stagnation time (Foster, 1977).
6. Clear aeration of the sludge due to decrease ration of exposed load.
7. The changeable hydraulic stagnation in this system does not influence mean removal constant vale K at constant local temperature.

8. This unit excludes the need for primary (initial) precipitation (sedimentation) tank as well as an economic benefit in small amount of sludge subsequently a recued requirements of sludge treated unit (David, et al, 1969).
9. The ability to obtain well exclusion even low ambient temperature (5-10) C° decrease organic load and in of mean of microbial cellular metabolism.

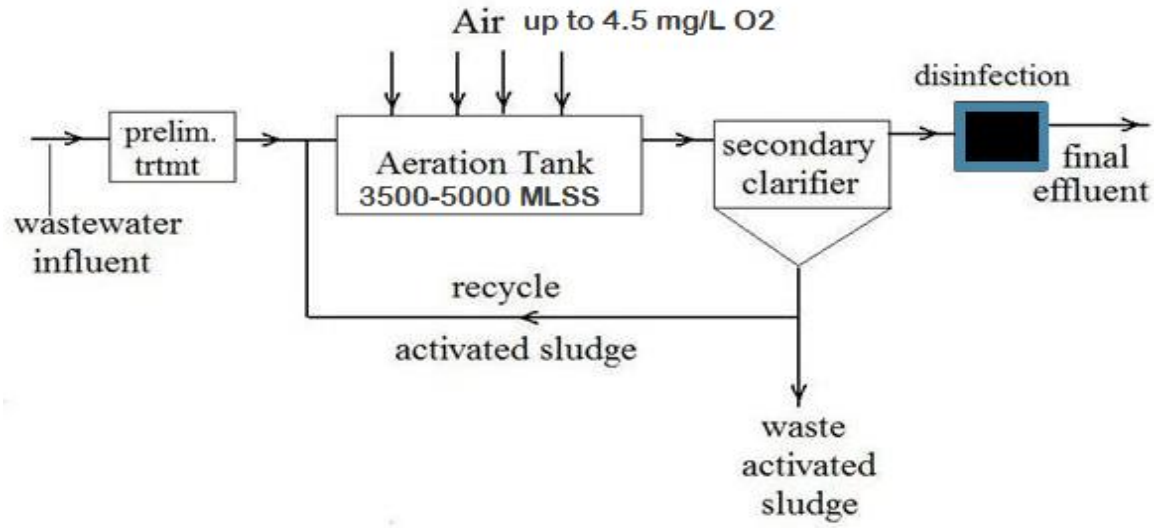


Figure 2.5: The extended aeration unit

2.2.6. The Oxidation Ditches

An oxidation ditch is a form of extended aeration activated sludge. The aeration basin is a large oval shaped tank that resembles a racetrack. Wastewater enters the ditch and is circulated around the track by means of a large horizontal brush/rotor. The rotor assembly is partly submerged in the ditch. As it rotates it pushes the mixed liquor around the "track". The rotor also provides the needed aeration to maintain a DO level of about 2 mg/L in the basin. The oxidation ditch effluent passes to the secondary clarifier and RAS is returned to the ditch. (Drinan, and Whiting, 2001; Gerardi, 2006; Sirianuntapiboon, et al. 2006; Han, 2012) as shown in the (fig.2.6).

Some ditches are designed with a concrete wedge at the exit of each bend. As the flow comes "out of the turn", the wedge forces the water at the outside to the inside as it comes down the "straightaway". This helps mix the flow and creates turbulence where settling is most likely to occur. Oxidation ditches, as with other extended air systems, do

not have primary treatment. Pretreatment maybe limited to bar screens. This means that grit will not be removed until it settles out in the oxidation ditch. The grit buildup in the ditch can result in odors and loss of detention time. It should be removed anytime the unit is drained for service (Drinan and Whiting 2001; Wisconsin Department of Natural Resources Wastewater Operator Certification, 2010; Davis, 2010).

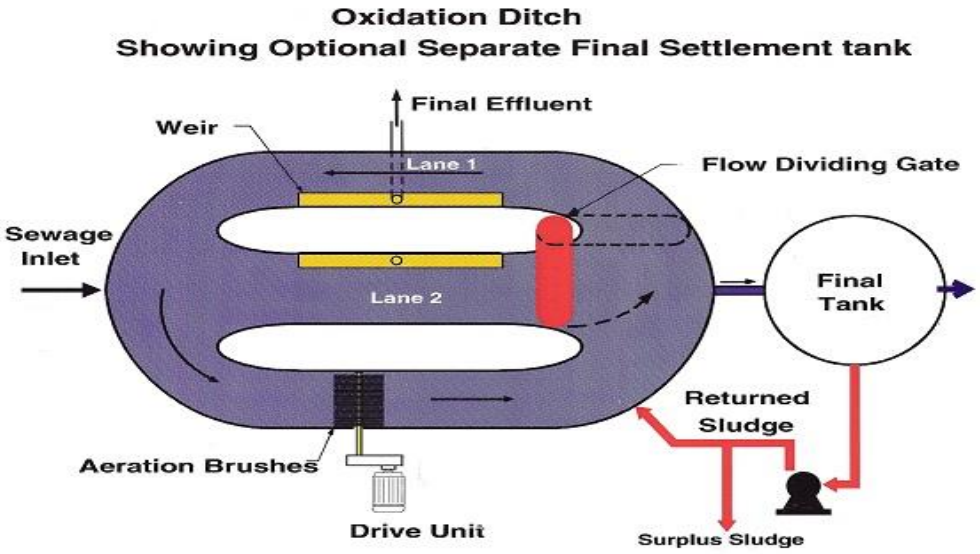


Figure 2.6: The oxidation ditch activated sludge unit

2.2.7 Sequencing batch reactor (SBR)

A sequenced batch reactor is a process that is used in small package plants. It is not a continuous flow process. The reactor basin is filled and then aerated for a certain period of time, usually 1-3 hours. After the aeration cycle is complete, the reactor is allowed to settle and effluent is decanted from the top of the unit.

When the decanting cycle is complete, the reactor is again filled with raw sewage and the process is repeated. These processes are popular because entire process uses one tank. Most plants do not have clarifiers or RAS systems. A large equalization basin is required in this process, since the influent flow must be contained while the reactor is in the aerating cycle (Arrojo et al. 2004; Farabegoli, et al., 2004; Ganjidoust, et al. *2004*; Cassidy, et al. 2005; Sirianuntapiboon, et al. 2006; Vaigan, et al. 2009).as shown in the (Fig.2.7).

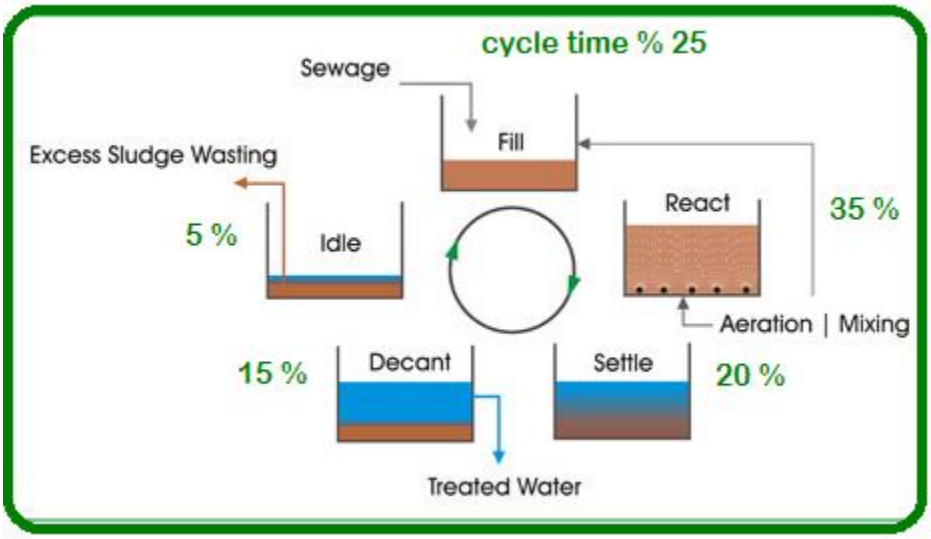


Figure 2.7: The sequencing batch reactors principle

2.3. Nitrification Processes

Biological nitrification is the oxidation of ammonium ions to nitrite ions and then to nitrate ions. During the oxidation of ammonium ions and nitrite ions, oxygen is added to the ions by a unique group of organisms, the nitrifying bacteria ,Nitrification occurs in nature and in activated sludge processes (Corbitt, R. A. 2004) Nitrification in soil is especially important in nature, because nitrogen in absorbed by plants as a nutrient in the form of nitrate ions. Nitrification in water is of concern in wastewater treatment, because nitrification may be required for regulatory purposes or may contribute to operational problems, Although ammonium ions and ammonia are reduced forms of nitrogen, that is, are not bonded to oxygen, it is the ammonium ion, not ammonia, that is oxidized during nitrification. The quantities of ammonium ions and ammonia in an aeration tank are dependent on the pH and temperature of the activated sludge (Austin, 1988 Bitton, 1994; Gerardi, 2006; Davis, 2010).

In the temperature range of (10- 20)°C and pH range of 7- 8.5, which are typical of most activated sludge processes, about 95% of the reduced form of nitrogen is present as ammonium ions. The oxidation of ammonium ions and nitrite ions is achieved through the addition of dissolved oxygen within bacterial cells. Because nitrification or the biochemical reactions of oxygen addition occur inside biological cells, nitrification occurs through

biochemical reactions. The nitrification steps are shown in equation 1 and (Fig.2.8) (Celenza, 2000; Metcalf and Eddy 2003; Gerardi, 2006).

$$2NH_{3+} + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2 + 2H + 2H_2O \text{ …….. (1)}$$

$$2NO_2 + O_2 \xrightarrow{Nitrobacteria} 2NO_3 \text{ …….. (2)}$$

2.4. Denitrification

The use of nitrate ions by some facultative anaerobes (denitrifying bacteria) to degrade substrate, which use nitrate ions and sometimes nitrite ions to degrade substrate of wastewater actually evolved before the use of free molecular oxygen. Although denitrification often is combined with aerobic nitrification to remove various forms of nitrogenous compounds from wastewater, denitrification occurs whenever an anoxic condition exists, Therefore denitrification can promote favorable operational conditions or can contribute to operational problems. The denitrification steps are shown in the equation 3 and (Fig. 2.8). (Delwiche, 1981; Metcalf and Eddy 2003; Shaar, et al., 2010).

$$\mathbf{2NO_3 \rightarrow 2NO_2 \rightarrow N_2} \text{…….. (3)}$$

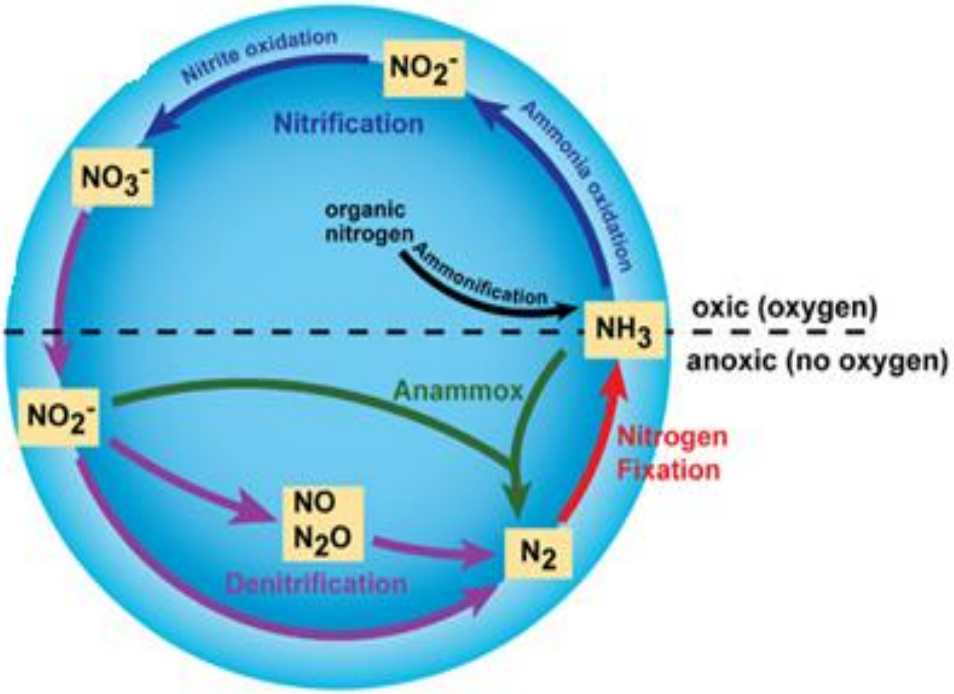


Figure 2.8: The nitrification and denitrification process

2.5. Phosphorus removal

Phosphorus removal can be achieved both biologically and by chemical addition. The basic idea is to incorporate phosphorus into suspended solids. This can happen either by microorganisms or precipitation chemicals such as iron or aluminum salts. The chemical reactions for precipitation with aluminum and iron can be seen in equations 4 and 5 (Lydia, 2006; Gerardi, 2006; Cordell, et al. 2009; Davis, 2010).

$$Al^{3} + H_nPO_4 \leftrightarrow ALPO_{4+n}\, H^{+} \text{..... (4)}$$

$$Fe^{+3} + H_nPO_4 \leftrightarrow FePO_4 + nH^{+} \text{..... (5)}$$

Biological phosphorus removal can be achieved with many different methods. The biological phosphorus removal processes include, in the biological suspended growth process, an aerobic zone followed by an anaerobic zone. The biological removal of phosphorus can also be achieved by modifications of this basic principle (Cecchi, 2003; De-Bashan, and Bashan, 2004; Bitton, 2005; Einschlag, and Carlos, 2013).

2.6. Pharmaceuticals and personal care products in environment

Pharmaceuticals and personal care products (PPCPs) are chemicals that are discharged from household usage, airport and industrial manufacturing waste. This large group of PPCPs consists of non-prescription drugs, prescription drugs, veterinary medicines, growth promoters, diagnostic agents, cosmetics, fragrances, sun screen agents and disinfectants used in industry, households, slaughterhouses, dairies, tanners and agricultural practices (USEPA, 2014). Pharmaceuticals can also be excreted via feces and urine as well as the disposal of expired medicine via toilets (Ternes, et al 2002). (Fig. 2.9) explains the routes for PPCPs; involving their origin and how they enter into drinking water stream. Notably, all PPCPs have the potential to be excreted, disposed of, or washed into sewage systems and from there discharged to aquatic or terrestrial environments.

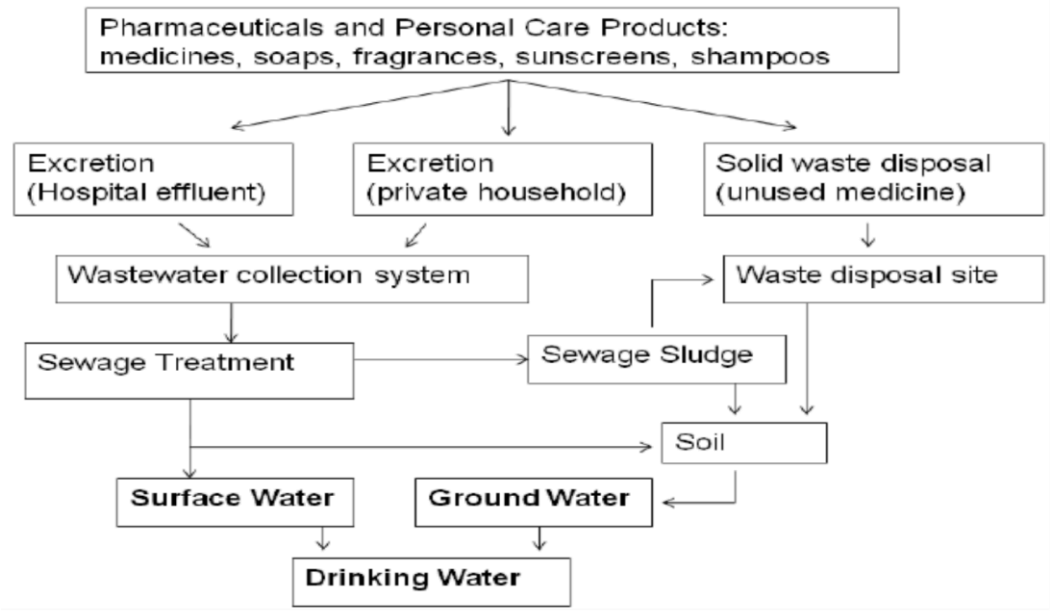


Figure 2.9: the pathways for PPCPs (Bound, and Voulvoulis, 2004; Nicholas, 2010 adapted from EPA 2008).

2.6.1. The Pharmaceuticals

All pharmaceuticals are in general applied for a chemically and structurally various group of substances administered to human and veterinary medicine. Their only common denominator is that they are all manufactured to interact with certain biological pathways, leading a specific functional response (ABPI, 2008) this is clearly a favorite quality from a medicinal view, but might be of importance for non-specific organisms when pharmaceuticals are released into the ambient environment (Dibner, and Richards, 2005; Kummerer, 2009a, b; Halling-Sørensen, 1998).

Pharmaceuticals are classified according to the organ or system on which they served and/or their therapeutic and structural features in the Anatomical Therapeutic Chemical (ATC) Classification System, which is advocated by the WHO Collaborating Centre for Drug Statistics Methodology (WHOCC). One such group is the anti-infective (group J), which includes antibacterial, antibiotics, antifungals, antiprotozoans and antivirals. They are different from most other pharmaceutical groups in that they are "licensed to kill", i.e. they are meant to eradicate microbes harmful for e.g. the human body. (Lawrence, 2004) they are in this sense closely related to the biocides used in these

chemicals compounds, e.g. triclosan which will investigate later. (Fent, et al 2006; Schnittker, and Karandinos, 2010).

After application most pharmaceuticals are metabolized to some degree in the body, the extent depending on the chemical properties of the drug, e.g. of the antibiotic amoxicillin 80–90% is excreted unchanged (Bound, and Voulvoulis, 2004). Therefore, a certain amount of the active substance will be excreted together with more or less active metabolites enter the sewage system and finally end up in a wastewater treatment plants. A small contribution to the overall load into the sewage system is also unused drugs that are improperly disposed of (Bound, and Voulvoulis, 2004; Daughton, and Ruhoy, 2009). Hospital wastewaters constitute a special case, where generally higher concentrations of pharmaceuticals are detected (Lindberg, et al., 2004; Martins, et al., 2008). They can either be connected to the municipal WWTPs or have a separate hospital WWTP, the latter not necessarily ensuring higher removal rates of the pharmaceuticals (Bound, and Voulvoulis, 2004; Kosma, et al., 2010).

2.6. 2. The Personal care products

Chemical Compounds used in personal care products have lately been frequently detected in water supplies. Personal care products, including fragrances, hygiene products, cosmetics and sunscreens may include compounds that have negative environmental effects and act as EDCs (Kümmerer, 2004; Suárez, et al., 2008). Personal care products consist of a lot of different compounds, including preservatives and antibacterial compounds, and these can cause harmful influence both to the environment and the wastewater treatment process. Also, sunscreen agents and mask can contain PHCs (Swedish Environmental Protection Agency, 2008; Gary 2010). Municipal wastewater treatment plants are not designed to remove antibiotics or other pharmaceuticals, but to limit the release of nutrients and organic matter into the aquatic environment. Even so, some pharmaceuticals are removed during the treatment process due to adsorption, photolysis and biodegradation. However, due to the chemical properties of the pharmaceutical removal can differ quite substantially, *e.g.* the β-blocker atenolol is not removed at all, whereas paracetamol is removed almost completely (Miege et al., 2009; Li, et al. 2010). In the common case, the treated sewage effluent is released by the WWTPs into a nearby river, still containing small

amounts of pharmaceuticals. When pharmaceuticals are used within veterinary medicine, the ingested drug will be excreted directly onto a pasture, potentially being flushed into nearby streams during rainfall; it was recently shown that also the production of pharmaceuticals can lead to environmental contamination when insufficiently controlled. Extreme concentrations of ox tetracycline (43 μ mol/L) in WWTPs effluents connected to production facilities in China was reported by Li and colleagues (Li, et al., 2008) and Larsson and co-workers reported a total concentration of fluoroquinolone antibiotics of 100 μ mol/L in effluent from drug production facilities in India (Larsson, et al., 2007).

2.6.3. The occurrence of PPCPs in the environment

Pharmaceuticals and Personal Care Products (PPCPs) have been recognized as a potential environmental problem (Kümmerer, 2004; Suárez, et al., 2008). The research on the occurrence and on the fate of PPCPs in the environment has been active particularly in Europe and USA (Carballa 2005; Lishman, 2006). A bundle of all analytical works on pharmaceuticals and personal care products in the environment emphasize on concentrations detected in WWTPs effluents and surface waters. However, these chemicals compounds have been trace in all aquatic compartments even if the comparative knowledge on their presence in groundwater, drinking water and sea water is low. (Lindberg, et al., 2004; Enick, and Moore, 2007; Martins, et al. 2008). The detection of pharmaceutical substances is not a measure of the number actually present, since most studies do not have the aim to estimation all, but are targeting a certain group. Pharmaceuticals from all therapeutic groups have been detected in WWTPs effluents, mainly in the Pico n mol/L concentration range. Highest concentrations are generally related to their high volume drugs, e.g. anti-inflammatory drugs. As a consequence, the highest environmental concentrations are found in surface waters (Coetsier, et al., 2009). Still, the groundwater concentrations of the antiepileptic drug carbamazepine have been detected up to 5 n mol/l (Heberer, 2002). For instance, the presence of clofibric acid, propylphenazone and diclofenac were determined in the drinking water of Berlin in the nmol/l concentration range (Khetan, and Collins, 2007). Due to the leaching behavior of antibiotics applied in veterinary medicine, sulfa-antibiotics have been detected in ground waters (Blackwell, et al., 2009), however it should be noted that antibiotics still have not been detected in

drinking waters (Kummerer,. 2009b). Finally, e.g. salicylic acid at 5 nmol/L was detected in the marine environment (Wille, et al., 2010). When it comes to environmental detection data on antibiotics, a certain background concentration can be expected in soil, since several of the "natural" antibiotics are produced by soil living organisms, e.g. streptomycin by the bacterium Streptomyces's. However, no such production has been showed for the aquatic environment so far (Kulik, et al 2008; Kummerer, 2009a), which means all measurable concentrations detected there are most likely introduced through human use.

A similar study carried out by the United States Geological Survey (USGS) on 139 stream samples of 30 different state referred measurable levels of prescribed and non-prescribed including steroid, reproductive hormones either as parent or their metabolites. Consequently, such study alongside with other studies focus the detecting of PPCPs in surface and drinking water indicating an important trend relating public health with subsequent adverse environmental consequences (Kolpin, et al 2000; Williams, 2005). Also, an overview was given by WWTPs showed different influents and effluents concentration ranges of pharmaceuticals found in numerous researches (Table 2.1). The concentrations are dependent on several factors which can be different for each country, WWTP, *etc*. (Bound, and Voulvoulis, 2004; Fent, et al 2006; Brausch, and Rand, 2010).

Table 2.1: The measurement influent, effluent concentrations of some common pharmaceuticals. (Fent, 2006; Petrovic, and Barcelo, 2006 (modified)).

Compound	***Influent concentration µg/L)***	***Effluent concentration (µg/L)***
Acetylsalicylic acid	3.2	0.6
Salicylic acid	57-330	0.05-3.6
Ibuprofen	2-38.7	0-4
Diclofenac	3.0	2.5
Carbamazepine	0.7-1.5	0.7-1.5
Metoprolol	-	0.08-0.73
Clofibric acid	0.15-1	0-0.88
Paracetamol	285-420	5-10
Bezafibrate	0.42-5	0-0.84
Fenofibric acid	0.44	0.22-0.4
Triclosan	0.029-0.47	0.02-0.058

The PPCPs are released in the in surface water at relative low concentrations, in general in the range of ng/l up to low µg/l; and these chemical compounds will be further diluted when they come in contact with surface water. Because of the continuous input of these chemicals even readily degradable pharmaceuticals are measured in rivers and other surface waters, especially near WWTPs effluents. Less easily degradable pharmaceuticals do also enter the sea. For example carbamazepine was detected in the North Sea (Bester, and Weigel, 2001). Also in groundwater pharmaceuticals can enter. Multiple pharmaceuticals were measured in drinking water at low ng/L range. In figure (2.10) the occurrence of pharmaceuticals in small streams and rivers in Germany is reported (Ternes, 1998). the measured concentrations are in the low µg/L range.

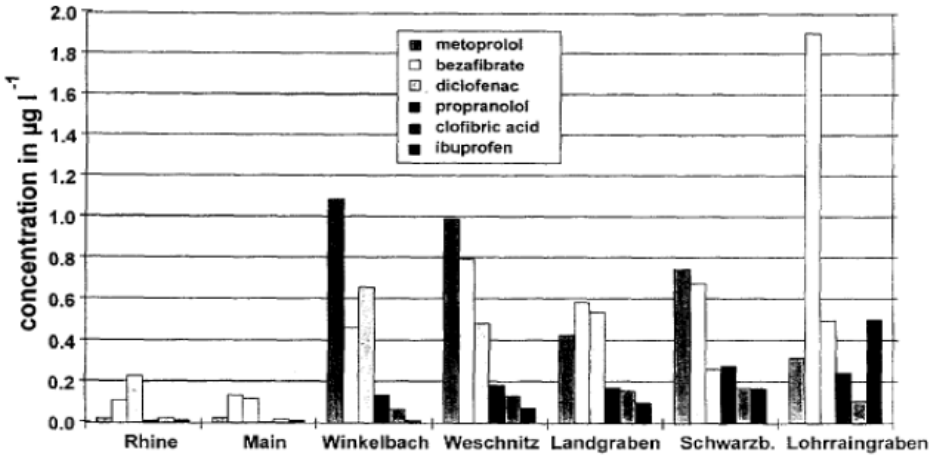


Figure 2.10: Concentrations of some drugs in different rivers and brooks in Germany (Ternes, 1998).

It is difficult to determine the effects of pharmaceuticals in the environment. Some acute effects have been determined for aquatic organisms but these occur at pharmaceutical concentrations of several mg/L, and therefore they are not likely to occur at present situation. For instance, for ibuprofen a LC50 (96 h) is determined at 173 mg/L for the bluegill sunfish (Hansen, and Jensen, 1998). Because of the low pharmaceutical concentrations in the environment but their continuous input, chronic effects of pharmaceuticals are much more likely. However, these effects are more difficult to predict because of the long time period is required before effects become clearly visible. Especially endocrine disruptors are known to disturb the functioning of organisms at very low

concentrations. Some effects occurring at environmental realistic concentrations have yet been determined also for non-hormones.

2.6.4. Use of human PPCPs

The consumption of pharmaceuticals has been increasing over the last years. This trend is likely to continue in future due to e.g. the growth and the aging of the population. The increasing number of users of drugs over the last years is shown in table (2.2) for the various situation. The pharmaceuticals are divided into 14 classes based on their functional use.

Table 2.2: Classes of drugs and the number of users (x 1000) in the Netherlands from 2002- 2006 (CVZ, 2006).

Pharmaceuticals	2002	2003	2004	2005	2006
A Alimentary tract and metabolism	2910	3004	2769	2969	3441
B Blood and blood forming organs	1655	1663	1667	1673	1944
C Cardiovascular system	2676	2759	2910	2982	3630
D Dermatologicals	3421	3465	3193	3166	3484
G Genito urinary system and sex hormones	2774	2703	1419	1412	1594
H Systematic hormonal preparations	828	854	890	927	1043
J Antiinfectives for systematic use	3840	3826	3775	3945	4229
L Antineoplastic and immunomodulating Ag.	145	157	169	180	221
M Musculo-skeletal system	3403	3423	3322	3136	3369
N Nervous system	3584	3598	3345	3308	3555
P Antiparasitic agents, insecticides, repellents	144	148	161	162	170
R Respiratory system	3149	3064	3033	3099	3481
S Sensory organs	1785	1802	1759	1755	2137
V miscellaneous	34	37	40	43	60

Types of some effects of pharmaceuticals maybe shown ass the effects between and within species sex, inter- and intraspecies between organisms of the different developmental stages may influence the toxicity of a pharmaceutical (Daughton, and Ternes, 1999).

Also, light effects, such as genetic or behavioral changes are much more difficult to detect while they can have important sequel. At especially at low concentrations, pollutants can disturb the chemical signaling. (Bester, and Weigel, 2001). Pharmaceuticals could also cause this and interfere in the information transfer between or within organisms. However, combined effects of different pharmaceuticals together can exhibit unexpected effects based on one compound assessment which can be seen in veramapil (a pharmaceutical used for the cardiovascular system), which increases the intercellular concentrations of other pharmaceuticals in organisms mode of actions of pharmaceuticals plays an important role similar targets of pharmaceuticals in humans and other organisms could have possible effects to these creatures. (Daughton, and Ternes, 1999). Finally, the effects of metabolites have a serious influence hence some pharmaceuticals may be degraded to metabolites which have bioactive and/or persistent characters. For example clofibric acid is the metabolite of clofibrate and is quite persistent and can be classified as harmful to aquatic organisms (Fent, et al 2006). Also, the consumption of some widely used pharmaceuticals in Finland during 2010 is present in (Table 2.3) the consumption was calculated according to the following equation 6 (Vieno et al, 2007).

Table 2.3 The Pharmaceutical consumption in Finland 2010 (Vieno, 2007)

PPCPs	Cons.(kg)	PPCPs	Cons.(kg)	PPCPs	Cons.(kg)
EE2(Estrogen)	57	Ketoprofen	604	Ciprofloxacin	639
Ibuprofen	113232	Bezafibrate	118	Paracetamol	151947
Diclofenac	1079	Ofloxacin	31	Triclosan	416
Naproxen	6230	Metoprolol	4732	Carbamazepine	3754

$$\mathbf{Consumption_{(Kg)}} = \mathbf{DDD_{(g)}} \times \frac{\mathbf{DDD}}{\mathbf{1000_{inh}}} \times \frac{\mathbf{population}}{\mathbf{1000000}} \times \mathbf{366} \ldots\ldots (6)$$

2.6.5. The destination of Environmental PPCPs and their biotransformation

PPCPs may introduce to the environment either in their unchanged parent forms or as metabolites. Dissociation of PPCPs in the environment can occur via biological or chemical processes that include oxidation, hydrolysis, reduction, or alkylation. Additionally, sorption to particulate matter, complexion with metal ions, thermolysis, photolysis, and volatilization may further degrade them or simply make them biologically

unavailable. Properties of the environment itself can affect degradation of anthropogenic compounds (pH, salinity, dissolved oxygen, temperature, presence/quantity of organic matter, and existing microbial communities) (Aga, 2008).

In an ideal situation, anthropogenic compounds will undergo total degradation in the environment, or "mineralization." However, certain factors may inhibit mineralization. Evidence from research on other organic compounds suggests the potential for PPCPs to become trapped in microsites of solid matrices, inhibiting biological degradation (Alexander, 2000; Jjemba, 2008). Adsorption and complexion of PPCPs also inhibit degradation in a similar manner. Interestingly, some PPCP metabolites that have been conjugated into less biologically active forms within the human body become deconjugated back into their active forms during the wastewater treatment process or in the environment due to microbial action (Ternes, 1998; Ternes, et al. 1999b; Huang, and Sedlak, 2001; Khanal, et al. 2006; Jjemba, 2008). Overall, relatively little is known about the fate of PPCPs and their metabolites once released into the environment, and more specifically, saline environments, various aspects of the receiving aquatic environment itself, such as physicochemical characteristics, presence of particulate and dissolved organic matter, and overall flux of water may differentially affect the fates of these compounds. (Kolpin, et al. 2002; Benotti, et al. 2006).

2.6.6. Evaluation of PPCPs to Non-target Organisms

PPCPs drain in the environment as combination of several compounds via effluent, runoff, and hospital drainage, etc. A more logic viewpoint of non-target organism exposure must evaluate the mixed acts of PPCP mixtures vs. exposure to single compound. A study assessed the individual toxicities of some pharmaceuticals on three different organisms, then compared these results to binary mixtures of the compounds (Cleuvers, 2003). The findings indicated stronger effects for some of the mixtures than predictions based on single effects, i.e. concentration addition vs. independent action. This results may demonstrate a potential for increased toxicity of mixtures of compounds, especially those with similar modes of action (i.e. additive effects), where the compounds themselves may have low individual toxicities. Such combinations of chemicals may not only show additive effects, but synergistic effects and antagonistic effects must also be expected (Marking, 1977).

Some workers hypothesize that although the levels of PPCPs obtaining in toxicity used in experimental studies are much higher than environmental levels. Hence, the fact that PPCPs are typically observed in mixtures in the environment could lead to toxicity at levels lower than expected. (Gomes, et al. 2004; Quinn, et al. 2009). Bioaccumulation of specific PPCPs has also been shown to occur in a large range of aquatic organisms. For example, the antimicrobials triclosan and triclocarban accumulate in the alga *Cladophora spp*. found downstream from WWTP discharges (Coogan, et al. 2007). Laboratory experiments by (Delorenzo, et al. 2008) showed accumulation of methyl-triclosan in grass shrimp and (Fair, et al. 2009) speculated that triclosan accumulated in dolphin plasma based on higher levels in tissues compared to environmental concentrations in surrounding surface waters (Metcalfe, et al. 2010) noted potential accumulation of antidepressants in fish that were caged and placed downstream of WWTP effluent discharge. The less that the compound was ionized, the greater the bioaccumulation, which is the general trend for many organic contaminants (i.e. less ionization and higher lipophilicity results in greater bioaccumulation potential; commonly estimated based on acid dissociation constant and octanol -water partition coefficient, or pKa and Kow, respectively). However, (Delépée, et al. 2004) saw a large accumulation of various antibiotics in the freshwater bryophyte 7 *Fontinalis antipyretica* and suggested that the more antibacterial agents are ionized, the more they were bio accumulated.

2.7. The Removal mechanisms of PPCPs

There are four different things that can take place to organic compounds in a WWTP. A compound can break down (biodegrade), sorb to sludge, volatilize or end up in the effluent. Compounds can be destructed completely (mineralize) or transfer to other elements. Various operational conditions have been observed to affect the biodegradation of a compound. Some compounds biodegrade better with a long SRT, HRT and the biodegradation is usually faster when a high concentration of the compound is present. (Vazquez, et al 2006; Swedish Environmental Protection Agency, 2008).

The biotransformation of compounds depend on many different factors. A biodegradation rate constant can be used to describe the biological transformation. On the other hand, the compounds sorption potential has also a big impact on its fate; the sorption coefficient k_d

describes this. Compounds with high k_d values require a longer SRT to fulfill their biodegradation. (Suárez, *et al.*, 2008). Xenobiotic compounds are particularly persistent to biodegradation and microbes. They are often halogenated organic compounds that are especially hard for microbes to degrade. Halogenated organic compounds include halogenated hydrocarbons, halogenated aromatics, pesticides and PPCPs (Bitton, 2005).

2.7.1. The Biodegradation of PPCPs

Biodegradation is biological degradation by either aerobic or anaerobic microorganisms that leads to the reduction of a parent compound or metabolite. WWTPs have a high potential to decrease PPCPs and their metabolites via biodegradation. Biodegradation will mostly occur during secondary treatment in the wastewater treatment process, where the compounds will be exposed to the most activity by microorganisms. The biodegradability of a compound is highly dependent on its chemical structure. Unbranched compounds with short side chains are more likely to biodegraded than compounds with a large number of branched side chains. (Jones, et al., 2005; Alexander, 1999). Many of the compounds, foreign to the biological systems, that have been introduced to the environment during the last century are not readily biodegradable. Many factors share to the resistance to biodegrade. Not only the chemical structure but also ecological and environmental factors, toxicity to microbes, unavailability of nitrogen and phosphorus, low level concentration and unavailability of the substrate due to sorption (Bitton, 2005). Two main mechanisms of biodegradation are probable. Co-metabolism takes place when a compound biodegrades only when other organic compounds are present and are serving as substrate for the microorganisms. The second mode is called catabolic metabolism and it happens when the compound in itself can be the only origin of substrate for the microorganisms (Stasinakis, et al., 2005). Biodegradation is also highly dependent on the microbial communities. If the cultures are not acclimated to the compound they start to select the microbes that can degrade the compound. This is why a period of is adaptation sometimes needed before the foreign compound ensues to biodegrade (Bitton, 2005). However, some studies focus the microorganisms' role in the biodegradation of compounds, it is still vague which have the main responsibility in degrading the compound. Consequently, it is apparent that optimization of WWTPs for PPCPs removal is not easy. (Lapertot, and, Pulgarin, 2006;

Roh, *et al.*, 2009). Biodegradation of compounds in WWTPs can be stated by pseudo first order reaction illustrated in equation (7). (Ternes, 2004, Ternes, and Joss, 2006):

$$\frac{dCi}{dt} = K_{biol,i} \times SS \times Ci \quad \text{..... (7)}$$

Ci is the concentration of the soluble substances of the compound,

K_{biol} is the kinetic constant (biodegradation rate constant)

SS is the Suspended Solids concentration.

Biodegradability relies not only on the constants but also the diversity and total share of the biomass. Optimally, the biodegradation rate constant in a classical WWTP mean the following removal rates: (Ternes, 2004) as shown in the following table (2.4).

Table 2.1 The Biodegradation rate constant

$K_{biol} < 0.1$	no removal due to biodegradation
$0.1 < K_{biol} < 10$	removal due to biodegradation is dependent on treatment configurations
$K_{biol} > 10$	at least 95% removed by biodegradation

A bundle of work was devised to measure the biodegradation of compounds without mentioning their metabolites that may form as in our study. Some studies emphasized study the parent compound and not metabolites that can be even more injurious than the original compound. Hence, serious facts may appear unnoticed. Biodegradation does not explain if a compound mineralizes or transforms to metabolites (Fogler, 2009; Fatta-Kassinos, et al., 2011; Solen, and Harb, 2011). One way to determine the reaction order and rate equation is to guess and then integrate the equations that are used to describe the system. When the reaction order is correct, the plot of the data will be linear. (Fogler, 2009).

In a first order reaction:

$$\frac{Ln\, C_0}{C_A} = Kt \quad \text{..... (8)}$$

C_0 is the concentration in the beginning

C_A is the concentration at time t.

This means that when **(Ln C_0/C_A)** is plotted as function of time, the slope is linear. The reaction rate constant k is the slope of the line. In a second order reaction, a plot of $1/C_A$ against the function of time gives a linear slope (Fogler, 2009). In a pseudo first order reaction, that is often used to describe the biodegradation of pharmaceuticals, a reaction that is initially second order is changed to first order as the other variable, the suspended solids concentration, can be considered to remain constant (Ternes, 2004; Fogler, 2009).

When the reaction rate/degradation constant, K_{biol}, is known, it is possible to calculate the relative amount degraded in a batch reactor with the Equation (9). C_{out} is the concentration at the end. (Ternes, 2004).

$$\boldsymbol{C_{out} \div C_0 = e^{-Kbiol \times ss \times HRT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The total biological transformation can be calculated with Equation (10).

$$\boldsymbol{Removal}\% = \left(\mathbf{1} - \frac{\boldsymbol{C_{out}}}{\boldsymbol{C_0}}\right) \times \mathbf{100} \quad \ldots\ldots (10)$$

Since the reaction rate constant $\mathbf{k_{biol}}$ is expressed per suspended solids concentration, it not only depends on the degradability of each specific compound, but also on the sludge composition. In this behalf the sludge age is assumed to take influence in three independent ways:

- Biodiversity of the active biomass: According to the specific growth rate, each species of microorganisms has its characteristic minimal sludge age (*i.e.* average residence time inside the reactor) required to allow the settlement of a stable population. For the elimination of a significant number of micro pollutants ≥ 10d sludge age (nutrient removal) has shown to be crucial for biodegradation.
- Share of active biomass within the total suspended solids: the higher the sludge age, the more the sludge is being stabilized and correspondingly also the fraction of inert and inorganic matter increases. Therefore k_{biol} is expected to slightly decrease with increasing sludge age.
- Decrease of specific sludge production due to the increasing effect of sludge decay with increasing sludge age, as shown in (Fig. 2.11).

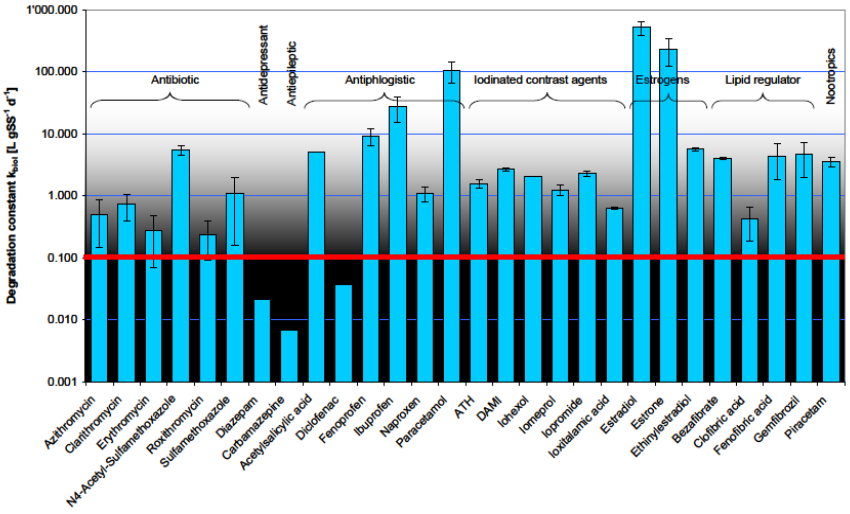


Figure 2.11: The degradation rate constants k_{biol} observed in aerobic batch experiments run with activated sludge from plants with a sludge age ≥ 8d. In the case of several observations being available, error bars indicate variation

2.7.2. The Sorption of PPCPs

Sorption to sludge can be an important removal mechanism especially when a pharmaceutical and personal care products is persistent and has a high sorption potential. Lipophilic properties and the electrostatic state are important for the amount of pharmaceutical that is sorbet to the sludge. Two different kinds of sorption mechanisms can take place: absorption and adsorption (Worch, 2012).

2.7.2.1. The Absorption of PPCPs

Absorption is related to hydrophobic interactions of aliphatic and aromatic groups of a compound with the lipid fractions of the solids (Ternes, 2005). The hydrophobic character of a compound can be indicated with the K_{ow} value. K_{ow} is the partition coefficient between octanol and water for a specific compound. The higher the log K_{ow} value, the more hydrophobic a substance is. Three groups can be distinguished for their sorption behavior based on the Log K_{ow} values (Jones, 2005; Swedish Environmental Protection Agency, 2008; Worch, 2012).

Table 2.2 The sorption potential

Log K_{ow} < 2.5	Low sorption potential
Log K_{ow} > 2.5 - 4.0	Medium sorption potential
Log K_{ow} > 4.0	High sorption potential

The values of log K_{ow} of the some pharmaceuticals are listed in table (2.6) Bezafibrate and fenofibrate are the most hydrophobic pharmaceuticals, with a log K_{ow} >4.0 from all the selected pharmaceuticals, removal due to absorption is expected be the most important for these two compounds. Aspirin will be the least absorbed to sludge, (Ternes, 2006).

2.7.2.2. The Adsorption of PPCPs

Adsorption is related to electrostatic interactions with the substance and the surface of microorganisms. Because sludge is negatively charged, it will attract positively charged molecules and reject negatively charged molecules. Most of the selected pharmaceuticals of the current study are acidic and therefore at neutral pH, negatively charged. This decreases their adsorption affinity to the sludge. The pKa value indicates the acidity of a pharmaceutical (Worch, 2012).

Table 2.3 Physical-chemical properties of the chosen pharmaceuticals (Ternes, 2006).

Pharmaceutical	Log K_{ow}	pKa value at T = 20 °C
Paracetamol	0.46	9.38
Aspirin	1.426	3.5
Bezafibrate	4.25	3.6
Carbamazepine	2.69	13.9
Clofibric acid	2.57	3.0
Diclofenac	0.7-4.5 depending on pH	4.15
Fenofibrate	5.191	n.a.
Ibuprofen	3.481	4.5-5.2
Metoprolol	1.9	9.7
Triclosan	4.6	7.9

2.7.3. The Volatilization /stripping of PPCPs

Many PPCPs are able to evaporate to the atmosphere and stay there for various periods of time. A compound's ability to evaporate is determined by its volatility. A volatile PPCPs can travel from the original pollution source and end up in another part of the world. (Swedish Environmental Protection Agency, 2008) Volatilization, or air stripping, transfers mostly VOC and ammonia from water phase into air phase (Bitton, G., 2005).The percentage of a compound that is vaporized during wastewater treatment depends on Henry coefficient and the amount of air getting in contact with the treated wastewater. The Kaw is the water-air partitioning coefficient for a certain compound and defined in the following equation.

$$\boldsymbol{K_{aw} = \frac{C_{air}}{C_{water}} = H/RT} \quad \text{..... (11)}$$

K_{aw} = partitioning coefficient (-)

C_{air} = concentration of pollutant in air (mg/L)

C_{water} = soluble concentration of pollutant (mg/L)

H = Henry's law constant (atm m^3/mol)

R = gas constant (atm.m^3/mol/K)

T = Temperature (K)

A partitioning coefficient between air and water of >3 * 10-3 is required for effects of stripping to air in a reactor with fine bubble aeration. (Ternes, 2006). Table (2.7) shows that the Henry Law constant and the Kaw of pharmaceuticals are very low.

Table 2.4 Demonstrates the Henry law constant and the Kaw of certain pharmaceuticals.

Pharmaceutical	Henry's Law constant (atm.m3/mol)	Kaw (-)
Acetylsalicylic acid	$1.30*10^{-9}$	5.32E-08
Metoprolol	$2.19*10^{-8}$	8.96E-07
Clofibric acid	$1.08*10^{-10}$	4.42E-09
Carbamazepine	$4.73*10^{-12}$	1.93E-10
Diclofenac	$1.50*10^{-7}$	6.13E-06
Ibuprofen	$1.40*10^{-13}$	5.73E-12
Triclosan	$2.1*10^{-8}$	4.76
Paracetamol	$6.5*10^{-8}$	log P, 0.31

2.7.4. The Abiotic transformation of PPCPs

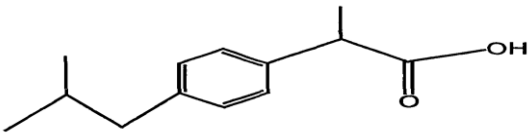
Abiotic transformation may occur via the processes of hydrolysis and photolysis. (Andreozzi, et al 2003) has determined half-lives of carbamazepine, clofibric acid and diclofenac for photolysis. In a test with glass-disk reactors in a thermostatic bath at a temperature of 25 C^o direct photolysis was analyzed in various seasons and at several latitudes ($20N^o$ – $50N^o$). During winter and $50N^o$ latitude the half-lives of carbamazepine and clofibric acid were in the order of 100 days. Half-live of diclofenac was in the range of 5 days. In summer the t 1/2 for DCF was lowered to approximately 0.5 d (Andreozzi, et al 2003). Another research showed the rapid degradation of diclofenac in the lake Greifensee (in Switzerland). The removal of diclofenac in this lake was over 90% (inflow and outflow concentration of max. 370 ng/L and max. 12 ng/L resp.), most likely due to photo degradation (Buser, and Poiger, 1998). A first order degradation rate was determined in a laboratory experiment with a half-live of less than 1 hr in autumn at a latitude of 47 N° (Buser, and Poiger, 1998). Metabolites were not studied in this case, thus this elimination of diclofenac could result from the production of OH-diclofenac to a much more advanced degradation. Photolysis of diclofenac in lakes can thus be significant. For WWTPs, this process is however not so relevant because there is (almost) no light in activated sludge tanks (Ramil, et al 2009; Kosjek, et al 2007).

2.8. The Properties of the chosen PPCPs

Three pharmaceuticals were chosen for this research, ibuprofen, paracetamol and triclosan. Certain criteria of these compound include their possibility to purchase and use without a prescription, their potential to transform into substances that cause bioaccumulation representation of wide variety of therapeutic categories. Also, their occurrence is highly reported in the environment with high consumption rates in the worlds. However, many studies reveal their toxicity which may be acute or chronic. Pharmaceuticals and personal care products have (hydrophobic/hydrophilic) physical-chemical properties with their possible susceptibility to biodegradation (Zhu, et al 2010; European Commission Health and Consumers, 2010; Verlicchi, et al 2010).

2.8.1. Ibuprofen IBU

Table 2.5 The most properties of Ibuprofen (a. Ternes and Joss, 2006; b. Ternes 2004; c. Smook, et al. 2008; d. Suárez, et al.2008; e. Urase, and Kikuta, 2005).

INCI Name	Ibuprofen		
Chemical Name	Benzeneacetic Acid, alpha-Methyl-4-(2-Methylpropyl)-		
Scientific name	a-Methyl-4-[isobutyl] phenyl acetic acid		
Trade Names	Advil, Children's Advil/Motrin, Medipren, Motrin, Nuprin, Pedia Care Fever.		
Molecular Formula	$C_{13}H_{18}O_2$		
Molecular Weight	206.28082		
Biodegradation Kbiol	21-35 [a]	23 ± 10 [b]	6.8 ± 3.3 [c]
Sorption coefficient log kd	0.007 ± 0.002 [a]	0.9-1.4 [d]	
Sorption potential log kow	3.97 [e]	3.5-4.5 [d]	3.5 [b]
Physical form	Colorless, crystalline stable solid		
Chemical structure			

Ibuprofen is a non-steroidal acidic anti-inflammatory drug that is largely used throughout the world (Lischman, et al 2006). It is an analgesic, anti-inflammatory, antipyretic and antirheumatic drug as diclofenac. It can be sold over-the-counter or consumed by prescription. The administration of ibuprofen is wide, it has over 1 million users and its amount sold each year is the second largest of all selected pharmaceuticals. Excretion of ibuprofen takes place almost completely via the urine. About 1% is present as parent compound (Thomas, and Foster, 2005).

The therapeutic dose of the drug is large (up to 1200 mg/d) and 70-80% of this is voided un-metabolized after use. Consequently, large proportion of ibuprofen is reaching to WWTPs (Smook, et al., 2008). The compound has been detected in Finnish surface water

in concentrations up to 65ng/l and in WWTP influents and effluents 20µg/l and 4µg/l, respectively. This report denotes that their occurrence is higher than in the most other European countries (Ternes, 2004).

Many studies have shown that ibuprofen does not volatilize or sorbs to the sludge. The only main removal method of ibuprofen is therefore biodegradation. Most of the drug biodegrades in the aeration tank during secondary treatment in a conventional WWTP with activated sludge. The total removal of ibuprofen in WWTPs can be up to 99% (Smook, et al., 2008). As well as, other studies have indicated that occurrence and removal of pharmaceuticals in three different wastewater treatment plants were not affected by the change in temperature between 7-22°C. In this study the SRT was well over 10 days and the food per mass ratio (F/M) was low, 0.02gCOD/gTSS.

The removal of ibuprofen was over 90%. However, at another plant, that had an SRT of only 2 days and a high F/M ratio of 1.7gCOD/gTSS, no ibuprofen removal took place. The plant was designed for only organics removal. The influent concentration of ibuprofen in both WWTPs was around 2400ng/l (Clara, et al., 2005). The drug oxidizes to hydroxyl and carboxyl metabolites in WWTPs and this often contributes to the high removal rates (Paxéus, 2004). In spite of the fact that the drug has a high removal rate in activated sludge WWTPs, it is still detected in environmental waters due to the high influent level and currently low detection limits is observed (Urase, and Kikuta, 2005).

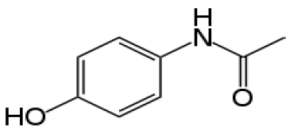
The drug has also been found to bio accumulate in pH values below 5.5, It was discovered that ibuprofen was not degraded by the ammonia-oxidizing bacteria *Nitrosomonas europaea* but it did degrade in nitrifying activated sludge. On the other hand, some studies have detected ibuprofen-degrading bacteria, without identification strains are responsible for the biodegradation of ibuprofen in WWTPs (Roh, et al., 2009).

The study made by Ternes, and Joss, 2006 about the biodegradation of ibuprofen in laboratory experiments at 17 ± 1°C temperature. Wastewater from WWTPs was spiked to certain levels of ibuprofen and the biodegradation of the compound was tested in a batch with MLSS concentration of 3.2g/l. The sludge used from a WWTP had a sludge age of 11 ± 1 days and COD concentration of the influent wastewater was 275mg/L. the result concerning their removal value were of 21-35 l/gSS/d k_{biol} (Ternes, and Joss, 2006).

However, (Ternes, 2004) studied many different WWTPs in Europe who found that when the sludge age was over 5 days, the K_{biol} values were 23 ± 10 l/gSS/d. The third experiment was carried out by (Smook, et al. 2008) relating the biodegradation in the aeration tank in a WWTP that uses conventional activated sludge process for nutrient removal. The HRT in the aeration tank was 7 hours and the MLSS concentration was on average of 2.33g/l. (Kimura, et al 2007; Smook, et al., 2008; Falas, et al 2012).

2.8.2 Paracetamol

Table 2.6 The most properties of the Paracetamol (a: Ternes, and Joss, 2006; b: Jones, et al. 2006).

INCI Name	Acetaminophen
Chemical Name	N-(4-hydroxyphenyl)
Scientific name	Hydroxyacetanilide
Trade Names	Tylenol Panadol, Mapap
Molecular Formula	$C_8H_9NO_2$
Molecular Weight	151.17
Physical form	crystalline stable solid
Biodegradation (Kbiol)	58-80 (a)
Sorption coefficient (log kd)	0.0004 (a)
sorption potential (log kow)	0.46 (b)
Chemical structure	

Paracetamol (acetaminophen) is used as antipyretic, non-steroidal analgesic, and anti-inflammatory. Chemically, 4-Hydroxy Acetanilide, it is one of the most popular over-the-counter analgesic and antipyretic drugs (Chandral and Dutt 2013).

Paracetamol is available in different dosage forms: tablet, capsules, drops, elixirs, suspensions and suppositories even known as acetaminophen. Contrary to ibuprofen and diclofenac, it has a low anti-inflammatory effect. It is metabolized in the liver and can in high doses be toxic and cause liver failure (Rang, et al. 1995; Kumble, and Singh, 2012).

It is given for fever, headaches, pain of arthritis, aches, colds, flu and period pain. Its saturated aqueous solution has a pH of about 6 and is stable (half-life over 20 years) but stability decreases in acid or alkaline condition due to being slowly broken down, via a base or acid hydrolyzed hydrolysis of the amide bond, into acetic acid and p-aminophenol (Fig. 2.12) (Reynolds, 1996; The United States Pharmacopoeia., 2000).

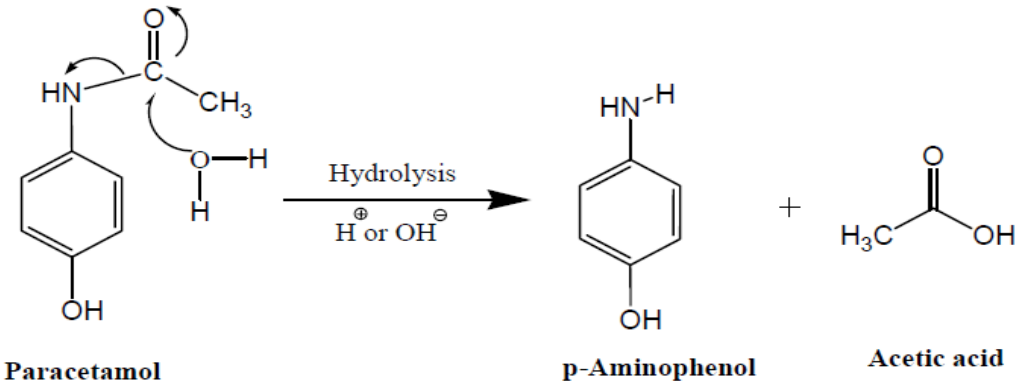


Figure 2.12: The chemical structure and the hydrolysis of paracetamol (Reynolds, 1996).

Paracetamol was ranked as one of the top three drugs prescribed in England, and the mass of paracetamol through prescription alone totaled more than 400 tons in that year (Roberts, and Thomas, 2006). Paracetamol has been detected with a concentration of up to 6 mg·L-1 in European STP effluents, up to 10 mg·L-1 in natural waters in USA and even more than 65 mg·L-1 in the Tyne River, UK. (Kolpin, et al 2002; Roberts, and Thomas, 2006).

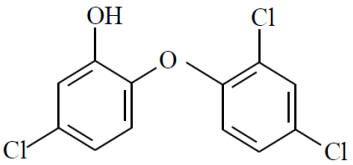
Furthermore, according to a reconnaissance study of organic wastewater contaminants in USA waters, paracetamol was determined to occur at a frequency of 23.8% in surface water with a maximum concentration of 10 µg·L-1 (Kolpin, et al 2002; Satoskar, et al 2001).

In a study made at a WWTP in Spain, paracetamol was found at levels of 7.1-11.4µg/l in the influent. The WWTP received both municipal and industrial wastewaters, which included pharmaceutical industry. The WWTP used activated sludge as secondary biological treatment, with both anoxic and aerobic zones. The SRT during the time of sampling was 10 days and the HRT 11.5 hours. They detected that paracetamol was removed to up to 99.9 ± 0.1% from the aqueous phase in the WWTP. The study concluded

that due to the fast biodegradation, paracetamol does not sorb to sludge in significant amounts (Radjenovic, et al. 2009). A similar study carried out at a southern English WWTP using activated sludge treatment as their secondary biological treatment process, paracetamol was removed on an average of 92% over a four day sampling period. The mean temperature at the time of sampling was 20.6°C and the sludge age 3 days. The concentration found in influent wastewater was 2-3µg/l. (Jones, et al., 2005). Paracetamol biodegrades fast and has as high k_{biol} of 58-80 in activated sludge. (Ternes, and Joss, 2006). The properties of paracetamol are summarized in Table 2.9.

2.8.3. Triclosan

Table 2.7 The most properties of the Triclosan (a: Nakada, et al 2010; b: Thomas et al. 2005).

INCI Name	Triclosan
Chemical Name	2,4,4'-trichloro-2'-hydroxy-diphenylether
Scientific name	(5-chloro-2-(2,4-dichloro-phenoxy)-phenol
Trade Names	Irgasan® DP300, Irgasan® PG60, Irgacare® MP, Irgacare® CF100, Irgacide® LP10; Cloxifenolum, Irgagard® B 1000, Lexol 300, Ster-Zac
Molecular Formula	$C_{12}H_7Cl_3O_2$
Molecular Weight	289.5
Sorption coefficient (log kd)	3.7-5.1 (a)
sorption potential (log kow)	4.6 (b)
Physical form	White crystalline powder
chemical structure	

Triclosan (5-chloro-2-(2,4-dichloro-phenoxy)-phenol, a broad spectrum antibacterial, was early synthesized by Ciba-Geigy Company, Switzerland, under its trade name IRGASAN DP300 (Bhargava, and Leonard, 1996). Triclosan is an antimicrobial agent that has been used for more than 40 years as an antiseptic, disinfectant or preservative

in clinical settings. Triclosan has been used since 1972, and is now found in the following products: soaps, hand-washes, dish-washing products , laundry detergents and softeners, plastics (e.g., toys, cutting boards, kitchen utensils), toothpaste and mouth washes, deodorants and antiperspirants, cosmetics and shaving creams, acne treatment products, hair conditioners, bedding, trash bags, apparel like socks and undershirts, hot tubs, plastic lawn furniture, impregnated sponges, surgical scrubs, implantable medical devices and pesticides. (Glasser, 2004). It has a broad range of activity that encompasses many, but not all, types of Gram-positive and Gram-negative non- sporulating, bacteria, some fungi (Jones, et al. 2000; Schweizer, 2001). *Plasmodium falciparum* and *Toxoplasma gondii* (Mcleod, et al. 2001). It has also been shown to be Eco toxic, particularly to algae in aquatic environments (Tatarazako, et al. 2004). Additionally, it has been shown to interfere with the cycling of nitrogen in natural systems (Fernandes, et al. 2008; Waller, and Kookana, 2009). Triclosan is bacteriostatic at low concentrations, but higher levels are bactericidal (Suller, and Russell, 1999, 2000). At sublethal concentrations, it acts by inhibiting the activity of the bacterial Enoyl-acyl carrier protein reductase (FabI), a critical enzyme in bacterial fatty acid biosynthesis (Heath, et al. 2002, Zhang, et al. 2004). At bactericidal concentrations, it is suggested to act through multiple nonspecific mechanisms including membrane damage (Gilbert, et al, 2002).

A study on the removal of triclosan in five primary settling WWTPs using activated sludge in Europe. He noted that triclosan had high removal rates in WWTPs, with an average of 73% and the lowest removal of 58%. (Paxéus, 2004) It has also been artificially approved that triclosan does not biodegrade under anoxic or anaerobic conditions (Chen, et al., 2011). Another study on ammonia-oxidizing bacteria for the biodegradation of triclosan, bisphenol A and ibuprofen revealed that triclosan was biodegraded by the ammonia-oxidizing bacteria *Nitrosomonas europaea*. However, the test indicated that, due to competitive behavior or toxicity effects, the presence of triclosan reduced nitrate production (Roh, et al 2009).

A work on the fate of triclosan in a conventional activated sludge WWTP. It was observed that up to 85-95 % of the influent triclosan biodegraded and 1.5-4.5% sorbed to sludge. It was concluded that triclosan was biodegradable in both high and low

concentrations in activated sludge and that triclosan did not disrupt the activated sludge processes in the WWTP, not even in high concentrations (Federle, et al., 2002).

Table 2.8 The concentrations of triclosan in different environmental matrices.

Environmental matrix	Triclosan concentration	References
Surface water : Lake / river /streams with known input of raw waste water	1.4 ng/L - 0.004mg/L	Kolpin, et al. 2002, Lindström, et al. 2002, Kolpin, et al. 2004, Bendz, et al. 2005, Glassmeyer, et al. 2005, Zhang, et al. 2007, Halden, and Paull, 2005, Chau, et al. 2008, Coogan, et al. 2007, Coogan, and La 2008.
Wastewater Influent Effluent	20 ng/L –0.0086161 mg/L 23 ng/L -0.005370 mg/L	Samsoe-Petersen et al. 2003, Lishman, 2006, Heidler and Halden, 2007, Kantiani, et al. 2008; Bester, 2003; Kanda et al. 2003; Sabaliunas, et al. 2003, Bendz, et al. 2005, Thompson, et al. 2005, Ying and Kookana 2007.
Sea water	<0.001-100 ng/L	Xie, et al. 2008, Fair, et al. 2009
Lake/River/other Marine	<100-53000 µg/kg 0.02-35 µg/kg d.w.	Fjeld, et al. 2004; Morales, et al. 2005; Miller, et al. 2008.
Biosolids from WWTP	20-133000 µg/kg d.w.	Svensson, 2002; Kinney, et al. 2006; Chu, and Metcalfe, 2007, US EPA 2009, Cha, and Cupples, 2009, Ying and Kookana 2007.
Activated/digested sludge	580-15600 µg/kg d	McAvoy et al.2009, Singer et al. 2002, Chu and Metcalfe 2007, Chu and Metcalfe 2010
Pour water	0.201-328.8µg/L	Chalew and Halden 2009

2.8.3.1. The Mechanism of Triclosan Action

Triclosan works by blocking the active site of the Enoyl-acyl carrier protein reductase enzyme (ENR), which is an essential enzyme in fatty acid synthesis in bacteria (Roujeinikova, et al. 1999). By blocking the active site, triclosan inhibits the enzyme, and therefore prevents the bacteria from synthesizing fatty acid, which is necessary for building cell membranes and for reproducing. Since humans do not have this ENR enzyme, triclosan has long been believed to be fairly harmless to them. Triclosan is a very potent inhibitor, and only a small amount is needed for powerful antibacterial action. (Aiello, et al 2004; Rodricks, 2010; APUA, 2011).

2.8.3.2. Triclosan in the Environment

Triclosan, as well as other antibacterial agents and their degradation byproducts, are now found throughout the environment, including surface waters, soil, fish tissue, and human breast milk (Adolfsson-Erici, et al 2000). Over 95% of the uses of triclosan are in consumer products that are disposed of in residential drains. In a U.S. Geological Survey study of 95 different organic wastewater contaminants in U.S. streams, triclosan was one of the most frequently detected compounds, and in some of the highest concentrations.
(Glasser, 2004).

In 1999-2000 study by the U.S. Geological Survey, triclosan was detected in 57 percent of the 139 U.S. waterways that were thought to be prone to agriculture or urban activities including surface and wastewater. (Kolpin, et al 2002; Halden, 2005).

A subsequent study indicates that triclosan can persist through wastewater treatment and can be discharged into waterways and/or biosolids (Aiello, et al 2004; Halden, 2006). When domestic wastewater is treated before discharge to surface waters, there is proof that up to 95 percent of triclosan is removed via the wastewater treatment plant processes (Samsoe-Petersen, et al 2003). This removal efficiency is dependent on treatment plant operations. Swiss researchers observed a 94 percent removal rate of triclosan at wastewater treatment operations that employed mechanical clarification, biological treatment or nitrification, flocculation and filtration (Kolpin, et al 2002; Halden, 2005). It was estimated that 79 percent of the triclosan was removed via biological degradation while 15 percent adsorbed to the sludge. The remaining 6 percent in the effluent resulted in a concentration of 42

ng/Liter (Singer, et al 2002). The transport of triclosan to wastewater treatment plants occurs via different routes *ie*. Using and application of antibacterial sanitary products containing triclosan .However, some scientists have raised concerns about bacterial resistance related to exposure to triclosan (Levy, 2000). Unlike wastewater, most runoff that enters storm drains is untreated and directly flows into creeks, rivers and ultimately to the ocean. Triclosan may be transported into the storm water system through commercial or residential washing of equipment outdoors with antibacterial soaps. Although, our present understanding of triclosan environmental effects is little, there is evidence that triclosan can be toxic to aquatic organisms (Orvos, et al 2002, Chalew, and Halden, 2009). The presence of triclosan may influence both the structure and the function of algal communities in stream ecosystems receiving treated wastewater effluent (Wilson, et al 2003). These changes could result in shifts in both the nutrient processing capacity and the natural food web structure of these streams. According to Danish Environmental Protection Agency, triclosan bio accumulates in fish (Adolfsson-Erici et al 2000; Samsoe-Petersen, et al 2003) and human. The concentrations observed in fish are thousands of times higher than what is found in the water. Furthermore, at least one transformation product of triclosan -methyl triclosan- is stable in the environment, making it also available for bioaccumulation. Once methylated, the lipophiliccity of triclosan increases, meaning that it will be more likely to accumulate in fatty tissue and is not likely to photo degrade. On the other hand a study refers that in the presence of UV light, triclosan may degrade into a compound with dioxin-like characteristics (Rule, 2005).

A Swiss study, the lipid-based concentrations of methyl triclosan detected in fish were considerably higher than the concentrations in lake water, suggesting significant bioaccumulation of the compound with a thyroidal endocrine disruptor in these aquatic organisms (Veldhoen, et al 2006). For aquatic organisms, the potential uptake mechanism of lipophilic contaminants are direct uptake from water through exposed surfaces, mainly gills, and uptake through the consumption of food (Balmer, et al 2004; Rodricks, 2010; APUA, 2011).

In a medical point view and according to the American Medical Association, "the use of antimicrobial agents such as triclosan in consumer products has not been studied extensively. No data exist to support their efficacy when used in such products or any need

for them, but increasing data now suggest there is little evidence to support the use of antimicrobials in consumer products such as topical hand lotions and soaps, Considering the available data and the critical nature of the antibiotic resistance problem, it may be prudent to avoid the use of antimicrobial agents in consumer products." (Council of Scientific Affairs, 2000; Anderson, 2012).

2.9. The Oxygen Uptake Rate as A Toxic Biological Test

The contamination of water may be of organic or chemical sources. In order to remove these contaminant the oxygen consuming substances will increase in the aquatic life. This process performed by applying bacteria at wastewater treatment plants. Activated sludge is added which is a biomass consists of different types of bacteria. The heterotrophic bacteria are together with other microorganisms are responsible for the degradation of the main organic material (Eikelboom, 2000; Bitton, 2005). The aerobic degradation process of organic material can be determined by measuring the oxygen uptake rate (OUR) for the microorganisms. The main part of the organic material in the wastewater is degraded in aerobic environments (Le Bonté, et al 2005). Even though some bacteria are used for nitrogen removal in the denitrification step and some is reduced by the biological phosphorus removal process. Increasing discharge demands put higher pressure on process optimization and control of the wastewater treatment plant performance. For assessment and controlling of the process performance, oxygen uptake rate measurement is a useful device. Oxygen uptake rate parameters can provide much information concerning treatment plant performance, wastewater characteristics, degradability of special concentrated streams as well as measurements required for mathematical models, in order to expect possible optimizations of a treatment plant. Additionally it is beneficial for daily operation control (Corbitt, 2004; Le Bonté, et al., 2005; Gerardi, 2006). To extract wider information of the activated sludge, wastewater or the process performance, the OUR measurements are usefully combined with supplementary routes and additional analysis (Pierson, and Pavlostathis, 2000; Bitton, 2005; Hagman, M., and Jansen, J. C., 2007). The OUR depends on many factors and the most important factor is the temperature. Oxygen uptake rate is dependent on the temperature and generally the activity increases with the temperature (Roš, 1993; Henze, et al., 2002).

Hence, it is necessary to keep the temperature constant thought out the whole experiment. Laboratory experiments are often performed at 20°C, but in some cases it is preferable to keep the same temperature in the experiment as in the real plant. (Bitton, 2005; Chalasani, and Sun, 2007) another significant agent is the pH. The aerobic degradation of organic matter is depending on a pH 6- 9. Since CO_2 is produced during oxygen respiration, the pH will slightly increase and no adjustment for stabilizing the pH is normally needed. Also, carbon source is another factors. The OUR varies with the type of organic substrate available and therefore it is important to use the same substrate when comparing the capacity of different activated sludges. Acetate is often used as reference substrate because it is known to be a very easily degradable organic matter for heterotrophic bacteria. (Hagman, 2003). Nitrification inhibitor plays a great role in oxygen uptake rate. When the sludge from a nitrifying treatment plant is used some of the oxygen consumption depends on the oxygen used for nitrification instead of oxidation of organic matter, to avoid nitrification during measurements of organic degradation, a nitrifying inhibitor is used (Benes, et al., 2002; Bitton, 2005; Hagman, et al., 2006).

$$\boldsymbol{Oxygen\ Uptake\ Rate} = \frac{\boldsymbol{mgO_2}}{\boldsymbol{L}} \boldsymbol{/min} \times \boldsymbol{60 min/hr} \ldots\ldots \textbf{(11)}$$

Table 2.9: The values of oxygen uptake rate in activated sludge (approve by ASTM, 2004).

>40 high	This may indicate that there are not enough solids for the BOD loading
20-40 Normal	This range will usually produce a good BOD removal and a sludge that settles well in the final clarifier.
<20 low	This may indicate that there are too many solids or there has been a toxic occurrence

2.10. The Specific Uptake Rates (SOUR)

Specific Uptake Rates (SOUR) explain the amount of oxygen used by the microorganisms to consume one gram of food and is reminded as mg/L of oxygen used per gram of organic material per hour. The specific uptake rate is valuable when comparing one aquatic system with another. The performance of one aeration basin can be compared with another or the biological activity in a stream can be studied and compared both above and below a waste

outfall. Furthermore, toxic or high organic loads can often be detected before severe deterioration of effluent quality occurs. Changes in the SOUR on effluent samples will indicate changes in loading (Gerardi, 2006; Hagman, et al., 2006).

$$\boldsymbol{SOUR\ (mg/g)/h = OUR\ \times 1000/\ VSS\ (mg/L)} \text{…….. (12)}$$

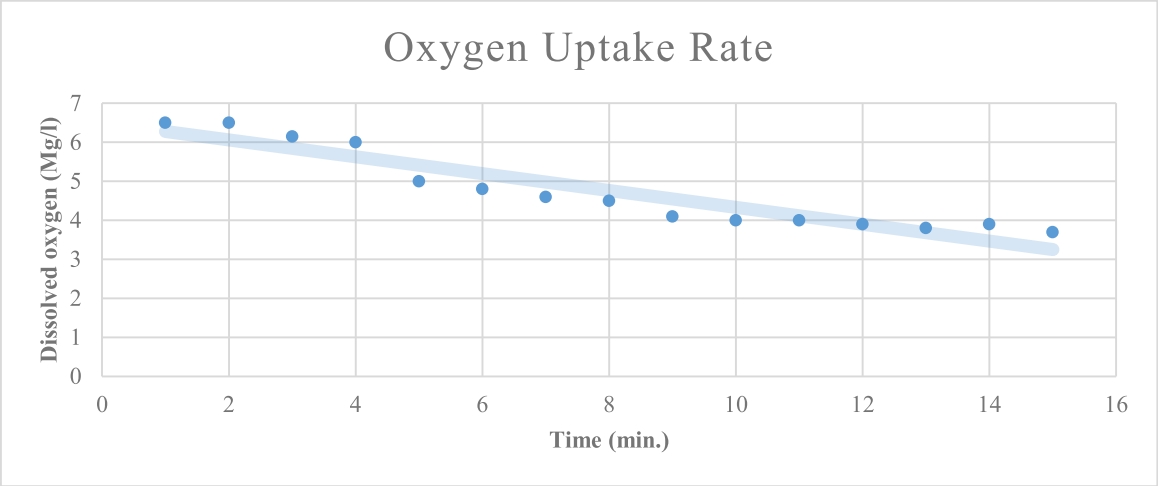


Figure 2.13: The OUR data for activated sludge during the study

2.11. Toxicity of PPCPs to the biological wastewater treatment

Running of any biological system is need a sufficient supply of oxygen, it is a very important factor, Biodegradation of the waste is not enough with the less supply of oxygen. There are two kinds of biological wastewater treatment. The first one is a mechanical method which is intended to create contact between wastewater, cells and oxygen applying rotational movements with mixing. The second method is followed without using mechanical tools that doesn't involve cells and oxygen. (Gaur, 2008; Kim, et al 2009). A study showed a significant transformation of chemicals that occurs in nutrient- removing wastewater treatment plants. The same performance is observed in configurations of the reactor as wide as conventional activated sludge (Keller, et al, 2005). Activated sludge processes using microorganisms for mineralizing the pollutants to water and carbon dioxide (CO_2) are used degrade these pollutants to the certain acceptable forms. Removal of clofibric acid is poor as it contains chlorine in its structure. It is identified as a refractory contaminant in many investigations of municipal sewage influents and effluents. Membrane

bioreactors were used and were proved as efficient for removal of clofibric acid which would increase the feasibility of the technology MBR is an advanced technology for the wastewater treatment process (Kimura, et al. 2007). Another study has been shown that Diclofenac has a poor biodegradation rate. The sorption behavior of Diclofenac onto sludge is same like Carbamazepine. Removal efficiency of Diclofenac could be up to 80% and the carbamazepine below 10%. This is because the Carbamazepine is extraordinarily persistent to biodegradation at low concentrations and the biodegradation of Diclofenac may be possible under some conditions (Zhang, et al 2008).

2.12. The advanced treatments for PPCPs

Traditional WWTPs were not engineered to exclude the pharmaceuticals and personal care products contaminants that recently have important impact. Subsequently, more developed techniques are being investigated to define if these could shield PPCPs from introducing the circumstance. Some probable developed tools may include, membrane bioreactors, Powdered Activated Carbon Treatment (PACT),Reverse Osmosis, Micro-filtration Techniques-Membrane Bioreactor (MBR),Activated Sludge-secondary treatment system, Thermophiles Treatment for Biosolids-aerobic and anaerobic, Solar Treatment for Wastewater Effluent, oxidation with ozone, ultra violet photolysis and ion exchange. (Bolong, et al., 2009; Waghulkar, 2010; Einschlag and Carlos, 2013).

All the aforementioned methods have been examined on various kinds of pharmaceuticals and personal care products contaminants have higher efficient removal than conventional treatments. However, such technique is expensive, trading course, experience and highly qualified personnel. The findings are however extremely dependent on the structure and chemical of the compound. Some, like ion-exchange and UV photolysis have proven to be good but ineffective (Bolong, et al 2009).

Some workers noticed that it did not exclude large quantities of micro pollutants and the photogenic agents. The application of ozonation promoted the exclusion of diclofenac and carbamazepine (Shaar, et al 2010).

According to (Jones, et al 2007). The application of well-developed devices for the exclusion of PPCPs, may not be efficient. However, the removal rate may be very accepted with highly advanced treatment. The increase in CO_2 production and high costs may lead to

more adverse influence than the PPCPs would have caused. As conventional treatment methods may not be as reliable, they can still remove considerable levels of PPCPs, if operating properly (Jones, et al, 2007; Saritha, et al 2007; Einschlag, and Carlos, 2013).

2.13. Disposal of Undesired PPCPs

Consumer pharmaceutical wastes are created from prescription drugs for a variety of reasons; a change in prescription, patient's health improves before finishing treatment, patient death, expired drugs and patient non-compliance. OTC medicines are often sold in bulk and may contain more than is needed before the expiration date or the consumer may switch brands or prescriptions. Many of these expired of unwanted medications are disposed of in the trash or down the drain (Ahmed and Bayoum, 2014).With few exceptions, countries do not have clear and consistent guidelines on how to properly dispose of unwanted pharmaceuticals, especially when it comes to the general public. In February 2007, the White House Office of National Drug Control Policy released the Federal regulations on the Proper Disposal of Prescription Drugs.(White House Office of National Drug Control Policy, 2014) These general recommendations suggest unused pharmaceuticals be mixed with coffee grounds or kitty litter, placed in an impermeable bag, and thrown out in the trash. They also recommend certain drugs be flushed down the toilet coming in last on their list, they suggest taking unused medications to a community pharmaceutical take-back program. Burning is now regarded as the best disposal option for expired or unwanted medications, but it is not a commonly available option for the general public. A report on how expired medications are being disposed of found that 1.4% of residents returned medications to a pharmacy, 54% disposed of medications in the garbage, 35.4% flushed medications down the toilet or sink, 7.2% did not dispose of medications, and 2% related they used all medication before expiration (Kuspis and Krenzilok, 1996) (Fig. 2.14). Studies have reported that approximately one third of the total volume of pharmaceuticals sold in Germany and about 25% of that sold in Austria are disposed of with household waste or down the drain (Kümmerer, 2004). This significant contribution from private individuals turns the focus from industry to the activities, actions, and behavior of consumers on their surrounding environment. Some consider that flushing of undesired medications down the toilet is more preferable than throwing medications in the

trash where children or illicit drug users might get approach of them. However, such practice in particular may be more closely associated with causing environmental damage. By recommending the medications be crushed, combined with another substance, and placed in the trash reduces the poisoning risk but it has the potential to enter the water through landfill leaching. Even pharmaceuticals captured in leachate at lined landfills are typically transported to wastewater treatment plants, where some pass through untreated.

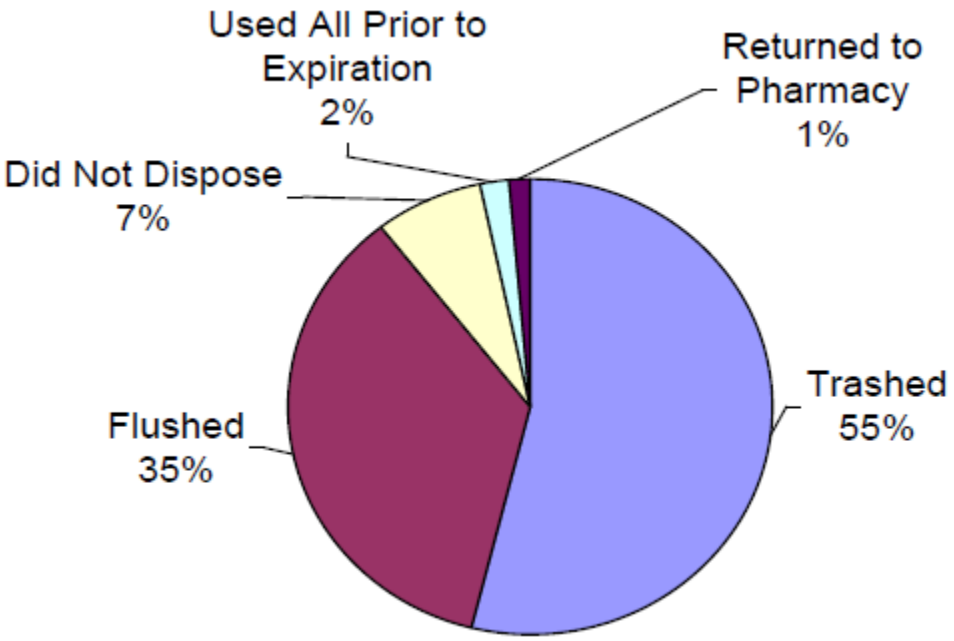


Figure 2.14: Household Expired Medication Disposal Methods (Kuspis and Krenzilok, 1996).

2.14. Toward less pharmaceuticals pollution

One trend of removal the probable advance impacts that pharmaceuticals have on the ecology is to initiate environmentally safer and more sustainable pharmaceuticals i.e. "green" pharmaceuticals. In Sweden an advance toward more sustainable use of pharmaceuticals has begun with a new approach of classification. Regulatory authorities together with the chemical industry have initiated a labeling system that observed the persistence, bioaccumulation and toxicity (PBT) of a pharmaceutical. The scale goes from 0-9 and the higher the score, the more dangerous the compound is for the environment (Fatta-Kassinos et al., 2011). In this context, doctors and consumers can decide to use a

drug that has less environmentally risks than another but with similar physiological effects. A study carried by authors sampled the drainage of a WWTP in Patancheru in India that received the disposed water from 90 bulk drug manufacturers. The study referred high levels of pharmaceuticals, especially of the antibiotics (fluoroquinolones), were found Ciprofloxacin was noticed at concentrations of 28000-31000µg/l.

Unfortunately, this concentration is higher than the largest therapeutic concentration in human plasma. Formerly, it was thought that the municipal WWTPs and improper disposal of drugs were the largest origin of pharmaceuticals in the environment. Currently, little studies have been made of the effluents from drug manufacturers. The drugs are manufactured in this region of India are distributed internationally and are used in the products of other pharmaceutical companies. (Larsson, et al., 2007)**.**

2.15. Green pharmaceuticals will be the future

Pharmaceutical and personal care products PPCPs are trace environmental pollutants formed essentially from consumer use rather than manufacture drainage. Their occurrence was firmly established since the beginnings of 1980 of the last century .these compounds included suspended particulates sediments and sewage sludge which can pollute both the surface and ground water having their relatively high affinity to water. Although that such substances are prone to be degraded and disassociated (Seyler, et al 2006). Their continual exposure and pouring to water receiving plants can cause widespread, prevailed and combined use by individuals and domesticated livestock, offering PPCPS false existence in the ambient circumstance. Risks of ecological or human health due to exposure to these material are poorly identified which may be occurred owing to prolonged or sub therapeutically concentration of these bioactive substance or the possible transformation products. The need for fresh water and its importance for proper health is growing which ascertain the absence of these products in household water i.e. to exclude the impacts of any presence or synergistic of water supplies. There is scarcity relating to the long term combined exposure to light levels of xenobiotic (a strange and foreign biotic), abroad pattern of proactive activity should be applied to minimize the introduction of PPCPs to the ecology. A whole guardianship program overseen should be followed by both health care industry and consumer. Notably, application of such

supervision program would benefit not only the environment but also will reduce medication expenses and making patient health better with safety. The stewardship program for PPCPS should ecologically be oriented to solve PPCPs problems based on scientific background for such phenomenon. Disposition of PPCPS to the environment should be minimized to the lowest levels as recommended by health care industry authority. Also, the release of PPCPS to the environment should be controlled and reduced which are cohesively captured. A successful approach to life cycle stewardships of PPCPs are of great importance and should be actively included to plan and apply a fruitful project (Daughton, 2003).

In the few years ago, a huge progress applying "green chemistry" which means the application of light ecologically hazardous substances and planning alternate synthesis pathways. Green chemistry is largely based on aqueous chemistry. Drug manufacturers are advised to apply environmentally friendly and economically advantageous pharmaceutical industry. Such principles should be extended to include drug design, delivery distribution and disposal all the processes and to the end user and not only for the manufacturer. The aims of these processes are to lessen the flow of PPCPs to the environmental. Many opinions to reduce the release of PPCPs to the environment had already been suggested forwards. Such ideas are repeatedly mentioned and much emphases are important due to its significance. However, there are several routes of scientific advancement to apply bases towards green health care system. The transfer of new technique to clinical practice is slow. Some studies concluded that new technology is acquired from clinical experiments which may be in an average of 17 years to be incorporated into traditional practice.

New PPCPs should be designed and formulated for analysis in new decision for "environmental friendliness" or "environmental proclivity" researches must be carried out on green PPCPs products not only to improve therapeutic or cosmetic action but also to maximize their ability to biodegradation, photolysis or other physicochemical changes to produce harmless end products. Such alteration should be directed to produce more labile drug which would normally degraded or poorly transferred across the stomach in order to decrease excretion. The available drugs which do not decomposed into their initial structure and have no alterations mostly produce wide well selected groups of metabolites. However,

some of them have real active ingredients and other are environmentally stable compared with those of their parent metabolites. Trends are applied to design drugs having better functional sorption features which aims to decrease direct excretion of their parent metabolites. Goals being followed in many fields are to use small doses by promoting drug delivery definitely to the target site or receptor. This mechanism involved better drug design to accommodate existing membrane transporters and forming in situ synthetic transporters. Occasionally, the formulation of drug can hinder its absorption particularly these who are sick or people of abnormal gastrointestinal function. Improvement the formulation of a drug can hinder or avoid its dissolution which can be seen clearly in rapid dissolved tablets containing common excipient of stearic acid which mostly acts as anti-dissolving agent. Even though, it is advised that new formulation are currently needed for insoluble drugs. It is known that 30 % of U.S pharmacopeia convention Inc. (USP) drugs and 50 % of prospective drugs are not well absorbed in water (Daughton, 2003; Aleong, 2008; Yanlong and Francois, 2010).

3. MATERIALS AND METHODS

3.1. Activated sludge samples

The activated sludge was taken from the wastewater treatment plant WWTP of Gaziantep, Turkey. The Gaziantep WWTP, serving about 1,150,000 PE, and this activated sludge treatment was plant designed for biological removal. The plant is operated at a low solids retention time (SRT), 2-4 days. The flow to the plant was 230,000 m3/day. The sludge samples were brought immediately to the laboratory which were located at the bioreactor. The sampling and the experiments were carried out after acclimatization the microorganisms.

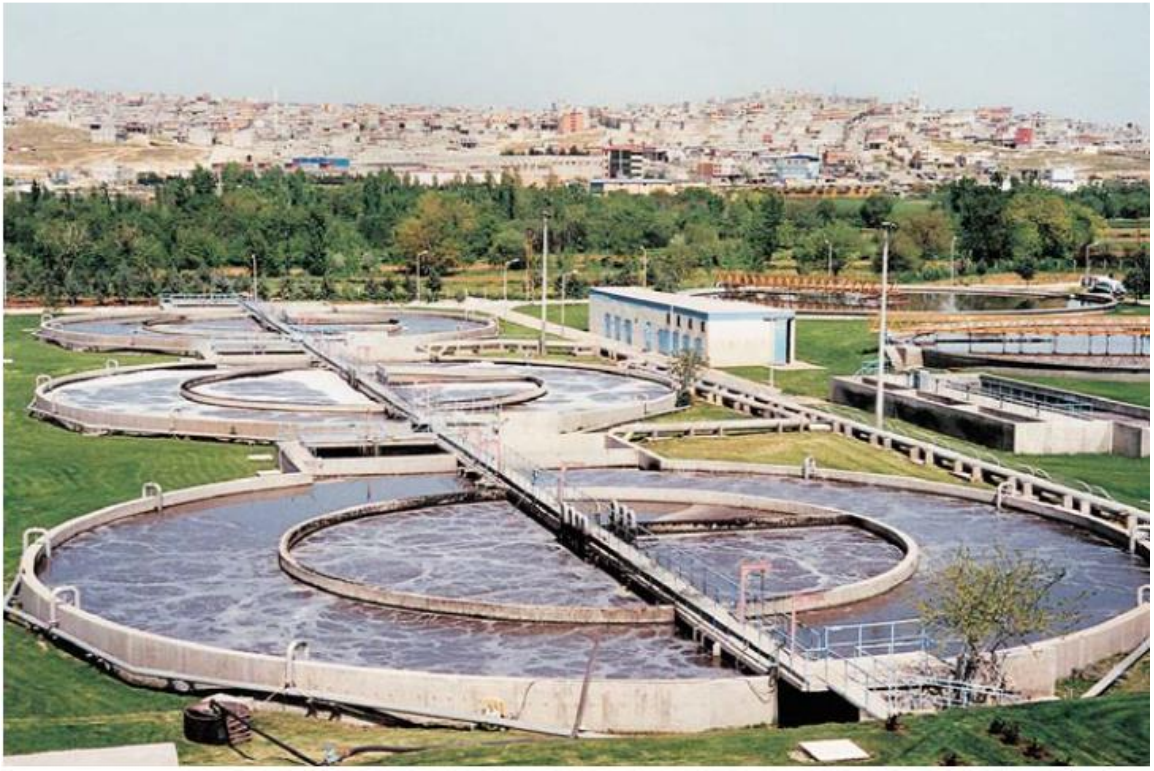


Figure 3.1: Shows Gaziantep wastewater treatment plan

3.2. Acclimatization of activated sludge

The activated sludge seed was obtained from Gaziantep wastewater treatment plant that received no industrial wastewater and was acclimatized in the laboratory by feeding in synthetic wastewater with no excess sludge removal. The composition of these synthetic wastewater was explained in the following table, the bioreactors were built 5L cylindrical

shape to ensure the distribution of the largest possible amount of air, also air diffusers were used by connecting to the air pumps via plastic tubing. The plastic tubing was providing airflow to the diffuser and was placed in a plastic pipe taped to the reactor wall. These were professional diffusers, which gave us instant and bubbles to act as the oxygen supply.

Table 3.1: The Composition of the synthetic wastewater added to the bioreactors as (mg/L) (Ahlgren, 2012).

Composition of the synthetic wastewater added to the bioreactors as (mg/L)		
Chemicals	Mg/L	Company produced
$MgSO_4$ * 7 H_2O	60.9	Sigma-Aldrich®
$NaHCO_3$	218.75	Merck
NH_4Cl	38.2	Tekkim
Yeast extract	209.7	Merck
Peptone	184.68	Sigma-Aldrich®
CH_3COONa * 3 H_2O	130.8	Sigma-Aldrich®
KH_2PO_4	35.1	Sigma-Aldrich®
$CaCl_2$ * 2 H_2O	70	Merck
$NaHCO_3$	218.75	Merck

3.3. Experiment procedures

The Activated sludge process was modified from an aerobic process which consisted of 5 aerobic reactors for one bioreactor for control and 4 bioreactors for aerobic process. The bioreactor of aerobic processes operated with HRTs of the aerobic stages of 18, 24, 36 h and 52 h. To evaluate pharmaceutical and personal care products removal performance of the extended activated sludge process under high DO condition, the DO concentrations of the all aerobic reactors were controlled at 5.0 ±0.75 mg/L (Basnyat, 2011). In order to improve these chemicals removal performance further.

During the operation of the extended activated sludge process, the SRT was controlled at 20 d and the sludge concentration was around 4000- 5000 mg MLSS/L. The total HRT was kept at 52 h. The sludge return ratio was kept at (0). The temperature was about 20.0 ± 1.5 C°. The influent pH was not controlled and varied between 6.5 and 8.3, the

operation of the process consisted of four reactors, namely A, B, C and D. All reactors as shown in the figure # at the same condition, just HRT was different.

Figure 3.2: The bioreactors of this study

3.4. Experimental methods

All the experiments included soluble COD (5220 D. Closed reflux, Colorimetric method), MLSS and MLVSS (2540 G. Total, Fixed and Volatile Solids in solid and semisolid samples), TSS (2540 D. Total Suspended Solids dried at 103~105°C), Dissolved Oxygen (DO) (4500-O G. Membrane Electrode method) and pH (4500-H+ B. Electrometric method), were carried out according to the Standard Methods for Water and Wastewater Examination (APHA, AWWA and WEF, 1992,1998). METHOD 1683 Specific Oxygen Uptake Rate in Biosolids (EPA-821-R-01-014, 2001).

3.4.1 The daily experiments

Many experiments had been tested every day to ensure that the plant was worked as it was plan, also to know more details about the activated sludge properties and what the fate of bioreactor when we add these chemicals drugs.

3.4.2. Sludge Volume Index

(SVI) is an indication of the sludge settle ability in the final clarifier. It is a useful test that indicates changes in the sludge settling characteristics and quality. By definition, the SVI is the volume of settled sludge in milliliters occupied by 1 gram of dry sludge solids after 30 minutes of settling in a 1000 ml graduated cylinder or a settle meter. A liter of mix liquor sample is collected from bioreactors every day, settled for 30 minutes in a 1 liter of graduated cylinder, and the volume occupied by the sludge is reported in milliliters. The SVI is computed by dividing the result of the settling test in ml/liter by the MLSS concentration in mg/L in the aeration tank times 1000, the common range for an SVI at activated sludge plant should be between 50 and 150. Optimum SVI must be determined for each experimental (ALFA 1989; Jenné, et al., 2007).

$$\boldsymbol{SVI\,\frac{mL}{g} = settled\ sludge\ volume\ in\,\frac{mL}{L}\,after\ 30min \times \frac{1000}{MlSS}\,mg/L} \quad \ldots\ldots (12)$$

3.4.3. Sludge Age

The concentration of the activated sludge solids and the condition of those biological solids determines the effectiveness of an activated sludge process. Too few or too many organisms in a system will cause operational control problems, reducing treatment plant efficiency ,To successfully maintain a viable biological population and to maintain the proper concentration of solids, the system requires continuous observation and monitoring by the operator. Sludge age is one of the methods or tools available to the operator to help maintain the desired amount of solids in the aeration tank. Sludge age is a relatively easy control parameter to monitor because the suspended solids in the aeration tank are easy to measure. Sludge age considers the solids entering the aerator; measured as primary effluent suspended solids in mg/L, and solids or organisms available to degrade the wastes; measured as Mixed Liquor Suspended Solids, mg/L The common range for sludge age for a conventional activated sludge plant is between 3 and 15 days. Sludge age is computed by:

$$\boldsymbol{Sluge\ Age\ (d) = \frac{MLSS(lbs)}{Primary\ Eff.SS(\frac{lbs}{d})}} \quad \ldots\ldots\ldots (13)$$

A low sludge age tends to produce a light, fluffy, buoyant type of sludge particle commonly referred to as straggler floc, which settles slowly in a final clarifier. This will be witnessed in a clarifier when these buoyant, fluffy sludge particles are being pulled over the weirs even though the effluent may be crystal clear. A high sludge age or too many solids in the system tends to produce a darker, more granular type of sludge particle, commonly called pin floc, which settles too fast in a final clarifier. Pin floc is observed as many fine tiny floc particles coming over the final clarifier weirs leaving a very turbid effluent. (Jenné, et al., 2007)

Table 3.2: The daily measured of some parameters

Parameters	2013		2014					
	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May.	Avg.
T °C	20	20	21	22	23	23	23	21.7
pH	6.65	7.2	6.8	7.1	7.8	8.1	8.4	7.4
TSS (mg/L)	256	269	307	360	343	441	447	346
COD (mg/L)	544	621	611	667	560	583	524	587
D.O. (mg/L)	3.2	4.5	4.5	4.6	4.5	4.7	5.5	4.5
MLSS (mg/L)	1700	2201	3807	4279	4390	5400	5324	3900
MLVSS (mg/L)	1393	1770	2171	2581	3567	3995	4209	2812
SVI (ml/g)	59	74	88	93	90	89	90	83.5
F/M gCOD/g MLSS/day	0.31	0.29	0.20	0.20	0.16	0.15	0.14	0.17
OUR (mg/L O2 per hour)	20	27	26	26	26	28	25	25

3.4.4. The Food/Mass Ratio

The Food/Microorganism ratio commonly referred to as F/M is based upon the ratio of food fed to the microorganisms each day to the mass of microorganisms held under aeration. It is a simple calculation, using the results from the influent BOD test to the aerator and the mixed liquor suspended solids test. Using the COD test may be preferred because the results are available sooner than the five day BOD. The F/M ratio is calculated

$$\boldsymbol{F/M = BOD\ (mg/L) \times Flow\ (MGD) \times 8.34/microbes\ (lbs)} \ldots\ldots (14)$$

3.5. Oxygen uptake rate and Specific Uptake Rate test

The measurements and respirometry of the current study have demonstrated to be a useful tool at wastewater treatment plants in many aspects. The measurements can be performed using simple equipment, although more advanced and expensive equipment is available on the market. Compared to many other methods it is relatively easy to apply and the data could be used for simpler characterization and process control as well as for more complex tasks like simulation and plant design. (Takeshi, et al 2006)

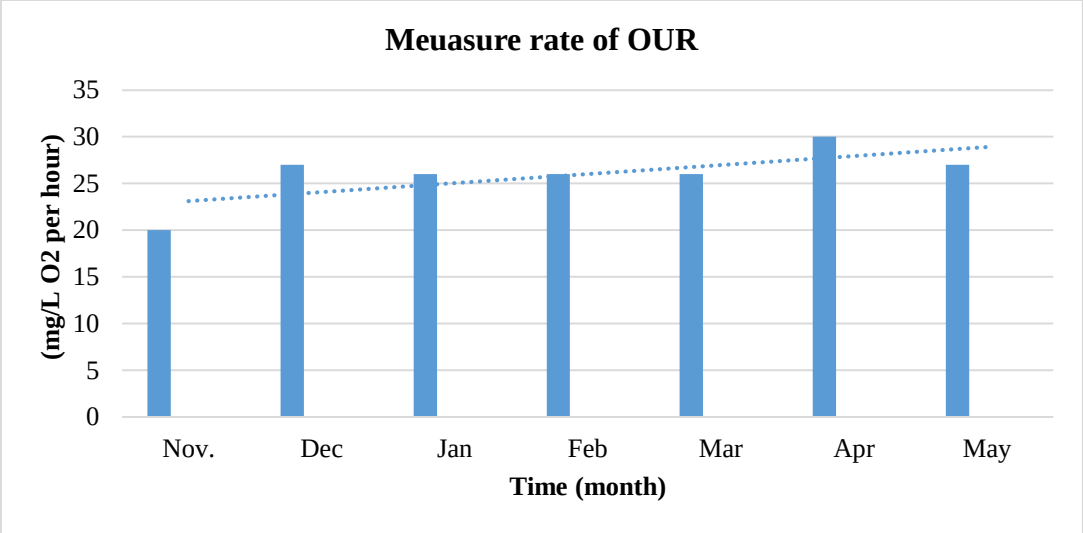


Figure 3.3: The monthly data for oxygen uptake rate

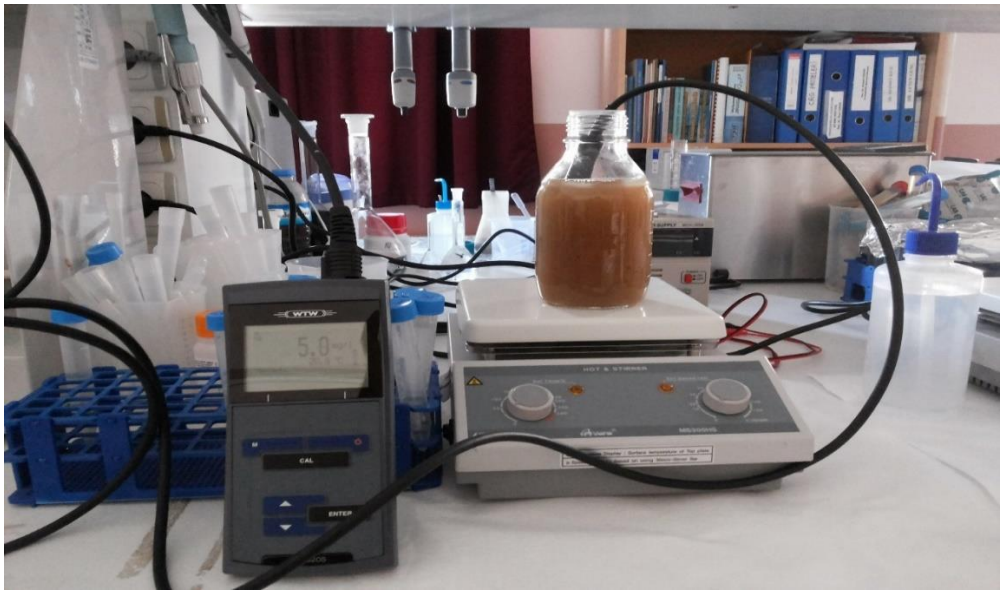


Figure 3.4: The method for measure the Oxygen uptake rate in laboratory

3.6. Experimental evaluation for PPCPs

EPA Method 1694 determines pharmaceuticals and personal care products (PPCPs) in environmental samples by high performance liquid chromatography combined with tandem mass spectrometry (HPLC/MS/MS) using isotope dilution and internal standard quantitation techniques. This method has been developed for use with aqueous, solid, and biosolids matrices (USEPA 2007). Three type of PPCPs have been added (Paracetamol, Ibuprofen and Paracetamol) to the bioreactors, every bioreactor had a four different HRT 12h, 24h, 36h and 52h, after the time of HRT passed away 50 ml from bioreactor was taken and store at refrigerator, subsequently took to measure by HPLC. The method for spit these chemicals compound shown in table (3.3).

Table 3.3: The quantities of PPCPs that addition to bioreactors

PPCPs	Concentration add mg/L									Temperature °C	D.O. mg/L
Triclosan	0.01	0.02	0.1	0.2	0.3	0.5	1	5	10	21±1.2	5±0.75
Ibuprofen	0.01	0.02	0.1	0.2	0.3	0.5	1	5	10	21±1.2	5±0.75
Paracetamol	0.01	0.02	0.1	0.2	0.3	0.5	1	5	10	21±1.2	5±0.75

3.7. Solid Phase Extraction

After centrifugation the samples which were pulled at different hydraulic retention times, from the aerobic system .The samples were first through a 10-cm P5 filter paper (Fisher Scientific, PA, USA) to remove suspended solids, isolated by solid phase extraction using 3 mg Oasis hydrophilic-lipophilic balance cartridges (Waters, United Kingdom). (Kvanli, et al, 2008). The samples were pre filtered through glass fiber filters (Scheicher and Schuell).The cartridges were preconditioned with 1 mL methanol and 1 mL of ultra-pure water. The samples were drawn through the cartridges at an approximate flow rate of 1 mL/ min. The cartridges were washed with 1 mL 5% methanol to remove any loosely bound contaminants, and then they were eluted with 2 mL methanol (Shang, et al 2013).

3.8. LC /MS analysis of PPCPs

3.8.1. Preparation of Standards and Calibration Curves

As we know every drugs, PPCPs, or any chemicals compounds have a total of different solvent to prepare the stock solution for instance, methanol, Acetone, alcohol, and

water in accordance with the chemicals structure and the type of compound as we shown in table (3.4).

Table 3.4: The preparation of standard for HPLC measure (Tixier, et al, 2002; Matuszewski, et al. 2003).

PPCPs	Pure chemical	Solvent volume	Solvent
Triclosan	25 mg	250 ml	Methanol
Ibuprofen	25 mg	250 ml	CAN
Paracetamol	50 mg	250 ml	Water

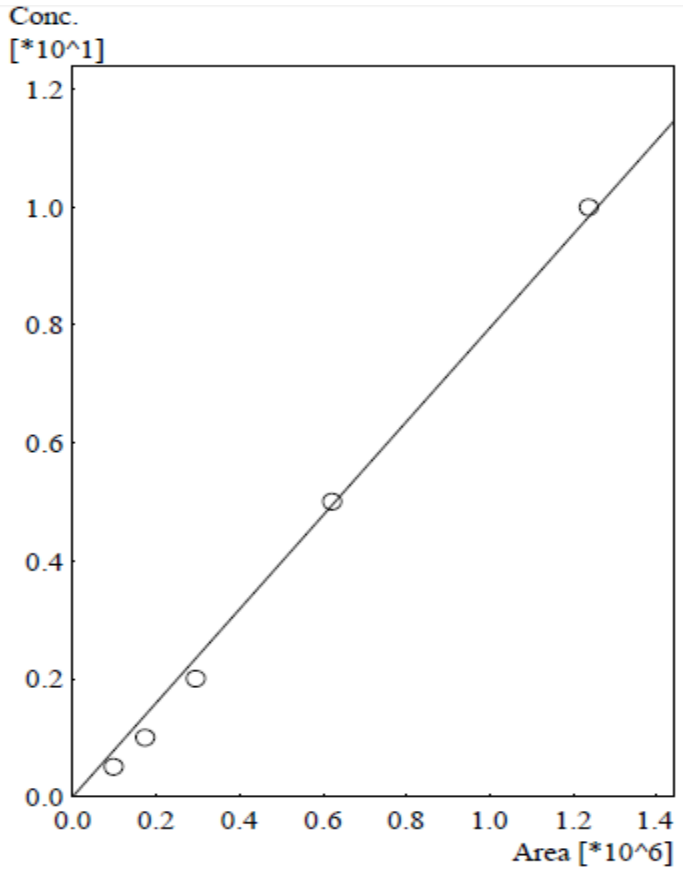


Figure 3.5: preparation of standard for Triclosan by HPLC measure

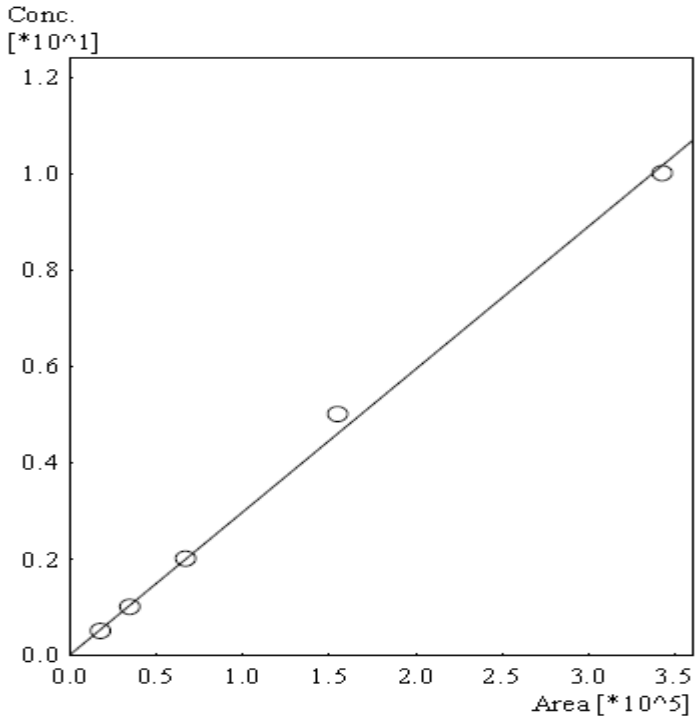


Figure 3.6: preparation of standard for Ibuprofen by HPLC measure

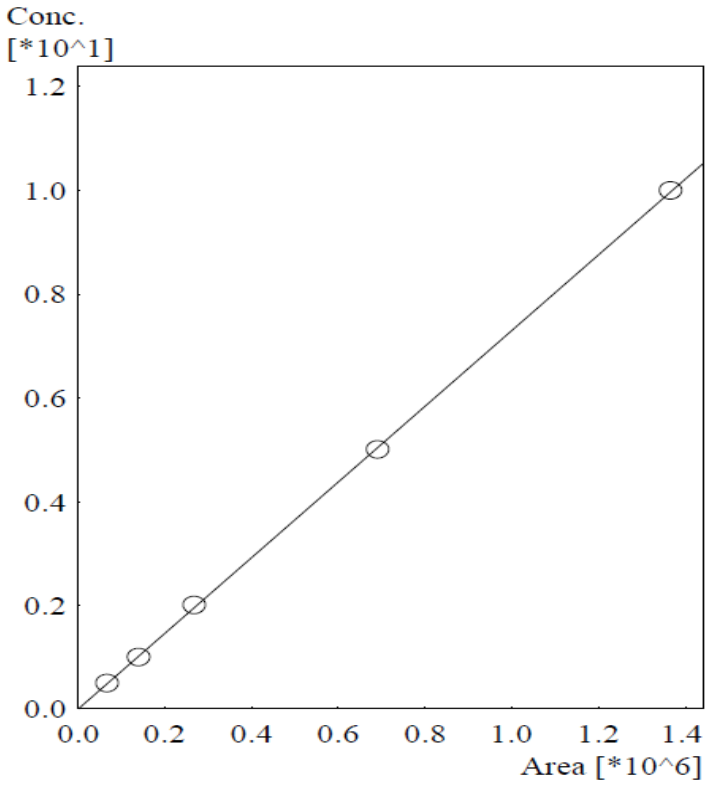


Figure 3.7: Preparation of standard for Paracetamol by HPLC measure

3.8.2. The LC /MS analysis of PPCPs

A method is presented for determinant three PPCPs compounds using LC-MS/MS. This method is a right forward process for the analysis and identification of these compounds with excellent sensitivity and acuity (Schreiber, 2009). Samples were analyzed by liquid chromatography with DAD, C18 Colum (250, 6.6, 5 um) Shimadzu LC 20AT, the methods, as summarized in Table 15, which were developed as a part of this work. Triclosan, Ibuprofen and paracetamol with a purity of 99.5% ±2%, as well as the UV detection at 210 nm, 210 nm, and 250nm respectively, were used to produce HPLC standards (Matuszewski, 2003; Vanderford, et al 2003).The method was successfully applied to determination these compounds in samples.

Table 3.5: The method used to determine PPCPs by HPLC

Chemical	Mobil phase	Flow rate (mL/ min)	Total time	T.	Retention time	U.V Detection
Triclosan	ACN : H_2O 90:10	1	7 Min	40 C°	4 Min	210 nm
Ibuprofen	CAN : phosphor buffer 60 : 40	1	5 min	40 C°	2.8 Min	210 nm
Paracetamol	CAN : H_2O 70 : 30	0.5	8 Min.	40 C°	5.4 Min	250 nm

4. RESULTS AND DISCUSSION

As stated before, the experimental work was divided into Five bioreactors were operated under the same conditions and at various HRTs, The effluent qualities and the activated sludge properties of the reactors are summarized in Table (4.1).

Table 4.1: The Effluent quality and the sludge properties of extended activated sludge process.

Reactor	A	B	C	D
Effective Volume (L)	5	5	5	4.5
SRT (d)	20	20	20	20
HRT (h)	12-52	12-52	12-52	12-52
Effluent COD (mg/L)	209	187	139	106
COD removal (%)	80	86	89	91.5
TSS (mg/L)	256	241	215	198
MLSS (mg/L)	4874	5012	5049	4450
MLVSS (mg/L)	4095	4229	4371	3647.5
MLVSS/ MLSS (%)	84	84.3	86.5	82
Excess sludge (g/d)	0.52	0.48	0.49	0.56
F/M Ratio	0.12	0.14	0.11	0.15
SVI (mL/ g)	91.5	95	88.9	90.7

4.1. The Sludge volume index results

Sludge volume index of 100 mL/g is mostly known as the boundary of well settling characteristics and bulking problem. All the reactors showed acceptable SVI for the extended activated sludge but the results were different as well as the structure and chemicals for the type of drugs that adding and effected by the activity of microorganisms toward the toxicity . The highest and the lowest average of SVI belonged to the sludge of reactor a (100 mL/g) and reactor C (51 mL/g), respectively. (Mines and Milton, 1998; Kargi and Uygur 2002). (Fig. 4.1) shows the values of sludge volume index of extended activated sludge bioreactors.

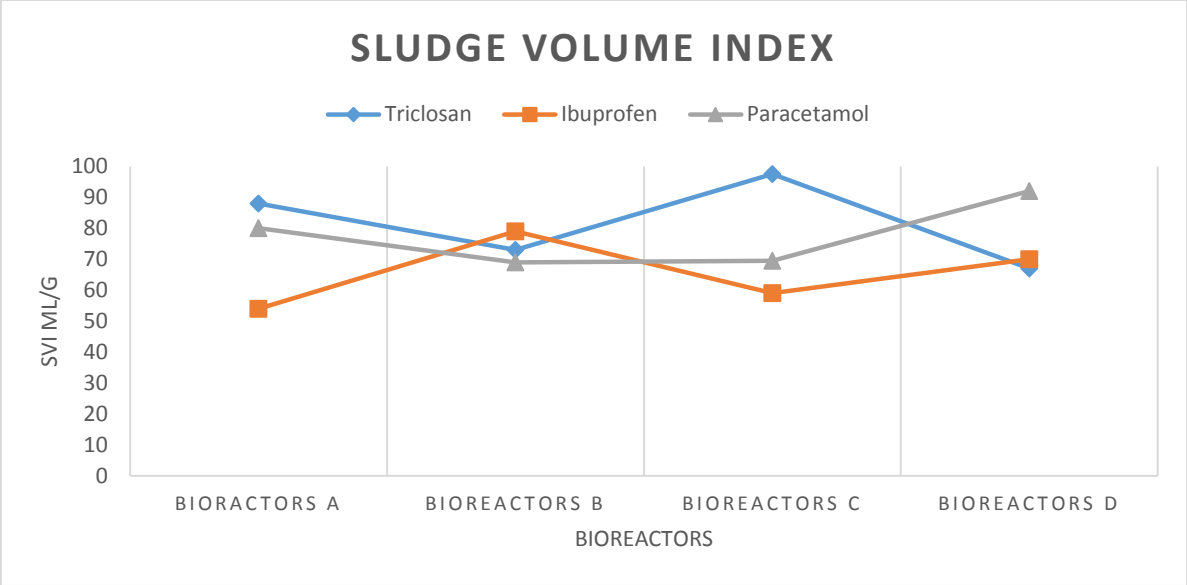


Figure 4.1 The values of sludge volume index in bioreactors with PPCPs

4.2. MLSS and MLVSS

The knowing of sludge concentration (MLSS and MLVSS) is important to know the effectual performance of the biological processes. (Fig. 4.2) shows the concentration of MLSS, MLVSS in the reactors from the first experiment to end. As well as shown in (Fig. 4.3) the high HRT had directly affected the biomass concentration of bioreactors by removing the PPCPs.

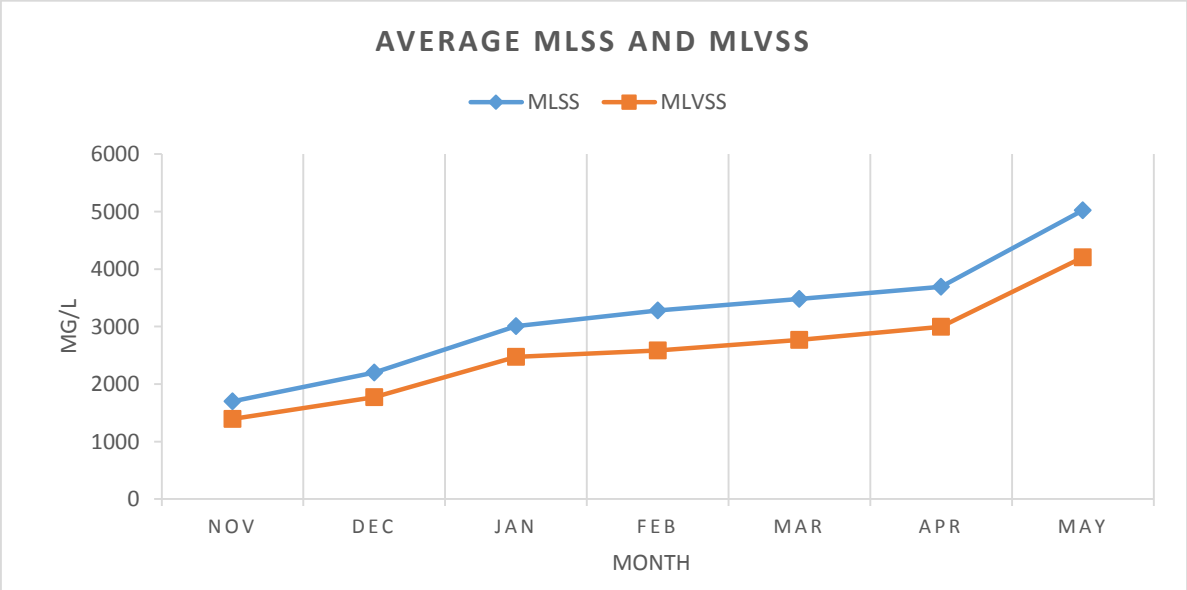


Figure 4.2: The average of MLSS and MLVSS during the study period.

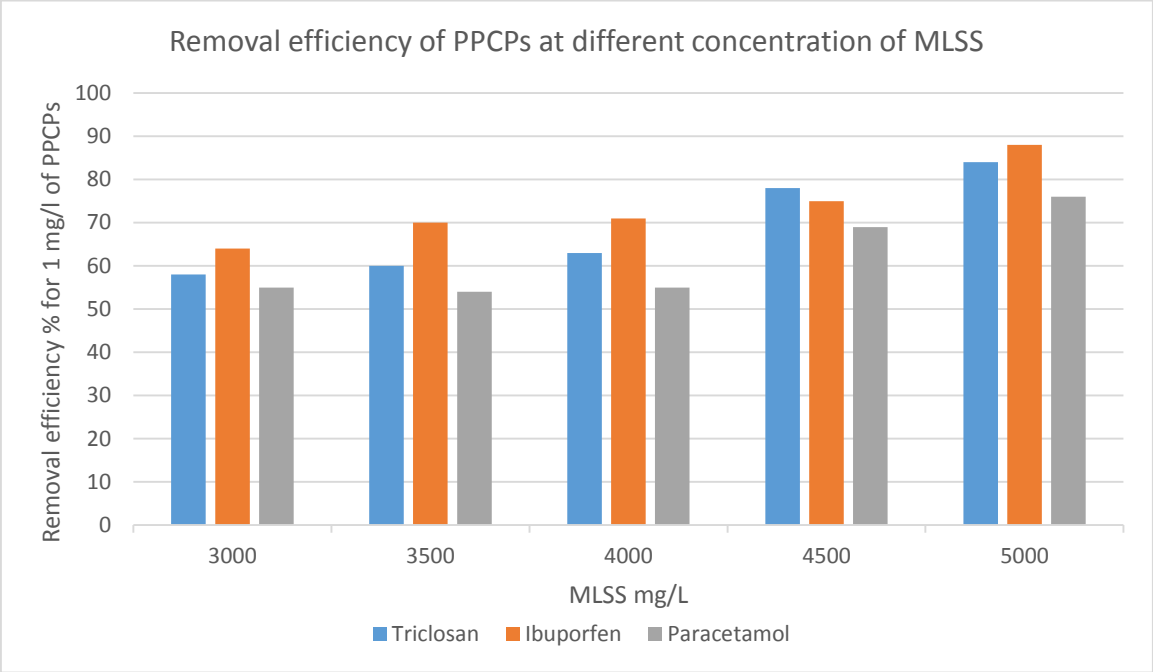


Figure 4.3: The Removal efficiency of PPCPs at different concentration of MLSS

4.3. The result of F/M ratio

The F/M values decreased with SRT. The highest and the lowest value of F/M were found in reactors A (0.79) and reactor D (0.42), respectively. Sirianuntapiboon, et al. (2006) obtained similar results where F/M of reactors with SRTs of 6.8, 8.5 and 10.1 d were 0.091, 0.047 and 0.029 d-1, respectively which indicates a decreasing rate of F/M via SRT.

4.4. Oxygen uptake rate OUR

The OUR results shown a clear difference when adding the doses of PPCPs, they indicates the inverse relationship between the oxygen uptake rate and the chemical complexity or Toxicity toward the microorganisms, because these microorganisms need more oxygen to degraded or convers the chemicals compound to Simpler by using the oxygen for oxidation.

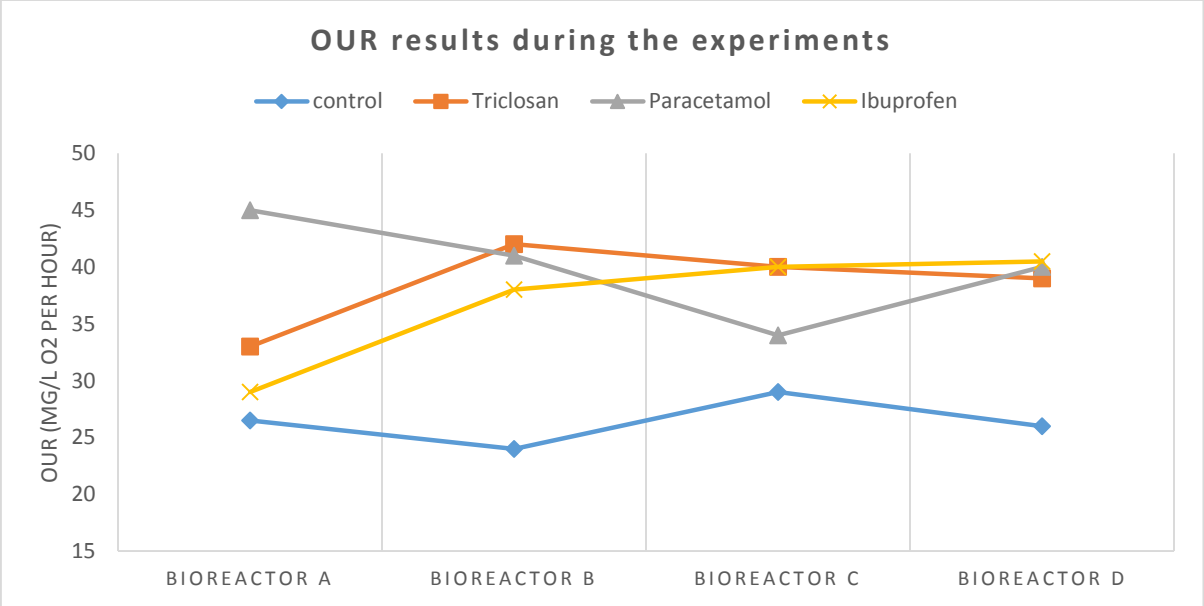


Figure 4.4: The results of OUR when adding the PPCPs

4.5. COD Removal

Fig.27 shows the influent and effluent COD concentration variations during the operation period of HRT 12h, 24h, 36h and 52h, there are several major factors that influence for COD removal efficacy. These are organic loading, hydraulic loading, temperature, pH, dissolved oxygen concentration, the MLSS, type of the treatment plane, the aerobic or anaerobic phase. The effluent COD of reactors decreased as the HRT increased. When the HRT at high level in all reactors phase 36h, 52h, Nevertheless It should be referring to that high HRT with high dissolved oxygen had a big effect on COD removal efficiencies, (AlBuraidi, 2013) get Almost similar results when he study the comparative between membrane and extended Aeration Activated Sludge the COD removal efficiency ranges between 89% and 91%., Also. Mardani, Sh., et al (2011) had the same result they were showed a COD removal efficiency ranging for conventional process between 83 and 92.5%, and the result for extended aeration process between 88 and 93.8%, and for contact stabilization process 77 and 92%.

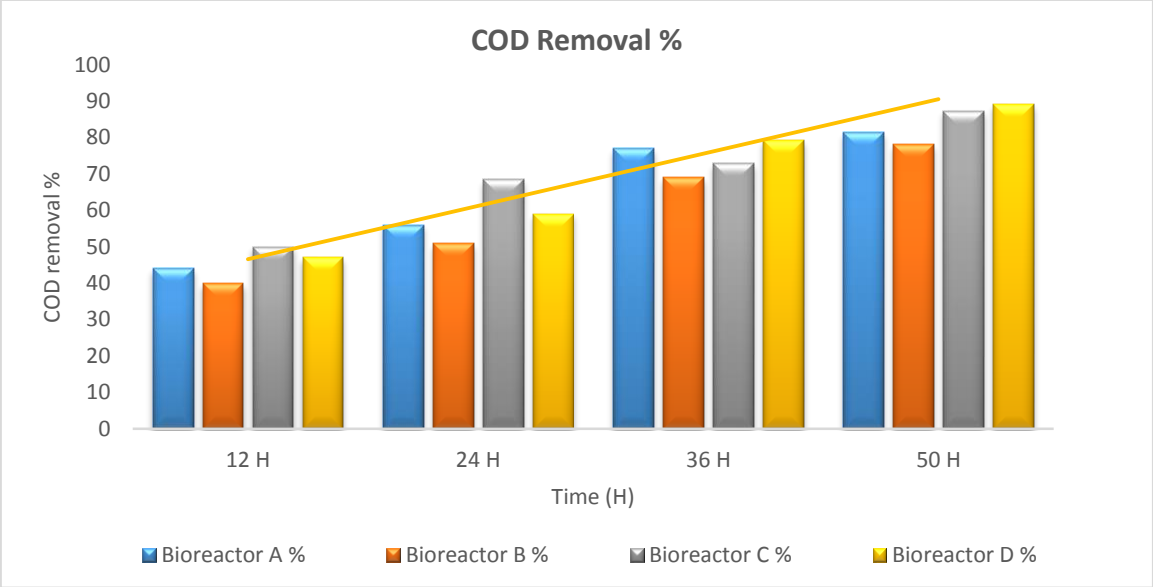


Figure 4.5: The COD removal at different HRT with four bioreactors.

4.6. Removal of PPCPs during Extended activated sludge Wastewater Treatment

The domestic WWTPs were mostly prepared to take away all organic and inorganic suspended solid and pathogens which mention earlier in the review of literature Water scarcity, population growth problems health and environmental hazard constitute topics of current researches. Nevertheless, economic factors of peoples or even of the whole institution play an important role for obtaining and selection of the best tools and of the most appropriate .Upon the findings of the available information, using of extended activated sludge had an important effect of highly qualified in their efficiency of removal certain selected PPCPs. Merits were exploited applying the activated sludge reflecting its relatively cheap processes as compared with those of advanced methods. Fortunately, five bioreactors of the present experiment were worked equally and the results showed that the bioreactors worked as it were planned.

4.7. LC /MS detection of PPCPs

Establishing the chromatographic retention time to select an appropriate precursor ion for the analytic was the initial step for developing a LC/MS method, the mobile phase was chosen after several trials with methanol, acetonitrile, water and buffer solutions in various proportions and at different pH values. A mobile phase consisting of ACN and water (90: 10) (v/v) for Triclosan, ACN: phosphor buffer 60: 40 for Ibuprofen and ACN:

H2O 70: 30 for Paracetamol were selected to achieve maximum separation and sensitivity. A flow rate of 1.0 ml/min for Triclosan and Ibuprofen, 0.5 ml/min for Paracetamol were given an optimal signal to raise ratio with a reasonable separation time. Using a reversed-phase C18 column, the retention times were observed to be (4.052, 2.08, 5.4) min for triclosan, Ibuprofen and Paracetamol. The total time of analysis was less than 6, 5, 8 min, respectively. The maximum absorption as was detected at 210, 210,250 nm respectively and these wavelengths were chosen for the analysis. The chromatogram below showed a complete resolution of all peaks.

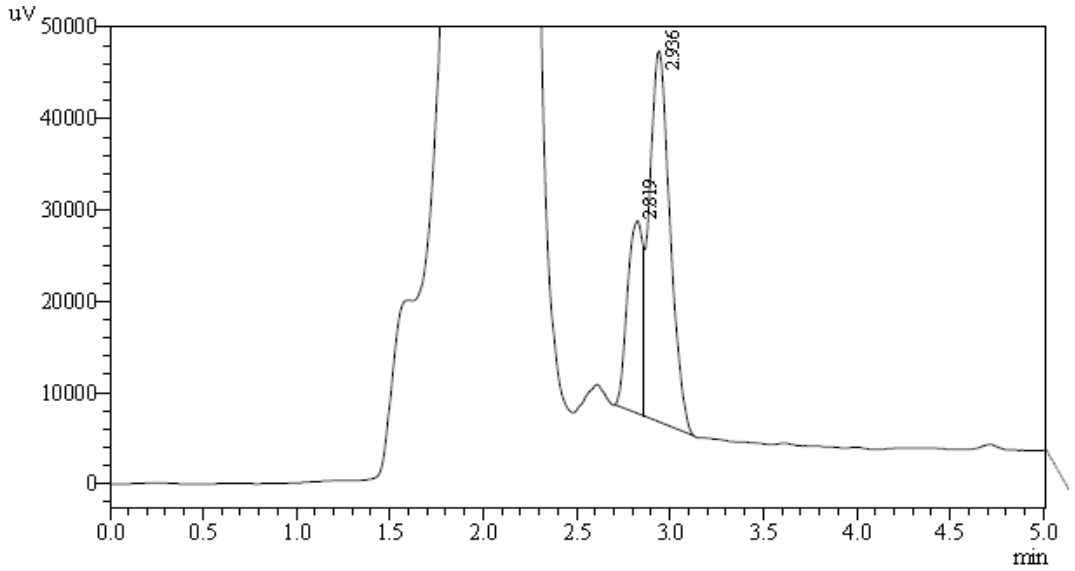


Figure 4.6: Detection of Ibuprofen by HPLC at 10 ppm

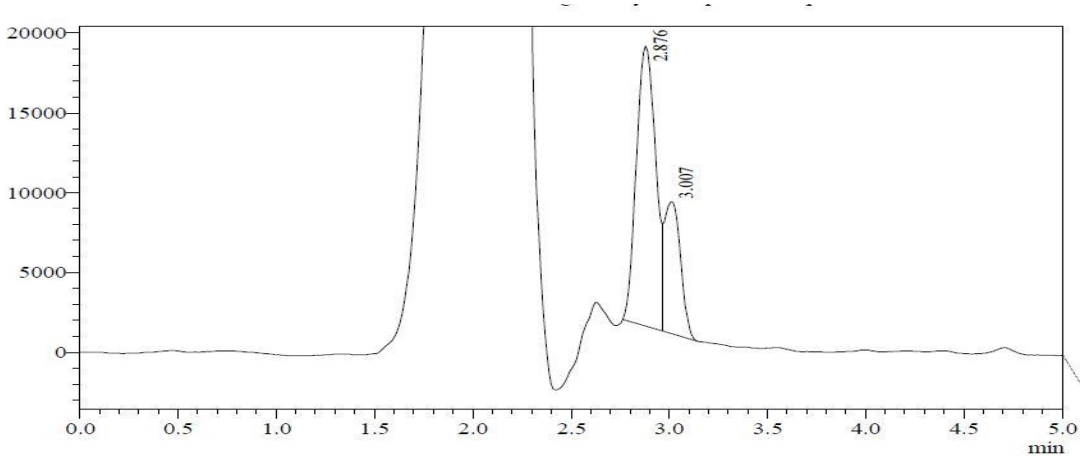


Figure 4.7: Detection of Ibuprofen by HPLC at 5 ppm

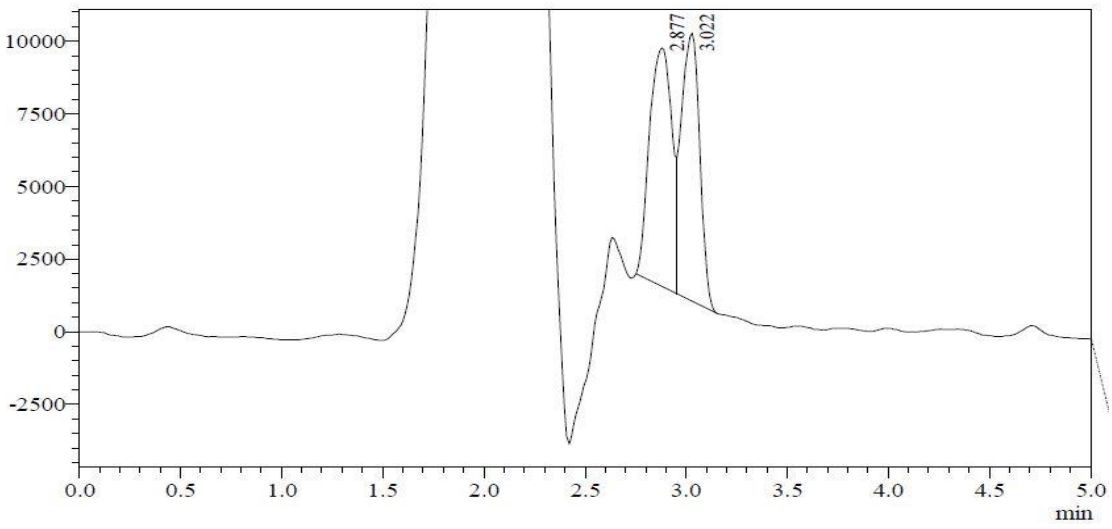


Figure 4.8: detection of Ibuprofen by HPLC at 2 ppm

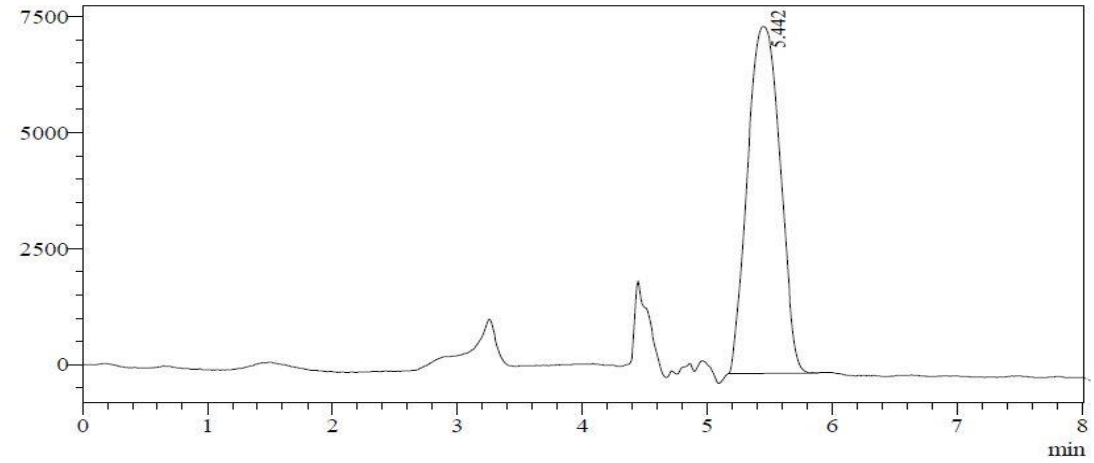


Figure 4.9: Detection of Paracetamol by HPLC at 10 ppm

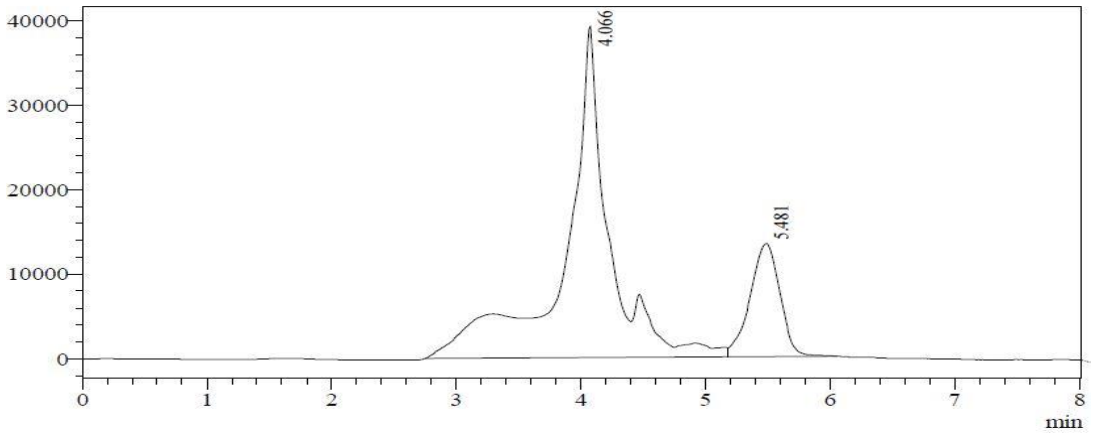


Figure 4.10: detection of Paracetamol by HPLC at 5 ppm

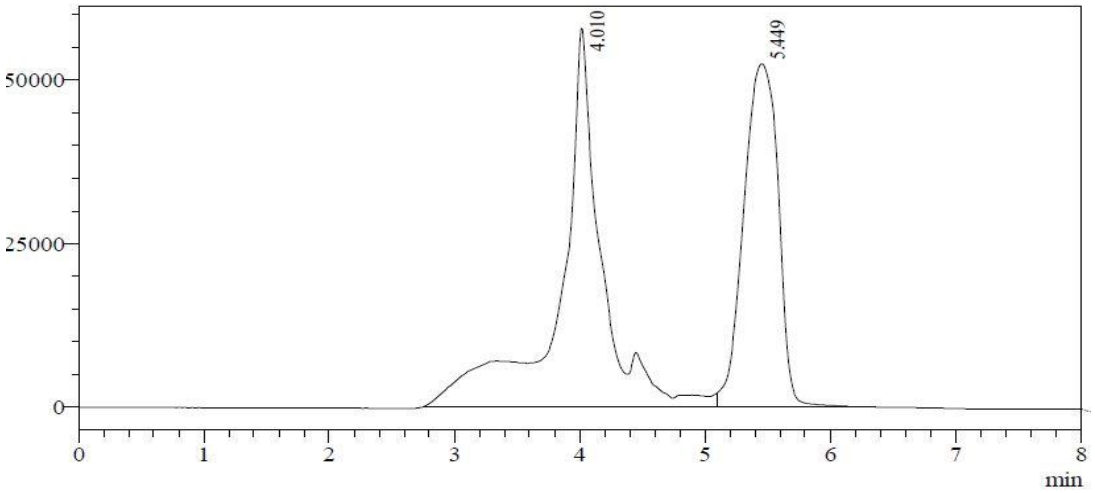


Figure 4.11: Detection of Paracetamol by HPLC at 2 ppm

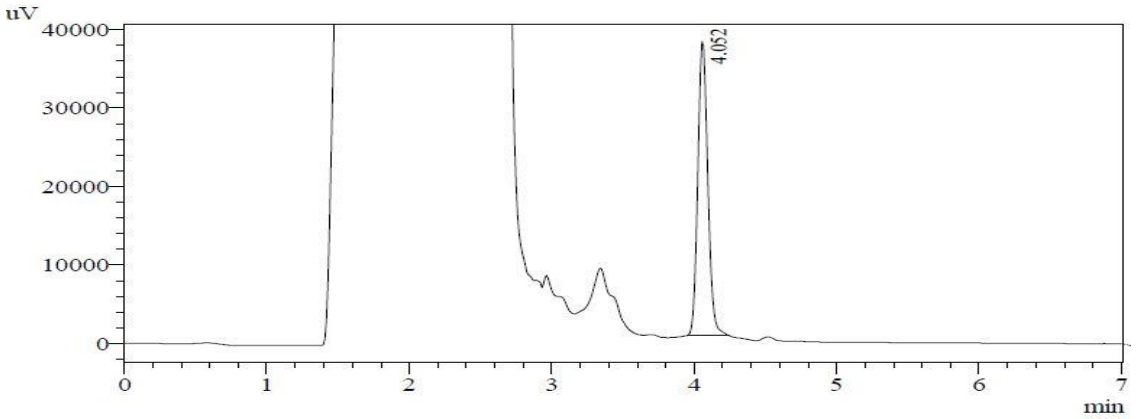


Figure 4.12: detection of Triclosan by HPLC at 10 ppm

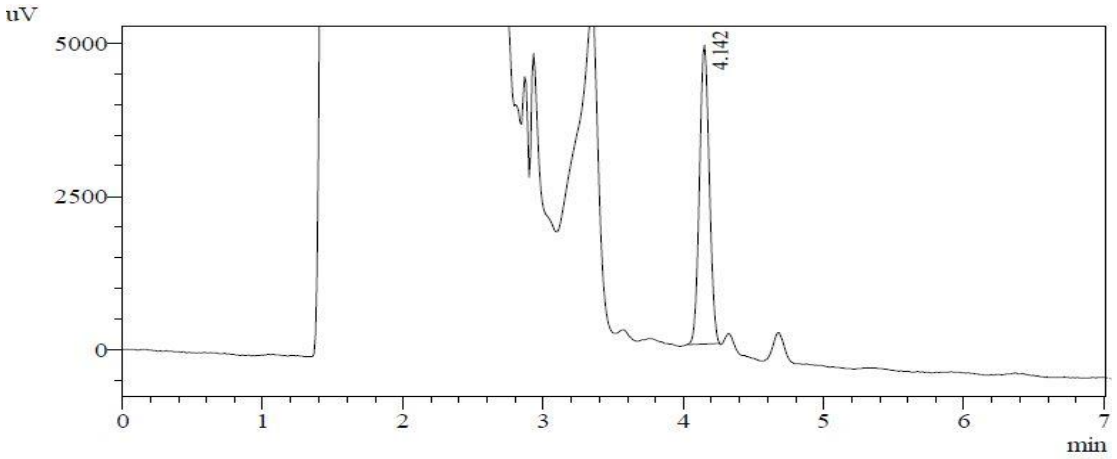


Figure 4.13 detection of Triclosan by HPLC at 5 ppm

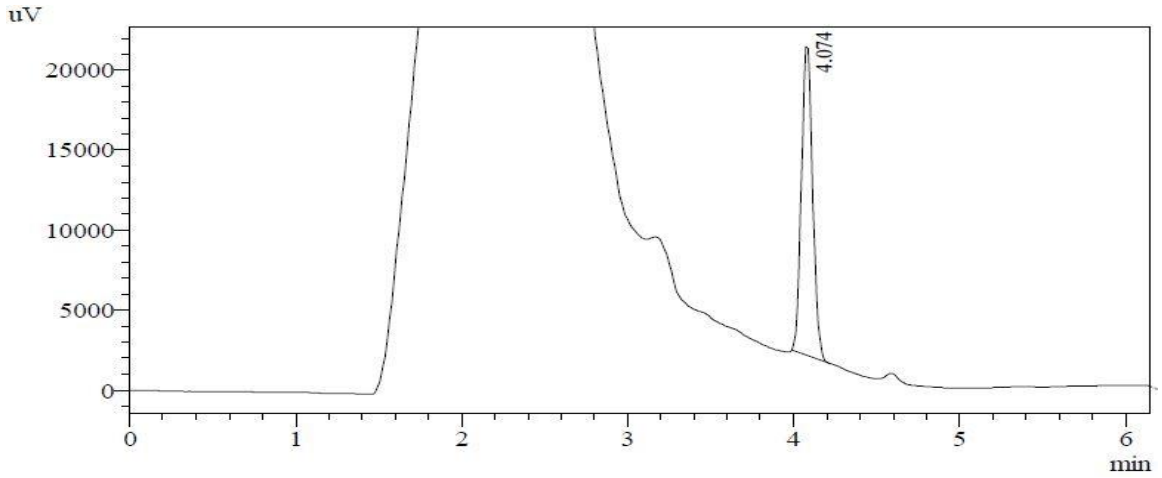


Figure 4.14: detection of Paracetamol by HPLC at 2 ppm

4.8. Removal of PPCPs from bioreactors

4.8.1. Triclosan Removal

Table 4.2 shows the HRT and removal of the concentration profiles of triclosan during extended activated sludge process, at different concentration of triclosan (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5and 10) mg/L in 250ml of bioreactor. The extended activated sludge system was worked at 22 C° ±1.5 and the mixed liquor suspended solids was 5000 mg/L. The observation revealed that triclosan compounds was fully biodegradable under aerobic condition after a time period of 52 H .The removal efficiencies in (Fig.4.15) were calculated from the added concentration of 0.01, 0.02, 0.1, 0.2 ppm and the triclosan was almost completely removed in bioreactors. Nonetheless, several workers, have reported that triclosan, despite being a relatively hydrophobic compound (log Kow¼4.76), is readily biodegradable under aerobic conditions (McAvoy, et al 2009). Also, the study carried by (Paxéus, 2004) has indicated the removal of triclosan in WWTPs in Europe. Notably, all the WWTPs used primary settling and activated sludge in their treatment. They observed that triclosan had high removal rates in WWTPs, with an average of 73% and the lowest removal of 58%.

Table 4.2: The final result for Triclosan removing efficiency.

Concentration Ppm	The hydraulic retention time of reactors (H)				
	0	12	24	36	52
	Triclosan Removal %				
0.01	0	69.5	74	86.2	99.99
0.02	0	69.05	74.8	86	99.85
0.1	0	65.09	71.2	84.04	99.79
0.2	0	59.7	70.07	81.73	99.75
0.5	0	57.06	66.5	79.01	90.5
1	0	43.79	58.01	70.59	88
5	0	39.7	58.2	68.06	85.06
10	0	30.04	47.06	64.06	81.2

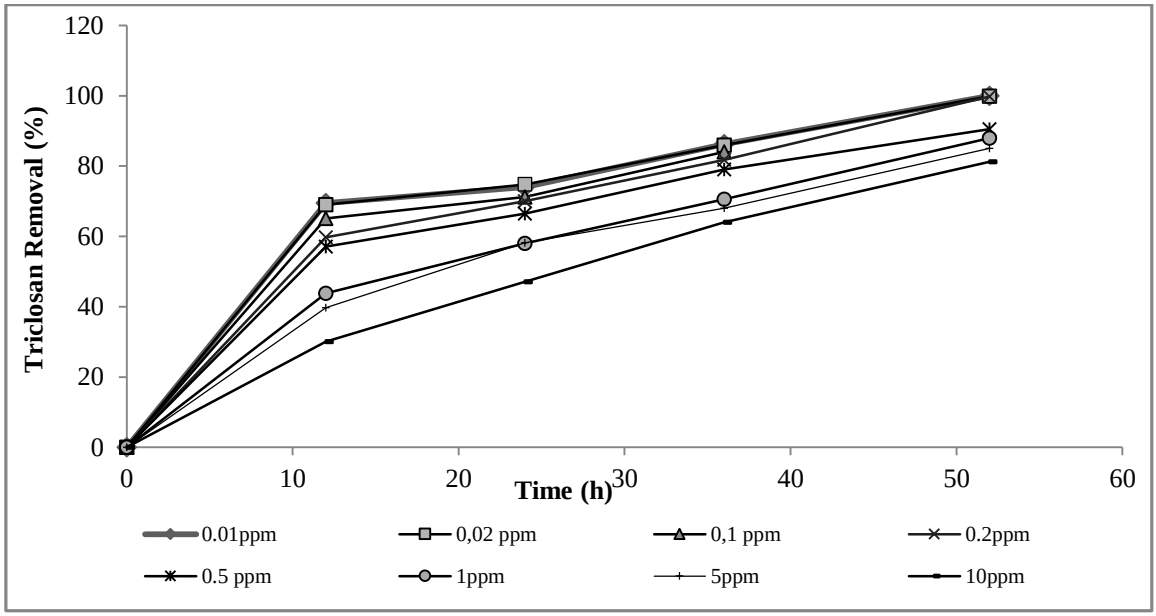


Figure 4.15: The removal efficiency of Triclosan at different time.

4.8.2. Ibuprofen Removal

The removal of ibuprofen (IBU) was shown in table 4.3. Within 52 hours the pharmaceutical was effectively eliminated to concentrations under or close to the detection limit. From the results presented in this study, the pharmaceutical ibuprofen was eliminated entirely over the experimental process at the low concentration, with a biodegradation removal efficiency of 99.9% which was shown in the (Fig. 4.16) On the other hand, the biodegradation of IBU is similar to those reported according to literature. The removal rates of IBU of more than 90% in WWTPs were reported by many worker (Kosjek, et al. 2007) for a pilot WWTP with a HRT of 24 hours.

Table 4.3: The final result for Ibuprofen removing efficiency

Concentration ppm	The hydraulic retention time of reactors (H)				
	0	12	24	36	52
	Ibuprofen Removal %				
0.01	0	77.9	85	94.73	99.99
0.02	0	73.2	81.2	93.7	99.99
0.1	0	70.02	79.8	89	99.99
0.2	0	67.09	78	86.6	99.99
0.5	0	64.12	74.03	82.67	98.09
1	0	59	66	75.91	89.02
5	0	48.88	62.67	73.08	84.11
10	0	48	57.09	69.72	81.87

Ibuprofen has shown to be easily removed by the extended active sludge reactor throughout the experiments. Ibuprofen has a low K_d value for secondary sludge (0.007± 0.002) and the highest biological transformation rate (Kbiol=21-35) of the substances. This means that ibuprofen can be degraded by microorganisms and degradation products of ibuprofen can be created.

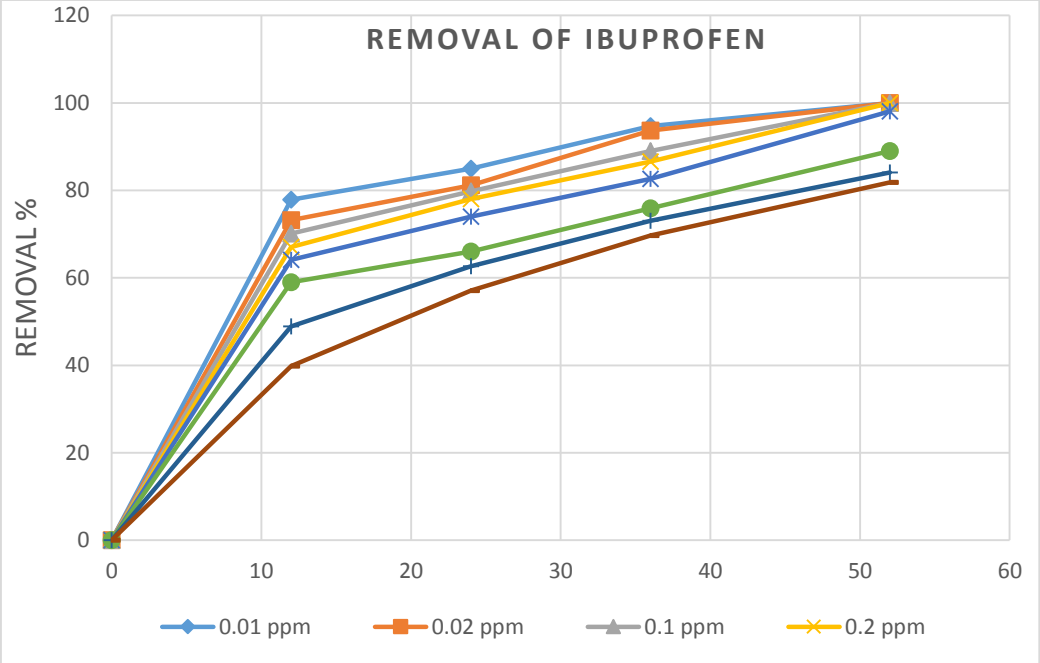


Figure 4.16: The removal efficiency of Triclosan at different time.

In the study made by (Ternes, and Joss, 2006) enough information was available to make some speculations. In the study they obtained the highest biodegradation rates, the MLSS was over double that of this study. Also the influent water had a lower COD load and the temperature was higher. As Clara, et al. (2005) concluded that the temperature should not have big effect on the biodegradation of ibuprofen, it is more likely that the SRT and organics load had a larger effect on the results.

4.8.3. Paracetamol Removal

Paracetamol was removed by used the extended activated sludge process it was on an average of 98.5% over a 52 h sampling period. (Fig. 4.17), the mean temperature at the time of sampling was 23°C and the sludge age 20 days. At The low concentration the removal that found 99.9%. Paracetamol biodegrades fast and has as high K_{biol} of 58-80 in activated sludge.

Table 4.4: The final result for Paracetamol removing efficiency

Concentration Ppm	The hydraulic retention time of reactors (H)				
	0	12	24	36	52
	Paracetamol Removal %				
0.01	0	75.11	84.95	94	99.9
0.02	0	69.2	83.09	91	99.1
0.1	0	67.2	81.5	89.9	99.01
0.2	0	56.6	80.29	89	99.05
0.5	0	59	79.65	86.26	95.71
1	0	54	70.09	80.01	89.3
5	0	50.05	67.42	75	87.6
10	0	41.5	59.81	69.79	84.03

From the table (4.4) there was a significant increase in removal efficiency, Also, another increase in the concentration of dissolved oxygen which was about 5.1 mg/L and high mixed liquor suspended solids (MLSS) which were 4620-5141 mg/L. The obtained indicated high and excellent removal rates. It was notice that there were an increase in the concentration of Paracetamol to 10 mg, a removal percentage was 84%. A study achieved by Ternes and Joss, 2006, they were used both conventional activate sludge and membrane bioreactor batch reactors found that the Paracetamol was biologically transformed by more than 90%.These finding mean that this compound should be readily biodegraded by the sludge found in wastewater treatment facilities.

stated that certain sludge characteristics were significant in the biodegradation of paracetamol, including the diversity of the activity of the biomass due to the differences in *Mixed liquor suspended solids* (*MLSS*) or the enzymatic activity, the fraction of active biomass within the total 9 suspended solids, and the floc size of the sludge for compounds being well degraded. (Ternes, and Joss, 2006).

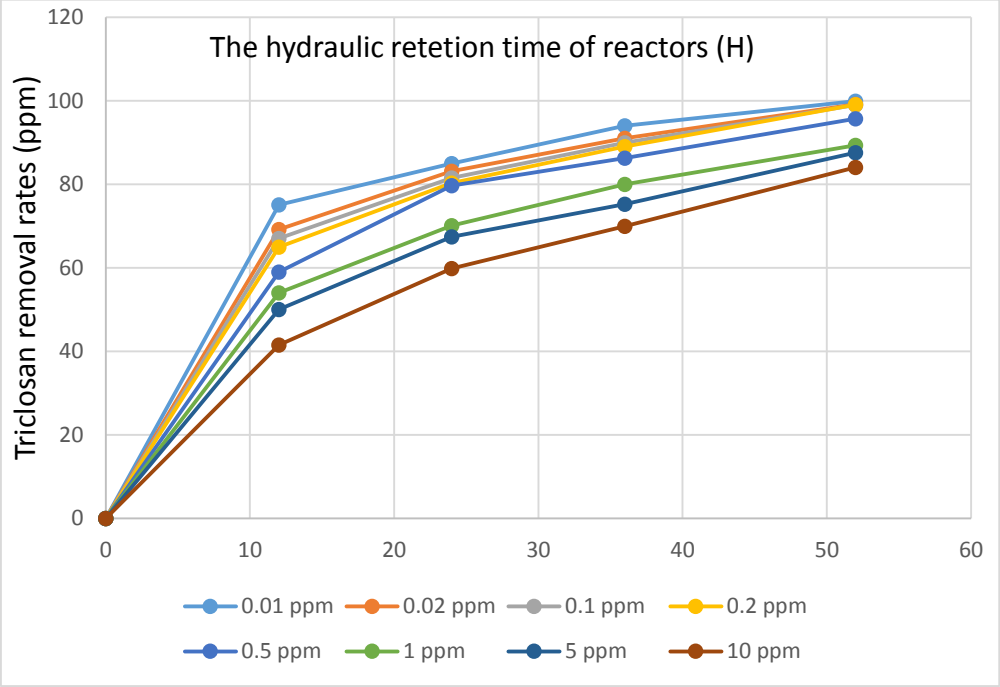


Figure 4.17: The removal efficiency of Paracetamol at different time.

In addition to this study, another study conducted by (Yamamoto, 2009) the on analysis concentration of Paracetamol and associated biodegradation, determined the persistence and partitioning of the pharmaceutical in aquatic environments. The samples used were collected from rivers located in Japan, and were inoculated with 100 µgL-1 Paracetamol. The resulting biodegradation rate, was found to be 0.014 hr-1, with a half-life of 50 hours. The removal rate by the microorganisms was found to be 96%. (Yamamoto, 2009) These biodegradation rates are very important in determining if Paracetamol will be removed during the wastewater treatment process.

5. CONCLUSIONS

A first approach to reduce the risk of PPCPS and their derivatives in wastewater is to avoid these substances from entering into the sewer systems. The removal of harmful substances from wastewater is another way and it can be achieved by different well-qualified wastewater treatment techniques, intended to remove suspended and colloidal dissolved components from wastewater.

In the current study it was observed that biological degradation and sorption are the main mechanisms for PPCP removal during municipal wastewater treatment. Hence, several studies showed that even though the conventional WWTPs meet the regulatory requirements for wastewater treatment, they are only moderately effective in removing pharmaceuticals. Removal efficiency of pharmaceuticals and personal care products will normally depend on their structural and biological properties, wastewater characteristics, operational conditions, and treatment technology followed. Consequently, a positive relationship was found between dissolved oxygen and removal capacity *i.e* availability of 4 mg/L of dissolved oxygen will remove 90% of PPCPs. Reversely, 2 mg/L of dissolved oxygen will cause 50% of PPCPS removal. Of all the operating measurements, the hydraulic retention time (HRT) and dissolved oxygen are the most significant parameters for extended activated sludge process and it was shown that longer HRT ameliorate the removal of the PPCPs during WWTP process. Although, the possible toxic effects of PPCPs in the future is not determined yet and their risk to the environment is not fully studied, their occurrence should not be ignored. Nevertheless, precautionary principles should be imply to prevent threats of injury to human hygiene or environment even if some aspects and effect relationship are not fully assessed.

Practically, a set of proactive source reduction measures should be consider to decline sum of active pharmaceutical compounds that are thrown to the aquatic environment, chiefly due to the practice of the general public which need a strict change of human policy in order to eliminate these activities.

Also, lessening the disposal pathways through take different programs could be more efficient and less expensive than broad wastewater treatment facility modifications or other remediation steps. Currently, realization of exposure from environmental sources of medication is not the concern of public health. However, chronic low dose for long period of active pharmaceutical compounds that many people may subject especially those of sensitive populations may have hazardous sequels. Nonetheless, such continual exposure to unspecific organisms could be crucial.

Further studies are required for better understanding the fate of PPCPs in wastewater treatment plants and their end products of degradation in aquatic environment. Nevertheless, certain chemical interactions are possible which need urgent environmental monitoring. Hence, Contribution of different activities and aspects including manufacturer, academic scientists, health care workers as well as the public. The continuing development of new medications, the escalating prescription of drugs, outbreak of emerging diseases and population increases will consequently act to exaggerate the occurrence of pharmaceuticals in the environment. It follows that an alternate solution for the risk of PPCPs polluting the environment may be achieved by application of "green pharmaceuticals".

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CURRICULUM VITAE

PERSONAL IDENTITY

Name, Surname:	**MOSSTFA MAAROOF**
Nationality:	**IRAQI**
Date and place of birth:	**17/3/1988/ MOSUL**
Marital Status:	**Marriage**
Telefon:	**+905535818806**
E-posta:	**mostafaal35@Gmail.com**

EDUCATIONAL BACKGROUND

Degree	Place of education	Date of graduate
Master degree	KSU, Graduate School of Natural And Applied Sciences, Department Of Environmental Engineering.	2014
Baccalaureate	University of Mosul/ Department of Environmental	2011
High school	Al- Shrqiya for high education	2007

LANGUAGE SKILLS

English

Arabic