UNIVERSIDAD DE VALLADOLID

ESCUELA DE INGENIERIAS INDUSTRIALES

MÁSTER EN INGENIERÍA QUÍMICA

# Study of PPCPs Biodegradability in a Completely Mixed Aerobic Activated Sludge Reactor

Autor:

Marín De Jesus, David Fernando

Tutor:
Irusta, Rubén
Departamento de Ingeniería Química y Tecnología del medio Ambiente
Cotutor:
García, Pedro
Departamento de Ingeniería Química y Tecnología del medio Ambiente

Valladolid, Septiembre 2016.

RUBEN IRUSTA MATA, profesor del Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Universidad de Valladolid, y PEDRO GARCÍA ENCINA, profesor del Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Universidad de Valladolid, INFORMAN:

Que D. DAVID FERNANDO MARÍN DE JESUS ha realizado bajo nuestra dirección el Trabajo Fin de Máster, del Máster en Ingeniería Química, titulado STUDY OF PPCPs BIODEGRADABILITY IN AN AEROBIC SLUDGE ASSETS REACTOR OF COMPLETE MIX.

Valladolid, 12 de Septiembre de 2016

Fdo. TUTORES

Reunido el Tribunal designado por el Comité Académico del Máster en Ingeniería Química, para la evaluación de los Trabajos Fin de Máster, y después de estudiar la memoria y atender a la defensa del trabajo “STUDY OF PPCPs BIODEGRADABILITY IN AN AEROBIC SLUDGE ASSETS REACTOR OF COMPLETE MIX”, presentado por el alumno D. DAVID FERNANDO MARÍN DE JESUS decidió otorgarle la calificación de _____.

Valladolid, 12 de Septiembre de 2016

El Presidente

Fdo.

El Secretario

:Fdo.:

Vocal

Fdo.**:**

# Study of PPCPs Biodegradability in a Completely Mixed Aerobic Activated Sludge Reactor

**David Marín De Jesus, Pedro Antonio García Encina, Rubén Irusta Mata**

D. Marín[1], P.A. García Encina*[1], R. Irusta Mata*[2]

[1]Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr. Mergelina s/n, 47011, Valladolid, Spain.

[2]Department of Chemical Engineering and Environmental Technology, University of Valladolid, Paseo del Cauce 59, 47011, Valladolid, Spain.

* Corresponding author: pedro@iq.uva.es (P.A. García-Encina), rubiru@eii.uva.es (R. Irusta Mata)

## ABSTRACT

Pharmaceutical and personal care product (PPCPs) are now one of the mayor contaminants in water. PPCPs are present in water that arrives into the wastewater treatment plant and is important to remove these contaminants before discharge to waters sources. For these reason was performed the assembly of a Completely Mixed Aerobic Activated Sludge Reactor during 142 days. The experiment was divided into two parts. The first stage is a preliminary stabilization of the system, in which it comes to system conditions as similar as possible to the operational conditions of a wastewater treatment plant. The second stage is the one where PPCPs were included in the inlet flow (IF) of the system. For these were selected six compounds, these are: Ibuprofen, Propylparaben, Salicylic Acid, Naproxen, Triclosan and Diclofenac, this stage was divided into 16 different experiments using the Taguchi Method of Quality Control. At the second stage the following parameters were determined: chemical oxygen demand (COD), concentration of each compound in the IF and concentration of each compound

in the effluent flow (EF). The values of PPCPs removal were obtained after analyzed the IF and EF in the gas chromatography mass spectrometry (GC-MS), the statistical analysis was made using a Mass Hunter Qualitative Analysis and a Mass Hunter Qualitative Analysis. After a statistical analysis of the results with Analysis of Variance (ANOVA) Taguchi Method and Signal/Noise Ratio (S/N) Taguchi Method for the mixture of the six compound, it was determined the best parameters values for the controls factors; hydraulic retention time (HRT), mean cell retention time (MCRT), recirculation flow (RF) and the values for the noise factors; COD, Ibuprofen Concentration, Propylparaben Concentration, Salicylic Acid Concentration, Naproxen Concentration, Triclosan Concentration and Diclofenac Concentration, all of them in IF.

**Keywords:** biodegradability, diclofenac; ibuprofen; naproxen; PPCPs; propylparaben; salicylic acid; triclosan; wastewater treatment.

**NOMENCLATURE SECTION**

ANOVA: analysis of variance

CC: compound concentration ($\mu g\ L^{-1}$)

COD: chemical oxygen demand ($mg\ L^{-1}$)

DO: dissolved oxygen ($mg\ L^{-1}$)

EF: effluent flow ($L\ d^{-1}$)

GC-MS: gas chromatography mass spectrometry

HRT: hydraulic retention time (h)

IF: inlet flow ($L\ d^{-1}$)

PF: purge flow ($L\ d^{-1}$)

PPCPs: pharmaceutical and personal care product

RF: recirculation flow ($L\ d^{-1}$)

MCRT: mean cell retention time (d)

S/N: ratio between the signal power and the noise power

SPME: solid phase micro extraction

TSS: total suspended solids (mg $L^{-1}$)

VSS: volatile suspended solids (mg $L^{-1}$)

## 1. Introduction

The mechanisms of incorporation of PPCPs in water bodies take place by discharges of the pharmaceutical industry, hospital waste, improper disposal of expired drugs and mainly urban wastewater to arriving drugs after being excreted by the urine and feces [1]. Several studies have demonstrated adverse effects form longstanding, low dose exposures in both, aquatic and terrestrial wildlife, although human toxicity related to trace levels of pharmaceuticals in the water supply remains unknown [2] [3].

The pharmaceutical and personal care product (PPCPs) are not always considered like an environmental contaminant. Was in the seventies when scientist identified the presence of Clofibric Acid in some wastewater of United States, this compound is the activate metabolite of several regulators of blood lipids [4]. In countries like Spain and France there are water discharges of approximately 500 tons of painkillers per year [2], where salicylic acid and diclofenac are the most important compounds presented in water [5].

In some cases the environmental damage of these contaminants are nor very clear. For example, diclofenac, has been associated with the disappearance of withe buzzards in India and Pakistan [4]. There are some studies for the elimination of Ibuprofen in a pilot wastewater treatment plant that has achieved a 60% removal of compound [6], other studies has achieved a 20% removal [7] and others a 94% removal [8].

The development of analytical methodologies for PPCPs in environmental matrices has boomed lately [9]. Gas Chromatography coupled to a single quadrupole Mass Spectrometry (GC-MS), is a technique far more common in routine analysis laboratories around the world. Despite PPCPs are mainly polar compounds and not readily analyzable by GC, shown how GC-MS is a valid instrumental technique for the analysis of emerging contaminants in environmental matrices like sewage water, when a derivatization step was included in the method [10].

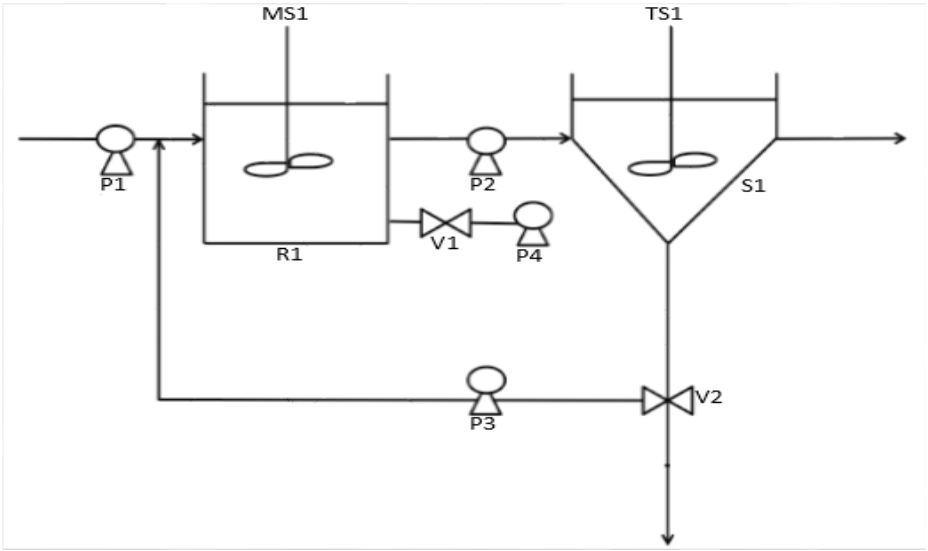
The main objective of this experiments is the study or the influence of the different control factors; hydraulic retention time (HRT), mean cell retention time (MCRT) and RF, and two noise factors; chemical oxygen demand (COD) in the inlet flow (IF) and compound concentration (CC) in the IF, in the elimination of 6 PPCPs in a completely mixed aerobic activated sludge reactor. There are only a few publications [11] [12] that proposed the use of this technique for the analysis of PPCPs in wastewater.

## 2. Materials and methods

### 2.1 Experimental set-up

The design of the experimental set-up was chosen according to a similar experiment made at the University of Valladolid (Spain) [13]. The experimental set-up consisted of a 5 L activated sludge reactor connected to a 16 L circular settler. In the activated sludge reactor a magnetic stirrer and an aeration pump was used to ensure a complete mixing in all the reactor. In the settler a stirrer was placed to prevent the creation of preferred paths and to ensure good recirculation of the sludge. In figure 1 can be seen a diagram of the experimental set-up.

The activated sludge reactor was fed with sludge from the wastewater treatment plant of Valladolid. The system was operated indoors at the Department of Chemical Engineering and Environmental Technology of University of Valladolid (Spain) at 23±1 °C.




| Code | Equipment | Code | Equipment |
|---|---|---|---|
| R1 | Reactor | P1 | Inlet Pump |
| S1 | Settler | P2 | Reactor-Settler Pump |
| V1 | Oxygen Valve | P3 | Recirculation Pump |
| V2 | Purge Valve | P4 | Oxygen Pump |
| MS1 | Magnetic Stirrer | TS1 | Timed Stirrer |

**Figure 1:** Diagram of Experimental set-up

### 2.2 Operational conditions

The experiment was divided into two parts. The first stage is a preliminary stabilization of the system, in which it comes to system conditions as similar as possible to the operational conditions of a wastewater treatment plant. The reactor IF was made with synthetic sewage as recommended formula by the Environmental Protection Agency (EPA) [14]. The feed compounds and concentration are listed in Table 1.

**Table 1:** Feed Compounds and Concentration

| Ingredient | Concentration (mg/L) |
|---|---|
| Casein Peptone | 8.18 |
| Meat Extract | 5.62 |
| Urea | 3.07 |
| Potassium Hydrogen Phosphate Trihydrate (K2HPO4.3H2O) | 2.86 |
| Sodium Chloride (NaCl) | 0.74 |
| Calcium Chloride Dihydrate (CaCl2.2H2O) | 0.41 |
| Magnesium Sulfate Heptahydrate (Mg2SO4.7H2O) | 0.12 |

This preliminary stabilization has a duration of 28 days, the HRT in this stage was maintained constant at a typical value of 4.2±0.2 hours. The recirculation flow (RF) from the settler to the reactor was maintained at 15.8±0.2 L $d^{-1}$ and the purge flow (PF) of the settler was maintained at 0.1±0.05 L $d^{-1}$.

The second stage is the one where PPCPs were included in the IF of the system. For these were selected six compounds, these are: Ibuprofen, Propylparaben, Salicylic Acid, Naproxen, Triclosan and Diclofenac. The selection of these compounds was due to their percentage of biodegradability, adsorption percentage and their solubility.

The design of the experiment was performed using the Taguchi Method of Quality Control [15]. This method uses standard arrays, called orthogonal arrays, that stipulates the minimal number of experiments which could give the full information of all the factors that affect the performance parameter [15].

The orthogonal array was developed taking into account three control factor´s; HRT, MCRT and RF, and two noise factors; COD in the IF and CC in the IF. This resulted in a design of 16 experiments. The orthogonal array for these experiments is presented in Table 2, where “1” means a lower parameter values and “2” means higher parameter values.

**Table 2:** Orthogonal Array

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | | | | |
| 1 | 2 | 2 | | | | |
| 2 | 1 | 2 | | | | |
| 2 | 2 | 1 | | | | |

The row CC taking into account a mixture of the six pharmaceutical compounds, each one of them in a low value or high value depending of the experiment to be performed. The order of the experiments begin with the lowest values of COD, CC and HRT, and finished with the highest values of COD, CC, and HRT. Table 3 represented the order of the experiments.

**Table 3:** Order of Experiments

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | **1** | **3** | **9** | **11** |
| 1 | 2 | 2 | **2** | **4** | **10** | **12** |
| 2 | 1 | 2 | **5** | **7** | **13** | **15** |
| 2 | 2 | 1 | **6** | **8** | **14** | **16** |

The values of HRT, MCRT, RF, COD, and CC for lowest and highest values are represented in Table 4 and Table 5 respectively. The value of each compound was designed taking into account the typical values that are in the different wastewater treatment plant in Spain [2] [7] [16].

**Table 4:** Lower Parameter Values "1"

| | | |
|---|---|---|
| **IF** | L $d^{-1}$ | 22.00 |
| **PF** | L $d^{-1}$ | 0.75 |
| **RF** | L $d^{-1}$ | 15.80 |
| **HRT** | h | 4.91 |
| **MCRT** | D | 6.00 |
| **COD** | mgO2 $L^{-1}$ | 400.00 |
| **Ibuprofen** | µg $L^{-1}$ | 8.10 |
| **Propylparaben** | µg $L^{-1}$ | 0.25 |
| **Salicylic Acid** | µg $L^{-1}$ | 21.60 |
| **Naproxen** | µg $L^{-1}$ | 0.50 |
| **Triclosan** | µg $L^{-1}$ | 0.28 |
| **Diclofenac** | µg $L^{-1}$ | 0.24 |

**Table 5:** Higher Parameter Values "2"

| | | |
|---|---|---|
| **IF** | L $d^{-1}$ | 15.00 |
| **PF** | L $d^{-1}$ | 0.45 |
| **RF** | L $d^{-1}$ | 10.10 |
| **HRT** | h | 7.20 |
| **MCRT** | D | 10.00 |
| **COD** | mgO2 $L^{-1}$ | 800.00 |
| **Ibuprofen** | µg $L^{-1}$ | 12.10 |
| **Propylparaben** | µg $L^{-1}$ | 0.37 |
| **Salicylic Acid** | µg $L^{-1}$ | 32.40 |
| **Naproxen** | µg $L^{-1}$ | 5.00 |
| **Triclosan** | µg $L^{-1}$ | 0.40 |
| **Diclofenac** | µg $L^{-1}$ | 0.36 |

### 2.3 Sampling and analytical procedures

a) First Stage

At this stage the following parameters were determined are: pH, temperature, dissolved oxygen (DO), COD, volatile suspended solids (VSS) and total suspended solids (TSS). The VSS and TSS were analyzed using the gravimetric method [17]. The COD was determined by the closed reflux method with dichromate as strong oxidant [18].

b) Second Stage

At this stage the following parameters were determined: COD, concentration of each compound in the IF and concentration of each compound in the effluent flow (EF). The COD was determined by the closed reflux method with dichromate as strong oxidant [18].

For the determination of the CC in IF and EF was used the technique of Gas Chromatography coupled to a single quadrupole Mass Spectrometry (GC-MS) with a Fiber Derivatization on Solid Phase Micro Extraction (SPME). The chromatography was performed by an Agilent 7890B GC system coupled to a 5977A MSD.

To each sample of IF and EF (100 mL) were added NaCl at 35% (wt./vol). After stirring for 20 min, the resulting sample pH was adjusted to 3 by adding few drops of HCl

(0.01%, 0.1% or 1%) as needed. Seventeen milliliters of the resulting solution were placed into a 20 mL SPME vial with 200 µL of aqueous mixture of the isotopically labelled internal standards of the six compounds.

The resulting vial was analyzed by the SPME method that consisted on a fiber preconditioning of 15 min at 270 ºC in the spare GC inlet, followed by 90 min of sample extraction at a penetration depth set at 60 mm. Next one fiber derivatization of the analytes absorbed into the fiber was carried out by introducing it for 45 min in another 20 mL SPME vial containing 1 mL of the derivatizing agent MTBSTFA at a penetration depth of 45 mm. These derivatizations took place with a constant temperature of 50 ºC and a stirring speed of 350 rpm with a cadence of 6s on and 30s off. Then the fiber was taken to the GC inlet at 270 ºC for 3 min. Finally the fiber was post conditioned for 15 min at 270 ºC in the spare GC inlet. The total analysis time for each GC run was 33.5 min.

This method was developed in a research at the University of Valladolid and the validation of the same was developed in this experiment.

At this stage also were determined: pH, temperature, DO, VSS and TSS. The VSS and TSS were analyzed using the gravimetric method [17].

The total analysis time in the GC of 33.5 min was divided into 3 different sections of time, the objective of this is to shows perfectly the exit of the characteristic ion of each compound into the chromatogram.

The first section going from minute 12 to minute 17, in this section we can observe the exit time of the characteristic ion of Ibuprofen, Propylparaben and Salicylic Acid. The second section going from minute 17 to minute 19.5, in this section we can observe the exit time of the characteristic ion of Naproxen and Triclosan. Finally the third section going from minute 19.5 to minute 33.5, in this section we can observe the exit time of

the characteristic ion of Diclofenac. Table 6 shows the retention time of each compound into the chromatogram.

**Table 6:** Retention Time of each Compound

| Compound | Section Time | Retention Time (min) |
|---|---|---|
| **Ibuprofen** | 1 | 13.69 |
| **Propylparaben** | 1 | 14.30 |
| **Salicylic Acid** | 1 | 14.79 |
| **Naproxen** | 2 | 17.97 |
| **Triclosan** | 2 | 18.49 |
| **Diclofenac** | 3 | 20.08 |

## 3. Results and discussion

### 3.1 COD Removal

Table 7 shows the precise values of COD percentage removal for each one of the experiments. The results shows that almost in the 16 experiments we ensure a high percentage removal respect to the IF with the EF.

**Table 7:** COD Removal (%)

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | **46.8** | **87.0** | **90.3** | **90.0** |
| 1 | 2 | 2 | **87.1** | **86.9** | **94.4** | **92.8** |
| 2 | 1 | 2 | **80.5** | **89.1** | **91.2** | **94.7** |
| 2 | 2 | 1 | **88.4** | **89.0** | **94.6** | **78.0** |

Figure 2 shows the evolution of the percentage removal of COD during the entire period of experimentation.

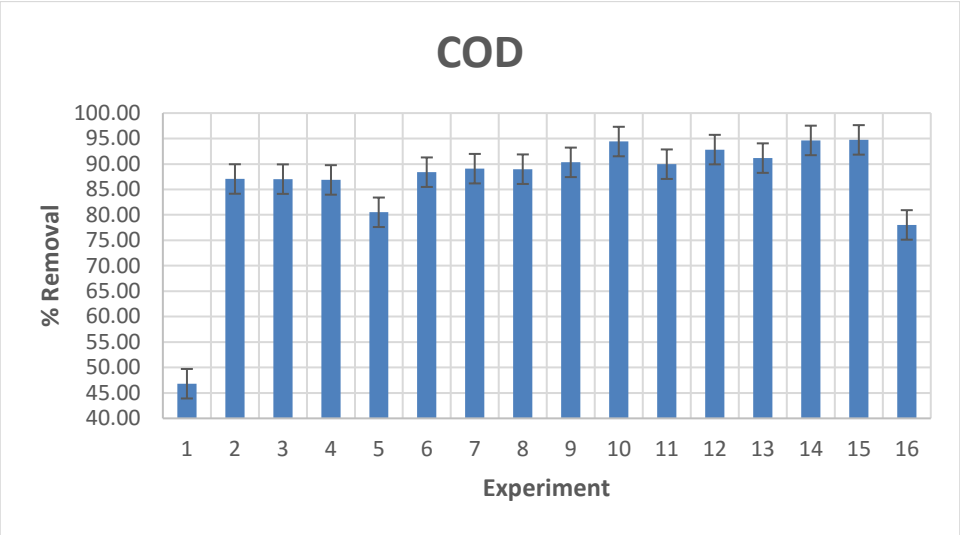



**Figure 2:** Percentage removal of COD

As can be seen in Figure 2 the behavior of the percentage removal of COD was between the 85% and the 95% in almost all the experiments. In the first experiment the income of a newest values of COD and PPCPs made that the system was not stabilized at all, which explain that the value of percentage removal it was so low, only a 46.8%. For the experiment number 16 the percentage removal value can be outside of the range because the parameter values of the control factors and noise factors are not favorable because the system is carried to the maximum limit of operation.

This values of percentage removal of Table 7 were analyzed with the ANOVA Taguchi Method and the Signal/Nose Ratio Taguchi Method.

a) Analysis of Variance Taguchi Method

The Analysis of Variance (ANOVA) Taguchi Method is a standard statistical technique which is used to provide a measure of confidence of the results obtained. This technique does not directly analyze the results, but rather determines the variability of this results [15]. Analysis provides the variance of control and noise factors, by understanding the source and magnitude of variance, robust operating conditions can be predicted.

The ANOVA work with a level of confidence of 95% for the variance ratio of each control factor to be considered like a good control factor. For these the control factor has to have a variance ratio over 4.7472 [15].

Once you analyzed the COD percentage removal with this method we obtained the Table 8 were is represented the ANOVA of Taguchi Method.

**Table 8:** COD ANOVA

| Effect | S | f | V | F |
|---|---|---|---|---|
| HRT | 57.0 | 1.0 | 57.0 | 0.4155 |
| MCRT | 108.0 | 1.0 | 108.0 | 0.7871 |
| RF | 172.3 | 1.0 | 172.3 | 1.2551 |
| Error | 1647.1 | 12.0 | 137.3 | 1.0000 |
| Total | 1984.4 | 15.0 | | |

Where *S* is Sum of Squares, *f* is Degrees of Freedom, *V* is Variance and *F* is Variance Ratio.

Analyzing the values of the Variance Ratio (F) in Table 8 we can see that these values are bellow that the expected value for the 95% level of confidence of the ANOVA. With this we can concluded that the 3 controls factors, in the parameters values analyzed, that are the typical values in the wastewater treatment plant in Spain, does not affect in a statistical way the process and can be considered like an error. This mean that exist some other control factors that has not taken into account that affects in a higher way the process.

b) Signal/Noise Ratio Taguchi Method

The ratio between the signal power and the noise power (S/N) is a way to analyzed the results obtained in the experiments using the Taguchi Method. The S/N Ratio uses a relation that said “Larger is Better”, this mean that the larger the target value is the better is the response of the system. For This S/N Ratio we used the following equation.

$$\frac{S}{N} = -10 * \log_{10} \frac{\sum_{i=1}^{n} \frac{1}{Y_i^2}}{n}$$

Where $n$ means the total number of experiments and $Y_i$ is the value of percentage removal for each experiment. With this S/N ratio we obtained the average statistics values for the lower parameter value and higher parameter value of HRT, MCRT and RF. Table 9 shows the average statistics values of lower parameter value and higher parameter value. Figure 3 shows average statistics values respect to the lower and higher parameters.

**Table 9:** S/N Values for COD

| | HRT | MCRT | RF |
|---|---|---|---|
| **Lower Parameter (1)** | 38.0 | 37.9 | 37.8 |
| **Higher Parameter (2)** | 38.9 | 38.9 | 39.0 |

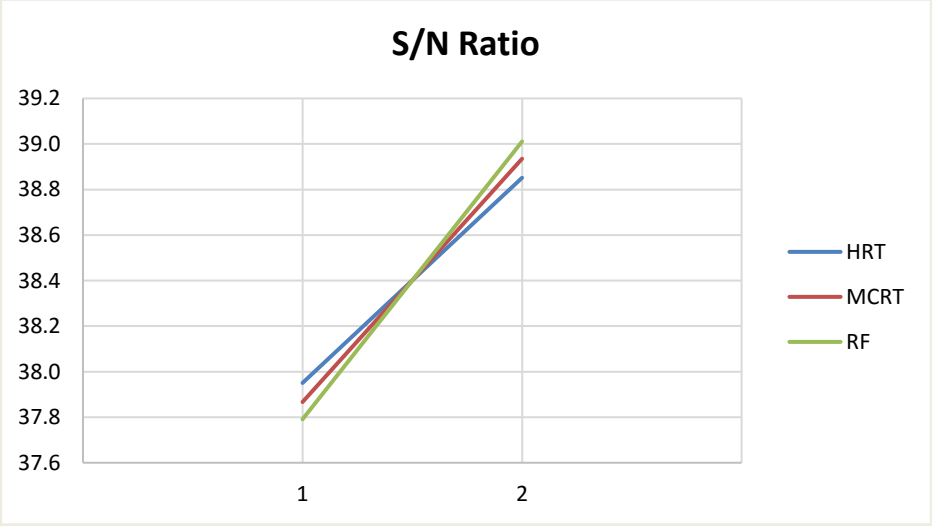



**Figure 3:** Values of S/N Ratio respect to the lower and higher parameters

Analyzing the results it can be concluded that for the COD removal the best option for experimentation is one where we have a higher parameter value of HRT, a higher parameter value of MCRT and a higher parameter value of RF.

### 3.2 PPCPs Removal

The values of PPCPs removal were obtained after analyzed the IF and EF in the GC-MS, the statistical analysis was made using a Mass Hunter Qualitative Analysis and a Mass Hunter Qualitative Analysis.

Figure 4 is an example of the chromatogram for IF and EF of the experiment number 7.

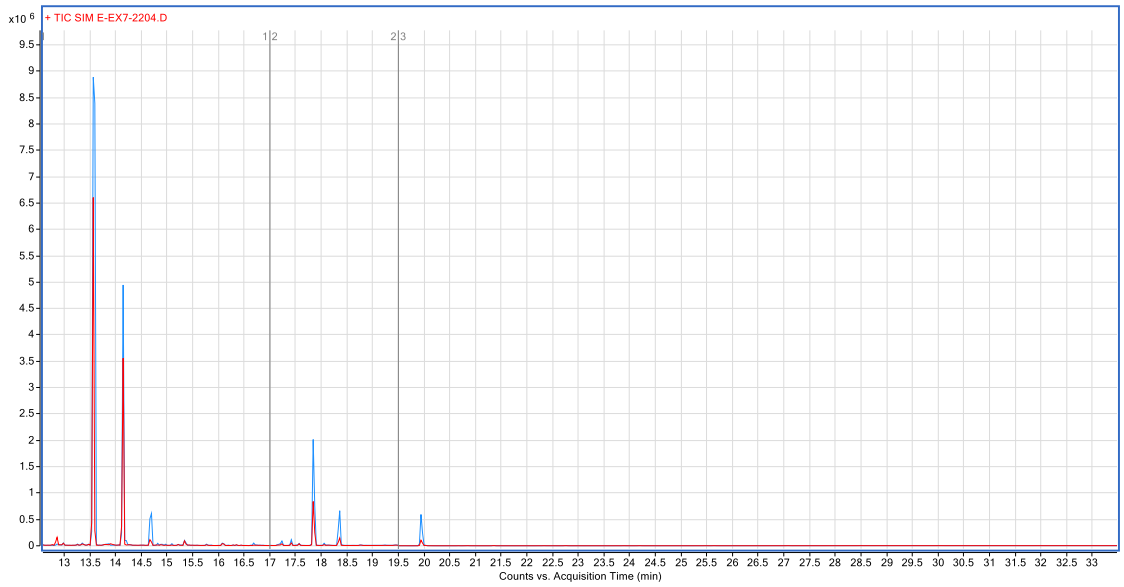



**Figure 4:** IF and EF Chromatogram - Experiment 7

In figure 4 you can see how was the behavior of the percentage removal for each compound between the IF and the EF, as can see there for some of them the percentage elimination it is significant.

In Tables 10, 11, 12, 13, 14 and 15 shows the precise values of CC percentage removal for Ibuprofen, Propylparaben, Salicylic Acid, Naproxen, Triclosan and Diclofenac, respectively, for each one of the 16 experiments.

**Table 10:** Ibuprofen % Removal

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | 65.5 | 39.6 | 92.5 | 76.2 |
| 1 | 2 | 2 | 86.4 | 61.7 | 83.3 | 76.0 |
| 2 | 1 | 2 | 95.6 | 96.6 | 97.0 | 90.1 |
| 2 | 2 | 1 | 93.2 | 92.0 | 97.1 | 74.9 |

**Table 11:** Propylparaben % Removal

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | 88.5 | 75.8 | 67.9 | 52.6 |
| 1 | 2 | 2 | 72.8 | 94.3 | 72.5 | 53.2 |
| 2 | 1 | 2 | 0.0 | 57.8 | 60.3 | 19.1 |
| 2 | 2 | 1 | 94.8 | 84.5 | 95.2 | 94.9 |

**Table 12:** Salicylic Acid % Removal

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | 86.5 | 89.2 | 86.0 | 94.5 |
| 1 | 2 | 2 | 86.8 | 12.2 | 95.7 | 77.9 |
| 2 | 1 | 2 | 84.7 | 88.7 | 3.3 | 3.1 |
| 2 | 2 | 1 | 96.8 | 95.7 | 2.8 | 7.5 |

**Table 13:** Naproxen % Removal

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | 69.2 | 69.8 | 64.9 | 40.5 |
| 1 | 2 | 2 | 60.4 | 80.0 | 56.4 | 34.2 |
| 2 | 1 | 2 | 83.4 | 8.3 | 70.0 | 72.0 |
| 2 | 2 | 1 | 6.7 | 85.1 | 70.7 | 74.4 |

**Table 14:** Triclosan % Removal

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | 65.5 | 68.7 | 83.3 | 70.3 |
| 1 | 2 | 2 | 55.7 | 16.9 | 71.7 | 54.1 |
| 2 | 1 | 2 | 0.0 | 76.5 | 73.1 | 93.5 |
| 2 | 2 | 1 | 53.2 | 86.0 | 92.5 | 48.0 |

**Table 15:** Diclofenac % Removal

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | 47.0 | 20.0 | 15.3 | 21.7 |
| 1 | 2 | 2 | 23.7 | 0.2 | 5.5 | 87.5 |
| 2 | 1 | 2 | 89.6 | 15.7 | 29.5 | 100.0 |
| 2 | 2 | 1 | 10.5 | 50.0 | 9.0 | 14.9 |

There is an important observation that we made for the experiment number five and it is that for some compounds were obtained a lower values of percentage removal, for this reason it was determined to repeat the analysis and was determinate that for second time the values of percentage removal was the same.

Figures 5, 6, 7, 8, 9, and 10 shows the time evolution of the percentage removal for Ibuprofen, Propylparaben, Salicylic Acid, Naproxen, Triclosan and Diclofenac, respectively, during the entire period of experimentation.

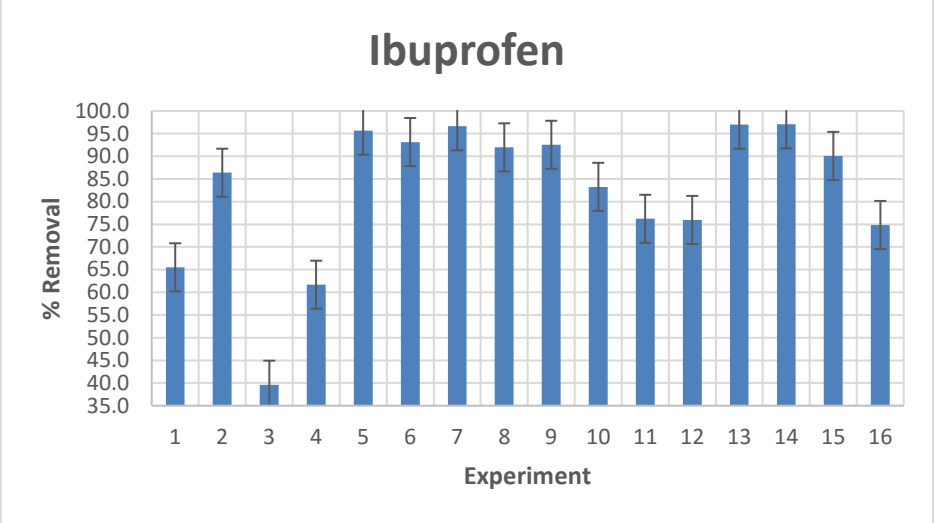



**Figure 5:** Percentage removal of Ibuprofen

As can be seen in Figure 5 the behavior of the percentage removal of Ibuprofen was between the 75% and 95% in almost all the experiments. Only in experiments 1, 3 and 4 this behavior change reaching minimal values of 40%.

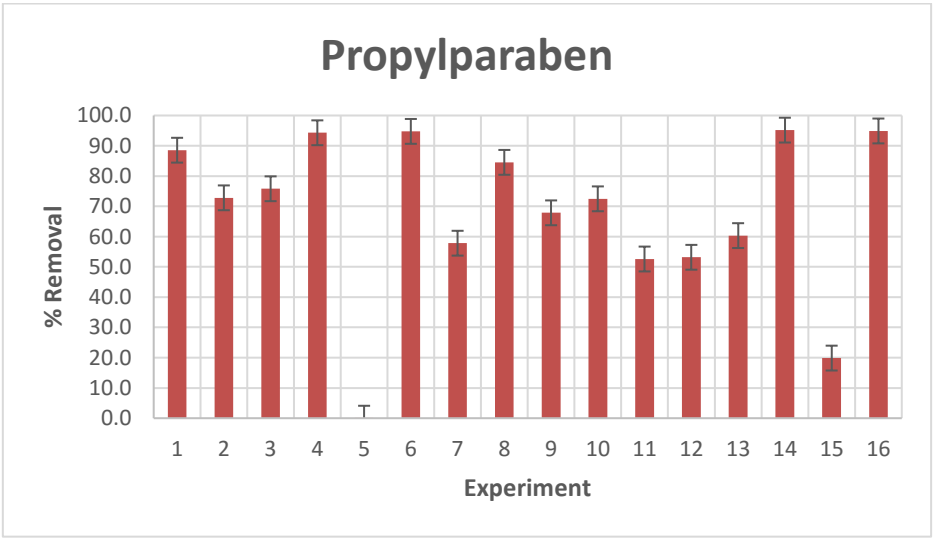



**Figure 6:** Percentage removal of Propylparaben

As can be seen in Figure 6 the percentage removal of Propylparaben it not have a standard behavior in the experiments, reaching extremely low values such as 0% and otherwise extremely high values such as 94.9%.

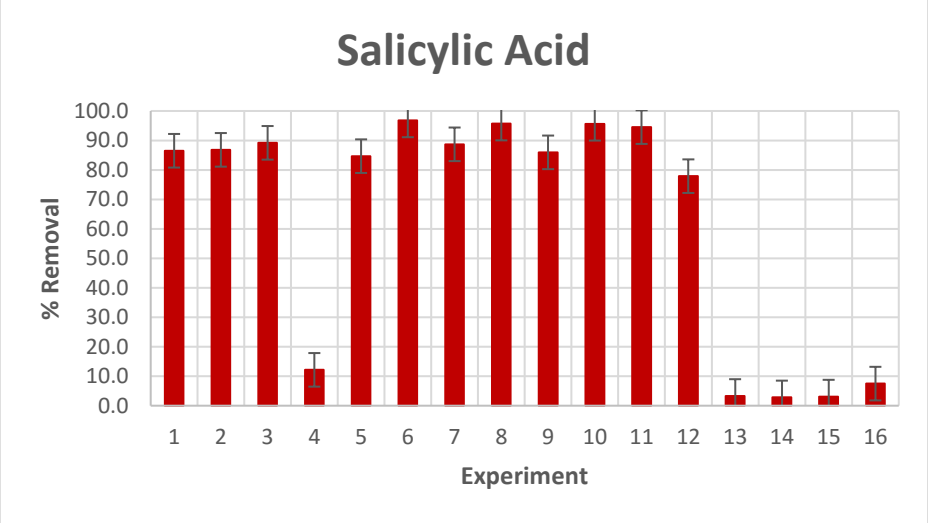



**Figure 7:** Percentage removal of Salicylic Acid

As can be seen in Figure 7 the behavior of the percentage removal of Salicylic Acid was between the 85% and 97% in almost all the experiments. In experiments 13 to 16 can be seen a decrease in these values, reaching values between 2% and 8%, this because the parameter values of the control factors and noise factors are not favorable because the system is carried to the maximum limit of operation.

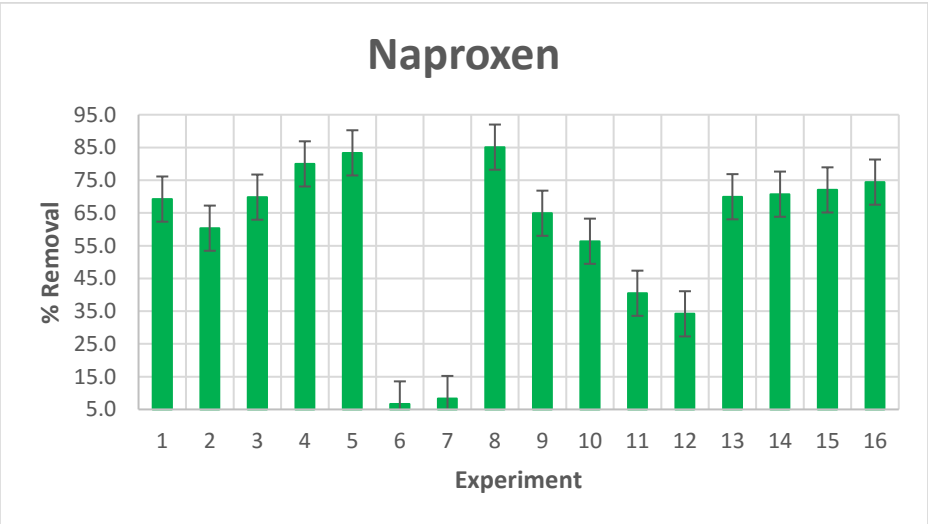



**Figure 8:** Percentage removal of Naproxen

As can be seen in Figure 8 the behavior of the percentage removal of Naproxen was between the 55% and 85% in almost all the experiments. In experiments 6 and 7 can be seen a decrease in these values, reaching values between 6% and 8%, this because the parameter values of the control factors and noise factors are not favorable.

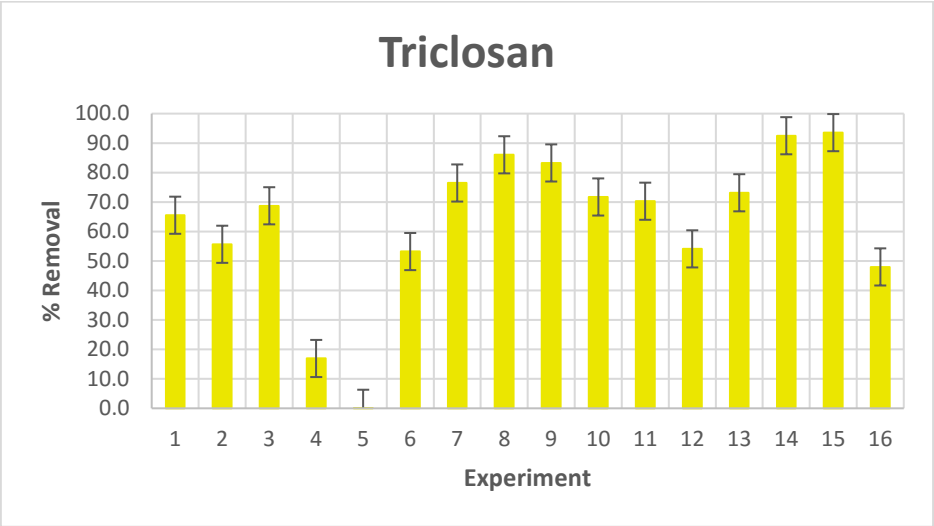



**Figure 9:** Percentage removal of Triclosan

As can be seen in Figure 9 the percentage removal of Triclosan it not have a standard behavior in the experiments, reaching extremely low values such as 0% and otherwise extremely high values such as 92.5%.

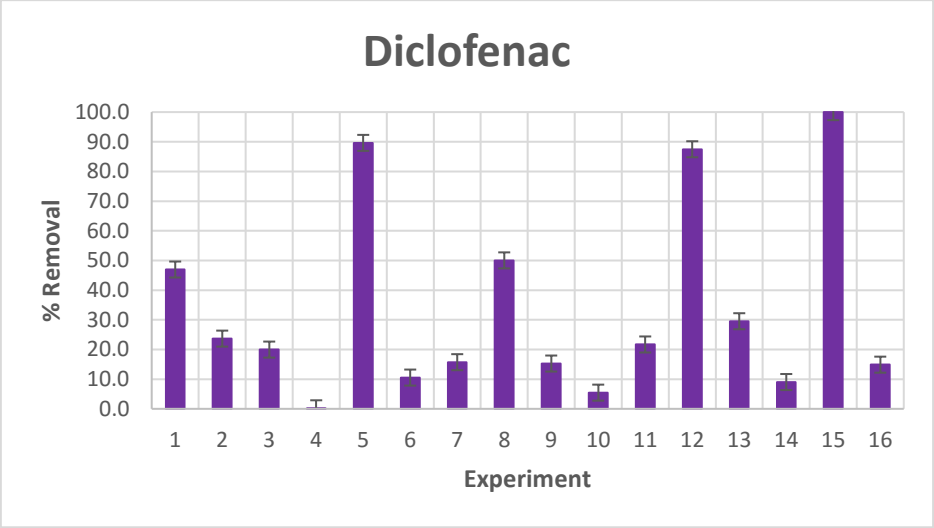



**Figure 10:** Percentage removal of Diclofenac

As can be seen in Figure 10 the percentage removal of Diclofenac it not have a standard behavior in the experiments, reaching extremely low values such as 0.2% and otherwise extremely high values such as 100%.

As can be seen in the below figures we do not have the same behavior in the percentage removal for all the compounds in the same experiments. For example, in experiment number 6 we have a 93.2% removal for Ibuprofen, 94.8% removal for Propylparaben, 96.8% removal for Salicylic Acid, but only a 53.2% removal for Triclosan, 10.5% removal for Diclofenac and 6.7% removal for Naproxen.

For these reason and as the goal of the experimentation it is to have the higher value of percentage removal of each compound in an only one experiment as a mix of them, we decide that for the application of Taguchi Method we have to made an average of the values of percentage removal of the 6 compounds. Table 16 shows the precise values of CC percentage removal for the mixture of the 6 compounds.

**Table 16:** Mix % Removal

| | | COD | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| | | CC | 1 | 1 | 2 | 2 |
| HRT | MCRT | RF | | | | |
| 1 | 1 | 1 | 70.4 | 60.5 | 68.3 | 59.3 |
| 1 | 2 | 2 | 64.3 | 44.2 | 64.2 | 63.8 |
| 2 | 1 | 2 | 58.9 | 57.3 | 55.5 | 63.0 |
| 2 | 2 | 1 | 59.2 | 82.2 | 61.2 | 52.4 |

As can be seen in Table 16 the behavior of the percentage removal for the mix of compound was between the 55% and 70% in almost all the experiments. In experiment number 8 are achieved the higher percentage removal for the mix of compound, for these reason we can concluded that this is the best experiment of all.

This values of percentage removal of Table 16 were analyzed with the ANOVA Taguchi Method and the Signal/Nose Ratio Taguchi Method.

a) Analysis of Variance Taguchi Method

Once you analyzed the PPCPs percentage removal as the same way that analyzed the COD percentage removal we obtained the Table 17 were is represented the ANOVA of Taguchi Method.

**Table 17:** PPCPs ANOVA

| Effect | S | f | V | F |
|---|---|---|---|---|
| HRT | 1.7 | 1.0 | 1.7 | 0.0224 |
| MCRT | 0.2 | 1.0 | 0.2 | 0.0023 |
| RF | 112.6 | 1.0 | 112.6 | 1.4759 |
| Error | 915.8 | 12.0 | 76.3 | 1.0000 |
| Total | 1030.3 | 15.0 | | |

Analyzing the values of the Variance Ratio (F) in Table 17 we can see that these values are bellow that the expected value for the 95% level of confidence of the ANOVA. With this we can concluded that the 3 controls factors, in the parameters values analyzed, that are the typical values in the wastewater treatment plant in Spain, does not affect in a statistical way the process and can be considered like an error. This means that exist some other control factors that has not taken into account that affects in a higher way the process.

b) Signal/Noise Ratio Taguchi Method

The S/N Ratio used was one more time the relation that said “Larger is Better”, this mean that the larger the target value is the better is the response of the system. For This S/N Ratio we used the following equation.

$$\frac{S}{N} = -10 * \log_{10} \frac{\sum_{i=1}^{n} \frac{1}{Y_i^2}}{n}$$

Where $n$ means the total number of experiments and $Y_i$ is the value of percentage removal for each experiment. Table 18 shows the average statistics values of lower

parameter value and higher parameter value. Figure 11 shows average statistics values respect to the lower and higher parameters.

**Table 18:** S/N Values for Mix of compound

| | HRT | MCRT | RF |
|---|---|---|---|
| **Lower Parameter (1)** | 35.6 | 35.7 | 35.9 |
| **Higher Parameter (2)** | 35.5 | 35.4 | 35.2 |

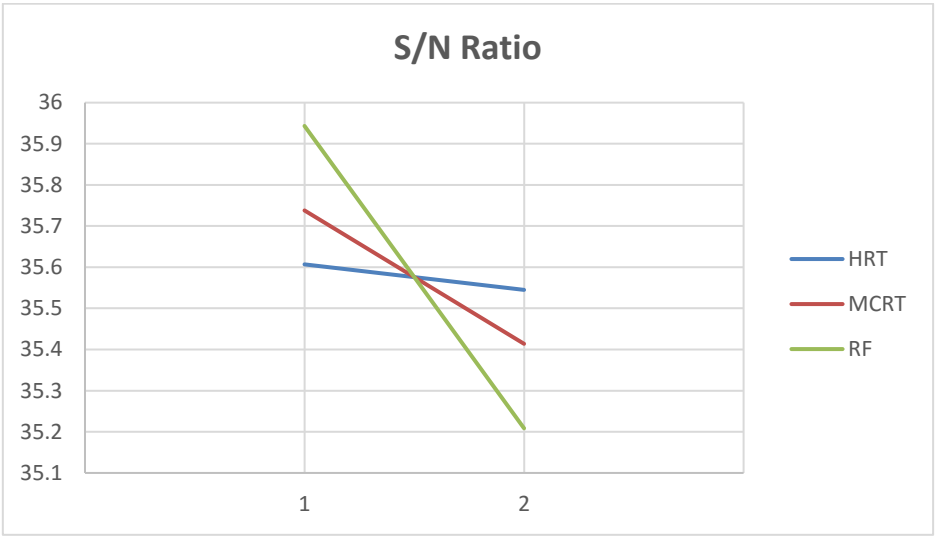



**Figure 11:** Values of S/N Ratio respect to the lower and higher parameters

Analyzing the results it can be concluded that for the removal of CC the best option for experimentation is one where we have a lower parameter value of RF, a lower parameter value of MCRT and a lower o higher parameter value of HRT.

It can be observed that the results obtained for PPCPs removal are totally different to the obtained for COD.

## 4. Conclusions

The research was successfully applied in a pilot scale of completely mixed aerobic activated sludge reactor. This research work development a method for the analysis of 6 different PPCPs in a wastewater and confirm the ability to remove it, with values of

97.1 % for Ibuprofen, 95.2% for Propylparaben, 96.8% for Salycilic Acid, 85.1% for Naproxen, 92.5% for Triclosan and 100% for Diclofenac in the optimal conditions studied. For the worst conditions we obtained values of 39.6 % for Ibuprofen, 0.0% for Propylparaben, 2.8% for Salycilic Acid, 6.7% for Naproxen, 0.0% for Triclosan and 0.2% for Diclofenac.

It has been determinate the possibility to remove a mix of compounds in only one process at the same time, with the same operating conditions for all of them, with values of percentage removal above of 85% for the optimal conditions studied and a 44% for the worst conditions.

With this we use the Taguchi Method of Quality Control and determinate that this analysis can be used for another compounds and evaluate the removal capacity for each compound. The results obtained after the analysis with the ANOVA Taguchi Method lead us to the conclusion that under these typical operational conditions the HRT, MCRT and RF have no a statistically significance influence on PPCPs removal. To determine this influence would be necessary structure of orthogonal array.

## 5. Acknowledgments

The authors would like to thank the Environmental Technology Group of the University of Valladolid for supporting this research and National Pedagogical University - Francisco Morazán, Honduras for the scholarship grants. To R. López Serna for her practical assistance.

**REFERENCES**

[1] L. D. Barceló, M. J. L. de Alda, Contaminación y calidad química del agua: el problema de los contaminantes emergentes. Informes CSIC, (2011)

[2] S. Ortíz de García, P. García Encina, R. Irusta Mata, Comsumption and occurence of pharmaceutical and personal care products in the aquatic environment in Spain. Science of the Total Environment, 444 (2013) 451-465

[3] C. J. Cartagena, Contaminantes orgánicos emergentes en el ambiente: productos farmacéuticos. Revista Lasallista de Investigación, 8 (2011) 2

[4] C. García Gómez, P. Drogui, Contaminantes emergentes: efectos y tratamientos de remoción. Revista Química Viva, 10 (2011) 96-105

[5] K. A. Strauch, Invisible pollution the impact of pharmaceuticals in the water supply. AAOHN, 59 (2011) 525-532

[6] M. Zupanc, M. Petkovšek, M. Dular, B. Kompare, Removal of pharmaceuticals from wastewater by biological processes, hydrodynamic cavitation and uv treatment. Ultrasonics sonochemistry, 3 (2012)

[7] C. Reyes Contreras, I. Ruiz, M. Soto, J.M Bayona, Evaluation of PPCPs removal in combined anaerobic digester-constructed wetland pilot plant treating urban wastewater. Chemosphere, 84 (2011) 1200-1207

[8] C. Zwiener, F. H. Friemmel, Short-term test with a pilot sewage plant and biofilm reactors for the biological degradation of the pharmaceutical compounds clofibric acid, ibuprofen and diclofenac. Science of the Total Environment, 309 (2003) 201-211

[9] C. Zwiener, F. H. Friemmel, LC-MS analysis in the aquatic environment and in water treatment – A critical review: Part I: Instrumentation and general aspects of analysis and detection. Analytical and Bioanalytical Chemistry, 378 (2004) 851-861

[10] A. Ballesteros Gómez, S. Rubio, Recent advances in environmental analysis. Analytical Chemistry, 83 (2011) 4579-4613

[11] A. Peña Álvarez, A. Castillo Alanis, Identificación y cuantificación de contaminantes emergentes en aguas residuales por microextracción en fase sólida-cromatografía de gases-espectrometría de masas (MEFS-CG-EM), TIP. Revista Especializada en Ciencias Químico-Biológicas, 18 (2015) 29-42

[12] G. Basaglia, M. C. Pietogrande, Optimization of a SPME/GC/MS method for the simultaneous determination of pharmaceuticals and personal care products in waters. Chromatographia, 75 (2012) 361-370

[13] J. Zambrano, Estudio de Ecotoxicidad y Biodegradabilidad de Ibuprofeno en un reactor aerobio de lodos activos de mezcla completa. Universidad de Valladolid (2013)

[14] Environmental Protection Agency (EPA), Transport and transformation test guidlines. OPPTS 835.3240 Simulation test – aerobic sewage treatment: a activated sludge units (2008)

[15] R. Roy, A primer on Taguchi Method (1990)

[16] C. Reyes Contreras, M. H. Valsero, R. Sidrach Cardona, J. M. Bayona, E. Bécares, Temporal evolution in PPCP removal form urban wastewater by constructed wetlands of different configuration: A medium-term study. Chemosphere, 88 (2012) 161-167

[17] American Public Health Association (APHA), Standard Methods for the examination of water and wastewater. 20 (1998)

[18] Universidad de Valladolid, Procedimiento normalizado de trabajo PNT-14-01 DQO (2013)