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**Analysis of changes introduced by final draft (2014) of reference
document “Common Waste Water and Waste Gas Treatment”
Application to wastewater treatments.**

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O. ABSTRACT

Within the work, an analysis of the changes appearing in the final draft (2014) compared with the actual reference 2003 document is presented. In order to detect the differences, it can be seen that there are no big distinctions regarding to the global structure. In both of them a general description is done about waste water, including general information about management systems and its treatment in the chemical industry. On 2003 document it is described the environmental and effluents management. On the other hand, 2014 document provides data and information about the environmental performance of Waste Water Treatment Plants (WWTPs). Regarding chemical industries; both documents explain all the techniques used for waste water treatments. It is important to stand out that in 2014 document there are 9 new techniques that don't appear in 2003 document.

In 2003 document, it is explained the BAT for each kind of pollutant, while in case of 2014 document it is said that BAT's conclusions are based in different sections of the previous chapter.

The associated emission levels for these BATs are narrower for 2014 document.

In 2014 document, there are six new emergent techniques in comparison with 2003 document, which deal with briefly only about one emergent technique, which appear as consolidated technique in 2014 document.

Finally, it has been more deeply analysed the emergent technique "Naturally Improved Microorganisms to Treat Refractory TOC/COD". This technique consists in improving microorganisms such as: prokaryotic cells (bacteria) or eukaryotes (yeasts, fungi and photosynthetic microalgae); to treat waste waters loaded with refractory TOC/COD.

Keywords: refractory TOC/COD, Bio-ROCs, Acclimation, Biostimulation, Bioaugmentation.

1. INTRODUCTION

It is important to know the problems regarding to wastewater produced in the chemical industries and the environmental impact that can cause. In this work, it is pretended to make a comparative analysis of the Best Available Techniques (BAT) in the treatment of wastewater in the chemical industry. These BAT's are proposed in the final draft of the 2014 "Common Waste Water and Waste Gas Treatment / Management Systems in the Chemical Sector" and are compared with the ones proposed in the actual reference document (2003) corresponding to the Integrated Pollution Prevention and Control directive of the European Union. These BAT's permit to analyse the levels of performance that can be obtained using these techniques and establish the emission levels.

In the last years, several new organic compounds have reached surface water and other aqueous bodies through intensive human activities such as petroleum and its derivatives, chlorinated and phenolic pesticides and industrial wastes, most of synthetic dyes, polyaromatic hydrocarbons, and active pharmaceutical compounds.

Different research studies indicated that some of these molecules are persistent in treated water because they are refractory to conventional biological treatment. They are called "Bio-Refractory Organic Compounds (Bio-ROCs)". This is mainly due to their toxicity that inhibits microbial metabolism completely or partially. That is the reason why it is been innovated with emerging techniques that allow to remove these new pollutants.

2. OBJECTIVES

The main objective of this work is to analyse the changes appearing in the final draft (2014) of the BREF (Best Available Techniques Reference Document) on waste water treatment and management in the chemical sector as compared with the actual reference document of 2003. Particularly the new BAT conclusions will be analysed and their influence on associated emission levels will be studied.

The overall objective will be addressed through the following sub-objectives:

- To detect what best available techniques for waste water treatments of the final draft (2014) are new respect to the actual reference document (2003)
- To deduce and summarize how these new techniques affect to emission limits indicated in the final draft (2014).
- To analyse in a deeper way the emergent technique: Naturally Improved Microorganisms to Treat Refractory TOC/COD.

3. ANALYSIS OF THE GLOBAL STRUCTURE OF BOTH DOCUMENTS.

In chapter 1 of both documents, a general description about residual water it is provided, including general information regarding to management systems and to the treatment in chemical industry. Document 2014 afford us a more detailed analysis about emissions of halogens, organic compounds, nutrients(nitrogen, phosphorus) and metals to water; giving a vision related to the relative importance of a specific pollutant to a particular industrial sector, as well as talks us about chemical industry and its relevance.

In chapter 2, it can be observed that document 2003 talks about Waste Water Management, Environmental Management Systems (EMS), stock management tools, operational management, strategic management, security and emergency tools. On the other hand, document 2014; provide very detailed information and data about the environmental performance of Waste Water Treatment Plants (WWTPs), chemical facilities, in terms of actual emissions, consumption, and the origin of raw materials, water consumption; analysis of the parameters (COD, TOC, BOD, COD, BOD5, TS, AOX, metals, nitrogenous compounds, phosphorus compounds, phenols, toxicity, etc.)

Chapter 03 of both documents provides a description of the most common Waste Water Treatment Techniques in the chemical sector; this techniques include a recuperation process divided in: Insoluble contaminants, /**mechanic separation**; soluble non-biodegradable or inhibitors contaminants/ **physic-chemical treatment**; soluble biodegradables contaminants/ **biological treatments**. In 2014 document, some techniques to avoid or reduce the impact on the nature of operative facilities are described in a deeper way, and were considered in order to determine the BAT; including **emission levels and consumption that can be achieved through the use of the technique**.

Chapter 4 of both document deals about the Best Available Techniques (BAT) for waste water treatment / management in the chemical sector, however in 2014 document talks about BAT conclusions. These conclusions cover the following topics:

- Environment management systems.
- Safe of water.
- Collection, treatment and wastewater management.
- Waste management.

Chapter 05 of both documents speaks about emerging techniques. It can be highlighted just one in 2003 in contrast with the six of 2014 document.

Chapter 06 of both documents are about conclusions and recommendations.

As it can be seen from analysis above, the global structure of the two documents is very similar, however content of chapter 2 is very different from one document to the other.

4. ANALYSIS OF WASTE WATER TREATMENT IN THE TWO DOCUMENTS.

4.1 Analysis of all waste water treatment techniques.

The techniques identified and described in the documents are those that are common in the chemical sector as a whole. They are introduced in a logical order, which follows the pollutant path.

The described Waste Water Treatment Techniques are:

- 1. Separation or clarification techniques:** which are mainly used in combination with other operations, either as a first step (to protect other treatment facilities against damage, clogging or fouling by solids) or a final clarification step (to remove solids or oil formed during a preceding treatment operation):

Grit separation	Sedimentation	air flotation
Microfiltration/Ultrafiltration	Oil – water separation	Filtration

In 2014 document it can be seen that two more techniques have been added:

Hydrocyclone	Electrocoagulation
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- 2. Physico-chemical treatment techniques** for non-biodegradable waste water, mainly used for inorganic or hardly biodegradable (or inhibitory) organic contaminants, often as a pre-treatment upstream of a biological (central) waste water treatment plant:

Physico - Chemical Treatment Techniques	
Adsorption	Hydrolysis
Chemical oxidation	Incineration
Chemical reduction	Ion exchange
Crystallization	Precipitation/sedimentation /filtration
Distillation / rectification	Nanofiltration / Reverse osmosis
Evaporation	Stripping
Extraction	Wet air oxidation

In 2003 document we have “*super-critical water oxidation*” as a technique already consolidated, however this appears in 2014 document as an emergent technique. In 2014 document it can be seen that four new techniques have been added:

Electrodialysis	Electrolysis
Pertraction	Pervaporation

3. **Biological treatment techniques** for biodegradable waste water:

Anaerobic treatment	Anaerobic treatment	Nitrogen removal by biological nitrification/denitrification
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In 2014 document it can be seen that three more techniques have been added:

Enhanced biological phosphorous removal	Phosphorous removal by chemical precipitation	Biological removal of sulphur compounds/heavy metals*
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*The last technique appears as emerging technique in 2003 document.

As it can be seen, many techniques are common to both documents, but 2014 document present some new techniques.

4.2 Analysis of the BATs for waste water treatment

In 2003 document, it is explained the BAT for each type of contaminant but in 2014 document is mentioned that the BAT conclusions are based in the different sections of the previous chapter.

Document 2003

Rainwater

Duct uncontaminated rainwater directly to a receiving water, by-passing the waste water sewerage system. Treat rainwater from contaminated areas before discharging it into a receiving water. Appropriate treatment facilities are:

* Grit chamber	* Retention pond
* Sand filter	* Sedimentation tank

Free Oil / Hydrocarbons

Oil/water separation by cyclone, microfiltration or API separator.	Microfiltration	Biological treatment.
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Emulsions

BAT is to break emulsions at source and recover the separated constituents or remove emulsions at source when they cannot be broken and can have adverse effects on downstream facilities.

Total Suspended Solids (TSS)

The ranking of treatment techniques is:

Sedimentation / air flotation to catch the main TSS load	Mechanical filtration for further solids reduction	Microfiltration or ultrafiltration when solid-free waste water is required.
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Heavy metals

The techniques that can be applied to achieve these requirements are:

Precipitation / sedimentation / filtration	Crystallization
Ion exchange	Nanofiltration (or reverse osmosis instead)

Inorganic Salts and/or Acids (Ionic Particles)

Appropriate treatment techniques (not including techniques for treating heavy metals or ammonium salts) are:

Evaporation	Ion exchange
Reverse osmosis	Biological sulphate removal

Pollutants unsuitable for biological treatment

There are the following choice:

- Choice 1: techniques that enable substance recovery:

- Nanofiltration or reverse osmosis.
- Adsorption.
- Extraction.
- Distillation / rectification.
- Evaporation.
- Stripping.

- Choice 2: abatement techniques without need of additional fuel, when recovery is not feasible:

- Chemical oxidation, but care must be taken with chlorine-containing agents
- Chemical reduction
- Chemical hydrolysis

- Choice 3: abatement techniques entailing considerable energy consumption, when there is no other choice to abate toxicity or inhibitory effects or when the process can be operated on a self-sustaining basis:

- Wet air oxidation (low-pressure or high-pressure variant).
- Waste water incineration.

- In cases where water supply and consumption are an environmental issue, techniques will be requiring considerable amounts of cooling water or wet scrubber systems for exhaust air treatment need to be assessed, such as:

- Extraction.
- Distillation / rectification.
- Evaporation.
- Stripping.

Biodegradable substances

Biodegradable substances

Is BAT to remove biodegradable substances by using an appropriate biological treatment system (or an appropriate combination of them), such as:

- Biological pre-treatment to relieve the final central biological waste water treatment plant from high biodegradable load (or as a final polishing step). Appropriate techniques are:

Anaerobic contact process	Upflow anaerobic sludge blanket process
Anaerobic and aerobic fixed-bed process	Anaerobic expanded-bed process
Complete-mix activated sludge process	Membrane bioreactor
Trickling (percolating) filter	Biofilter fixed-bed process

- Nitrification / denitrification when the waste water contains a relevant nitrogen load.
- Central biological treatment, avoiding the introduction of non-biodegradable waste water pollutants, when they can cause malfunction of the treatment system and when the plant is not suitable to treat them.

2014 Document

➤ **Environmental management systems**

BAT 1. In order to improve the overall environmental performance, BAT is to implement and adhere to an Environmental Management System (EMS).

BAT 2. In order to facilitate the reduction of emissions to water and air and the water usage, BAT is to establish and to maintain an inventory of waste water and waste gas streams, as part of the environmental management system.

➤ **Monitoring**

BAT 3. BAT is to monitor key process parameters relevant for emissions to water (e.g. influent to pre-treatment and final treatment) as identified by the inventory of waste

water streams (see BAT 2), including continuous monitoring of waste water flow, pH and temperature.

BAT 4. BAT is to monitor emissions to water in accordance with EN standards with at the minimum frequency given below. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

➤ **Emissions to water**

✓ **Water usage and waste water generation**

BAT 7. In order to reduce the usage of water and the generation of waste water, BAT is to reduce the volume and/or load of waste water streams, to enhance the reuse of waste water within the production process and/or to recover and reuse raw materials.

✓ **Waste water collection and segregation**

BAT 8. In order to prevent the contamination of uncontaminated water and the emissions to water, BAT is to segregate uncontaminated waste water streams from other waste water streams that require treatment.

BAT 9. In order to prevent uncontrolled emissions to water, BAT is to provide an appropriate buffer storage capacity for waste water incurred during other than normal operating conditions based on a risk assessment (taking into account e.g. the nature of the pollutant, the effects on further treatment, and the receiving environment), and to take appropriate further measures (e.g. control, treat, reuse).

➤ **Waste water treatment**

BAT 10. In order to reduce emissions to water, BAT is to use an integrated waste water management and treatment strategy that includes an appropriate combination of the techniques.

BAT 11. In order to reduce emissions to water, BAT is to pre-treat waste water that contains pollutants that cannot be dealt with adequately during final waste water treatment by using appropriate techniques.

BAT 12. In order to reduce emissions to water, BAT is to use an appropriate combination of final waste water treatment techniques.

As it can be seen from the analysis above, the structure of this chapter is very different from one document to the other. While 2003 document describe in detail each specific BAT for each specific pollutant, 2014 document establish only general BAT's, alluding to the previous chapter to choose the specific treatment to be applied.

5. COMPARATIVE ANALYSIS OF THE BAT-ASSOCIATED EMISSION LEVELS FOR EMISSIONS TO WATER IN BOTH DOCUMENTS.

In the following tables, which were elaborated in this work, a comparison of emission levels is shown.

Table N°01 BAT-AELs for direct discharges to a receiving water body

Parameter	2003	2014
	Concentration (mg/l)	Concentration (mg/l)
Total hydrocarbon content	0.05-1.5	
BOD 5	2-20	< 20
COD	30-250	< 30-100
TOC		<10-33
Total suspended solids (TSS)	10-20	5-35
Total nitrogen (TN)		5-25
Total inorganic nitrogen (Ninorg)	5-25	0.5-2
Total phosphorous (TP)	0.5-1.5	0.5-3
Absorbable organically bound halogens (AOX)	0.5-1.5	0.2-1.0

Table N°02 BAT-AELs for direct discharges to a receiving water body (heavy metals)

Parameter	2003	2014
	concentration (µg/l)	concentration (µg/l)
Chromium (expressed as Cr)		5-25
Copper (expressed as Cu)		5-50
Nickel (expressed as Ni)	1000	5-50
Zinc (expressed as Zn)	1000	20-300

As it can be seen, regarding to general parameters the differences are not very significant, with emission parameters, in some cases, slightly lower in 2014 document.

However, regarding to heavy metals, differences are very important. The emission levels are much lower for 2014 document. This decrease in emission levels cannot be attributed to new specific techniques for removing heavy metals, which do not appear in 2014 document. So, probably, the decrease can be explained for the increased awareness of the impact of heavy metals on environment. The new emission levels should be achieved through applying techniques already appearing in 2003 document.

6. COMPARATIVE ANALYSIS OF EMERGING TECHNIQUES DESCRIBED IN BOTH DOCUMENTS.

6.1 EMERGING TECHNIQUES 2003

Biological sulphur dioxide removal from exhaust gas: The biological sulphur dioxide removal system is a combination of a waste gas scrubber (absorber) and a biological waste water treatment facility. In the absorber, the waste gas stream containing sulphur dioxide is brought into contact with washing water.

6.2 EMERGING TECHNIQUES 2014

6.2.1 Removal of sulphate and other pollutants using ultrasonic reactors

The environmental benefits of using this technique is to remove the following contaminants from waste waters:

- ✓ Sulphate (up to 99.7 % reduction).
- ✓ COD (up to 55 % reduction).
- ✓ Phosphate (up to 99.9 % reduction).
- ✓ Heavy metals (up to 99.7 % reduction).

The resultant filter cake produced has lower moisture content and is often non-hazardous and can be disposed of in a suitable landfill site. It can sometimes be reused in the following applications:

- ✓ As an alternative raw material in the cement industry.
- ✓ As a treatment material for paint wastes, e.g. spray booth waste.
- ✓ In waste stabilisation/solidification.
- ✓ In the treatment of contaminated soils.

Sulphate-rich waste waters are treated using the following process steps:

1. Reaction of the sulphate in the water effluent with aluminium hydroxide chloride under acidic conditions (ideally with $\text{pH} < 1.3$). The quantity of aluminium hydroxide chloride that is required is proportional to the concentration of sulphate within the effluent.
2. Neutralisation with lime slurry or liquid lime (the optimum pH has been found to be 11.5).
3. Treatment in an ultrasonic reactor at a controlled rate where sulphate can precipitate. The amplitude and power of the ultrasonic vibrations are controlled to optimise the efficiency of sulphate removal. Within the ultrasonic reactor, the reaction chemistry and kinetics are altered so that calcium aluminium sulphate oxide is formed.
4. Clarification where sludge is removed and treated in a filter press and can then be disposed of or reused/recycled.

The technique can be applied as an end-of-pipe technique or included within a waste water treatment plant. An example of this is within a treatment plant, e.g. for chromium removal.

Example plants

Rimex Metals Ltd, London, United Kingdom.

6.2.2. Photocatalytic oxidation with titanium dioxide

The photocatalytic process can be applied to industrial waste waters for:

- ✓ General organic pollutant destruction.
- ✓ Specific pollutant degradation such as a pharmaceutical- or pesticide-contaminated waters.
- ✓ Toxicity reduction.
- ✓ Biodegradability improvement.
- ✓ BOD/COD removal.
- ✓ Odour and colour improvement.

The technique is a low-temperature system based on photocatalysis that can degrade a range of organic compounds as well as destroy microorganisms in aqueous effluents.

The technique is simple to operate and with few moving parts. It is also highly reliable and robust. The system is capable of being scaled to a variety of throughput requirements, from litres to cubic metres per day, and can be operated either on a continuous flow or on a batch basis, depending on the target material to be treated.

The basic configuration can use either a suspended photocatalyst that can be recovered for reapplication, or an immobilised photocatalyst coated on an inert substrate. The latter approach has, in general, a lower destruction efficiency than the former, but it reduces the need for a recovery plant, and is therefore simpler to build and to use.

6.2.3 Combined electrochemical oxidation

This technique allows toxic organic pollutants and non-biodegradable substances to be converted into more easily biodegradable organic components, or the total mineralisation of the organic pollutants (e.g. to convert them into water, salts and carbon dioxide).

The environmental performance of the technique is not only measured by the TOC, COD or specific component reduction but also by taking into account the biodegradability improvement for further biological treatment.

A major advantage of electrochemical waste water treatment is the use of the waste as an electrolyte.

Electrochemical processes can be classified into two main groups:

- ✓ Direct electrolysis (also called 'anodic oxidation', 'direct oxidation' or 'electrochemical incineration') by anodic oxidation in which the pollutant reacts at the anode surface with adsorbed hydroxyl radicals.

- ✓ Indirect electrolysis where the pollutant reacts in the solution with an electrogenerated reagent produced at the anode (e.g. O₃, ClO⁻, Cl₂ and ClO₂) or at the cathode (e.g. H₂O₂).

Combined electro chemical oxidation processes, combine electrochemical, photochemical and catalytic oxidation to achieve optimal results in the degradation of toxic and non-biodegradable organic substances.

The following combination can be used:

- ✓ Anodic oxidation and cathodic generation of hydrogen peroxide (H₂O₂).
- ✓ Cathodic generation of hydrogen peroxide and UV irradiation.
- ✓ Catalytic electrochemical oxidation (*in situ* generation of hydrogen peroxide and specific catalysts).
- ✓ Electrochemical generation of oxidising agents (e.g. H₂O₂, O₃), UV irradiation and varied catalysts.

The objective of these combined electrochemical oxidation processes is the creation of hydroxyl radicals, the ultimate cause of oxidation of the organic matter present in the waste water.

Identification of the most suitable electrode materials generally necessitates carrying out specific tests adapted to the nature of the waste water that has to be treated.

6.2.4. Supercritical water oxidation

Supercritical water oxidation (SCWO) is a special application of the high-pressure variant of wet air oxidation. The oxidation reaction takes place in the supercritical region of water, i.e. temperatures over 374 °C and pressures above 22.1 MPa.

Waste water is brought to the supercritical pressure by a high-pressure pump before it enters the economiser, where the feed is preheated by the reactor effluent. At start-up, or if the organic concentration in the waste water is less than 4 %, the feed has to be heated further to reach the supercritical temperature range. When oxygen is added to the feed, the temperature in the reactor will rise to about 600 °C.

The reactor effluent flows into the economiser, then through a heat recovery steam generator and through an effluent cooler. Finally, a control valve drops the effluent pressure to atmospheric conditions and the liquid and gas phases are separated.

The organic waste water content is reduced to carbon dioxide, water and nitrogen.

6.2.5. Membrane distillation

Membrane distillation (MD) is a thermally driven process in which only vapour molecules are transported through porous hydrophobic membranes. The liquid feed to be treated by MD must be in direct contact with one side of the membrane and does not penetrate the dry pores of the membranes.

The hydrophobic nature of the membrane prevents liquid solutions from entering in pores due to the surface tension forces. As a result, liquid/vapour interfaces are formed at the entrances of the membrane pores. In MD, the membrane itself acts only as a barrier to hold the liquid/vapour interfaces at the entrance of the pores and it is not necessary to be selective as required in other membrane processes such as pervaporation. The main requirements for the MD process are that the membrane must not be wetted and only vapour and non-condensable gases must be present within its pores. The pore size of the membranes used in MD lies between 10 nm and 1 µm.

6.2.6. Naturally improved microorganisms to treat refractory TOC/COD

The technique consists of the use of naturally improved microorganisms (e.g. prokaryotic cells or bacteria, photosynthetic bacteria or eukaryotes such as yeasts, fungi and photosynthetic microalgae) to treat waste waters loaded with refractory TOC/COD.

This technique is deal with more profoundly in next chapter. Also, as antecedent of this technique, in next chapter the treatment of TOC/COD as described in 2003 and 2014 documents is deal with, as well as an analysis of how this pollutant is referred to in legislation.

7. TREATMENT OF TOC/COD

7.1. Removing of refractory TOC/COD according to 2003 and 2014 documents

Water quality is questionable when looking at the emerging pollutants that accumulate in hydrosphere day after day.

The effective suppression of refractory organic pollutants in wastewater is a major problem whose solution is really urgent, because it affects to the natural water resources. It exist, according to 2003 and 2014 documents, different techniques of elimination of refractory TOC/COD, as the following ones:

Table N° 03 Techniques of elimination of refractory TOC/COD

N°	Technique
1	Chemical precipitation
2	Chemical oxidation (pre)
3	Wet air oxidation (pre) (1)
4	Nanofiltration (NF)/Reverse Osmosis (RO)
5	Electrodialysis
6	Adsorption
7	Extraction
8	Pertraction

9	Distillation/rectification
10	Pervaporation
11	Waste water incineration (FT)

There can be waste water that contains non-biodegradable organic compounds, by conventional methods, and refractories to the biological oxidation. These waste waters are mainly industrial, but these pollutants are also appearing in domestic wastewater although in a minor concentration.

The effective elimination of these organic contaminants in residual waters is a really important problem which requires an urgent solution, as affect to the natural water resources.

This kind of pollution happens due to the presence of aromatic hydrocarbons polynuclear (PAH), phenolic compounds, halogenated hydrocarbons (AOX), pesticides, dyes, etc.

All of them can be grouped under the COD refractory parameter that includes all this organic charge.

Law 16/2002, about Integrated Prevention and Pollution Control (IPPC), is the transposition of the European Directive 2008/1, that establish the mainly pollutants substances to be considered as pertinent to fix emission limit values. In the case of water, we can distinguish between:

- Persistent hydrocarbons and persistent toxic organic and combinable substances.
- Elements that have a negative influence over oxygen balance (and computable, taking account parameters as BOD, COD, TOC).

Confronting this problem, 2003 and 2014 documents establish the action lines that must follow the companies in order to reduce water emissions. We must highlight that pollutants are divided in three big groups, and to each group is assigned a list of erase techniques (considered as end of pipe techniques)

- Insoluble techniques: mechanical treatment.

- Non-biodegradable or inhibitory soluble contaminants: physic – chemical treatments.
- Biodegradable soluble contaminants: biological treatment.

This same documents point the principal pollutants groups to take into account: TSS (total suspended solids), BOD-COD-TOC, DQO refractory, AOX, N Total, NH4-N (NH3), PO4-P, heavy metals, phenols and fats.

The Royal Decree 509/1996, that expands the Royal Law – Decree 11/1995, which set up the relevant rules to the processing of urban wastewater. (Last modification: 09/12/2015); bases the criteria to wastes originating from urban wastewater treatment facilities. As it is shown in the next Table N° 04.

Table N° 04. The criteria to wastes originating from urban wastewater treatment

Parameter	Concentration (mg/l)	Minimum reduction percentage	Reference method of measurement
Biochemical Oxygen Demand (BOD 5 at 20°C) without nitrification	25 mg/l	70 – 90	Sample homogenised, unfiltered decant. Determination before and after five days of incubation at 20 ° C ± 1 ° C in complete darkness. Applying a nitrification inhibitor.
Chemical Oxygen Demand (COD)	125 mg/l	75	Sample homogenised, unfiltered decant. Potassium dichromate.

A comparative analysis is done for both documents, in which it can be observed that the associated emission levels for the different BATs are lower in document 2014 in comparison with document 2003. Also, it can be observed that Spanish legislation still has not been updated to this new COD concentration limits, which must be taking into account by the firms in order to adapt themselves to this new limits and seek for better methods to comply with the law; just like is shown in the following table:

Table N ° 05. BAT-AELs for direct discharges to a receiving water body in comparison with Spanish legislation

Parameter	2003	2014	Royal Decree 509/1996
	concentration (mg/l)	concentration (mg/l)	concentration (mg/l)
BOD 5	2-20	< 20	25
COD	30-250	< 30-100	125

The current legislation establish as a limit of COD concentration of 125 mg/l. This limit would permit to accomplish recommendation of 2003 document; however, Spanish legislation would require to be adapted to the limits indicated in 2014 document. For accomplish these new limits, in some cases, methods for treating refractory TOC/COD a described below, could be needed.

7.2. Naturally improved microorganisms to treat refractory TOC/COD

This emergent technique consists in improving microorganisms such as: prokaryotic cells (bacteria) or eukaryotes (yeasts, fungi and photosynthetic microalgae); to treat waste waters loaded with refractory TOC/COD.

The technique consists of a three-step process:

- ✓ Selection of naturally occurring microorganisms.
- ✓ Generation of microbial variants with enhanced characteristics to treat the targeted pollutants in waste waters.
- ✓ Introduction of the improved microorganisms into the water treatment process.

The technique is an alternative to other techniques such as chemical oxidation or incineration to treat waste waters which contain COD/TOC.

A reduction of TOC/COD levels in water effluents is the environmental benefit of the technique. Refractory TOC/COD abatement efficiencies associated with naturally improved microorganisms is given in Table N°06

Table N°06 Abatement efficiencies associated with naturally improved microorganisms to treat refractory TOC/COD

Characteristics of the waste water treated	Abatement efficiency (% of COD removed)	Comments
Effluent loaded with dimethylformamide	98 COD	Laboratory development
Effluent loaded with metformin	60 COD	2 days retention time on effluent which contain 95 % COD of metformin
Effluent loaded with aliphatic acids and phthalic acid derivatives	Up to 100 TOC	

There are no significant cross-media effects associated with this technique. The technique is generally applicable to new and existing installations in the industrial or municipal sectors.

Investment costs are made up of the treatment tank and the decanting system. The technique can provide significant savings compared to incineration. At a plant producing acrylate resins in France, the total cost reduction is evaluated at 50 %.

The return on investment is expected to be less than 2 years.

The use of microorganism for the treatment of different contaminants and, in this particular case, of refractory COD/TOC is a new technique that it has been used in several laboratory jobs as well as an industrial pilot scale.

Semrany, S.; Favier L., Djelal, H.; Taha, S.; Amrane, A. (2012) describe three different kinds of procedures for treating refractory TOC/COD:

- 1 **Acclimation:** To survive exposure to a hostile medium containing one or more pollutants, a microorganism may regulate its metabolism toward using the pollutant as a source of carbon and/or electrons for energy and growth or toward tolerating the stress created by the pollutant by changing its own morphology and/or physiology.

- 2 **Biostimulation:** It consists in a spiking with some compounds such as minerals, easily biodegradable organic nutrients, or even air or dissolved oxygen, which can enhance microbial growth so the formed biomass may eliminate pollutants. Microorganisms produce enzymes to degrade a primary substrate but some of these enzymes appear to be able to attack other secondary substrates, among them the refractory pollutants.

- 3 **Bioaugmentation:** It is the addition of a specially prepared bacterial culture to a biological reactor (for example, an activated sludge system). The goal of bioaugmentation includes objectives such as: 1) increasing the density of more desirable bacteria, 2) achieving a specific operational goal such as degrading complex organic compounds, 3) increasing the overall organic removal rate, and 4) recovering from an upset in the biological treatment system.

Basing on the origin of additional seed, three approaches can be distinguished:

- (a) “**Autochthonous Bioaugmentation (Auto-BA)**” where used microorganism(s) are isolated from the contaminated water but prepared in an enriched culture and then reinjected in the original environment.

- (b) “**Allochthonous Bioaugmentation (Allo-BA)**” or “**bioenrichment**” when seeding material is isolated from another medium.

- (c) “**Gene Bioaugmentation (Gen-BA)**”: “**Genetically Engineered Microorganisms (GEM)**” are living cells where a specific portion of DNA (gene) coding to a protein related to some desired function, was introduced.

Example of emergent pollutant with Bioaugmentation

- **Pharmaceutical active compounds**

Pharmaceutical Active Compounds (PhACs) may be considered to be, among emergent pollutants, the most looked anxiously by population. Acetaminophen (better known as paracetamol) is one of the most used human pharmaceuticals in the world. Elimination of increased quantities found in water was investigated in a MBR alimented with the target pharmaceutical as sole carbon source; two bacterial strains (*Delftia tsuruhatensis* and *Pseudomonas aeruginosa*) were isolated from a nitrifier enrichment culture. *D. tsuruhatensis* was found able to survive on acetaminophen as a sole carbon source and to mineralize the toxic metabolite hydroquinonein. The following table shows a work reported using bioaugmentation.

Table N°07 Works reporting usage of bioaugmentation: Pharmaceutical pollutants.

Authors	Setup	Pollution level	Augmented seed	Results
De Gusseme et al.	20 L MBR	Acetaminophen (100 µg L ⁻¹)	<i>Delftia tsuruhatensis</i> ; <i>Pseudomonas aeruginosa</i>	>99.9% abatements were observed and isolation of <i>D. tsuruhatensis</i> able to use Acetaminophen as sole carbon source

Example of plants using improved microorganism

- **TOTAL, France:** effluent loaded with acrylic acid (industrial pilot phase)
- **CIBA, Germany:** effluent loaded with 4,4'-dinitrostilbene-2,2'-disulfonic acid (laboratory phase).
- **Pharmazell, Germany:** effluent loaded with sulfanilic acid (industrial pilot phase)
- **Solvay, Belgium:** effluent which contains phthalic acid (industrial pilot phase).

As it can be seen, this technique is emergent, and it is not yet applied at industrial scale. However, in our opinion it is a very promising technique, which probably will be widely applied in a next future.

9. CONCLUSIONS

Within the general task of the analysis about the changes introduced in the final 2014 draft, an exam of both documents has been done regarding to the situation of the differences; in which significantly differences has not been observed related to the structure although there are differences in specifics situations, like the following ones:

- Regarding to all waste water treatment techniques that are described, some were found as new inside the 2014 document, like the next ones: hydrocyclone, electrocoagulation, electrodialysis, pertraction, pervaporation, enhanced biological phosphorous removal, phosphorous removal by chemical precipitation and Biological removal of sulphur compounds/heavy metals*. The last technique was described as emergent in 2003 document and it appears as consolidated in 2014 document.
- Significantly, inside 2003 document we have a *super – critical oxidation* as physical – chemical consolidated treatment technique that appears as emergent in 2014 document.
- 2003 document BAT's are explained for each kind of pollutant and in the 2014 document, only the global actions are mentioned (BAT conclusions) and it shows that those conclusions are based in the different section of the previous chapter.
- A comparative analysis is done for both documents, in which it can be observed that the associated emission levels for the different BATs are lower in document 2014 in comparison with document 2003.
- In 2014 document appear six new emergent techniques, that didn't exist in 2003 document.
- The Spanish legislation should be adapted to the new exigencies appearing in 2014 document.
- Methods for treating refractory TOC/COD could be needed to accomplish with legislation that is more exigent.
- Naturally improved microorganisms are a very promising technique for treating refractory TOC/COD, and probably will be widely applied in a next future.

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