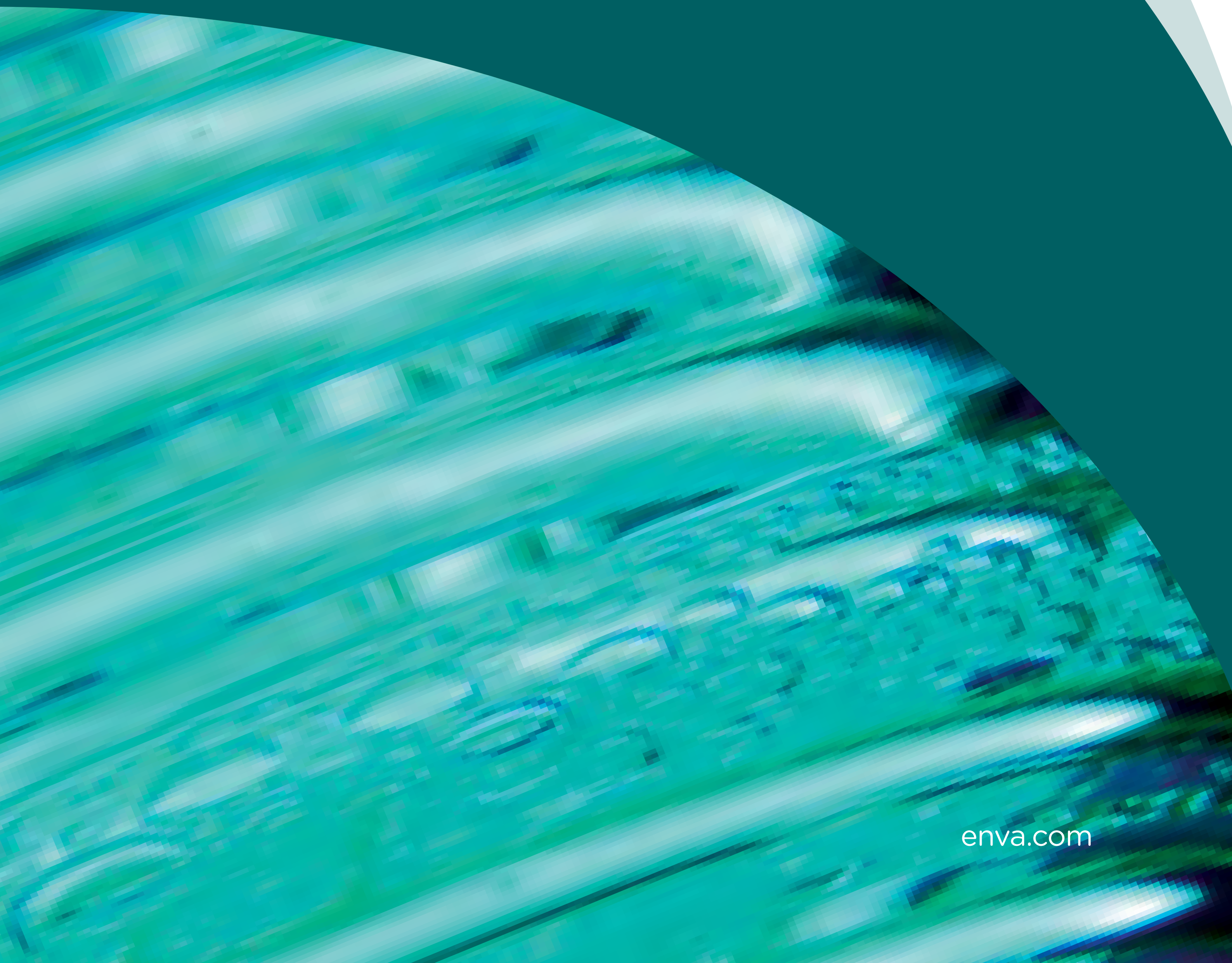
environment matters

Triton X-100

Treatment of Triton X-100 using UV-Oxidation



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Foreword

Triton X-100

Triton X-100 has wide ranging proven applications and benefits in the life sciences and biopharmaceutical production sectors. It is a non-ionic detergent that disrupts lipid interactions while leaving protein interactions intact. Triton X-100 is used in biopharmaceutical medicines to ensure they are safe by enabling the removal of potential viruses from medicines without affecting the quality of the active pharmaceutical ingredient.

Patient Safety is the primary driver for the application of Triton X-100 in the life sciences and biopharmaceutical production sector. Applications range from general purpose detergent to viral inactivation in medicinal products. Although other chemical treatments are known for monoclonal antibodies, some of the recombinant proteins that are manufactured by biopharmaceutical industry are not stable in contact with these chemicals. Triton X-100 is therefore the most suitable reagent known to allow for the regulatory requirement to ensure that biological medicines contain a suitable viral reduction manufacturing step.

Triton X-100 belongs to the substance group 4-(1,1,3,3-tetramethylbutyl) phenol, ethoxylated which through their degradation, have endocrine disrupting properties, for which there is scientific evidence of probable serious effects to the environment. As such, they give rise to an equivalent level of concern to those of other substances listed in points (a) to (e) of Article 57 of Regulation (EC) No 1907/2006 and, therefore, meet the criteria for inclusion in Annex XIV to that Regulation set out in Article 57(f) of that Regulation. On March 23, 2017 the European Parliament ratified the REACH vote to place Triton X-100 onto Annex XIV of the REACH regulation.

To prevent the release of Triton X-100 contaminated waste waters to the aquatic environment, environmental controls coupled with corporate compliance have resulted in the capture of the Triton X-100 contaminated waters for specific treatments and safe compliant disposal at many production facilities. The process of offsite tankering of the wastewater for thermal oxidation is the default disposal method of choice for those facilities without an onsite thermal oxidation infrastructure.

Treatment Solution

Enva, together with our partner Enviolet, offer an alternative and proven solution to the life science, chemical & biopharmaceutical sectors for the treatment of the Triton X-100 contaminated waste waters. The Enviolet UV oxidation system utilises UV and oxidation chemistry to destruct the complex organic species in aqueous waste, and to render them biodegradable. The system has been deployed in more than 600 locations across industries such as pharmaceutical, chemical, aircraft, automotive, surface treatment, metal finishing and waste management.

The UV oxidation system combines state of the art UV technology with additional chemical and physical process steps to create an innovative solution for the destruction of unwanted organic contaminants in wastewater. The process is ideally suited to the treatment of Triton X-100 contaminated waters generated by the biopharmaceutical and lifescience industrial sectors.

Robust pipes of borosilicate form the casing of the oxidation reactors. This prevents corrosion and allows viewing of the reactor chamber along its entire length. In addition the electronic performance control tunes the light characteristic by chip-card, guaranteeing optimal UV output and increased lamp life. Special flow devices create a rotational flow with high turbulence effect within the reaction chamber, which ensures that the optimum oxidation level is achieved.

Enva offer an offsite AOP treatment solution at our EPA licensed facility in Shannon, Co Clare. Alternatively we can offer installations designed to the customer scope of requirements in cased where capital expenditure requirements versus offsite treatment are more favorable. The units are provided as a turnkey package, including skid-mounted units or compact units for smaller applications. The units come complete with all mechanical components (measuring, controlling, dosing, cooling, tank construction, pipework etc.). The system also comes with user-friendly touchscreen PLC with visualization interaction with the process.

Client Assessment and Proposal

As a first step Enva review the waste stream with the client, gain an understanding of the clients specific aims and gather the relevant analytical data. The next step is a full laboratory scale evaluation on 10 litres of a representative sample of the waste stream, the evaluation is performed on a dedicated laboratory scale version of a full scale plant.

This laboratory trial allows us to determine if the waste can be treated successfully and will allow for optimisation of the treatment aims. The evaluation will also provide estimated budget capex and opex costs associated with the treatment of the waste stream. We also return treated samples to the client, if they wish, to carry out their own specific tests for internal review.

Once the above steps are completed successfully, we can organise and provide a live plant trial of the specific process wastewater at our AOP installation located our waste licensed site in Shannon.

The laboratory evaluation together with an agreed treatment scope, allows us to offer a commercial proposal to the producer of the waste stream.

Supporting Documentation

Please find overleaf examples and data relating to the successful treatment of Triton X-100 contaminated waste process water generated by the Biopharmaceutical industry.

Foreward by:
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Feasibility Study

UV-Oxidation of Organic Matter (COD) in a biopharmaceutical waste water

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Sample/Project:
Triton X-100 & Octylphenol degradation

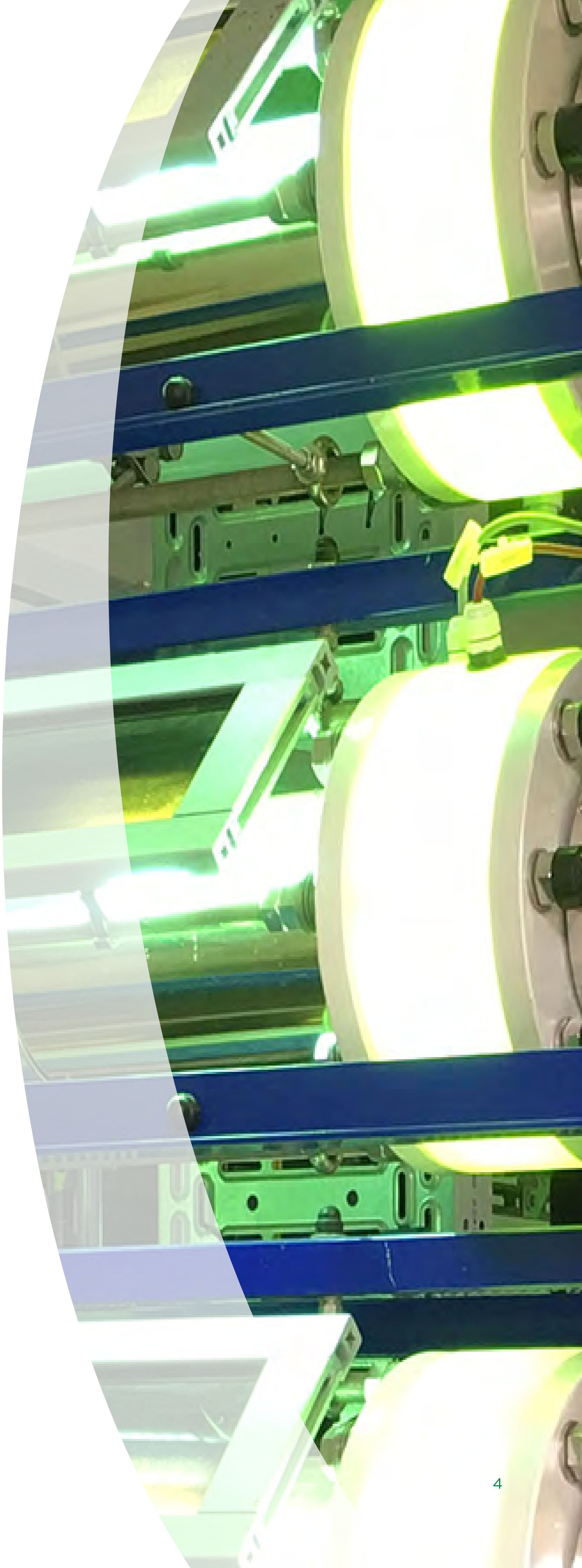
Increasing Bioavailability, Destruction of Triton X-100 and Octylphenol Compounds

Sample designation:
Biopharma Process Effluent

Treatment aim:

Increasing Bioavailability, Destruction of Triton X-100 and Octylphenol Compounds

Investigation Period:
15-27/11/2017



Introduction

UV-irradiation in combination with hydrogen peroxide has demonstrated its capability to oxidize organic and inorganic compounds in groundwater, process waters or industrial wastewater effectively. Successful industrial application by Enviolet® UV-oxidation plants has been exhibited for several years at BASF, DOW, Merck and many other multi international companies all over the world.

The Enviolet® UV-processes developed by a.c.k. aquaconcept GmbH / Enviolet GmbH provide technical solutions in the field of chemical synthesis and special applications not solely in a water matrix but also for gas phase applications.

Theoretical Principles

The basic requirement for any type of photoreaction of a molecule is absorption of light with sufficient energy resulting in R* with excited electrons. This means, initially, even very dark solutions can be treated by UV-Oxidation with reactors that are adequately designed and constructed.

$$R \xrightarrow{h\nu} R^*$$

R* may continue its reaction from this state, either directly or reverting to its initial state via reactive intermediates, or physically to photo products. Due to subsequent chemical processes, radicals, radical ions, ions or stable fragments are generated in aqueous solutions, the reactions maybe optimized by thermal processes due to the exothermic nature of the oxidation reaction. For instance, light of the correct wavelength can split hydrogen peroxide (H_2O_2) into highly reactive hydroxyl radicals by photolysis (UV/H_2O_2-process), which react quickly with organic and inorganic water compounds.

$$H_2O_2 \xrightarrow{h\nu} {}_2HO^\bullet$$

Such hydroxyl radicals (OH-radicals) are generated by the UV/H_2O_2-process with a minimum amount of chemicals and with the most economical energy input. For this reason, at high target-concentrations the OH Radicals are very effective for treatment of pollutants in aqueous solutions. The degradation of organic compounds via OH-radicals is initiated by hydrogen abstraction:

$$R\text{-}H + HO^\bullet \longrightarrow R^\bullet + H_2O$$

With the presence of Olefins an electrophilic addition of OH-radicals follows:

$$R{+}H + HO^\bullet \longrightarrow {}^\bullet R\text{-}ROH$$

These initiated reactions follow various reaction pathways of generated radicals. In presence of oxygen an organic peroxyl-radical is formed:

$$R^\bullet + O_2 \longrightarrow RHO_2^\bullet$$

Furthermore, various competitive reactions can occur:

$$R^\bullet + H_2O_2 \longrightarrow ROH + HO^\bullet$$
$$R^\bullet + HO^\bullet \longrightarrow ROH$$
$$R^\bullet + R^\bullet \longrightarrow R\text{-}R \text{ (Polymerization)}$$

Polymerization is avoided by proper process control and UV reactor construction.

Also the peroxyl-radical ($RHO_2^{\bullet}$) may for instance continue its reaction as follows:

$$2RHO_2^{\bullet} \longrightarrow RO + RH^{+} + HO^{-}$$

The resulting Aldehydes and Ketones oxidize to carboxylic acids via subsequent reaction processes leading to thermic or photo-chemical decarboxylation.

$$R'\text{-}CO_2\text{-}H \longrightarrow R'H + CO^{2}$$

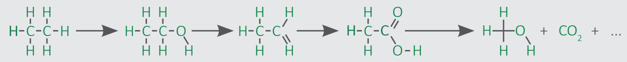
Finally, many of the reactions lead to a complete mineralization (CO_2 and H_2O) of the original organic compounds, in the intermediate stages of degradation the organics exhibit a substantial increase of oxygen containing groups. The intermediaries, which contain one or several –OH, =O und COOH – groups, are typically considerably less toxic than the original compounds and exhibit increased bioavailability characteristics. Therefore, Enviolet®-UV-Oxidation can often be combined with a biological degradation process.

The described degradation mechanisms can also be applied to organically bound halogens, resulting in mineralization resulting in the formation of chlorides as well as CO_2 and H_2O. From heteroatoms such as sulfur, nitrogen and phosphorus, sulfate, nitrate and phosphate are produced.

The oxidation reactions illustrate that carbon dioxide is not formed initially; this is why TOC (total organic carbon) reduction is rather slow at the beginning of the oxidation process. However, since Carbon atoms of the organic molecules have obtained a higher oxidation number, less oxygen is required for a complete oxidation to carbon dioxide and, therefore, COD (chemical oxygen demand) is reduced rather quickly thereafter. In conjunction with the observed COD reduction; the bioavailability of the aqueous solution increases and is confirmed by the observed increase in the BOD/COD ratio (BOD/COD*100%=bioavailability in %).

A COD/TOC ratio of approximately 3 to 4 is typically expected in an untreated aqueous solution containing various organic compounds. Of course, this ratio is also dependent on the presence and amount of bound heteroatoms. With increasing oxidation levels the COD/TOC ratio is typically reduced by the UV/H2O2 process to approximately 2.

Example:



Ethane-> Ethanol-> Acetaldehyde-> Acetic Acid-> Methanol -> Formic Acid and Carbon Dioxide

Obviously, the first 4 molecules in a hypothetical solution still remain at the same TOC level, whereas the COD is reduced. It is only with the dissociation of CO_2 the TOC level is reduced.

Analytical parameters and methods

TOC	total organic carbon (Teledyne Tekmar Phönix 8000)
COD	chemical oxygen demand, (Hach Lange LCK314, LCK514)
BOD5	biological oxygen demand, (Hach BOD Trak). For bacterial seed, activated sludge from our lab bioreactor is used. These bacterial cultures are more adapted to contaminants of industrial wastewater than activated sludge from municipal sewage plants that are typically used for BOD5 analysis. Therefor our results tend to simulate bio degradation in a biological step with adapted
Triton X-100	by client
Octylphenoles	external
H_2O_2	concentration of Hydrogen peroxide (titrimetric, a.c.k. method)
pH	pH-value
T	temperature

Feasibility Study

Carried out by Dr. Volker Hoffmann, Nicolai Friedrich and Frank Zegenhagen (Enviolet Corp).

Sample description: yellowish, turbid

For the laboratory treatment evaluations Enviolet® lab-scaled plants are utilised (Photo 2). The lab scale plants are of the same design as a full scale plant and as such the laboratory evaluation guarantees treatment conditions equal to that of a full-scale plant.

The main advantages of the Enviolet® reactor design are:

- A high turbulence in the UV-reactor guarantees very good mass transfer; that even when very strongly UV absorbing and turbid media are present that an optimal process treatment is achieved.
- The high velocity rotational flow prevents build-up of deposits on the UV-module (unit of quartz glass tubes and UV-lamp).
- Due to the high quality of the material of construction chosen; highly acidic and concentrated solutions such as copper or nickel electrolytes can be treated at high temperatures.

The system contains: Batch tank with integrated process equipment, dosing stations for chemicals required, static mixer, media pump, Enviolet®- UV – reactor, and continuous measurement for important parameters, piping, and heat exchanger.

Experimental Procedure

The tank is filled with a defined amount of the sample for evaluation. After adjustment of process conditions (H_2O_2-concentration etc.) the sample is pumped circulating via the UV-reactor. The UV-lamp is then switched on. The treatment is a batch process; that means the energy input is rising with treatment time.

Irradiation source: Enviolet® hump UV-lamp

Power: 40 W

Lab Treatment

Pre-tests: several, not documented

Main runs: irradiating the water in presence of H2O2 (process- controlled H_2O_2 dosing)

During the laboratory evaluation; processed samples were extracted at selected time intervals for analytical purposes of several parameters such as TOC, COD and BOD5. Samples were forwarded for 'Triton X-100' analyses to the producer of the waste as they have developed an in house analytical test method for Triton X-100. Samples were also forwarded to a chosen external lab for various octylphenol ethoxylate compounds analysis.

Laboratory scaled Enviolet® UV-plants (UV-reactors with different types of light sources)

Results

In the diagrams the “dimensionless treatment time” is used as a universal parameter for lay-out. This is an operating parameter determined by all lab investigations and related to Enviolet’s central database. When all necessary design information for the commercial plant are known, e.g. charge volume, volume of effluent per day and power requirement of the plant treatment; the dimensionless treatment time can be transformed into treatment hours of the related commercial unit.

Diagram 1

Concentrations of TOC,COD and Octylphenols versus dimensionless treatment time.

Additionally biodegradability is displayed.

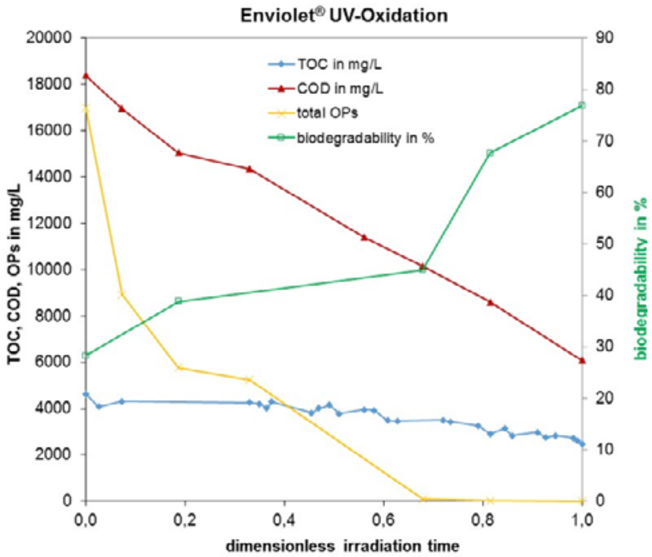


Diagram 1 shows the degradation curves of COD and TOC resulting from the laboratory UV-oxidation of the waste water. Additionally the sum of octylphenols is displayed and the biodegradability.

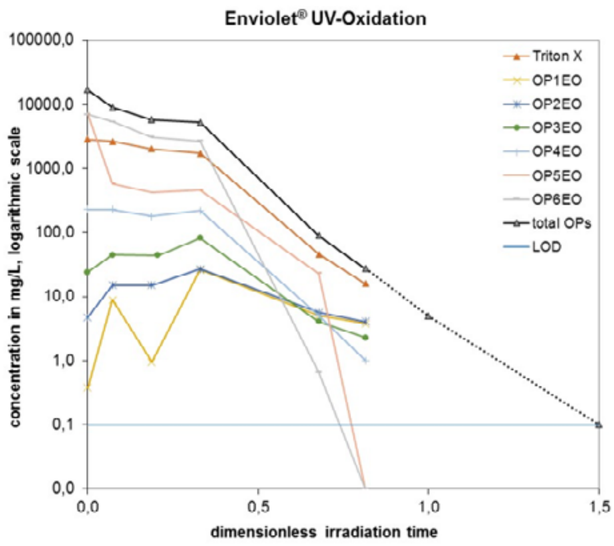
The oxidation of initial structures results in several degradation pathways leading to the formation of smaller molecules, mainly carboxylic acids. As the organic acids are degraded, the TOC is decreased as a result of the organic carbon being further oxidized to carbon dioxide. The change of the ratio COD/TOC from typically around 3 to 4 in the beginning of the reaction to lower ratios during the treatment is reflecting these reaction pathways.

With increasing treatment time, less oxygen (COD) is necessary to oxidize the remaining TOC as this carbon is extensively oxidized by the progression of the treatment process.

Octylphenol compounds degradation are observed, it is obvious that those with shorter polyethoxylate-chains are formed as intermediate degradation products as the reaction time increases (See diagram 2).

Diagram 2

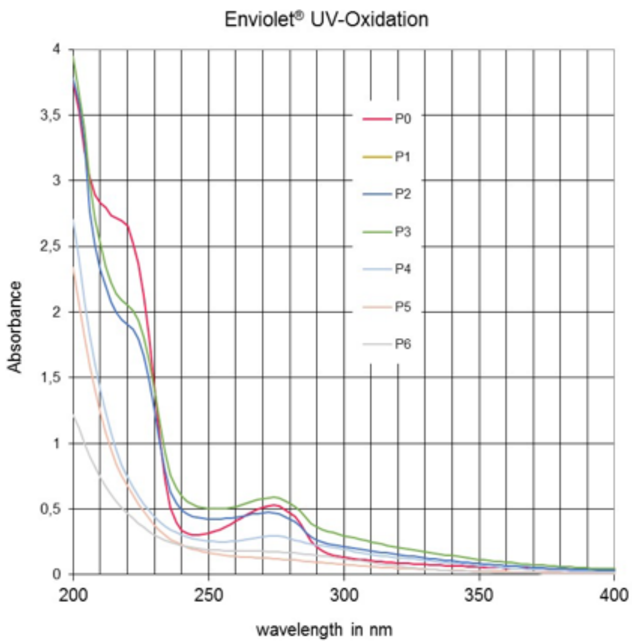
Degradation of Octylphenols



OP1EO	Octylphenol monoethoxylate
OP2EO	Octylphenol diethoxylate
OP3EO	Octylphenol triethoxylate
OP4EO	Octylphenol tetraethoxylate
OP5EO	Octylphenol pentaethoxylate
OP6EO	Octylphenol hexaethoxylate

Diagram 3

UV/Vis-Spectra of the samples (P0= original sample)



The laboratory evaluation was ended when a significant portion of the COD was oxidized. The endpoint was reached when there was no characteristic peak in the 260 to 290 nm wavelength area (Diagram 3).

As previously stated, the reaction pathways result in the formation of biodegradable products. This phenomenon can be quantified by the observed BOD/COD ratio and the resulting increased biodegradability (BOD/CODx100%).

Table 1

Relevant analytical parameters

Irradiation time, normalized	Sample	TOC in mg/L	COD in mg/L	BOD in mg/L	Bio-degradability in %
0,00	P0	4630	18400	5200	28
0,07	P1	4315	16950	n.a.	n.a.
0,19	P2	4280	15050	5840	39
0,33	P3	4250	14350	n.a.	n.a.
0,68	P4	3510	10150	4560	45
0,82	P5	2910	8600	5820	68
1,00	P6	2470	6090	4680	77

n.a. not analysed

Table 2

Octylphenols in mg/L

Irradiation time, normalized	Sample	Triton X-100	OP1EO	OP2EO	OP3EO	OP4EO	OP5EO	OP6EO	Total OPs
0,00	P0	2851	0	5	24	230	7000	6900	17010
0,07	P1	2639	9	15	45	230	580	5400	8918
0,19	P2	2012	1	15	44,0	180	420	3100	5772
0,33	P3	1727	26	27	83	220	460	2700	5243
0,68	P4	46	5,1	5,7	4,1	5,1	23	0,66	89
0,82	P5	16	3,8	4,1	2,3	1,0	<0,1	<0,1	27
1,00	P6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

LOD for OPs: 0,1 mg/L

Laboratory Evaluation Summary

The laboratory investigation was successful in achieving the evaluation scope; providing a significant increase in biodegradability of the aqueous solution and extensive destruction of the Octylphenol compounds. Optimisation is possible to further reduce the final reported Octylphenol concentration present in the treated wastewater

Note: Due to the aqueous matrix, the analytical method employed by the external laboratory for the detection of the Octylphenol compounds had a L.O.D. of 0.1 mg/L.

The laboratory evaluation of the wastewater allows for budget capex investment and opex costs of the wastewater treatment to be extrapolated and presented to the client.

Enva and Enviolet can if necessary, provide plant scale treatment validation of the AOP process of Triton X-100 process wastewaters at the Enva AOP platform located at our EPA waste licensed site (W-0041), Shannon, Co. Clare.

Footprint

The footprint of an installation to treat the volumes of Triton X-100 contaminated waste water as per the evaluation (60m^3 per week) is another positive of the Enviolet AOP offering. The demand for footprint for AOP installations is not overly onerous as the installations are of a compact design. In the case of the evaluation above, excluding the collection tank, a 6 Meters X 3.5 Meters footprint is required for the entire treatment plant.

We understand the value and demand for floor space availability. At design stage, Enviolet engineers will engage with the client to assess footprint availability and will design the installation, in so far as is practical, within any constraints identified. Both internal and external installation options or a combination of both are available.

See pages 15-18 for photographs of both internal and external installations.

Chemical Consumption - OPEX

Standard commonly used commodity chemicals are required for the AOP process; the chemicals typically used are acid and caustic for pH-adjustment and hydrogen peroxide and UV-light as the oxidant source. In the case of the evaluation of the Triton X-100 contaminated waste water as detailed above, estimated Opex is circa €25/m^3*, which includes chemicals, electricity and UV-lamps replacement.

The initial concentration of Triton X-100 in the evaluation is expected as being at the upper end of the concentrations present in biopharmaceutical process water. Therefore based on our expert experience in AOP treatment of such wastewater matrices we expect that the Opex will range from €10 to €25/m^3* for biopharmaceutical process wastewaters. The laboratory evaluation stage will determine precise Opex for each client wastewater matrix.

*Opex costs are based on current standard Irish market chemical costs of the required chemicals.

Existing Enviolet AOP installations in Europe for treating Triton X-100 contaminated Process Wastewater

Installation treatment capacity:

- Installations between 5 - 20 m³/d
- Concentrations of Triton X-types (e.g. Triton X-100) presented in 3 - 8 g/L
- COD of presented Water Matrix: 5 - 20 g/L

Aim of Installation treatment:

- Main aim: destruction of Triton X-compounds
- Reduction of COD and increase of BOD & Biodegradability

In two cases* the installations have been obliged to meet a treated COD consent of < 120 mg/L and < 400 mg/L respectively to allow discharge of the wastewater to sewer. In all other cases the AOP pre-treated wastewater is processed further by site WWTP before final release to the sewer.

*Names of customers must remain anonymous due to Confidentiality Agreements. Triton X Enviolet AOP Plants overview in operation in Europe.

FAQ	Answers		Comments
What flowrate and concentrations of Triton X-100 contaminated process wastewater have Enviolet AOP plants treated?	Flow rate: Company A: max. 8 MT/d Company B: 12 MT/d	Concentrations COD: ca. 20 g/L T-X-100: 3 – 8 g/L other components are: Glycine and Tween80 COD: ca. 15 g/L T-X-100: max. 3 g/L	All wastewater flow of this site is T-X-100 wastewater. We treat only the T-X-100 concentrate stream, other waste water go to biological site treatment
What is the removal efficiency in this plant?	Removal rates: Company A: < limit of detection. Depending on the water matrix the LOD varied between 1 … 10 µg/L. Company B: We not have received Technical information post installation to report efficiencies	Calculations would say: 99,9999% … 99,99999%, Company A is extremely satisfied by plant performance	The results from the analytical method are less than the LOD at the end of AOP treatment, we would suggest the removal efficiency is greater than that calculated.
How do you measure the removal if correlation to COD is not acceptable?	Customer A supplied developed in house analytical methodology Enviolet installed an DAD-online-monitoring system, which runs on a proven correlation		

On line Analytics options

DAD is a Diode-Array-Detector. DAD operation is similar to a photometer. With the aid of an additive Enviolet have achieved rather good selectivity on Triton X-100, as a result of the selectivity it is possible to monitor the destruction.

DAD is less accurate than HPLC-DAD, however it is much more cost effective method and in our view a solid working method for this type of wastewater.

Enviolet have offered different solutions including integrated online-analytics for Triton X-100 . Correlation studies are also possible to prove that using standard parameters eg. COD are consistent with Triton X-100 results

For batch processes, some customers have developed in-house analytical methods and test the wastewater before discharge release.

Internal Enviolet AOP Installation Example

External Enviolet AOP Installation

(core components supplied within unit-container)

External Enviolet AOP Installation

(core components supplied within unit-container)

Enva AOP Installation Shannon Co. Clare

EPA License W-0041

For further information please contact info@enva.com