Wastewater Treatment by UV-Oxidation at Oril API Manufacturing Site

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Abstract

This article shows the way of realizing a full scale UV-oxidation starting with feasibility study for Oril Industrie as manufacturer of Active Pharmaceutical Ingredients (API) within the biggest independent French pharmaceutical company Servier Laboratories.
The way from lab-testing at a German specialist for photochemistry to realization for the treatment of environmentally hazardous chemicals in wastewater from API-manufacturing is described for the combination of UV-oxidation and a following biological treatment.
The oxidative pre-treatment has to result wastewater with a non-toxic character, high biodegradability and elimination of two main components below low environments. Chemical ingredients that need to be oxidized in the described applications are for example Morpholine and N-Nitroso-Morpholine.
Apart from figures of the installed UV-plant, flow rates of the different treatment steps and concentrations are listed as well. The massive cost reduction in combination with huge environmental improvements have been the driving forces of this case.

Zusammenfassung

Behandlung des Produktionsabwassers der Wirkstofffertigung bei Oril mittels UV-Oxidation

Dieser Fachartikel beginnt mit der Machbarkeitsstudie und zeigt den Weg zur Umsetzung einer UV-Oxidation bei Oril Industrie als Hersteller pharmazeutischer Wirkstoffe innerhalb des Pharmakonzerns Servier Laboratories.
Der gesamte Weg von den ersten Laborversuchen bei dem deutschen Spezialist für Fotochemie zur Behandlung von umweltschädlichen Verbindungen im Abwasser der Wirkstoffproduktion wird für die kombinierte Anwendung aus UV-Oxidation und biologischer Behandlung aufgezeigt.
Die oxidative Vorbehandlung muss ein Abwasser liefern, das nicht toxisch, vollständig biologisch abbaubar ist und in dem 2 Hauptkomponenten unter sehr geringe Grenzwerte abgebaut werden. Zu diesen Verbindungen gehören z. B. Morpholin und N-Nitroso-Morpholin.
Neben Abbildungen der fertig installierten UV-Anlage und Volumenströmen der verschiedenen Prozessstufen enthält der Bericht auch Konzentrationen der einzelnen Schritte. Neben der massiven Kosteneinsparung war die erhebliche Verbesserung der Umweltverträglichkeit die zentrale Triebkraft in diesem Projekt.

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Table 1

Specs of untreated wastewater and requested limits after treatment.

Parameter	Range	Required limits
COD in mg/L	4,000–8,500	< 2,000
TOC in mg/L	1,600–2,700	< 1,000
Biodegradability in % B/C	10	> 60
Zahn-Wellens-Test in %	n. n.	< 90
API in µg/L	as low as possible	< 0.1
Morpholine (MOR) in µg/L	500,000–800,000	< 20
Nitroso-Morpholine (N-MOR) in µg/L	25–40	< 0.1
API in µg/L	as low as possible	< 0.1
TDS in mg/L	10,000–15,000	–
Flow rate in m^3/d	80–135	–
Toxicity (Daphnia)	high	< 5

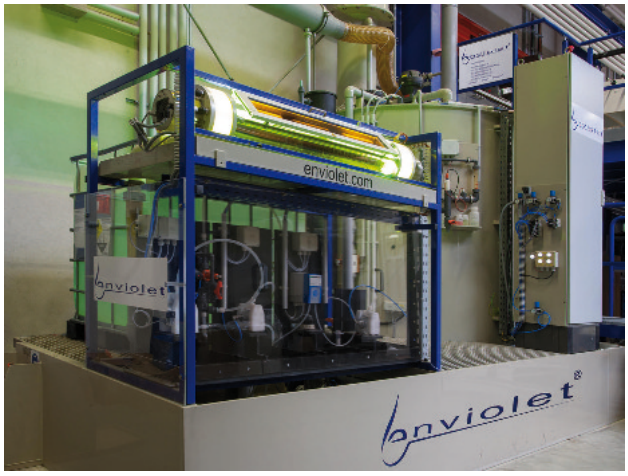

Figure 1: Demo and test-unit for semi-scale feasibility testing, installed at Enviolet's factory floor (Source: All figures were made by Enviolet.).

Introduction

Oril Industrie is a manufacturer of various API, situated near Le Havre within a nature reserve. Oril is part of Servier Laboratories SA, which is the leading independent French pharmaceutical company and the second largest French pharmaceutical company worldwide [1].

Due to the special hydrogeological location of Oril within an environmentally protected area, it is subject to very low legal limits for several substances used in the manufacturing process, in particular Morpholine (MOR).

Since MOR is an amine it is likely to turn into undesirable Nitroso-Morpholine (NMOR) in the station treatment plant.

Oril has two manufacturing sites within roughly 1.5 km of each other. The new API-manufacturing site is the Baclair site and the original manufacturing site is the Bolbec site, where a well-functioning biological wastewater treatment plant is also installed. The new Baclair site is connected to the biological treatment plant through a wastewater pipe.

In order to protect the environment and due to lack of a suitable and reliable treatment for the MOR wastewater, for many years Oril sent the wastewater from the new Baclair site to an external treatment company for incineration.

Enviolet is a globally-operating, Germany-based manufacturer and technology-provider in the field of photochemistry, specializing in preparative systems and a wide range of UV-oxidation processes (as well as wastewater treatment) for industrial use [2, 3].

Motivation

Oril's motivation for installing a new wastewater treatment process was to reduce MOR in the wastewater so that it could be treated in the biological treatment plant without risk of forming nitrosamines. Indeed the elimination of wastewater by incineration is not only environmentally unfriendly but also very expensive. The effective costs of the incineration amounted to approximately 300,000 EUR each month. These costs are a burden for any manufacturer, especially in an increasingly globalized market and faced with new requirements from many sides.

Therefore, Oril was looking to reduce the total costs of treatment in combination with an environmentally sustainable solution.

Case Concept

The Oril project team's concept was to get away from the high costs of external wastewater incineration treatment through the introduction of a new suitable process at the Baclair site, featuring a high removal rate of approx. 99.998 % for the critical substances, which could be adapted to varying operational

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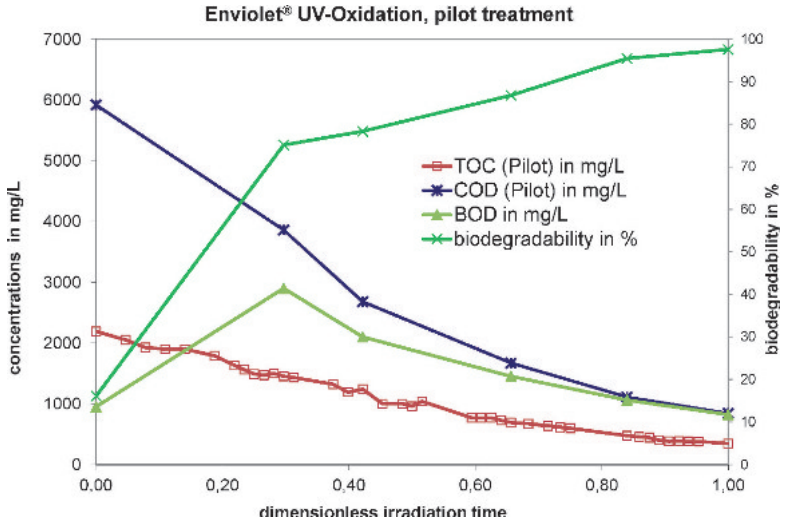

Figure 2: Specs for several summary parameters from pilot treatment.

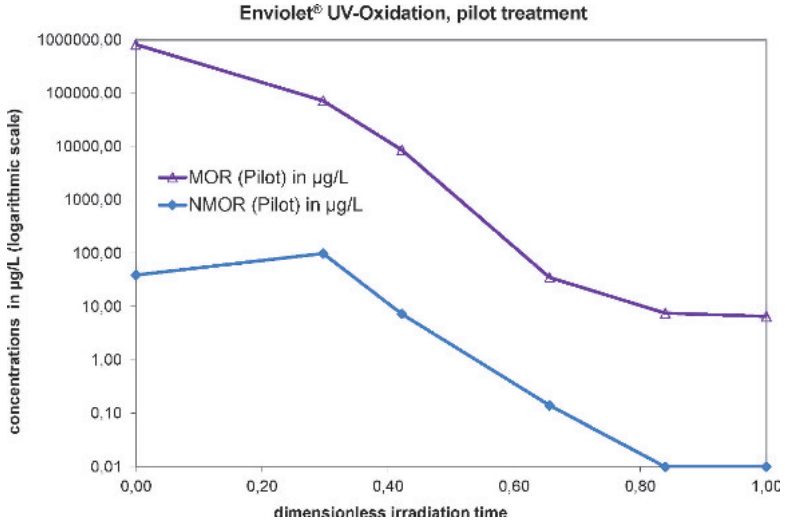

Figure 3: Specs for MOR and NMOR from pilot treatment.

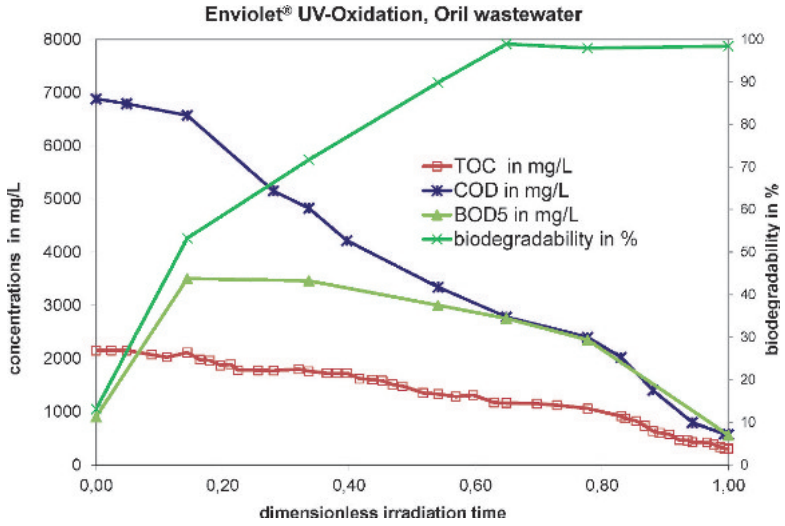

Figure 4: TOC, COD, BOD and biodegradability.

conditions of the manufacturing site.

The technology should also be cost-efficient and reliable in keeping concentrations of the two critical main components, MOR and NMOR, below the specified limits.

The legal limits are MOR = 15 µg/L and N-MOR = 100 ng/L.

The average flow of wastewater was 100 m^3/d, but could vary between 80 and 135 m^3/d.

The maximum capacity of the biological treatment plant on the Bolbec site is 500 m^3/d for lower-loaded wastewater.

Oril called upon several suppliers to submit concepts for a treatment process with specifications as shown in Table 1.

Several companies presented solutions and some of the results looked promising, but under practicable conditions, either the defined limits of treatment could not be adhered to, or the expected operational cost reduction could not be achieved.

A wide variety of solutions was offered, and some proposed a polishing of the effluent coming from Oril's biological wastewater treatment plant. These solutions carried not only high operational costs but also a significant investment of capital.

The German specialist for UV-oxidation achieved good result in a feasibility study in their application laboratory, treating the concentrated effluent. Subsequently, Oril requested reproduction of the results as well as a test implementation on a pilot scale. Therefore, several additional tests were performed, some in the presence of a process validation team from Oril and on a pilot-unit installed on Enviolet's factory floor (fig. 1–3).

All results from lab-testing on the scale of 10–15 L could be reproduced and confirmed various times in the pilot-unit (fig. 2 and 3), so that all concerns regarding the elim-

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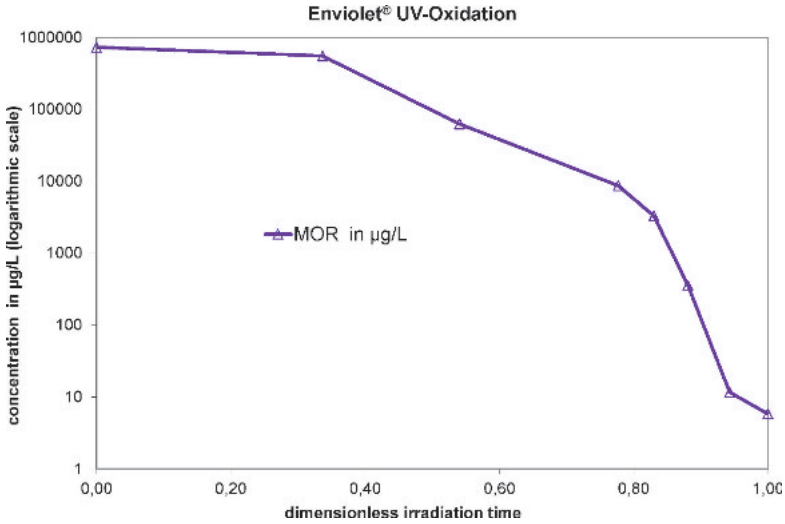

Figure 5: MOR degradation.

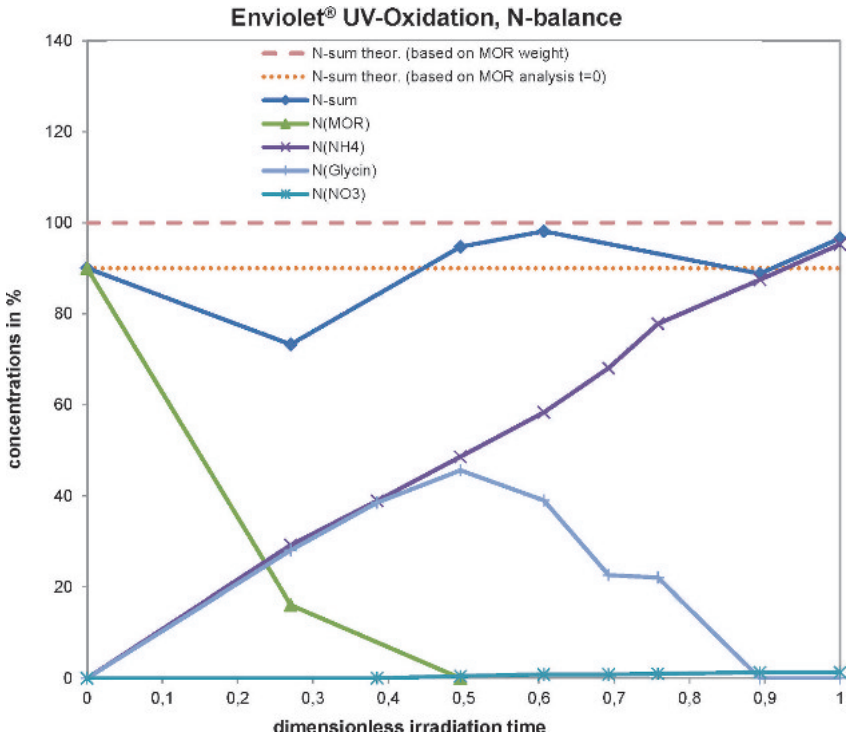

Figure 6: N-Balance MOR degradation.

ination of all critical substances and effective operational expenses (OPEX) could be dispelled and the project could proceed to the realization stage.

Additionally, Oril required that the solution provider should be able to show references of similar installations with a number of years of operational experience, and a commercial unit was visited.

Results

Figure 4 shows a typical change of total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD; incubated with bugs cultivated in a wastewater treatment plant of Enviolet's laboratory slurry) and biodegradability (= BOD/COD x 100 %) during the treatment of wastewater from Oril's production during the lab-test, but also as observed later in the full-scale plant. Figure 5 shows the degradation of MOR. The oxidation of initial structures is followed by several degradation pathways leading to smaller molecules, mainly carboxylic acids. As the organic acids are degraded, the TOC decreases as a result of the organic carbon being further oxidized to carbon dioxide. The change in the ratio COD/TOC, from typically around 3 in the beginning to 2 or less after the treatment, reflects these reaction pathways (fig. 2 and 4).

With rising treatment time less oxygen (COD) is necessary to oxidize the remaining TOC, as this car-

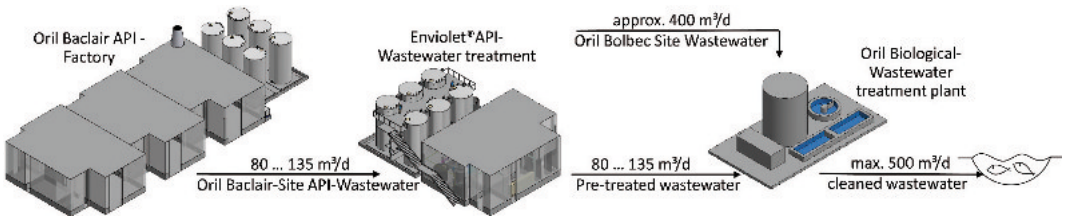

Figure 7: Treatment concept proposed by Enviolet: selective pre-treatment of the organically contaminated wastewater from the Baclair site and final polishing in the centralized biological treatment plant at Oril's Bolbec site.

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Figure 8: Samples during treatment by UV-oxidation.

bon has already been oxidized extensively.

The oxidation process also leads to a rise in biodegradability, as shown in fig. 2 and 4, which is due to the destruction of toxic compounds in the mixture. The critical components, MOR and NMOR, are N-heterogenic components which are shown in several diagrams (fig. 2–6). Additionally fig. 6 depicts the nitrogen balance that could be completed satisfactorily, proving only non-toxic intermediates. The beige fine particles of 2-(N-Morpholino) ethansulfonicacid (MES), which are always present in this wastewater, are also dissolved and oxidized during the oxidation process.

Figure 7 shows the treatment concept which was realized based on the test work performed during the development phase. The 80–135 m^3/d wastewater containing the critical substances is discharged into a 2,000 m^3 intermediate storage tank on the Baclair site, where the APIs are manufactured. Monitored detoxification by UV-oxidation takes place directly at the Baclair site and all 80–135 m^3/d are then transferred to the Bolbec site, where Oril's biological treatment plant is located. In this biological treatment plant all wastewater from the Bolbec site and the UV-pre-treated wastewater from the Baclair site are finally polished, before the cleaned wastewater is discharged into the aquatic system.

Operation and Results

The operation of the UV-oxidation plant is a continuous process, based on flow-chemistry, which usually stops for maintenance only. The process is fully automated and a centralized Programmable Logic Controller (PLC) controls all important process steps of the photo-oxidation treatment process. An online monitoring system feeds into the PLC to support automation. Additionally, daily samples are monitored in the lab and compared with specified set-values at dedicated process steps.

Figure 8 shows the typical appearance of the wastewater during the detoxification process: an initial dark turbid solution becomes nearly water-clear after processing. Also, the cooling power required to ensure that the maximum temperature is not exceeded during the oxidation is generated from the treated wastewater.

Figure 9 shows analysis results from samples taken during plant operation. Despite strong variations in initial concentrations, adherence to the MOR limit is achieved. Also, NMOR is always sufficiently degraded when the MOR concentration is below the target concentration.

Since final TOC concentrations correlate with MOR concentrations in this treatment process, the simple

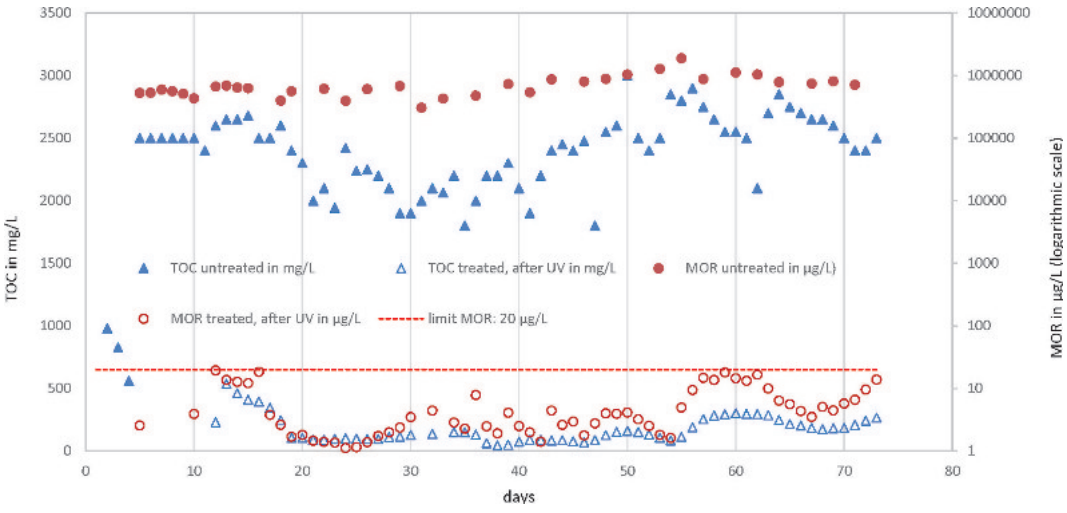

Figure 9: Treatment results of the industrial UV-plant over a period of 74 days of operation after hot commissioning. The inlet concentrations of TOC and MOR as well as the concentrations of TOC and MOR in the outlet of the UV-oxidation plant are shown.

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Figure 10: New Wastewater treatment unit at Oril's Baclair site.

Figure 11: The photo-oxidation unit, the core of the new wastewater treatment plant placed at Oril's Baclair site.

analytical method for TOC can be used to indicate the MOR degradation.

Conclusion

The photo-oxidation plant (fig. 10 and 11) began operations in summer 2016. Since that time the UV-oxidation completely detoxifies the wastewater; API and toxic components like MOR and NMOR are removed and, ultimately, only bio-available compounds remain in the treated effluent. The nitrogen balance, starting with the partially very toxic N-Organic compounds in the untreated wastewater, could be completed with non-toxic intermediates, which were also removed by the new treatment process.

The huge savings achieved by a reduction in the costs for wastewater disposal lead to a return of investment significantly lower than one year.

This is another good example for the industrial application of UV-oxidation plants [4–6].

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The link was accessed for the last time on 21 March 2018.

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