How UV with electrochemical H_2O_2 generation leads to autonomous, safe and sustainable removal of micropollutants

The opportunity

Strong population growth, contamination from industrial and municipal uses, and critical regional droughts are placing great stress and challenges on global water resources and, consequently, on water purifiers. In addition to decades of proven drinking water treatment processes of surface and ground waters, there is a strong future need to recycle municipal wastewater in order to relieve the growing pressure on water resources.

For this purpose, Advanced Oxidation Processes (AOPs) are an essential part of the treatment chain. AOPs are used to remove harmful trace substances (e.g. 1-4 Dioxane, ibuprofen) that find their way into the water cycle for example through the use of hygiene products, medicines or industrial production, and that would accumulate to critical concentrations in drinking water if not removed. In addition to eliminating micropollutants, established AOPs act as an effective disinfection barrier against viruses, bacteria and protozoa.

AOPs can be efficiently used in groundwater treatment applications and as a 4th treatment step in wastewater treatment to either meet discharge limits, or in water reuse applications to create potable water.

Xylem Inc. (Xylem) is committed to this challenging technology as an international water treatment company offering many years of ozone and UV light-based AOP experience. With thousands of UV, ozone and AOP installations worldwide, Xylem, along with its other water treatment, transport and analytical technologies, is making a significant contribution to safe water supply and wastewater treatment.

A key component of AOPs are hydrogen peroxide (H_2O_2). This is converted by ozone or UV light into highly reactive, extremely short-lived hydroxyl radicals, which remove

harmful trace substances in an environmentally friendly, economic and efficient manner.

Hydrogen peroxide is one of the many products manufactured and marketed by Evonik, one of the world's leading specialty chemicals company. Evonik is producing large quantities of mainly high concentrated hydrogen peroxide in strategically located plants and ensures a safe transportation to the place of use, such as drinking water plants. There, it is stored at concentrations of between 35 and 50 percent by weight.

In addition to this portfolio, on-site generation of hydrogen peroxide holds strong benefits to logistical, handling safety and regulatory challenges and can complement today's established hydrogen peroxide production and supply chain. The Danish company HPNow has developed and brought to market a technology solution for this purpose, branded as HPGen. Utilizing proprietary direct electrochemical synthesis, HPGen generate H_2O_2 directly at the point of use, in a secure and sustainable manner. In 2017, Evonik and HPNow entered into a cooperation agreement to combine respective strengths, innovative technology and industry expertise in a first drinking water treatment project.

The collaboration

The degradation of micropollutants in water treatment by means of AOPs has become established as state of the art, with realized flow rates > 5,000 m³/h. The innovative approach of this project is to produce the hydrogen peroxide directly at the point of use, thus verifying the safe and reliable integration of this technology into a typical water treatment scheme using a UV AOP solution.

For this purpose, a HPGen – UV AOP was installed in April 2021 at Evonik's premises in the Industrial Park in Hanau-Wolfgang, Germany. The test plan was focused on evaluating the removal efficacy of four emerging contaminants using this unique combination of in-situ H_2O_2 and UV.

The main components of the set-up were HPNow's HPGen A1000 model, which produces a nominal 1 kg of H_2O_2 per day (100wt% equivalent), at a low concentration output. The UV reactor was a Xylem's Spektron 6 UV reactor, branded Wedeco, and is equipped with a 70 W low-pressure UV lamp. This type of reactor is a designed for small flow rates. On a large scale, Xylem installs 300 - 800 W powerful UV emitters.

The HPGen consumable materials are only tap water, electricity, and oxygen - from the ambient. With these, the HPGen A1000 produced the nominal 1 kg / day at a safe and stable output concentration of 0.15w%.

Figure 1: Top: Complete test setup. Lower left: HPGen H_2O_2 generator from HPNow. Lower right: Spektron 6 UV-reactor from Xylem

Xylem's Spektron 6 UV reactor contains a low-pressure UV lamp, which emits UVC light monochromatically at 254 nm wavelength. This wavelength "activates" the H_2O_2 into the desired hydroxyl radicals, while also disinfecting the water. The UV reactor used applies UV-AOP typical UV doses at the selected flows of this pilot project. Due to the very high reactivity of the hydroxyl radicals with the micropollutants and other water constituents, the substances are oxidized within fractions of a second and no hydroxyl radicals remain in the water.

Ibuprofen, caffeine, dichlorobenzamide and 1,4-Dioxane were spiked to the process water as target pollutants and the degradation behavior was investigated in UV-AOP using the environmentally friendly oxidant H_2O_2. Within this process, hydrogen peroxide decomposes into oxygen and water only.

- Ibuprofen is an intensively used analgesic and anti-inflammatory.
- Caffeine has a stimulating effect on the human nervous system and is a component of various foods.
- Dichlorobenzamide is a persistent and highly mobile degradation product of the herbicide dichlobenil, which is no longer permitted in Europe. Because of its persistency dichlorobenzamide can still be found in ground waters in concerning concentrations.
- 1,4-Dioxane is an industrially used solvent and a component of various production processes. Because of its poor degradability by conventional water treatment processes and its widespread use, 1,4-Dioxane serves as a design guidance parameter for UV-AOP in wastewater reuse under California's Title 22 Indirect Potable Reuse: Groundwater Replenishment Rule. California's

standards are being adapted worldwide for particularly effective wastewater treatment to potable water.

A total of two sets of experiments were conducted at different UV and hydrogen peroxide doses of 5 mg/l (Experiment 1) and 10 mg/l (Experiment 2) to investigate the effect of different H_2O_2 doses on trace contaminant degradation rates. UV dose A of experiment 1 with 5 mg/l H_2O_2 was equivalent to the same UV dose A in experiment 2 with 10 mg/l H_2O_2. This was also true for UV doses B and C. The highest UV dose D was applied exclusively in experiment 1, because the decreasing AOP performance at low hydrogen peroxide doses can be compensated by higher UV doses. The applied H_2O_2 and UV doses corresponded to representative doses used in UV-AOP applications.

The substances explained in the previous section were enriched to concentrations typical for drinking water treatment cases of about 5 µg/l 1,4-dioxane and about 3 µg/l of the other substances in the tap water used. During this process, an electric agitator ensured sufficient mixing of the trace substances in the water.

A peristaltic pump dosed the hydrogen peroxide produced by the HPGen on site from the H_2O_2 holding tank (1 m³) into the water flow, which was between 330 and 1,350 l/h depending on the targeted UV dose. A centrifugal pump conveyed the water through the UV reactor into the collection IBC of the treated process water and also ensured good mixing of the H_2O_2 with the process water.

The results

Both test series 1 and 2, with 5 and 10 mg H_2O_2/l, respectively, showed good to very good degradation results of all substances. In both tests, the same pattern was revealed with the strongest reduction of ibuprofen, followed by caffeine, dichlorobenzamide and finally 1,4-dioxane, with the double H_2O_2 dose increasing the log reduction by a factor of about 1.4.

In experiment 2, the limits of quantitation of ibuprofen and caffeine were exceeded at the highest UV dose C applied. For ibuprofen, the detected degradation in the 10 mg/l H_2O_2 experiment was lower than the reduction obtained in experiment 1, because the input concentration of the substance was slightly lower in the 10 mg/l experiment.

For the individual trace substances, the following reductions were achieved depending on the UV and H_2O_2 doses.

Table 1: Reduction ranges of the target compounds in percent

Substances	5 mg/l H_2O_2	10 mg/l H_2O_2
Ibuprofen	79,6 – 98,9%	89,5 – 99,4% (< LOQ)
Caffeine	74,9 – 96,8%	85,5 – 98,4% (< LOQ)
Dichlorobenzamide	54,2 – 89,0%	71,2 – 95,2%
1,4-Dioxan	45,0 – 85,2%	67,6 – 92%

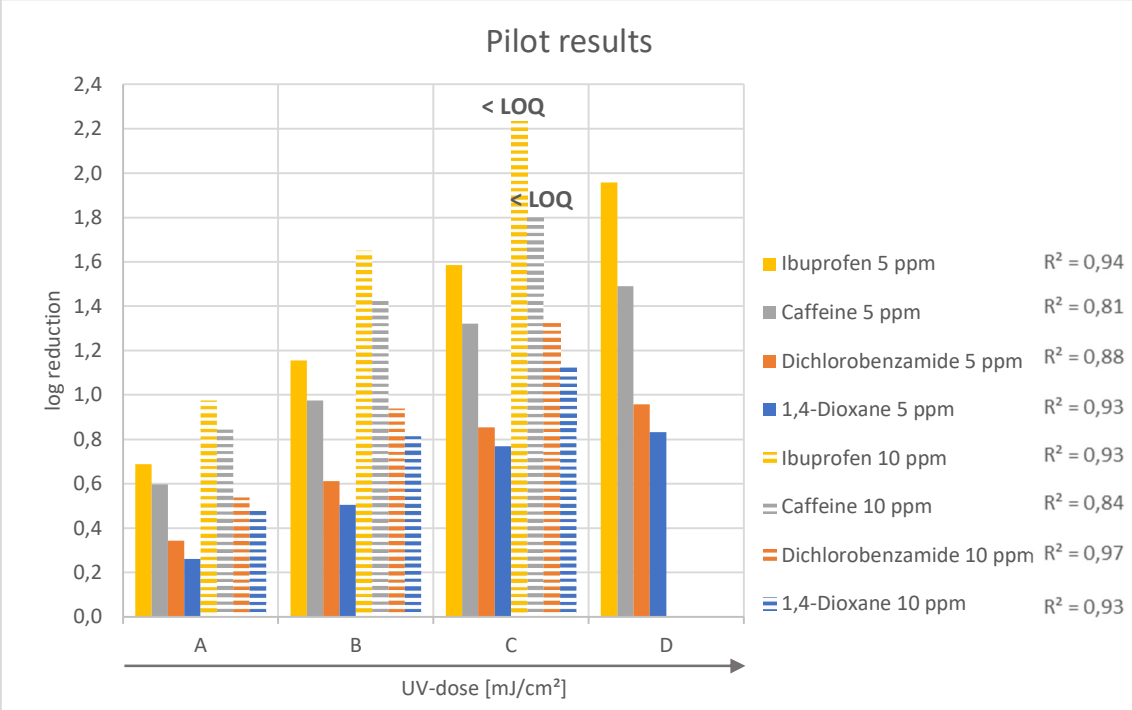

Figure 2: Log reductions of the tested compounds in each experiment

Benefits for users

The test results support the treatment processes practiced worldwide with AOP to produce drinking water. 1,4-Dioxane is a particularly resistant micro-pollutant to oxidative wastewater and drinking water treatment processes. Consequently, good 1,4-dioxane reduction suggests even better reduction of most other trace and micropollutants. This is also illustrated by this series of experiments. With the trace substances degraded in this project, these are representative surrogates of their use

classes. It could thus be proven that UV-AOP is an efficient and highly effective treatment technology for water contaminated with micropollutants.

By combining Xylem's globally established AOP solutions with HPNow's decentralized HPGen hydrogen peroxide generators, this advanced and environmentally friendly technology can be implemented in regions where hydrogen peroxide supply is difficult to access. Another advantage is the low concentration of H_2O_2, which eliminates the need for on-site storage of high concentrated hydrogen peroxide. Of no less importance is the positive impact on sustainability. Substantially reduced carbon footprint is achieved through the combination of highly efficient direct electrochemical generation, as well as elimination of transportation. In fact, with the use of green electricity, HPGen-UV carbon footprint can be reduced next to zero.

This project has successfully demonstrated how combining the expertise, products and technologies of Xylem, HPNow, and Evonik opens up sustainable opportunities in treatment processes to reuse waste water for potable purposes and can provide people with healthy drinking water even in places where this was previously not feasible.

Learn more about the HPGen™ system and its benefits for AOP at:
https://www.hpnow.eu/advanced-oxidation/

Please contact us at sales@hpnow.eu for additional information.