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ACTINIUM CHEMICAL RESEARCH

PRELIMINARY STUDIES ON THE TREATMENTS OF HYDROPONIC WATER FROM SPACE GREENHOUSES

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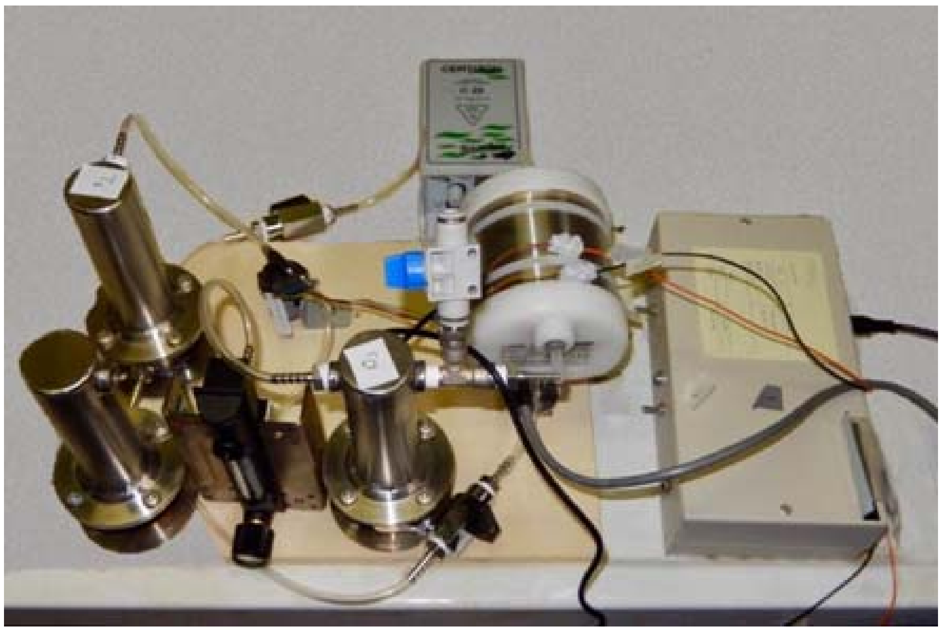
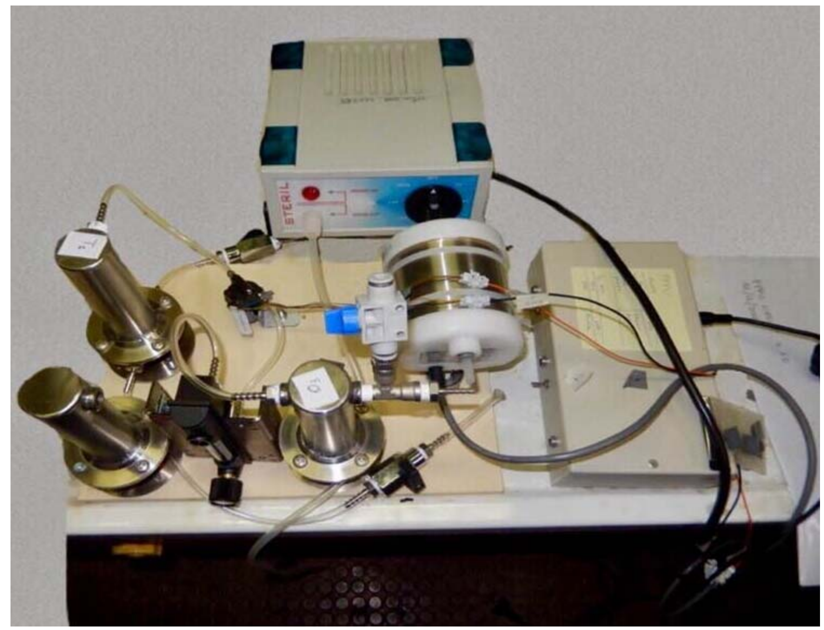
SUMMARY

- Evaluation of LED-UV flow reactor through uridine actinometry
- Evaluation of ozone generator through iodometry
- Determination of ozone solubility in water in our laboratory set-up
- Action of ozone on *Bacillus Subtilis*
- Action of LED-UV on *Bacillus Subtilis*
- Action of ozone on Hoagland-like solution
- Action of UV light on Hoagland-like solution
- Photo-ozonolysis of the Hoagland-like solution
- Summary and future outlook

Benchtop hydroponic water treatment plant





- Shown in two versions:

  Left with ozonizer 25mg O_3/h

  Right with ozonizer 250 mg O_3/h

Evaluation of LED-UV flow reactor by means of uridine actinometry

- **Uridine is a chemical actinometer useful for the determination of the number of photons or the energy released by an UV light source provided that the emission is comprised between 250 to 285 nm.**

- **When uridine is irradiated with UV-C light source it is transformed into a photohydrate as shown in Fig. 1, which does not absorb anymore in the spectral range comprised between 250 and 285 nm.**

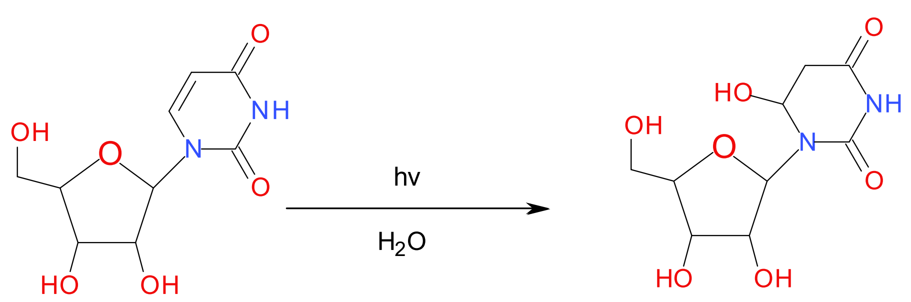


Figure 1. Uridine irradiated with UV light at about 260 nm yields exclusively uridine photohydrate with a known radiation chemical yield.

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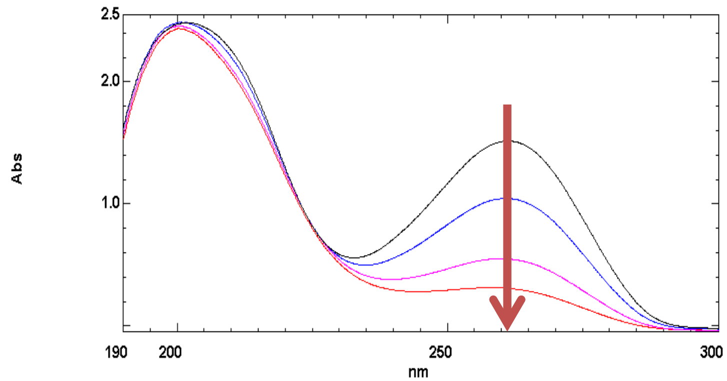
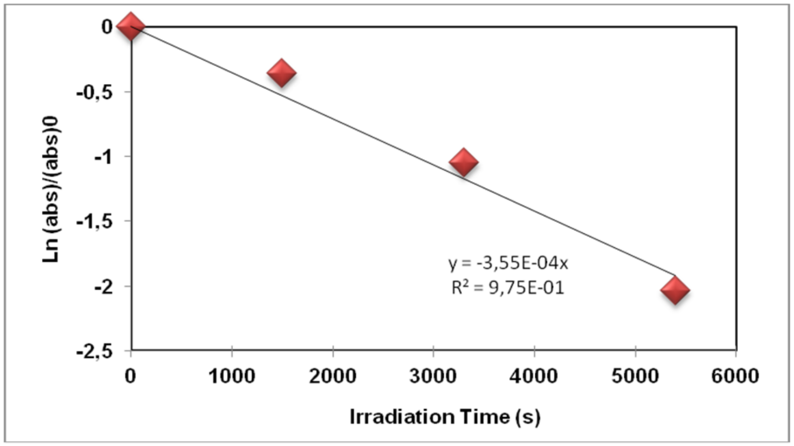
Uridine Actinometry on LED-UV reactor





- To photolyzed uridine it is necessary that the UV light source used emits in the wavelengths corresponding to the uridine absorption maximum. The commercial Aquisense Technologies LED-UV reactor employed in the present work is reported by specification to emit in the range comprised between 265 and 285 nm.
- The LED-UV flow reactor from Aquisense was able to photolyze uridine as shown in the top left picture. Thus, it is confirmed that its LED-UV emission is in the specification range between 265 and 285 nm.
- The uridine photolysis kinetics data were treated according to the pseudofirst order kinetics law and a straight line is obtained (top right picture) whose slope corresponds to the uridine photolysis rate constant in the UV-LED conditions offered by the Aquisense Technologies reactor. A rate constant value of $3.55x10^{-4}$ s^{-1} was determined.
- Knowing the quantum yield of uridine photolysis, it is possible to calculate the energy delivered to the uridine solution by the LED-UV reactor. It was found that such energy is in the range comprised between 1.0 and 2.3 mJ cm^{-2} s^{-1}.

Conclusion on LED-UV flow reactor

- The successful uridine photolysis in the LED-UV flow reactor from Aquisense Technologies , model PearlAqua 6D, demonstrates that the reactor is working properly irradiating in the wavelength range reported in the specification (around 275 nm).
- The photolysis rate constant of uridine in the tested reactor was found $3.55 \times 10^{-4}\ s^{-1}$ while the energy delivered to the uridine solution was found in the range comprised between 1.0 and 2.3 $mJ\ cm^{-2}\ s^{-1}$.

Evaluation of ozone generator by means of iodometry

- Ozone is a powerful oxidizing agent and is able to oxidize iodides to elemental iodine according to the following reaction:

  $O_3 + 2\ KI + H_2O \rightarrow I_2 + 2\ KOH + O_2$

- Iodine liberated by the action of ozone on potassium iodide is then titrated with sodium thiosulphate according to the classic volumetric analysis called iodometry:

  $I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$

Conclusion on ozone generator

- The iodometric titration is a suitable tool for checking the efficiency and the ozone production rate of the ozonizer.
- In the normal operative configuration, the ozone production rate of the ozonizer adopted (Certizone C25 from Sanders) was found in line with that expected by the specification.
- In fact the measured ozone production was 23.8 mgO_3/h against the specification value of 25 mgO_3/h.

Ozone solubility in water

- At 20°C the ozone solubility in distilled water at saturation is reported at 688 mg/L or 344 ml O_3/L (when P_{O3}=760 torr). However, these solubility values are by far achievable in practical conditions where P_{O3}<20 torr. In fact, typical ozone concentration in doubly-distilled water after ozone bubbing was found at 0.25 mg/L (1/2754 the ideal value).
- The typical ozone concentration in distilled water at room temperature, 0.25 mg/L is an extremely small value, in this case iodometry is not a suitable analytical tool but it is better to use a spectrophotometric-colorimetric method. We selected that of Lange.

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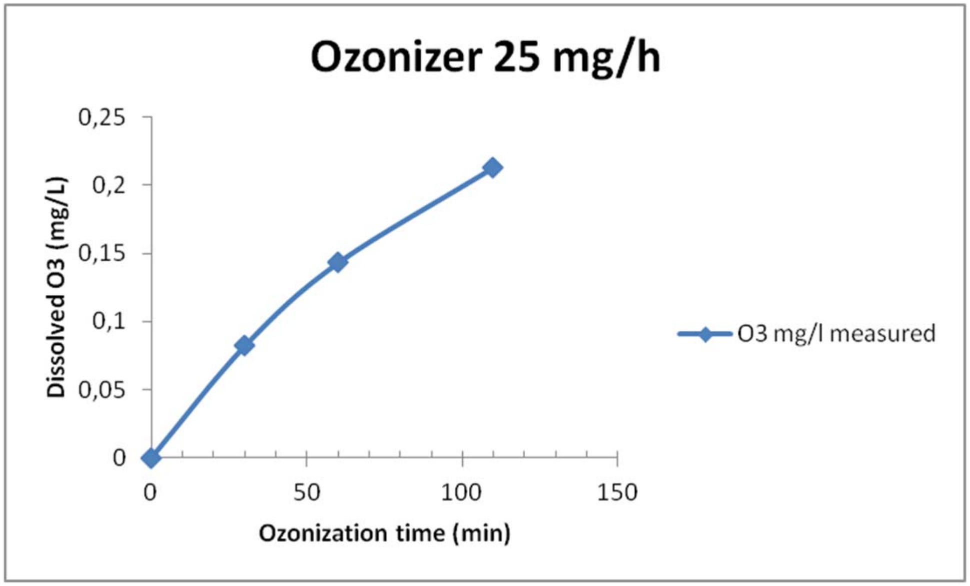
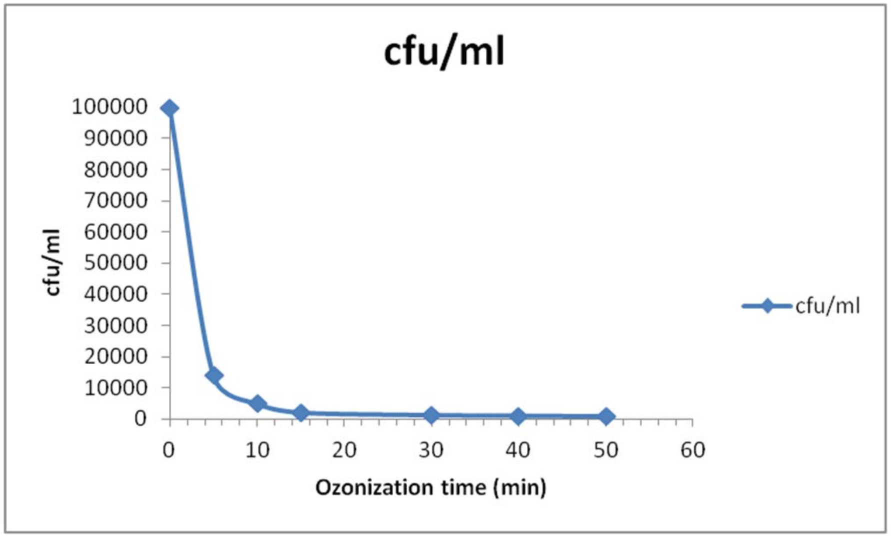
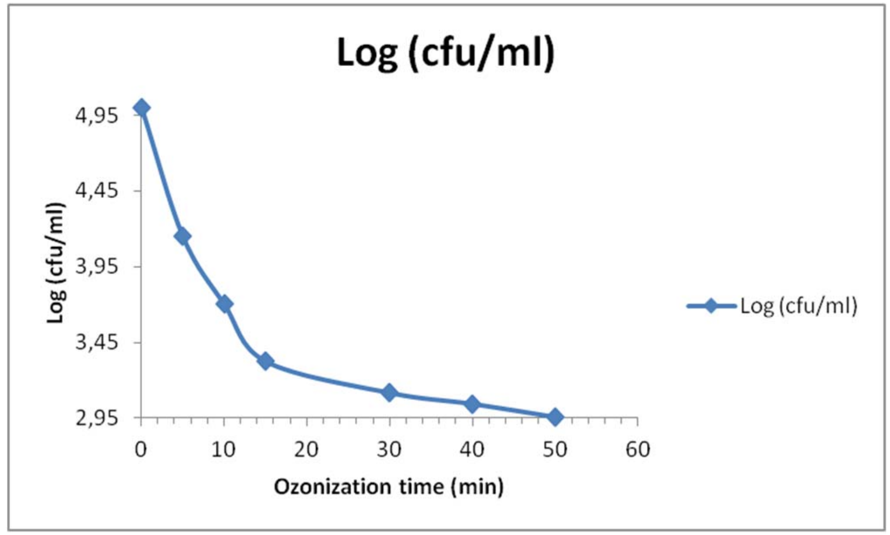
Ozone solubility in water



- Dissolved ozone in water as measured by the spectrophotometric-colorimetric test method after bubbling ozone (produced at 23.8 mg/h) through demineralized water (150 ml).

Action of ozone on *B. Subtilis*

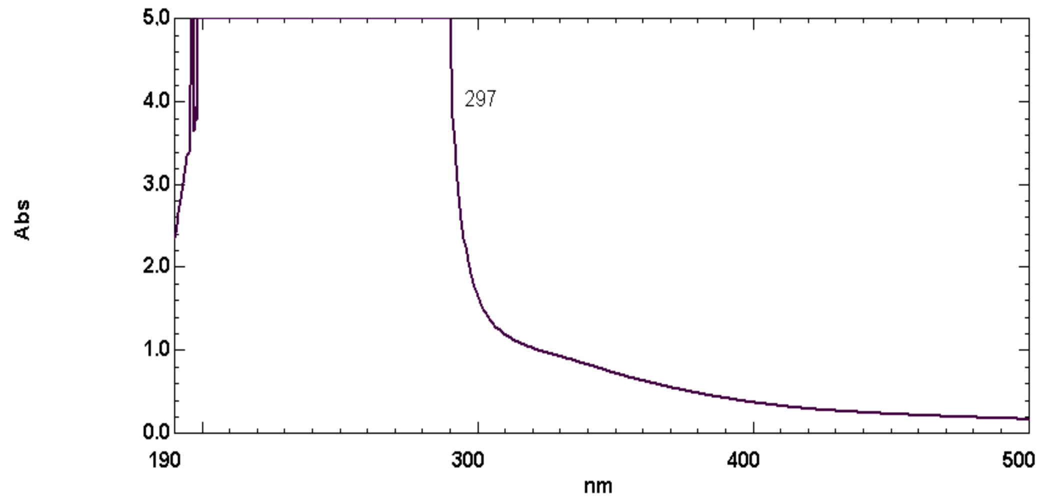




- In conclusion, it can be said that the ozonation of a standardized B. subtilis solution having a volume of 150 ml and a B.subtilis content of $1x10^5$ CFU/ml it requires a dose of 6 mg O_3 to abate the CFU by three orders of magnitude in the 150 ml volume. This corresponds to (1000/150)x 6 mg = **40 mgO_3/L i.e. 40 mg O_3 to treat 1L of B. subtilis solution $1x10^5$ CFU/ml.**

- **This result does not take into account the fact that together with B.subtilis the ozonized solution contains a mixture of nutrients utilized for the growth of the bacillus from its spores. It is completely unknown how much ozone is consumed by the nutrients present in the solution.**

Action of LED-UV on *B. Subtilis*



- The LED-UV irradiation of 10^5 cfu/ml *B. Subtilis* was completely not effective.
- The explanation of this was found by the UV-light cut off at 297 nm measured on the irradiated solution, as shown in the figure above.
- The solution was too opaque to the UV light because it was preparated using the nutrient solution to make the dilutions instead of the distilled water.

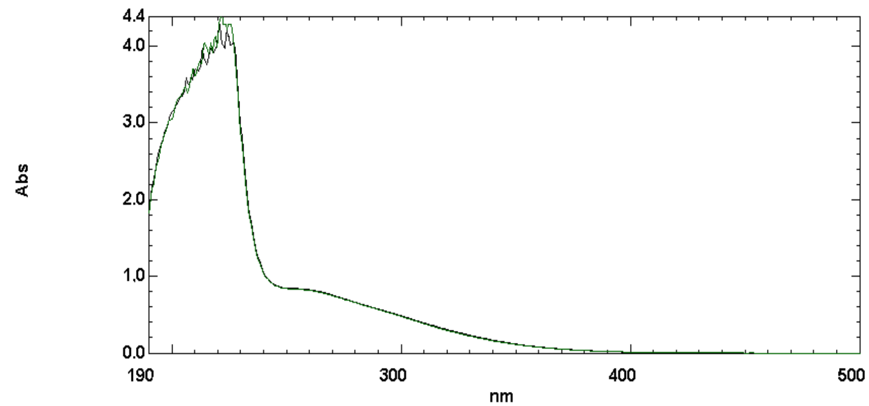
B. Subtilis experiment: photo-ozonolysis

- The photo-ozonolysis was not performed because the B.subtilis solution available was too opaque to the UV-C light.

- In these conditions the photo-ozonolysis was ineffective and the results should be expected identical to the simple ozonolysis.

Ozonation of the Hoagland-like solution

TABLE 1 - OZONE ON HOAGLAND-LIKE SOLUTION				
T (MIN)	pH	Electrical conductivity (mS/cm)	Dissolved O_3 mg/L	COD (mg/L)
0	4,73	1,518	0,000	77,9
10	5,30	1,472	0,122	
20	5,44	1,520		74,7
40	5,18	1,561	0,532	
60	5,33	1,534		73,1



- The action of ozone on the Hoagland-like solution <u>produces a yellow-orange precipitate</u>.
- It is well known that ozone is able to oxidize the transition metals from their lower oxidation state to the highest oxidation state which is less soluble or insoluble.
- Thus, transition metals micronutrients like for instance Fe^{2+} are oxidized to Fe^{3+} and the same could happens to other transition metals present in the solution as micronutrients.

- Despite the precipitate formed, the electronic absorption spectrum of the Hoagland-like solution does not change at all even after 1h ozonization at 24 mgO_3/h

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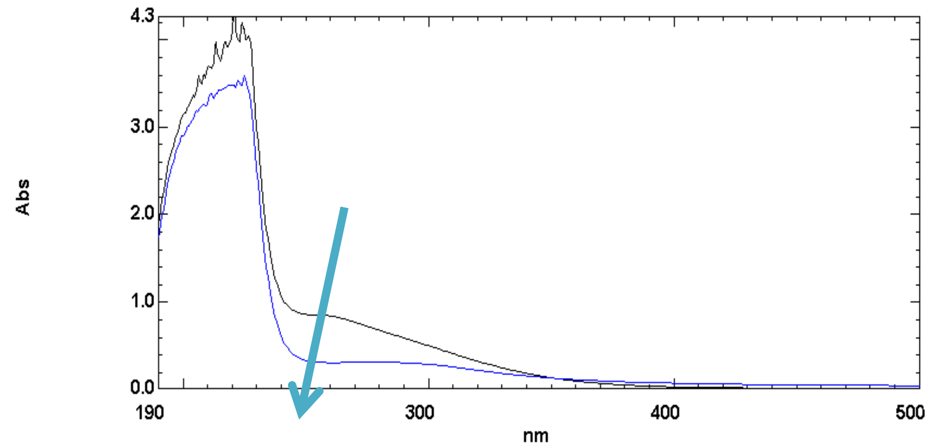
UV irradiation of the Hoagland-like solution

TABLE 2 - UV IRRADIATION ON HOAGLAND-LIKE SOLUTION			
T (MIN)	pH	mS/cm	COD (mg/L)
0	4,7	1,518	77,9
10	5,3	1,555	n.d.
20	5,4	1,605	n.d.
40	5,4	1,641	>160
60	5,5	1,720	>160
90	6,0	1,793	>160



- For problems with LED-UV reactor, use was made of a conventional Hg-lamp 17W working at 254 nm.
- The electronic absorption spectrum of the Hoagland-like solution was altered after 1h irradiation.
- One or more components of the Hoagland-like are photolyzed or photo-oxidized.
- Furthermore, also the electrical conductivity and especially the COD show dramatic changes which are probably linked to the photolysis and/or photoxidation of one or more components.

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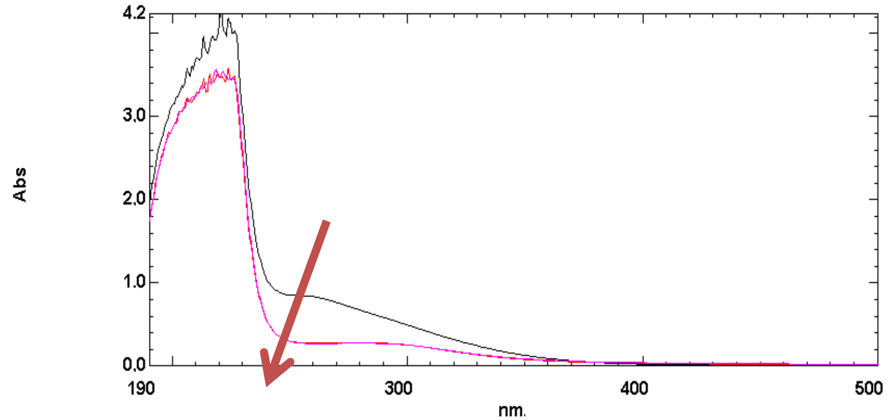
Photo-ozonolysis of the Hoagland-like solution

TABLE 3 - PHOTO-OZONOLYSIS OF HOAGLAND-LIKE SOLUTION			
T (MIN)	pH	mS/cm	COD (mg/L)
0	4,7	1,518	77,9
20	5,4	1,655	n.d.
40	5,8	1,721	n.d.
60	6,0	1,760	n.d.



- Photo-ozonolysis consists in the simultaneous action of UV light and ozone.
- The same problems as pure photolysis were observed: alteration of the electronic absorption spectrum due to photolysis and/or photoxidation, the increase in the electrical conductivity and pH value.

Summary and outlook-1

- Successful lab scale pilot plant was designed and built

The pilot plant was able to work:

1. only in the **ozonization mode** (keeping switched off the UV-LED reactor)
2. in the **UV-irradiation mode** (keeping switched off the ozonator)
3. in the **photo-ozonolysis mode** (when both the UV-LED lamp and the ozonator were kept switched on).

Summary and outlook-2

- **LED-UV reactor successfully tested with uridine actinometry: it works and irradiates at the right UV-C suitable for sterilization.**
- A series of problems has prevented to express in full the potential of the LED-UV unit.
- The LED-UV flow reactor presented an overheating problem which automatically caused the unexpected switch off of the lamp avoiding to make prolonged and more detailed kinetics studies.
- A new LED-UV flow reactor with supplementary cooling fan is recommented to be tested in a future work in place of the current model.

Summary and outlook-3

- **The ozone generator was successfully tested by iodometry**
- Ozonization, was found very efficient in the abatement of *B. subtilis* in the standardized solution.
- However, air-ozone bubbling into the solution with *B. subtilis* has produced a huge quantity of foam.
- This phenomenon can cause problems in a closed hydraulic circulation loop.
- The foaming phenomenon should be taken in account in the future developments of this device.

Summary and outlook-4

- The *B. subtilis* solution containing nutrients was too opaque for UV-light irradiation and hence also to conduct photo-ozonolysis.

- In case of future works, the *B. subtilis* standardized solution should be prepared (if possible) with the lowest nutrient load (e.g. NaCl solution) in order to make the solution suitable for UV irradiation and for photo-ozonolysis experiments.

Summary and outlook-5

- At present, with the experimental data derived from the present work we can conclude that ozone is effective in the sterilization of water solutions with high bacterial load.

- We cannot make conclusions about the effects of the UV-LED irradiation and about photo-ozonolysis on *B. subtilis* since the experiments were impossible to be performed. However, plenty of literature is available for the effect of UV-C on microbial load reduction.

- Only in the conditions outlined under the previous point 4 it will be possible to perform comparative tests between ozonation, UV-LED irradiation and photo-ozonolysis.

Summary and outlook-6

- The Hoagland-like solution was found unstable toward UV irradiation and similarly also under photo-ozonolysis conditions.

- In a future work, it is necessary to understand which component(s) of the Hoagland-like solution is (or are) photolyzed by UV irradiation and working at lower nutrient solution concentrations.

- This can be performed for example by careful component analysis and even HPLC analysis of the Hoagland-like solution before and after irradiation or by testing different versions of the Hoagland-like solutions without the presence of the component(s) suspected to be photosensitive.

Summary and outlook-7

- The steady increase in the pH value of the Hoagland-like solution was observed especially under UV irradiation and also in photo-ozonolysis conditions.

- Although less remarkable the phenomenon was observed also during simple ozonation.

- Further work should be addressed to understand the detailed reasons for these pH changes by purposely designed experiments.