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UV technologies in water purification systems

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Abstract: UV technologies are being increasingly used in water purification systems, taking advantage of the germicidal properties of UV and also its effect in reducing organic contaminants. This paper discusses the effectiveness of using UV technologies along a water purification chain and the parameters and configurations to be considered when selecting UV lamps for water purification systems. Also described are the effects of UV exposure on various types of bacteria and the effect of different UV wavelengths on organic molecules. Results are given on the germicidal effect of a 254 nm UV lamp, used for biofilm prevention in a pure water storage reservoir and on the effect of a dual-wavelength UV lamp (185 nm and 254 nm) in Milli-Q® ultrapure water systems for the reduction of organic contaminants.

Introduction

As early as 1801, scientists submitted the hypothesis that the lethal effect of the sun could be attributed to energy corresponding to the invisible ultraviolet (UV) bandwidth. Since then, many advances have been made in the understanding of UV light, and numerous UV-based technologies have been developed as a result. In particular, UV is now widely used in water treatment, both on a large scale for potable water and on a smaller scale for obtaining water suitable for analytical and research laboratories.¹ This paper describes the parameters to be considered when selecting UV lamps for water purification systems, the impact the configuration has on the efficacy of germicidal (254 nm) UV lamps, and the effect of dual-wavelength (185 + 254 nm) UV lamps on organic reduction.

Theory recall

The UV bandwidth occupies wavelengths of roughly between 100 nm and 400 nm in the electromagnetic spectrum; it is sandwiched between those of X-rays and visible light (Figure 1). The UV bandwidth is formally divided into UVA (black light), responsible for sun tanning and sunburn, UVB, which

is believed to induce skin cancer, UVC, whose energy has germicidal properties, and vacuum UV. The energy generated by the vacuum UV wavelengths is the highest and can induce the formation of ozone from oxygen.

Figure 1: UV bandwidth in the electromagnetic spectrum

According to quantum theory, energy is carried by photons. The photon energy is given by Equation (1), where h is Planck's constant, λ is the wavelength, and *C* is the speed of light. It is easily deduced from this equation that longer wavelengths (towards visible light) generate lower energy than shorter wavelengths (towards X-rays), which generate higher energy. The power of the UV lamp is defined by the photon energy and the number of photons delivered per unit of time.

$$
E = h \frac{C}{\lambda} \qquad \text{[Equation (1)]}
$$

Photons that hit organic molecules have an effect on the electrons in the chemical bonds and the atoms. Not all chemical bonds have the same energy or reactivity; therefore they are activated by the photons at different wavelengths. The energy absorbed to bring the electrons from their ground states to excited states corresponds to discrete and specific wavelengths. The passage from the ground state to a higher energy level is called a transition. Chemically,

UV lamp selection

In water purification systems, low-pressure mercury vapor lamps are used. Mercury is sealed inside tubes and is excited by electrical discharges. Mercury atoms come back to their ground state level by emitting energy corresponding to specific rays or wavelengths. At low pressure, mercury emits energy at three wavelengths: 254 nm (or more precisely 253.7 nm), 185 nm (184.9 nm), the principle radiation, and 194 nm (194.2 nm), a very low-intensity band. The 254 nm wavelength falls in the germicidal range, and the 185 nm wavelength, that induces ozone

transitions correspond to the passage of electrons from lower energy orbitals to higher energy orbitals. The most common transitions are σ to σ^* , n to σ^* , π to π^* , and n to π^* . Some examples of wavelengths corresponding to the energy required to induce these transitions are given in Table 1. Note that wavelengths of around 254 nm will activate and make aromatic systems reactive, but not C-O and C-C single bonds. On the other hand, hydroxyl (OH) groups will be activated by wavelengths close to 180 nm.

Table 1: Examples of wavelengths required to activate selected molecules and chemical groups

Molecules	Transition	Wavelength
H_3C - CH_3	σ to σ^*	135 nm
$H_2C = CH_2$	π to π^*	165 nm
H ₂ O	n to σ^*	167 nm
$H3C$ \rightarrow OH	n to σ^*	183 nm
R. R R^{\prime} R=alkyl	π to π^*	180-200 nm
	$n \circ \sigma^*$	190 nm
	π to π^*	2.54 nm

UV radiation is absorbed to different extents by the molecules it hits along the way, and thus by the media it crosses. For instance, air does not transmit UV as well as a vacuum, and water absorbs more UV radiation than air does. Thus, in UV-based technologies, the transmittance of UV through a specific medium is a primary factor to consider. This is particularly true for water treatment, where UV energy decreases very quickly.

formation from oxygen as well as water splitting, is used in the photo-oxidation of organic molecules. Regular glass absorbs all wavelengths below 320 nm, and therefore neither the 185 nm nor the 254 nm wavelengths would pass through. Thus, to allow these wavelengths to reach the water, the mercury lamp has to be made of quartz sleeves. These two wavelengths behave differently in water. While the 254 nm is fairly well transmitted because water molecules do not absorb the energy corresponding to this wavelength, the 185 nm intensity drops very quickly because it is absorbed by water molecules (Figure 2). Additionally, particulates and certain organic substances (such as humic and fulvic acids) stop or absorb UV light. It is particularly important, therefore, that the UV treatment is applied to clean water (in terms of particulates) which has already been purified for better efficiency.

Figure 2: Transmission of 185 nm and 254 nm wavelengths in water

In addition to these physico-chemical processes, other parameters, such as the quantity of gas sealed in the lamp, the partial pressure of mercury, the power, the electrical discharge process, and the lamp size have an impact on the effectiveness of the lamp. The combined effect of all these factors explains why differences can be found between UV lamps of the same nominal power from different suppliers. To systematically compare the efficiency of lamps at various flow rates, models were developed in Millipore's R&D Department. These models are based on lamp energy measurements in specific and reproducible conditions. This allows a quick and safe comparison of various lamps, and also permits estimating the effect of flow rate on the energy (in mW.sec/cm2) actually delivered to the water flowing around the lamp. Second order equations, taking into account the energy transmitted, the absorption, the lamp size, and the diameter of the housing, were related to the residence time of the water exposed to UV radiation and to the flow rate. An example of the relationship between the flow rate and the net energy delivered to the water is given for a 4 W UV lamp in Figure 3.

Figure 3: Effect of flow rate on the net energy delivered by a 4 W UV lamp

The efficacy of the lamps was experimentally tested. Data was obtained both for the germicidal effect of the 254 nm UV lamps (lamps that deliver almost exclusively the 254 nm wavelength), and for the total organic carbon (TOC) reduction by 185 + 254 nm dual wavelength UV lamps. Some of the data is presented here.

1- The germicidal effects of two lamps for various flow rates were compared (Figure 4) and plotted as the bacterial log reduction value (LRV). An LRV of 4 implies a reduction in bacterial growth by a factor of 10 000. Clearly both lamps behaved very differently. While Lamp 1 was fully efficient at low flow rates, and could not be used at flow rates higher than 5 liters per hour (lph), Lamp 2 was moderately efficient over a wider range of flow rates. Neither of these lamps was selected because they do not fit specifications required for Millipore water purification systems.

Figure 4: Comparison of germicidal efficiency (in terms of bacterial LRV) of two lamps as a function of the flow rate

2- Figure 5 shows a comparison of TOC reduction using two different [185 + 254 nm] UV lamps. The most efficient (Lamp 1) was selected to equip Milli-Q ultrapure water systems.

Figure 5: TOC reduction using two different dual-wavelength UV lamps

3- A comparison of the ballasts fitting the UV lamps in the water purification systems yielded similar differences. Ballasts are devices that generate optimized AC (voltage and frequency) to power

the UV lamp, then the electrical discharge in the low-pressure tube activates the mercury vapor to be energized by the electrical current. They are very important, not only for the lamp efficacy (as shown in Figure 6) but also for the UV lamp lifetime. Such devices are tested on a regular basis to equip water purification systems with the best ballasts available on the market. Ballast 2 was the one selected to equip current Millipore water purification systems.

254 nm UV lamps and germicidal effect

Effect on DNA

As was mentioned previously (Figure 2), the 254 nm wavelength is well transmitted through water. The 254 nm UV lamps have been widely used for several years to kill or inactivate micro-organisms and prevent bacterial growth and contamination in water purification systems. The most dramatic biological effect occurs at the genetic level.^{2,3,4} The maximum germicidal effectiveness lies around 265 nm (Figure 7), which is the wavelength of maximum absorption of pyrimidine bases such as thymine and cytosine.

Figure 6: TOC reduction using the same lamp with two different ballasts

Figure 7: Germicidal effectiveness curve relative to wavelength

Figure 8: DNA photoadducts generated by UV 254 nm

The 254 nm radiation delivered by mercury lamps induces many types of lesions in DNA. The two major photoproducts are the cyclobutane thymine-thymine dimer and the dipyrimidine (Thymine-Thymine, Thymine-Cytosine, Cytosine-Thymine or Cytosine-Cytosine) 6-4 photoadduct (Figure 8). The cyclobutane adduct resulting from a [2 + 2] cycloaddition, as well as its biological repair mechanisms, have been well studied and documented.

UV dose

The power, or UV dose, needed to inactivate each type of micro-organism varies significantly (Table 2). Bacterial DNA is quite accessible to UV radiation, which renders bacteria fairly easy to inactivate. The most resistant micro-organisms are mold spores and some viruses, because their DNA is well protected by capsids. The efficacy of a lamp to inactivate bacteria thus depends on the strain, on the power of the UV lamp, and on the radiation time, related to the residence time and to the flow rate when water passes a UV lamp.

Let us consider the inactivation of two bacteria strains, Escherichia coli and *Pseudomonas aeruginosas*, requiring respectively 6600 and 10500 µW.sec/cm2 UV doses. A water system was equipped with an in-line 6 W, 7 cm, 254 nm UV lamp, and the flow rate was fixed at 10 L/h. The energy measured at the quartz surface was 4.08 mW/cm2 . The net energy delivered to bacteria flowing through the lamp was calculated as $37600 \mu W/sec/cm^2$. This energy is sufficient to inactivate 99.9 % of both bacteria strains (see Table 2). Note that such a UV dose inactivates all bacteria strains cited in Table 2. This type of lamp is now installed in-line in pretreatment systems such as Millipore's RiOs™ reverse osmosis and Elix® systems. The Elix system employs reverse osmosis and electrodeionization. In accordance with previous calculations, experimental data was collected on an operating system and a bacterial LRV of 5 to 6 was

Figure 9: Bacteria LRV versus flow rate with an in-line UV lamp

measured up to 40 L/h (Figure 9).
In-line UV lamps and UV lamps for storage reservoirs

The importance of UV radiation on stored water was also considered. In the following set of experiments, a 60 L storage reservoir fitted with an air-vent filter and an 8 W, 254 nm UV lamp (Automatic Sanitization Module – ASM), was fed with Elix-type water. Two Elix systems were compared: one was equipped with an in-line 6 W 254 nm UV lamp, and the other system was not. Every day, half the water stored in the reservoir was drained and the reservoir was filled with freshly produced water from the Elix systems (Figure 10).

Figure 10: Schematic of the experimental protocol corresponding to results reported in Figure 11. Three samplings were done every 24 h. The reservoir was filled with water produced by an Elix system that did not contain an in-line UV lamp and then by an Elix system that contained an in-line UV lamp. The results are shown in Figure 11.

Three measurements were made at regular times. The first measurement was done on water stored since the day before. The second sampling was done after irradiation for 10 min (with the ASM lamp) of the water stored in the tank. Finally, the third measurement was made just after filling up the reservoir with freshly purified water. Performances of Elix systems with and without UV were compared regarding microbiological content of purified water over a two-month period. Analysis of the results highlighted different points (Figure 11). Clearly, the UV radiation in the storage reservoir reduced bacteria levels very significantly: in water purified without UV, by a factor of 50 (Figure 11A), and by 5 to 10 times in water already purified in-line by UV (Figure 11B).

Figure 11a Figure 11b

Figure 11: Bacterial count at the three sampling points (see Figure 10) in a system without a UV lamp (Figure 11A) and in a system equipped with an in-line UV lamp (Figure 11B)

in-line UV-treated was used. On the other hand, there was no difference between the bacterial counts, before and after emptying and refilling the reservoir with water that was not in-line UV-treated. Combining in-line UV lamp exposure with internal UV treatment in the storage reservoir is a safe and efficient way to control bacterial growth and to prevent build-up of biofilm in the reservoir.

Another potential way to control bacterial growth in storage reservoirs is to recirculate stored water in a loop equipped with a UV lamp.⁵ The efficiency of such a set-up was compared to previously discussed configurations, where stored water is not recirculated but is irradiated on a regular basis in the reservoir (Figure 12).

Set-up with UV lamp in recirculation loop

Figure 12: Experimental set-up of results reported in Figure 14. The UV lamp is installed either in-line or in the reservoir.

Results (Figure 13) show that the configuration with UV irradiation during recirculation and no UV treatment in the reservoir is not an efficient way of controlling bacterial contamination in the reservoir. Indeed, the UV efficacy is dependent on the flow rate, and contamination inside the reservoir is never reduced. So, although bacteria may be killed during the recirculation, water is re-contaminated when it comes back into the reservoir. The control of microbiological proliferation is performed much more efficiently by installing an immersed UV lamp in the reservoir.

Figure 13: Bacterial count in systems with a UV lamp either in the recirculation loop or in the reservoir.

Materials and methods

Bacterial analysis was done using a Milliflex® device with 0.45 micron rated membrane funnel and R2A agar pre-filled cassettes. Incubation was done at 30 °C for 72 h. The sample volume was adjusted from 0.1 mL up to 100 mL depending on the microbial content.

Photo-oxidation of organics using dual-wavelength [185 + 254 nm] UV lamps

Progress in instrument technology permits ever lower detection limits to be reached, and more and more experiments require very low sample quantities. The overall increased sensitivity of the methods has highlighted the importance of using high purity reagents. Mass spectrometry is a typical example of this evolution: organic molecules (TOC) at high ppb levels have an effect on UV detection. Mass spectrometry has detection limits a hundred times lower and is, therefore, more sensitive to traces of organic contaminants introduced during sample preparation, whether it is sample dissolution or

separation by liquid chromatography. So reaching the lowest possible TOC level has become very important for the success of experiments in areas as diverse as toxicology, pharmacokinetics, drug discovery, genomics, proteomics, and environmental analysis.

UV photo-oxidation technology

UV photo-oxidation using a dual-wavelength UV lamp is now a widely-utilized technology in water purification systems to decrease TOC to ppb levels (typically < 5 ppb).^{6,7,8} The 185 nm wavelength is

emitted from lamps made of synthetic quartz sleeves. The energy corresponding to both the 185 nm and 254 nm wavelengths is used during the chemical photo-oxidation process.⁶ As mentioned previously,

the 185 nm wavelength delivers higher energy that induces ozone formation from oxygen via singlet oxygen (Figure 14).

Figure 14: Effect of UV on oxygen and water molecules, and subsequent radical reaction. Reaction rates in sec¹.

The 185 nm wavelength can also induce homolytic water splitting and generate the hydroxyl radical (OH**.**).9 This radical has a very high oxidation potential (2.80 volts), and is believed to be a key species in the mechanism of organic molecule oxidation.

Once radicals are formed, the fastest chemical reaction rates are those involving the hydrogen radical with oxygen or a combination with a second hydrogen radical to generate hydrogen, and the reaction of the hydroxyl radical with organic molecules or a combination with a second hydroxyl radical to form hydrogen peroxide. Note that among all oxidizing species present, the hydroxyl radical has the highest oxidation potential (Table 3). It is difficult to ascertain which pathway occurs, and it is most likely that several pathways compete.

Possible chemical reactions are proposed to account for the oxidation of organic molecules. Methanol was picked as an example (Figure 15). Once again,

several pathways compete and Figure 15 describes reasonable chemical reactions that lead from methanol to carbon dioxide or a combination of carbon dioxide with water $(HCO_3^-$ or H_2CO_3). One organic carbon leads to one carbon dioxide molecule. Some organics, especially those with double bonds (π electrons), can also be activated directly by UV 185 nm and react with oxygen or the hydroxyl radical.

Table 3: Redox potential (volts) of various oxidative species

Oxidative species	Redox potential (Volts)
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	178
Permanganate	1.69
Chlorine	1.36
vaen	1.23

Figure 15: Chemical reaction accounting for oxidation of organic molecules

In water purification systems, the quartz sleeve mercury lamp is embedded in a 316 stainless steel housing and is installed upstream from the mixed-bed resin. The role of the resin is to retain the HCO_3^- ions and charged organic molecules formed during the photo-oxidation process. Indeed, the resistivity of purified water typically drops from 18 MΩ.cm to 5 – 10 MΩ.cm due to photo-oxidation and ionic species formation. Afterwards the mixed-bed resin resistivity rises to 18.2 MΩ.cm and the TOC level is typically < 5 ppb. Note that a very high concentration of TOC in the feedwater to the polishing system equipped with the UV lamp might generate higher TOC levels at the outlet of the system.

Effect of UV photo-oxidation in mass spectrometry

Data obtained by LC-MS is presented to show the efficacy and importance of UV photo-oxidation in technologies sensitive to TOC such as mass spectrometry. In a water polishing purification system, the 185 / 254 nm UV lamp was turned *on* or *off* and the total ion count (TIC) observed by mass spectrometry (MS) was recorded in both cases (Figure 16). TOC was measured at 4 ppb with the UV lamp *on*, and at 12 ppb with the UV lamp *off*. Clearly, TOC levels in water and the TIC recorded by MS are related.

The mass spectrum of a selected peak (at 13.1 min) was recorded for both configurations. The most important difference between the two spectra is the intensity of the detection signal. It is ten times lower when the UV lamp is *on* (4 ppb TOC). Figure 17A and 17B compare spectra on the same scale of intensity, and it is quite obvious that the UV-treated water brings much less organic contamination. When the spectrum recorded with the UV lamp *on* is expanded to full scale (Figure 17C), very minor peaks become visible. These peaks could not be detected with the UV lamp *off*. So, using clean water in terms of TOC lowers the detection limit of the MS.

Figure 16: Total Ion Count obtained by mass spectrometry of water treated with and without UV photo-oxidation.

Figure 17 A : Mass spectrum of non UV-irradiated water at time 13.1 min on the TIC tracing.

Figure 17 B : Mass spectrum of UV-irradiated water, at the same absolute scale as Figure 17A, at time 13.1 min on the TIC tracing.

Figure 17 C : Full scale expansion of Figure 17B.

Figure 17: Mass spectra corresponding to time 13.1 min on the TIC tracing.

TOC monitoring

In order to run experiments under optimum conditions, to control the water quality, and to take full advantage of TOC reduction, it is very useful to be able to monitor the TOC level at the outlet of the water polishing purification system. A TOC monitor can be installed in-line just before water delivery. The TOC monitor installed in Millipore systems was developed in collaboration with Anatel®. The principle of the TOC monitor is also based on photo-oxidation using a dual wavelength [185 / 254 nm] UV lamp. After purging a cuvette, water is brought into this cuvette and resistivity is measured. Water is then irradiated by a dual-wavelength UV lamp and the time extended to

ensure complete oxidation of all organic molecules to $CO₂$. The time necessary for full oxidation was determined experimentally using various types of organic molecules. The $CO₂$ formed reacts with water to generate HCO_3^- (predominantly). The resistivity is measured again and the difference in resistivity before and after UV photo-oxidation is related to the TOC initially present in the water. This principle can work because one organic carbon atom leads to one $CO₂$ molecule (Figure 15). For accurate measurement, a temperature sensor is also present in the cell, and the resistivity is compensated to 25 °C.

Figure 18: Localization of UV lamps in a schematic of a water purification chain

Conclusion

A schematic of a complete water purification chain is presented on Figure 18 and the different types of UV lamps that can be found in such a chain are highlighted. An initial germicidal 254 nm UV lamp is installed in-line in the pretreatment system, and a second germicidal 254 nm UV lamp is set up in the storage reservoir. The role of both these lamps is to control and prevent bacterial contamination in the water purification chain. A dual wavelength [185 /

254 nm] UV lamp is incorporated in polishing systems to reduce the TOC level via photo-oxidation processes. Note that this lamp also emits UV at 254 nm and, therefore, additionally has a germicidal effect. Finally, monitoring of TOC levels is also performed by a dual-wavelength UV lamp, installed at the outlet of the water purification system to ensure water quality.

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