

TREATMENT OF GROUNDWATER WITH

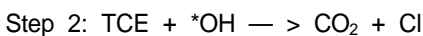
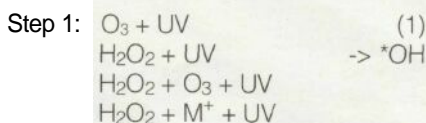


THE THIRD GENERATION UV SYSTEMS

**Alex Wekhof
Edwin N. Folsom Jr.
Yuval Halpern**

Treatment of aqueous solutions containing toxic organic compounds is of widespread concern, and established methods of toxic treatment have to be re-evaluated under increasingly restrictive regulations. Ultraviolet technologies offer the advantage of being very effective when compared with other processes, because the UV-aided process destroys the contaminant compounds leaving no residue (1). Traditional UV technology—described below as first and second generation UV systems—has advantages and limitations.

The basis of the first generation UV technologies is the use of 254 nm light emitted by conventional mercury vapor lamps. This wavelength generates active radicals from peroxide or ozone added during treatment of contaminated water. The mixture must be kept under UV light until the oxidants are converted into free radicals, which subsequently destroy toxic organic compounds. This is a conventional advanced oxidation process (AOP); for example, the destruction of TCE is known to proceed as follows:



The first-generation UV-assisted process shown above has drawbacks, including the bulky size of units.

UV photons can be used to destroy organic toxic compounds directly—without the use of oxidant additives—by breaking chemical bonds in organics through photodissociation. This process requires photon energies from 4 to 7 electron volts (eV), achieved at wavelengths from 300 to 175 nm. Direct UV photolysis of TCE is shown as follows:



For dissociation to occur, the UV wavelength must match up with the target compound's optimal absorption band, which can be as narrow as 1 nm or as wide as 20 nm. If a complex organic compound undergoes photodissociation, it may generate byproducts that also are toxic, and the byproducts do not have the same optimal dissociation wavelength as the parent molecule. This condition, as well as the presence of many different toxic compounds in a contaminated medium, requires a dense

structure of UV emission lines to effectively support the direct photolysis.

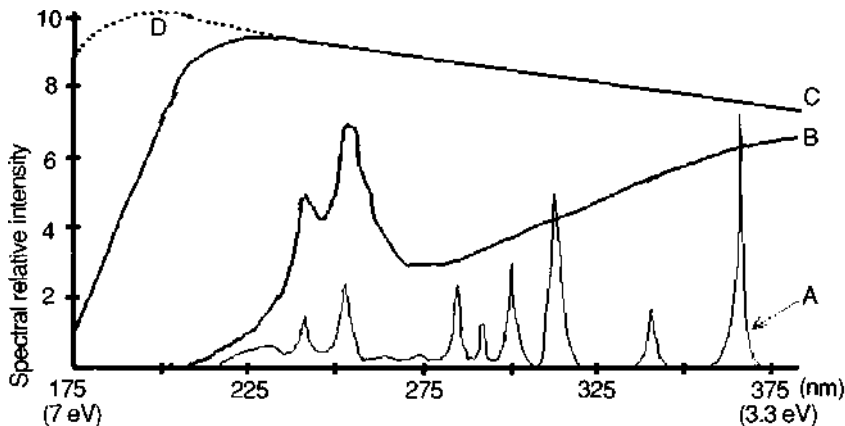
Traditional medium and high pressure mercury vapor lamps having input powers over 200 watt per lamp inch (80 watt/cm) generate few additional lines (2) (Figure 1 A). The number of UV lines in the deep UV region can be slightly increased with dopants like iodides and magnesium placed into medium or high pressure mercury lamps. Such lamps are known as metal halide lamps. Systems that employ lamps with dopants, which became known as second generation UV systems, can be more effective than the first generation UV systems (3); they can treat organic toxic compounds with or without adding an oxidant.

Wekhof Process - The third generation UV systems

This method is the alternative to processes based on UV lamps with a line emission. Instead, it is based on a pulsed source of the UV continuum. Since the UV continuum overlaps absorption bands of all toxic compounds present, then the only requirement for the process is that the UV light has to be of sufficient intensity (4). If these conditions are met, this process destroys all toxic organic compounds through both AOP and direct photolysis.

FIGURE 1

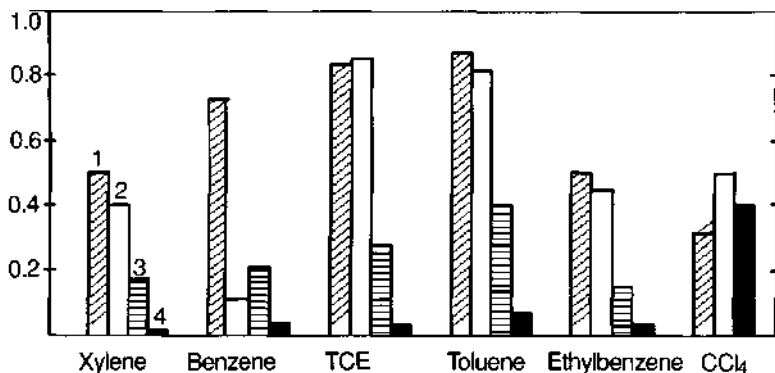
Comparison of spectral intensities



A: Spectrum of medium pressure mercury lamp at 60 watts per lamp cm.
 B: Spectrum of xenon flashlamp pulsed at current density of 8.5 kA/cm²
 C: Approximation of spectrum of Wekhof lamp pulsing at average load of 60 watts per lamp cm, current density 12 kA/cm².
 D: Black body spectrum at conditions as in C.

FIGURE 2

Destruction of toxic organic compounds



Standard xenon flashlamps generate approximately the required spectrum. However, standard xenon lamps have to be operated at elevated parameters to generate the spectrum (2, 4), as shown in Figure 1B. A more efficient spectrum can be generated by a Wekhof Flashlamp (Figure 1C) without sacrificing the lamp lifetime and at less energy consumption [(4), Patent 5,144,146 granted September 1, 1992.]

Experiments

We conducted two series of tests. The first series was in cooperation with the Lawrence Livermore National Laboratory, and was performed with groundwater from their wells. For these tests we used a specially designed test apparatus fully described in (4).

It consisted of an elliptical reflector to encircle a lamp and a processing reactor. The reactor was a 1.5-in. diameter quartz tube. A pump circulated one liter of contaminated water between this

reactor and a back-up container. This system allowed a simple mounting for each of two different lamps. However, the simplified mounting resulted in substantial optical losses (equal for both lamps). These losses did not affect the comparative nature of these measurements, but prevented us from making accurate estimates of absolute values of removal rates of organics. The pH was maintained at 7.0 in these tests.

In the second series of tests, conducted with Chemical Waste Management and Canonie Environmental, we used a cylindrical stainless steel processing vessel as our UV reactor. We performed these tests with only a Wekhof Flashlamp mounted along the vertical axis of the 4-in. diameter by 7-in. long reactor. The batch volume was 1 gallon. These tests were designed to measure absolute values of various processes with the lamp only, since the effectiveness of a conventional AOP is well known.

In the second series of tests we also measured the UV absorption of each water sample to estimate UV utilization. We also adjusted the pump speed to create necessary turbulent flow in the reactor to equalize the UV exposure along the reactor radius. In all tests during this series, groundwater samples came from customer sites and pH was adjusted to 4.5 before runs.

Results

Series 1 tests with LLNL for GSW-15 well. We ran more than 150 samples. A portion of the data from tests involving both lamps is presented on the histogram of Figure 2.

These tests demonstrated an improved (or at least equal) performance by the Wekhof Lamp without adding peroxide to the water in comparison with the similar exposure of a medium pressure mercury lamp plus peroxide in water. Carbon tetrachloride data did not follow this trend; however, the additional tests showed encouraging CCU results (Figure 6). The data also show a higher than directly proportional increase of removal rates of organics with the applied pulsed UV power.

Series 2 tests Tests were conducted with CWM and Canonie Environmental. We tested the following conditions: (a), the action of UV pulsing of this lamp alone; (b), pulsed UV plus the addition of 80 ppm peroxide to the water; and (c), conditions as in a plus the addition of TiO₂ as a catalyst. Results for 1,1,1 trichloroethane (TCA) are presented in Figure 3. Results for 1,2 dichloroethane (DCA) were similar to those for TCA.

We did not use maximum allowed loads for the lamp. Therefore, exposure times on Figures 3-6 can be reduced three-fold by increasing the lamp power

from 60 W/cm to 180 W/cm, the power projected for a commercial unit. The energy consumption in both cases remains the same, and can be calculated using the lamp pulse energy, its repetition rate, the system electrical efficiency, and its degree of UV utilization. The optimal UV utilization for each case-calculated by measuring the UV absorption of treated water samples-was 20 watt hours per gallon for 100 sec. of exposure for Figures 3-6.

Figures 4-6 present removal rates of other VOCs from the same groundwater for the pulsed UV combined with the action of peroxide and when such action was enhanced by the catalyst (TiO_2) added to the groundwater.

Exposure times on Figures 4-6 can also be reduced by increasing the lamp power without changing the energy consumption per gallon of treated water. The data show from 100-fold to well over 1000-fold removal of organic toxic compounds. Carbon tetrachloride was more difficult to remove than other organics. The data show a significant improvement in removal rates with the use of the catalyst. Removal rates are also linear with the exposure time. Phenols and TCE removal rates were similar to each other and were largest amongst all the tested organic compounds: more than 10,000 times for 100 sec of exposure (20 W hour/gal).

Discussion

Data presented give extra support to the conclusion in (4) that the variety of organics disintegrated by a pulsing UV continuum shows the process' universal application. These tests also show that removal rates of organic toxic compounds are different. For example, removal rates for phenols, methyl ethyl ketone and for TCE were up to 100 times higher than that for chloroform and carbon tetrachloride at the same exposure conditions. The best results were when both peroxide and the catalyst (TiO_2) were added to the water and pH was adjusted to 4.5. The process efficiency for TCA and DCA with such dopants was good and can be improved further. The observed linear dependence of removal rates for the exposure time allowed projection of the energy consumption necessary to achieve the removal goal for each toxic organic compound.

The performance of the pulsed lamp was better in the presence of peroxide in the treated water. This is because peroxide absorbs one part of the UV spectrum and toxic organic compounds

FIGURE 3
TCA removal from groundwater

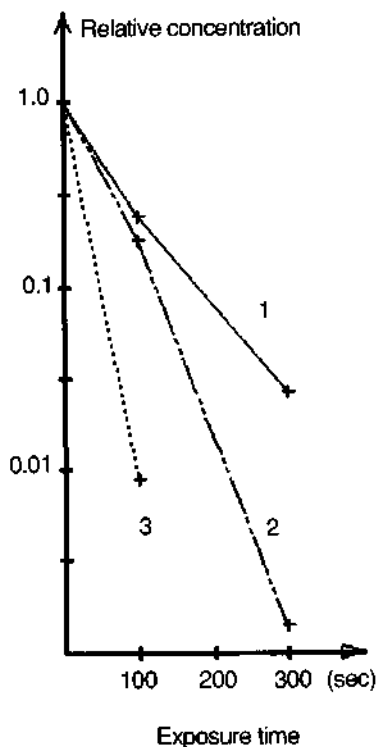


FIGURE 4
MEK removal

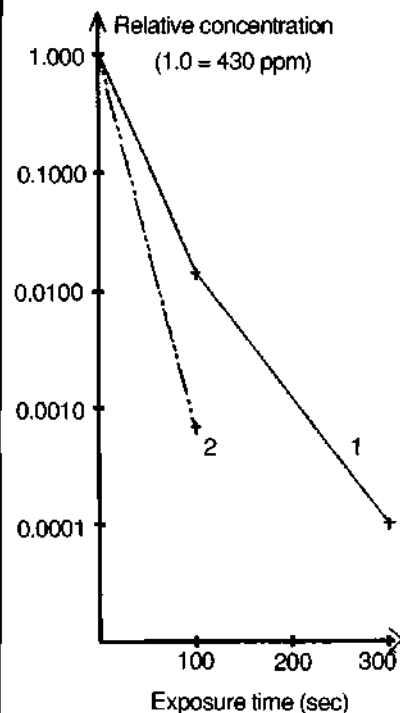


FIGURE 5
2-Chlorophenol removal

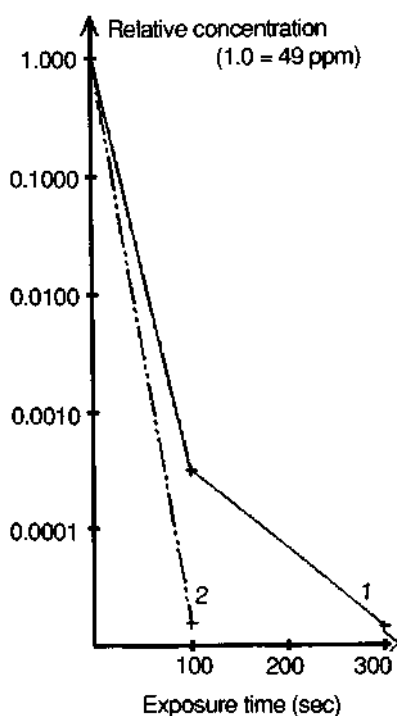
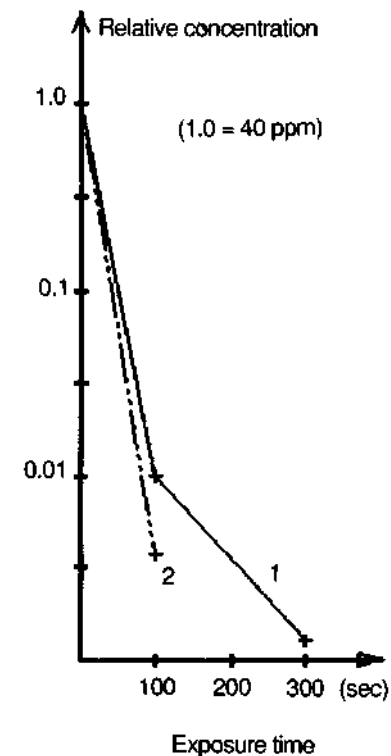


FIGURE 6
CCl4 removal



absorb another part of the spectrum, improving use of the lamp energy.

The presence of the catalyst, TiO₂, increased the process efficiency even further because of the catalyst's ability to create OH radicals on its surface under UV light with wavelengths above 300 nm. Since these photons are not capable of dissociation of either VOCs or peroxide, their use by the catalyst simply improves the overall energy efficiency.

The rate Γ of the photodissociation process, or the rate of creation of OH radicals in water or on the surface of catalyst grains can be simply calculated with the following correlation (4):

$$\Gamma = \Phi \times \sigma \times n \quad [\text{cm}^{-3} \text{sec}^{-1}]$$

Φ : UV flux within an absorption band of an organic toxic compound, or peroxide, or a catalyst in photons/cm² •sec.

σ : cross-section for a photodissociation of an organic toxic compound, peroxide or of the reaction on a catalyst surface that has to be measured or calculated.

n : concentration of reacting compounds per cm³ of the carrier

medium.

Test results show the Wekhof Lamp provided sufficient UV fluxes Φ within absorption bands—at least 0.1 watt/cm²•nm within the treated media. Thus, commercially acceptable rates of toxic compound destruction such as ($\Gamma = 1 \text{ mg/L} \cdot \text{sec}$) were achieved. Similar fluxes were generated in tests with mercury medium pressure lamps, but their few UV lines did not have sufficient matching with absorption bands of target compounds. That is one reason why they performed poorly compared with the UV flashlamps of the same power.

There is another important advantage in using a pulsed UV source. It is the ability to produce very high photon fluxes, with energy thousands of times higher than the energy per second emitted continuously. This changes the kinetics of the photochemistry in a way that speeds up targeted reactions (4), and may be a reason for a faster increase in removal rates of organic compounds with pulsing UV power, as shown on Figure 2.

We suggest the following mechanism: During each pulse, the intense UV light creates intermediate

products or states from a portion of the toxic organic compounds. Their lifetimes are comparable with the time between UV pulses. Subsequent bursts of photons cause a further energy consumption by these intermediate products, followed by a full photodissociation. In other words, some toxic organic compounds experience a two-step photodissociation, with UV photons with wavelengths above 300 nm contributing to the process. Since the population of these intermediate products drops sharply with time, a decrease in the time between pulses (i.e., a higher pulse repetition rate) affects these products in the observed non-linear fashion, more efficiently utilizing the lamp output.

Process applications

In our tests, the 100-to more than 10,000-fold reduction in the removal of VOC's, even such stable VOC's as TCA and CCU, was achieved for 20 watt hours per gallon exposure, or at the electrical costs of \$1.40/1000 gallons (at \$0.07/kWH). Chemical costs for such treatment were not estimated and are assumed to be equal to 30% of electrical costs. A further

cost reduction is possible by improving the process through adjusting the lamp power, pH, and concentrations of peroxide and the catalyst.

The treatment of groundwater can be done directly with this method, if water is filtered to remove solid compounds and has no significant coloration.

Another way to treat groundwater is with air stripping towers with a pulsed UV process to cleans the exhaust. This approach offers an advantage where an air stripping tower is already in place and needs to be upgraded. Some data on air treatment by the pulsing UV are presented in (4). The advantage of converting water flow to air flow can also be justified by a lesser dependance of this treatment on the UV absorption properties of the treated water. However, in this case one has to deal with byproducts such as ozone or acids.

It is important to maximize the use of the ultraviolet energy, allowing no more than 15% of UV light to end up on the reactor walls. The geometry of the processing reactor (its diameter for a cylindrical reactor) has to be determined as a function of the absorption spectroscopy of the treated water or air. In such a case, one has to compensate for a lower UV flux in places near the reactor wall by moving the water (or air) flow through the reactor with a high degree of turbulence. A turbulent flow will equalize the UV exposure of the treated medium by passing it through regions of a different UV intensity.

The analysis of the correlation for the rate r of the UV photodissociation suggests yet another important approach for a better UV utilization. Since this rate is directly proportional to the concentration of targeted organic compounds n (cm^{-3}) one should try to increase the concentration. Volume reduction can usually be achieved with filtration or air-stripping.

Conclusions and recommendations

The use of a pulsing UV continuum generated by the Wekhof flash lamp is more energy-efficient than the standard oxidation process with peroxide combined with the 254 nm UV line from a medium-pressure mercury lamp.

The use of a pulsing UV continuum (Wekhof Process) for waste and groundwater treatment is more efficient in combination with peroxide and a catalyst.

The UV utilization can be improved by adjusting the size of the processing chamber to absorption of the UV light by the treated medium.

The UV utilization can be improved if the concentration of toxic organic compounds is increased by a known technique of volume reduction such as filtration or air-stripping. Therefore an optimal concentration of organic toxic compounds can be achieved to maximize utilization of UV light.

Acknowledgements

The authors appreciate test arrangements from Mr. Gary Cox of Canonie Environmental Services, Mountain View, CA; help in testing from Mr. Craig of BC Analytical (Emeryville, CA); and thank Ms. Linda Richter, of ILC Technology, Inc. (Sunnyvale, CA) for providing flashlamps.

References

- (1) Roy, Kimberly. "Series on UV/oxidation technologies," *HAZMAT WORLD*, 3, 5; 1990.
- (2) Phillips, Roger. *Sources and Applications of Ultraviolet Radiation*, Academic Press, London: 1983.
- (3) Lyandres, S.E.; Rees, John T.; Folsom, Edwin N.; Boegel, Anthony J. "Treatment of Ground Water Contaminated with Volatile Organic Compounds Using Second Generation UV Light Technology,"

presented at HAZMACON 1991, San Jose, CA.

(4) Wekhof, Alex. "Treatment of Contaminated Water, Air and Soil with UV Flashlamps," *ENVIRONMENTAL PROGRESS*, 10, 4; 1991. (Patent allowed; U.S. Patent Office, February 1992.)

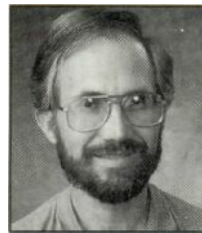
Dr. Alex Wekhof, Ph.D., is president of UVERG, 285 Fifth Street, Oakland, Cal. 94607; 510-272-0547. He has more than 25 years of experience in theoretical and applied research in the fields of plasma



Alex Wekhof

physics and application of UV energy. His developments of a novel UV remediation process, a new UV flashlamp, and a new UV reactor have each been awarded patents by the U.S. Patent

Edwin Folsom is a project manager for the Environmental Restoration Division of Lawrence Livermore National



Edwin Folsom

Laboratory. He is responsible for design, construction and testing of treatment systems for groundwater and soil vapors contaminated with fuel hydrocarbons and halogenated hydrocarbons.

Yuval Halpern, Ph.D., is manager of advanced waste technology with Chemical Waste Management. As director of the Advanced Technology Group, he is responsible for long-range chemical studies at CWM. He has published 38 scientific papers, and has been awarded 36 foreign and U.S. patents.



Yuval Halpern