AN ULTRA-PURE SOLUTION FOR INDUSTRIAL WATER APPLICATIONS

Water Convention 2009 – Best Poster Winner (1st Prize)

Richard Woodling, Karthik Sathrugnan, Bruce Coulter; Siemens Water Technologies (now Evoqua Water Technologies)

Many industries rely on the availability of clean water for its processes, and perhaps none more so than the semiconductor industry which requires ultra-pure water for the production of the critical components that reside in our everyday electronic devices. In 2009, Siemen Water Technologies (now Evoqua) won the Best Poster Award for their study which compared UV treatment along with various oxidation methods for the selective removal of organic compounds for high purity and water reclamation applications. Their research eventually led to the development and commercialisation of the Vanox AOP system, now used in the most demanding applications in the production of ultra-pure water, and removal of persistent contaminants in water and used water.

Water treatment technologies remain a passion of Dr Richard Woodling, then the lead researcher and author of the paper, who is now the Senior Vice President and Global Head of Water Services at TUV SUD. He believes that the trend of the future will be associated with the development of new or hybrid membranes and the application of these membranes to overcome different challenges: “I am particularly interested in graphene and its applications as it has great promise in water purification and energy reduction. Most technologies being developed, such as forward osmosis, dialysis, and electrodialysis, currently utilize membranes in one form or another. I also feel new materials for trace contaminant removal will be developed.”

In addition, he also believes “the digital era for water is coming of age and will lead to new technological breakthroughs related to optimising performance of treatment systems. Finally, the conversion of biomass to energy will continue to improve and net zero waste water treatment in the municipal space is in the horizon.”

The abstract and poster submitted by Siemens Water Technologies (now Evoqua Water Technologies) for the Water Convention 2009 have been included in this article for your reference.

Editorial Manager(tm) for IWA Conferences
Manuscript Draft

Manuscript Number: IWA-1003

Title: Advanced Oxidation for the Removal or Organic Contaminants in Industrial Waters

Article Type: Submission for Oral Presentation

Keywords: advanced oxidation; high purity; microelectronics; organic destruction

Corresponding Author: Dr Richard Woodling, Ph.D.

Corresponding Author's Institution: Siemens Water Technologies

First Author: Richard Woodling, Ph.D.

Order of Authors: Richard Woodling, Ph.D.; Karthik Sathrugnan, Ph.D.; Bruce Coulter

Manuscript Region of Origin: SINGAPORE

Abstract

Advanced Oxidation for the Removal of Organic Contaminants in Industrial Waters

Dr. Richard Woodling, Dr. Karthik Sathrugnan and Mr. Bruce Coulter, Siemens Water Technologies, 82 Toh Guan Rd. East, Singapore 608576

Trace organic removal, either in high purity waters such as in the microelectronics and pharmacuetical industries or in municipal waters for drinking or discharge has long been a challenge to treat in both an economically and selective fashion. UV irradiation can be utilized to mineralize these materials to carbon dioxide and water. In many circumstances additional oxidizing species such as ozone, hydrogen peroxide or titanium oxide are required in order for complete removal. The electrical energy per order of magnitude, ee/o, is utilized to evaluate the efficiency of these processes as a comparative tool. In this paper, a baseline study is reported which compares these and other technologies for the selective removal of organic compounds for high purity and water reclaimation applications such as in the microelectronics industry. The focus of the research is on Ultra-high purity and reclaimed water applications such as in the semiconductor industry. EE/o's are reported for a variety of methods and compared based upon the chemical, electrical and equipment life cycle costs. Potential applications will include high purity water for pharmacuetical and microelectronics applications, reclaim and recycle streams and industrial discharge streams.

Advanced Oxidation for the Removal of Organic Contaminants in Industrial Waters

R. Woodling*, J. Feng, D. Arifin, C. Garcia, K. Sathrugnan, B. Coulter

Water Technologies

SIEMENS

Introduction

The manufacturing of electronic products involve the use of ultrapure water for silicon wafer cleaning, rinsing, and process equipment cleaning, etc. Most of the semiconductor companies are recycling the used ultrapure water for the economic and environmental benefits. The challenges in ultrapure water treatment and reclamation are the fluctuations of concentrations of organic contaminants in source water and the need to stabilize the total organic carbon (TOC) value at 1.0 to 0.5 ppb level.

Three different technologies have been used to treat the ultrapure water for semiconductor companies, namely activated carbon systems, media filtration systems, and membrane systems. However, these three methods are all non-destructive method, which transfer the contaminants to another medium. Advanced oxidation processes (AOPs) have been developed as destructive method for water reclamation. Most of AOP's combine with UV light to activate the oxidants (e.g. hydrogen peroxide, ozone, and etc.) to generate the hydroxyl radical. The hydroxyl radical is usually less selective and scavenging ions, such as carbonate ions, can seriously decrease the treatment efficiency of AOP's. Therefore, persulfate, with higher selectivity and lower health side effects can be a possible candidate to substitute hydrogen peroxide and ozone for water reclamation and TOC destruction.

In this study, batch experiments were carried out with persulfate as the oxidant in the UV mediated AOP system. The main TOC contaminants in the semiconductor plants were specified to be urea, trihalogenated methanes (e.g. chloroform), acetone, and isopropanol alcohol (IPA). Low pressure mercury lamp with wavelength A and wavelength B were used as the light sources to activate the persulfate.

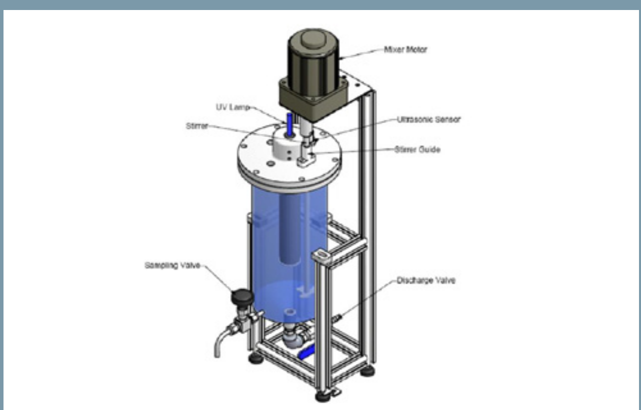

Fig. 1. UV batch reactor

Singapore International Water Week

Results & Discussion

Direct Oxidation: $S_2O_8^{2-} + 2H^+ + 2e^- \quad 2HSO_4^-$ (OPR=2.1V) (1)

Indirect Oxidation:

$S_2O_8^{2-} + hv \rightarrow SO_4^{-}\bullet + SO_4^{-}\bullet$

$SO_4^{-}\bullet + SO_4^{-}\bullet \rightarrow S_2O_8^{2-}$

$SO_4^{-}\bullet + S_2O_8^{2-} \rightarrow SO_4^{-}\bullet$

$SO_4^{-}\bullet + e^- \rightarrow SO_4^{2-}$ (ORP=2.6V) (2)

The λ_{max} of both persulfate and hydrogen peroxide is in the range of 194 to 200 nm. The molar extinction coefficient (ε) of persulfate is 950 M^{-1} cm^{-1}, which is around four times higher than that of hydrogen peroxide (ε = 265 M^{-1} cm^{-1}). It indicates that persulfate might be a better oxidant for UV mediated AOP process.

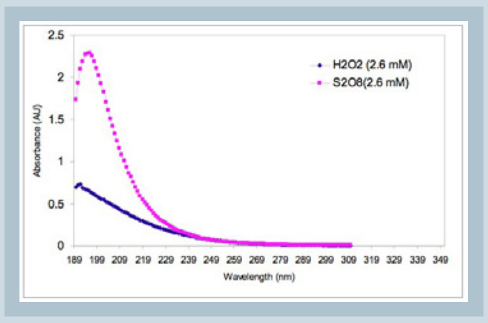

Fig. 2. Absorption spectra of persulfate and hydrogen peroxide.

The efficiency of a batch UV reactor to degrade the contaminant is dependent on the fluence rate distribution within the reactor, and the degradation/inactivation kinetics of the target compounds/species. In this study, discrete ordinates model for the UV lamp was used to calculation the fluence rate inside the reactor. Figure 3 presents the fluence rate distribution and average fluence rate for the batch reactor with low pressure lamp. UV fluence rate decreased with the increase of distance from lamp to the wall of the cylinder. Thus, in order to increase the average fluence rate in the reactor, the most possible choices are to decrease the diameter and the dark area of the batch reactor.

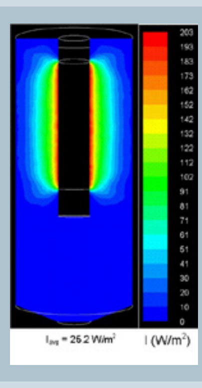

Fig. 3. Fluence rate distribution of low pressure UV lamp (wavelength A) in the UV batch reactor.

Figure 4 indicated:

- Persulfate/UV system can effectively oxidize the trace TOC contaminants in the ultrapure water system of semiconductor industry.
- The oxidation rate will increase with the increase of oxidant dose.
- In the presence of UV lamp with wavelength B, less oxidant dose can be used to achieve similar mineralization rate of the TOC concerned.

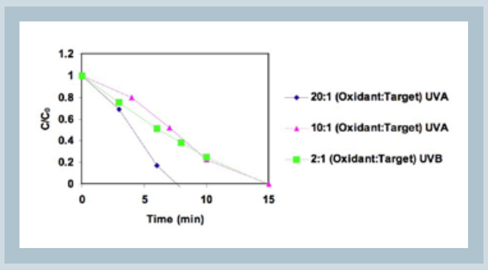

Fig. 4. Oxidation of IPA at 100 µg l-1 with different oxidant dosages and different UV lamps (the concentration of IPA was expressed with µg TOC per liter).

Light source	Target compound	Initial concentration	Oxidant dosage	UV dose	E_{EO}
		μg TOC l^{-1}	Molar Ratio to TOC	J m^{-2}	kWh mg^{-1}TOC
UV A	Urea	20	30	13910	0.035
		20	40	10282	0.026
		100	6	36288	0.018
		100	20	14666	0.007
	Chloroform	20	10	17237	0.044
		20	20	10735	0.027
		100	2	45360	0.023
		100	10	10130	0.005
	IPA	20	20	15120	0.038
		20	30	12096	0.031
		100	10	21924	0.011
		100	20	11642	0.006
	Acetone	20	20	15422	0.039
		20	30	11340	0.029
		100	10	18144	0.009
		100	20	9828	0.005
UV B	Urea	100	5	15120	0.008
	Chloroform	100	2	9072	0.005
	IPA	100	2	22680	0.011

Table 1. Chemical and UV dose for four representative target compounds of semiconductor industry

Conclusions

Persulfate/UV system has been proven to be effective to treat the trace organic contaminants in the ultrapure water of semiconductor industry. Compared to low pressure mercury lamp with wavelength A, the lamp with wavelength B would be beneficial to increase the persulfate activation efficiency, and could achieve similar treatment efficiency as lamp of wavelength A with accordingly less oxidant dose and less energy consumption.

*Siemens Pte Ltd, Water Technologies, Global R&D Centre
82 Toh Guan Road East, #C1-30 WaterHub, Singapore 608576
(E-mail: richard.woodling@siemens.com)