Pure Appl. Chem., Vol. 73, No. 8, pp. 1237–1241, 2001.

Green chemistry and the global water crisis*

Dennis L. Hjeresen

The Green Chemistry Institute, American Chemical Society, 1155 Sixteenth Street NW, Washington, DC 20036, USA

Abstract: Among environmental issues facing the world today, land-based sources of water pollution is one of the most pressing. Adequate supplies of satisfactory-quality water are essential for the natural resources and ecological systems on which all life depends. Green chemistry offers a scientifically based set of solutions to protect water quality.

INTRODUCTION

Green chemistry combines critical elements of environmental improvement, economic performance, and social responsibility to address global environmental problems. The growing global crisis in water resources provides an important illustration of the influence of upstream pollution prevention. For the past decade, scientists have sought to raise an alarm concerning the unsustainable use of the planet's water resources [1–4]. A key United Nations report indicates that water shortages will touch 2.3 billion people, or 30% of the world population, in four dozen nations in 2025 [1]. Exacerbating the shortfall is the extensive pollution of water resources, rendering significant amounts of water unfit for human use.

RELATION OF WATER TO CHEMISTRY

Green chemistry can provide tools to protect water quality in the face of increasing global pressures on water quantity. A 2001 report by the Organization for Economic Cooperation and Development (OECD) [5] indicates that within the industrialized (OECD) countries the chemical industry was the single largest consumer of water (43%) followed by metals processing (26%), pulp and paper (11%), with other uses accounting for 20%. Critical sources of water pollution include chlorine for both water treatment and pulp and paper bleaching, metals processing, pharmaceutical manufacturing, textile dying and cleaning, corrosion control, and processes as varied as photography and photolithography. Green chemistry science and technology offers economically viable alternatives for water applications. New processes and products submitted to the U.S. EPA for the annual Presidential Green Chemistry Challenge Award offer illustrative examples [6–9].

INDUSTRIAL WATER TREATMENT

There is no questioning that chlorine, as a domestic water treatment, has been effective and a mainstay in reducing water-borne diseases worldwide. However, chlorine from manufacturing almost inevitably makes its way to aquatic ecosystems and impacts organisms that are integral to food chains. Once present in the environment chorine compounds interact with other compounds that can lead to the formation of carcinogenic chloramines, which bioaccumulate within the food chain.

Industrial wastewater treatment deals primarily with three simultaneously occurring surface-fouling processes: microbial, scaling, and corrosion. In the United States alone, over 50 million lb./yr. are

*Lecture presented at the IUPAC CHEMRAWN XIV Conference on Green Chemistry: Toward Environmentally Benign Processes and Products, Boulder, Colorado, USA, 9–13 June 2001. Other presentations are published in this issue, pp. 1229–1330.

sold to over 500 000 individual users. These chemicals are often mammalian or aquatic toxins and many of the corrosion inhibitors are incompatible with biocides, requiring industrial operations to use multiple chemical approaches to the same systems. The most common corrosion inhibitors are azole materials, typified by tolyltriazole (TTA). Herein lies the problem: the oxidizing halogens chlorine and bromine introduced into industrial water systems to address microbial contamination react with TTA, yielding a chlorinated by-product that does not protect copper alloy piping. Doses of TTA are then increased to overcome this effect, and the net result is increased chemical usage and release. Another issue in industrial water treatment deals with separation of suspended solids and contaminants. At least 200 millions lbs. of acrylamide-based polymers are used annually in a variety of industrial and other water facilities. In order to make these polymers water-soluble, an emulsion of water, oil, and surfactants in roughly equal amounts is formed. Unfortunately, neither the surfactant nor the oil have any value beyond their polymer-carrying function and are ultimately discarded to the environment in amounts in excess of 90 million lbs. annually. Several alternative approaches are under development and distribution:

- Albright and Wilson Americas has developed Bricorr® 288, a phosphonocarboxylate mixture that is entirely organic and thus rapidly biodegrades when released into the environment. The compound is water-soluble and therefore will not bioaccumulate, reducing risk to higher organisms. An added green chemistry advantage is increased handling safety.
- Nalco Chemical Company developed STABREX microorganism control based on a stabilized hypobromite compound designed to mimic bromine antimicrobials produced in the human immune response system. The STABREX compound is based on the antimicrobial *N*-bromoaminoethanesulfonic acids produced by eosinophils in the enzymatically catalyzed oxidation of bromine with H_20_2 reacting with 2-aminoethanesulfonic acid (taurine). Over 100 billion gallons of industrial wastewater have been treated with STABREX since 1997, replacing 20 million lbs. of chlorine. Relative to chlorine, STABREX is 10 times less toxic, yields half of the disinfection by-products, and is more effective for its designed applications.
- BetzDearborn, Inc. developed a halogen-resistant azole (HRA) that does not react with chlorine. Because of the lack of reactivity with either chlorine or bromine, less of each oxidizing halogen is needed. Further, significantly less HRA is needed to protect cooling systems when compared with TTA. In tests at a nuclear power plant, a five-fold reduction of copper release was achieved with 33% less inhibitor. 90% of the HRA was recovered, compared to 9% of the TTA because of the lack of reaction with chlorine. Finally, the HRA demonstrated only a fraction of the aquatic toxicity of TTA. Thus, less inhibitor, microbial agent, and money are required, while decreasing the environmental impact.
- Another Nalco process was developed to address the problem of acrylamide-based polymers. Nalco developed a new polymerization technology that reduced the particle size. Particles are then suspended in aqueous solutions of ammonium sulfate, an inorganic salt. This allows the same active polymers to be delivered as colloids in water. Eliminating the oil eliminated flammability, handling, transport, and worker safety issues. This process has accounted for utilization of 3.2 million lbs. of ammonium sulfate between product introduction in 1998 and 1999. During this same period, over a million lbs. of hydrocarbon solvent and surfactants were prevented from entering the environment.

PULP AND PAPER PROCESSING

The annual world market for bleached pulp approximates $50 billion. The bleaching of pulp depends on the systematic separation of lignin from cellulose. The chemical processes of the pulp and paper industry are primarily directed to separating these two components. In nature, the biodegradation process accomplishes this using a limited suite of enzymes: ligninase, glyoxal oxidase, and Mn peroxidase. To achieve the same oxidation for which nature uses O_2, industry has substituted chlorine compounds, resulting in the release of phenoloic compounds and environmentally persistent organochorine compounds.

- Dr. Terry Collins at Carnegie-Mellon University has developed oxidant activators derived from iron called tetraamido-macrocyclic ligands (TAML™). When combined with hydrogen peroxide in water, the TAML activators produce a reaction equivalent to oxidizing enzymes in nature.
- Craig Hill (Emory University) and Ira Weinstock (USDA) developed a catalytic approach designed to mimic the processes of nature. The process utilizes nontoxic and inexpensive organic compounds called polyoxometalates. First, the lignin is removed from the wood pulp through oxidation with polyoxometalates. Then, O_2 is added to the bleaching liquor and the same polyoxometalate catalyzes the mineralization of the dissolved lignin fragments. The result is an effluent-free process.
- Union Camp, a large U.S. pulp and paper company, has tested ozone as a primary oxidant in pulp bleaching and built a $6 million demonstration facility. Relative to chlorine bleaching, Union Camp reported reduction of effluent biological oxygen demand by 73%, chemical oxygen demand by 83%, absorbable organic halides by 99%, color in the water by 98%, and chloroform by 99%. Further, no reportable levels of dioxin or chlorophenols appear with this process.

SEMI-CONDUCTOR MANUFACTURING

Much of the enormous amount of water consumed in the manufacturing of semiconductors is utilized for cleaning at multiple stages of the photolithography process. This water is typically deionized and, therefore, has a significant energy investment as well. As chip architecture moves to finer and finer scaled structures the surface tension of the liquids no longer permits ready diffusion. Surfactants can be used to reduce surface tension, but this necessitates a subsequent rinsing and drying step, requiring additional amounts of ultrapure water. An approach developed by Los Alamos National Laboratory working with semiconductor and equipment manufacturers has been with the replacement of conventional clean techniques with supercritical CO_2 ($SCCO_2$). $SCCO_2$ offers a variety of advantages to address the new processes in this area. The gas-like properties, high diffusivity, and low viscosity allow the $SCCO_2$ fluid to reach the small architectural features of the new wafer designs.

PHOTOGRAPHIC PROCESSING

The billions of photographs developed every year via the silver halide process use primarily aqueous processes that produce huge amounts of chemical, solid, and liquid waste. In the United States alone, over 400 million gallons of fresh water are sent to treatment works after single use in the developing process. This water contains up to 15 million gallons of chemical photographic developer laden with contaminants such as hydroquinone, ammonia, and silver. The DuPont DuCare® system first reduces wash water volume 99% by sending the used water to the fixer. Then the system replaces the traditional hydroquinone developer with erythorbic acid, 75% of that is recycled. The developer and a recyclable fixer are then returned to a central facility where the silver is recovered with up to 99% efficiency. Estimated fresh water savings in the United States alone would be 395 million gallons per year.

PHARMACEUTICALS MANUFACTURING

Roche Colorado Corporation produces an antiviral agent ganciclovir (Cytovene®) to treat patients whose immune systems have been compromised, including those with AIDS. By substituting the guanine triester process (GTE), Roche reduced the number of chemical reagents and intermediates from 22 to 11, increased the product yield by more than 25%, eliminated the (only) 2 hazardous solid waste streams, and eliminated 11 different chemicals from the hazardous liquid waste streams; of the 5 ingredients not incorporated into the final product, 4 of the ingredients were efficiently recycled and reused. By modifying the production process, the company was able to increase production output without new capital plant expansion costs while eliminating significant environmental liabilities.

Pharmacia & Upjohn redesigned their process for the synthesis of the steroid bisnoraldehyde which is an intermediate chemical in the manufacturing of progesterone and corticosteroid pharmaceuticals. First, a new fermentation process was developed that increased the use of a renewable biofeedstock from 15 to 100%. Then, a new oxidation reaction was developed that eliminates many of the hazards and by-products of the original process. This combined process reduced solvent use and entirely eliminated the need to maintain an inventory of 60 000 gallons of ethylene dichloride, a known carcinogen. Pharmacia & Upjohn report maintaining the same product yield with 89% less organic solvent waste and 79% less aqueous waste.

AGRICULTURAL CHEMICALS

Few green chemistry applications are more important than those for the agricultural chemicals industry. The economic and human costs of crop losses on a global scale drive the estimated $12 billion annual market for insect control chemicals. The persistence of many pesticides, herbicides, and fertilizers in the ecosystem and the evidence of their biological impacts are a significant consequence of the synthetic organic chemical approach to the problem. Further, the resistance that develops among insect species to these pesticides also argues for a fresh approach. Dow Agrosciences has developed a large-scale testing program to systematically ferment and screen samples for natural microorganisms with insecticidal properties. The microorganism *Saccaropolyspora spinosa*, isolated from a Caribbean island soil sample, exhibits neurotoxic effects on a range of chewing insects in trees, fruits, cotton, vegetables, and other plants. Environmentally, Spinosad represents a major improvement over synthetic organic pesticides. It does not leach bioaccumulate, volatilize, or persist in the environment. Dow studies indicate that 70 to 90% of beneficial insects are not harmed. Worker risks are also lowered with the decreased mammalian toxicity. This is also the case with aquatic species.

METALS PROCESSING

Metals can enter the environment through multiple vectors in the processing life cycle: mining, smelting, forming, plating, and following use. Mine tailings and abandoned mines represent an ongoing legacy of environmental contamination long after the commercial value of metals has been extracted. Electroplating to protect surfaces is a common industry practice especially in defense and aerospace industries. These processes generate large quantities of sludge and liquid effluents. Cadmium and chromium have superb characteristics when it comes to protecting steel, but are known carcinogens that persist in the environment. A medium-sized electroplating operation may discharge 100,000 gallons of effluents daily and up to 20 tons of hazardous sludges per week. Several different approaches are using green chemistry to address these problems:

- The approach used by IonEdge Corporation incorporates a dry plating technology that does not use liquid chemicals and recycles all of the solids. By vaporizing the cadmium and controlling the direction, the process allows deposition only on intended parts. The amount of water used and treated is decreased by an order of magnitude while energy consumption drops by 65%. In U.S. facilities, estimated daily savings in waste treatment and disposal is over $1000.
- The approach used by NALCO creates a chelating polymer ligand specific to the target metal in the waste stream. This is marketed in a liquid form as NALMET®, and the levels in the processing system are monitored by and controlled through an automated delivery system. This prevents excess use and reduces ultimate waste volumes. The company claims 25 to 90% reductions in

sludge volume. The precipitated sludge is then removed by NALCO, and a partner company recycles the target metal.

SUMMARY

Green chemistry offers a variety of mechanisms to address globally important environmental problems such as water contamination at their source. Such source reduction has proven more cost-effective than either abatement or remediation approaches.

REFERENCES

1. P. Gleick. *The World's Water: The Biennial Report on Freshwater Resources 1998–1999*, Island Press, Washington, DC (1998).
2. P. Gleick. "Basic Water Requirements for Human Activities: Meeting Basic Needs", *Water International* **21** (1996).
3. S. Postel. *Last Oasis: Facing Water Scarcity*, Worldwatch Institute, W. W. Norton, New York (1992).
4. A. Outwater. *Water: A Natural History Basic Books*, HarperCollins, New York (1996).
5. OECD Environmental Outlook for the Chemicals Industry. Organization for Economic Co-operation and Development, Paris (2001), available on-line at http://www.oecd.org/ehs
6. U.S. Environmental Protection Agency—Office of Pollution Prevention and Toxics, The Presidential Green Chemistry Challenge Awards Program: Summary of 1996 Award Entries and Recipients, EPA744-K-96-001 (1996). Also at www.epa.gov/greenchemistry
7. U.S. Environmental Protection Agency—Office of Pollution Prevention and Toxics, The Presidential Green Chemistry Challenge Awards Program: Summary of 1997 Award Entries and Recipients EPA744-S-97-001 (1998). Also at www.epa.gov/greenchemistry
8. U.S. Environmental Protection Agency—Office of Pollution Prevention and Toxics, The Presidential Green Chemistry Challenge Awards Program: Summary of 1998 Award Entries and Recipients EPA744-R-98-001 (1998). Also at www.epa.gov/greenchemistry
9. U.S. Environmental Protection Agency—Office of Pollution Prevention and Toxics, The Presidential Green Chemistry Challenge Awards Program: Summary of 1999 Award Entries and Recipients EPA744-R-00-001 (2000). Also at www.epa.gov/greenchemistry

Green chemistry has become a target for cutting-edge research into sustainable technologies. These may reduce (or eliminate) the production and use of hazardous substances in mining and in the design, manufacture and application of chemical products, and may also lead to energy savings and a better environment and health. Research in green chemistry and allied areas in biochemistry, geochemistry, biotechnology, ecology and healthcare give young scientists ample opportunity to demonstrate their inventiveness and provide important input to sustainable development. What is a Water Crisis? Did you know that only 2.5% of all the water in the world is freshwater? And that only 1% is accessible, by accessible, I mean water trapped in glaciers and snowfields. We only have real access to 0.0007% of the planetâ€™s water, thatâ€™s all we have to feed and fuel over 6.8 billion people. The lack of clean water is a plague that affects 1.8 billion people every year. A water crisis is when there is not enough potable water for a population, which in turn leads to drought, famine, and death. Today safe drinking water has become a luxury for people living in drought-hit re Today the Water Crisis affects BILLIONS around the world. 844 million live without access to Safe Water, while 2.3 billion live without improved sanitation. Learn what Water.org is doing to combat the Global Water Crisis and join our cause today!Â The power of water. Water connects every aspect of life. Access to safe water and sanitation can quickly turn problems into potential â€“ empowering people with time for school and work, and contributing to improved health for women, children, and families around the world. Today, 785 million people â€“ 1 in 9 â€“ lack access to safe water and 2 billion people â€“ 1 in 3 â€“ lack access to a toilet. These are the people we empower. Learn more about the global water crisis >. Learn more about the global sanitation crisis >. The report notes that the global demand for water has been increasing and will continue to grow significantly over the next two decades due to population growth, economic development and changing consumption patterns. If we do nothing, some five billion people will be living in areas with poor access to water by 2050 â€“ UNESCO chief. Due to climate change, wetter regions are becoming wetter, and drier regions are becoming even drier. At present, an estimated 3.6 billion people, nearly half the global population, live in areas potentially water-scarce at least one month per year, and this popula Green chemistry offers a scientifically based set of solutions to protect water quality. Discover the world's research. 17+ million members. 135+ million publications. 700k+ research projects. Join for free. No full-text available.Â In that respect, in this chapter green chemistry and its principles are reviewed in relation to green technologies for the removal of emerging compounds from water and wastewater. View. Show abstract. ChemInform Abstract: Additiveâ€Free Decarboxylative Coupling of Cinnamic Acid Derivatives in Water: Synthesis of Allyl Amines. Article. Feb 2015. ORG LETT.