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# COTTON TEXTILE WASTEWATER TREATMENT BY ULTRAVIOLET-ENHANCED OZONATION

**S. Edward Law**
**Department of Biological and Agricultural Engineering**
**The University of Georgia**
**Athens, GA**

## Abstract

Ozonation has been proven by many past studies to be an effective treatment for removing color and improving other water-quality attributes for textile wastewaters. Recent research and development efforts have combined simple ozonation with ultraviolet irradiation to synergistically enhance wastewater treatment in the food-processing sector; similarly dramatic increases in treatment efficacy may be possible for textile wastewaters. Technical details are thus presented describing our advanced oxidation process of UV-enhanced ozonation and the mobile, pilot-scale prototype developed for on-site evaluations of this improved water-treatment method.

## Introduction

Cotton yarns and fabrics are colored in dyebaths using direct, acid, and reactive type dyes. Wastewater from dyehouses carries appreciable concentrations of such dyes which fail to attach to fibers. Conventional public-owned waste-treatment plants utilizing biological processes do not satisfactorily remove color, leaving these effluents as a major difficulty in the textile industry's efforts to meet environmental regulations. Transfer of reactive dyes to cotton fibers requires quantities of NaCl or other salts often exceeding the mass of fiber being dyed; the *ca.* 2/3 billion kg of salt discharged annually in US textile wastewater adds significantly to the environmental concern regarding potential toxicity to aquatic life.

Efforts are underway internationally to develop methods for renovating the spent dyebath in order to recycle its water, heat and salts for reuse. Researchers at the University of Georgia and others have applied nanofiltration for salt recovery and ozonation for color abatement [Carriére et al., 1993; Rearick et al., 1995]. Our earlier work concentrated upon applications of electric-discharge-generated ozone ($O_3$) for effectively decolorizing cotton dyehouse effluent and investigated aquatic toxicity following the ozonation treatments [Law et al., 1996; Hitchcock et al., 1998; Wu et al., 1998; Perkins et al., 2001].

Ozone reacts vigorously and selectively with organic dyestuffs, exhibiting an oxidizing capability greater than that of chlorine [Rice and Netzer, 1982]. Decolorization results directly from ozone reaction with dye molecules as well as indirectly from the dye's reaction with hydroxyl and other highly reactive free radicals formed as ozone decomposes is water [Langlais et al., 1992]. Ozone effectively breaks double bonds (*e.g.*, N=N and C=C) in long conjugated chains of organic dye molecules. Because dye color is attributable to visible light absorption by these long chains of double bonds, ozonation shifts the dominant wavelengths of absorption to shorter values, hopefully, outside the visible band. Decolorization is thus achieved.

Our laboratory tests on simulated cotton dyehouse wastewaters have confirmed ozonation to be a highly effective decolorization process. As summarized in Fig. 1 for a 7.81 mg/L·min dosage of ozone sparged into 30°C wastewater, decolorization obeyed an exponential decay attaining 85% color removal in ~ 9, 16 and 30 min, respectively, for Acid Red and #4 and #9 reactive dyes; corresponding first-order appartent rate constants were ~ 0.22, 0.11 and 0.06/min. Ozonation for 1 h removed greater than 98% of the color from all wastewaters tested. The presence of NaCl salt had no significant effect upon either the rate or degree of decolorization. Likewise, for salt-free reactive dyes, ozonation had no significant effect upon toxicity to the text organism *C. elegans* immersed in the wastewaters. In contrast, toxicity of the Acid Red wastewater increased as ozonation treatment time was increased. In all cases, NaCl in the wastewaters proved 100% lethal to the test organism–with or without ozonation; ozonation did not alter the response.

While the straightforward ozonation process reported above proved beneficial for decolorization, our more recent work at the University of Georgia has been directed toward significantly increasing the beneficial action of ozone, and hence its efficiency of application, beyond that achieved by simple ozonation. In aqueous solution ozone chemically acts upon water-borne contaminants by both: a) direct reaction with molecular $O_3$; and b) indirect reaction with free-radical species, especially the increased concentration of hydroxyl radicals (OH·), formed when $O_3$ decomposes in water in the presence of ultraviolet photons. UV irradiation at ozone's 253.7 nm peak absorption photolytically drives this process. Additionally, photon irradiation itself in the UV-band can deactivate contaminants as well as sensitizing them for a more effective oxidation by ozone. To realize these combined benefits on a practical level, we have thus developed an advanced oxidation process (AOP) of UV-enhanced ozonation to synergistically improve the simple ozonation process we formerly used and take it to the next level of increased effectiveness.

At this stage of our work we have extensively evaluated the advanced oxidation process for deactivating pathogenic microorganisms to synergistically improve the microbiological safety, turbidity, and water-use efficiency of food-processing wastewaters allowing their reconditioning for reuse [Diaz and Law, 1997 and 2001]. Figure 2 illustrates our typical bench-scale results for the AOP applied to 250 mL batches of poultry-broiler overflow chiller wastewater being sparged by 0.5 wt% $O_3$ in an $O_2$ feed-gas stream and irradiated by 254 nm UV. The antimicrobial effects achieved against an inoculated strain of *Salmonella typhimurium* at the indicated treatment conditions are plotted as functions of treatment duration. At 4 to 8 min treatment times a synergistic bactericidal effect is documented between $O_3$ and UV acting simultaneously as compared with the sum of the separately acting $O_3$ and UV bactericidal effects; the synergistic effect provides an additional >1.1 Log (*i.e.*, 13-fold) reduction in *Salmonella*. Statistically significant differences ($P<0.01$) are shown for all main treatment effects as well as their interactions, with $O_3$xUV exhibiting the greatest interaction – indicating synergism.

It is hypothesized that the synergistic effect of UV-enhanced ozonation we have documented for deactivating water-borne pathogens will similarly prove beneficial for increasing the efficacy and energy efficiency of ozonation for textile wastewater treatment. In an effort toward developing collaborative cotton-textiles industry evaluations of this improved process on-site, this paper briefly summarizes technical aspects of the design, fabrication, and preliminary operational evaluation of our mobile, self-contained engineering prototype which scales up our wastewater-treatment AOP from 250 mL bench-top batches to continuous 60 L/min on-stream pilot-scale operation [Law and Diaz, 2001].

## Pilot-Scale Prototype

A schematic diagram of the interconnected system components incorporated into our AOP prototype is presented by Fig. 3. To implement UV-enhanced ozonation on a pilot-scale, a 60 L/min (16 gal/min) continuous side flow from real-life wastewater streams can be diverted through the prototype for treatment and evaluation at the plant site. From concept to prototype our AOP design provides for a modular, self-contained, skid-mounted unit (Fig. 4) which can be operated within a mobile trailer (Fig. 5) parked adjacent to, or installed on-line within, the plant. The only input connections required are electrical power and the wastewater stream to be treated and evaluated.

The 60 L/min wastewater stream is initially subjected to three stages of suspended-solids removal in order to optimize the effectiveness of the subsequent ozonation and the UV irradiation treatments; namely, hydrosieving (0.5 mm, 0.020 in. slots) and sedimentation (2 min @ 4 cm/s, 8 ft/min) at atmospheric pressure, and micron-size particulate removal (98% mass removal @ 74 μm diameter) by a hydrocyclone after pressurizing the liquid to typically 503 kPa (73 psi). In order to independently and simultaneously apply various combinations and treatment levels of $O_3$ and UV to a common effluent stream, the prototype divides the liquid flow into three parallel treatment pathways (not shown) following solids removal. These 20 L/min (5.3 gal/min) streams each pass through separate ozonation, irradiation, and ozone-contacting stages at a predetermined back pressure imposed by a throttling valve. Ozone gas is infused by in-line venturi injectors supplied by an electric-discharge type ozone generator giving 5-15 wt% $O_3$ in $O_2$ feed-gas, respectively, for ozone outputs of 6.54-1.5 kg/day (14.4-3.4 lb/day). Irradiation of the water is facilitated by 40-s exposure in a coaxial ultraviolet reactor (30 mW/cm$^2$ @ 254 nm). Optimal ozone utilization is ensured by over 8-min residence time in separate contact columns. Subsequently, the three test streams converge at the throttling valve and, when required by specific applications, residual dissolved ozone is removed downstream by a centrifugal-type degasser and catalytically converted to $O_2$ for exhausting. The treated wastewater stream is discharged at atmospheric pressure for reuse.

The various liquid flowrates, pressures, ozone injection rates, and UV intensities are electronically sensed and these signals are input to a programmable logic controller (PLC) for overall system management. Installed instrumentation continuously monitors gaseous and dissolved $O_3$ concentrations, UV intensities, turbidity, and pH/ORP throughout the overall process. Additionally, liquid samples drawn at progressive sites through the process can be laboratory analyzed to experimentally determine the effects which varying operational parameters have upon treatment efficacy and water-quality characteristics.

## Summary

Technical details have been presented describing our recently developed mobile, pilot-scale, ultraviolet-enhanced ozonation system for synergistically treating wastewater streams on-site. This trailer-mounted prototype, which draws a 60 L/min (16 US gal/min) continuous side flow from real-life processing-water streams, incorporates three parallel treatment pathways for independently and simultaneously applying various combinations and treatment levels of $O_3$ and UV for experimental purposes. Ancillary processes of the self-contained prototype are: pretreatment separation of solids by hydrosieving, sedimentation, and hydrocycloning; contact-column residence and reaction; and, when required, degassing and catalytic abatement of residual ozone in the treated effluent. Installed instrumentation continuously monitors UV intensities, gaseous and dissolved $O_3$ concentrations, turbidity, and pH/ORP throughout the overall process. This advanced oxidation process has

proven very effective in treating food-processing waters for recycling; we invite collaborative on-site evaluations across the cotton-textiles sector to likewise experimentally determine treatment efficacy and water-quality improvements achievable.

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## References

Carriére, J., J.P. Jones, and A.D. Broadbent. 1993. Decolorization of textile dye solutions. *Ozone Sci. and Engr.* 15(3):189-200.

Diaz, M.E. and S.E. Law. 1997. Ultraviolet photon enhanced ozonation for microbiological safety in poultry processing water. *ASAE Paper No. 97-6054*. 12 pp. St. Joseph, MI.

Diaz, M.E. and S.E. Law. 2001. Control of pathogenic microorganisms and turbidity in poultry-processing chiller water using UV-enhanced ozonation. *Ozone Sci. and Engr.* 23(1):53-64.

Hitchcock, D.R., S.E. Law, J. Wu, and P.L. Williams. 1998. Determining toxicity trends in the ozonation of synthetic dye wastewaters using the nematode *Caenorhabditis elegans*. *Archives of Environmental Contamination and Toxicology* 34:259-264.

Langlais, B., D.A. Reckhow, and D.R. Brink. 1992. Ozone in Water Treatment: Application and Engineering. Lewis Publ., Boca Raton, FL.

Law, S.E. and M.E. Diaz. 2001. Implementation of UV-enhanced ozonation for recycling food-processing wastewaters: mobile prototype case study. *Proc. of Internat. Ozone Assoc. 15th World Congress* 2:306-312. London, UK.

Law, S.E., J. Wu, D.R. Hitchcock, and M.A. Eiteman. 1996. Ozone decolorization of cotton dyehouse wastewater. *ASAE Paper No. 96-1016*. 11 pp. St. Joseph, MI.

Perkins, W.S., S.E. Law, M.C. Smith, P.V. Winger, and P.J. Lasier. 2001. Biological treatability and environmental impact of ozonation of spent reactive dyebaths. *Textile Chemist and Colorist* 1(2):39-43.

Rearick, W.A., L.T. Farias, and H.B.G. Goettsch. 1995. Water and salt reuse in the dyehouse. *Proceedings of COTTECH Conference '95*. Cotton, Inc., Raleigh, NC.

Rice, R.G. and A. Netzer. 1982. Handbook of Ozone Technology and Applications. Butterworth Publ./Ann Arbor Science, Stoneham, MA.

Wu, J. M.A. Eiteman, and S.E. Law. 1998. Evaluation of membrane filtration and ozonation processes for treatment of reactive-dye wastewater. *Jour. of Environmental Engineering* 124(3):272-277.

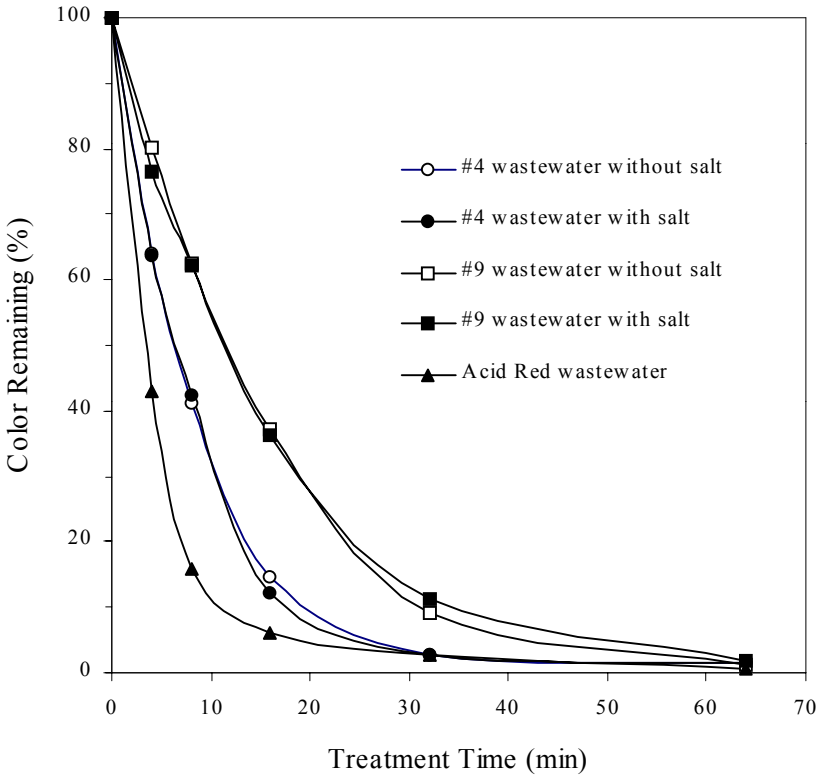


Figure 1. Percent color remaining in cotton wastewater as a function of ozonation time at 7.81 mg/L·min dosage rate [Law *et al*., 1996].

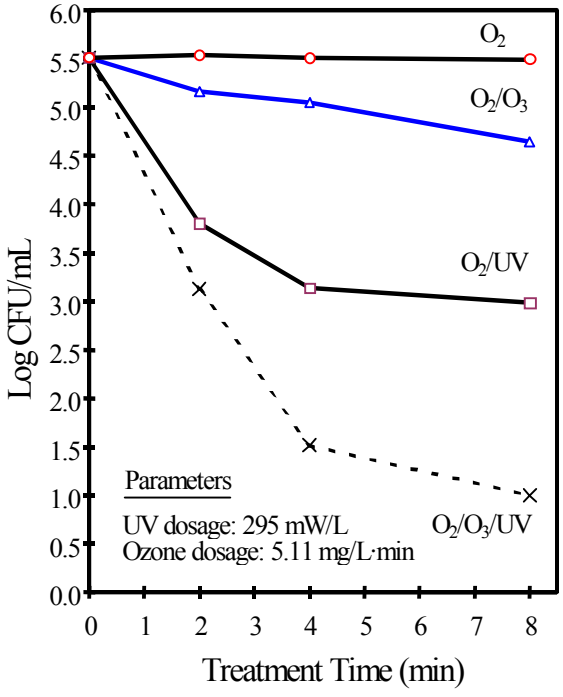


Figure 2. Bactericidal effect of three different treatments on *Salomonella typhimurium* inoculated poultry chiller wastewater as functions of treatments duration [Diaz and Law, 2001].

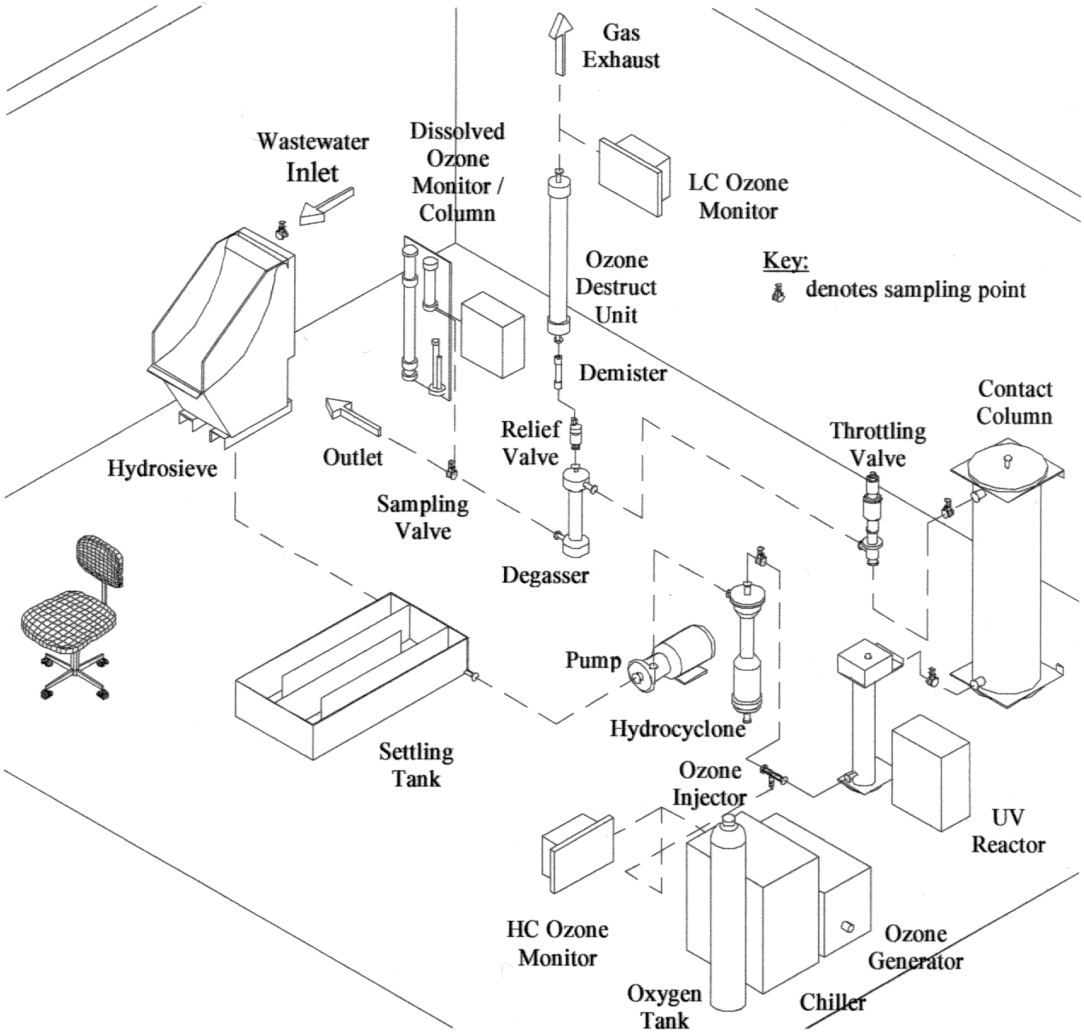


Figure 3. System components comprising pilot-scale prototype for UV-enhanced ozonation treatment of wastewater [Diaz and Law, 2001].

Figure 4. Skid-mounted prototype for UV-enhanced ozonation of wasterwaters.


Figure 5. Transport trailer for pilot-scale prototype.