Environ. Eng. Res. Vol. 10, No. 2, pp. 71~78, 2005
Korean Society of Environmental Engineers

FIBER OPTIC SENSOR FOR *IN-SITU* AND REALTIME MONITORING OF TRANSPORT OF GAS PHASE OZONE IN UNSATURATED POROUS MEDIA

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(received October 2004, accepted April 2005)

Abstract : A series of column experiments was conducted to develop a monitoring system for *in-situ* and realtime measurement of ozone transport in unsaturated porous media using a fiber optic sensor. The calibration of the fiber optic transflection dip probe (FOTDP) system was successfully carried out at various ozone concentrations using a column with length of 30 cm and diameter of 5 cm packed with glass beads, which don't react with gaseous ozone. The breakthrough curves (BTCs) of ozone were obtained by converting the normalized intensity into ozone concentration. The FOTDP system worked well for *in-situ* monitoring of gas phase ozone at various water saturations and in presence of soil organic matter (SOM). However, the FOTDP system did not measure the ozone concentration at more than 70% water saturation.

Key Words : fiber optic sensor, transflection dip probe, unsaturated porous media, ozone

INTRODUCTION

Contamination of subsurface system has increased due to the spill and leakage of oil.[1)] *In-situ* ozonation is effective for the remediation of unsaturated soils contaminated with organic pollutants.[2~9)] It offers many advantages in comparison with conventional technologies, including rapid removal of contaminants and gas phase application. Contaminants in soils react not only with ozone, but also with hydroxyl radicals generated from the catalytic reactions of ozone with metal oxides on soil surfaces.[8)] Several successful field applications of *in-situ* ozonation have been reported.[10,11)] Recently, mathematical models describing the fate and transport of gas phase ozone in variably saturated porous media have been developed.[12,13)] An efficient method for monitoring the transport of gaseous ozone in the contaminated site is essential to properly determine the effectiveness of the *in-situ* ozonation technology for field applications. Conventional techniques to perform such tasks typically require both sampling and lab analysis that are laborious and costly. Fiber optic sensors, on the other hand, could be used as a new method for *in-situ* monitoring, resulting in reduced sampling and analysis cost.

Various fiber optic sensors have been studied for environmental applications, since their initial development approximately thirty years ago. Their main advantages over conventional methods for monitoring can be summarized as: 1)

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small size, 2) continuous real-time measurement, 3) rapid and remote detection, 4) no sampling requirement, and 5) easy and portable installation.[14] This innovative technique is based on the basic principles of monitoring absorbance, reflectance, luminescence, reflective index change, or light scattering caused by a target material either flowing or deposited at the end of the sensor. Fiber optic sensors have been used for monitoring various physicochemical parameters in water such as, oxygen, pH, carbon dioxide, ammonia, detergents, biochemical oxygen demand, pesticides, and humidity.[15~17] To a lesser extent, some fiber optic sensors have been applied to detect or monitor organic contaminants, pH, and water content in subsurface environments.[15.18.19] Ge et al. (1995)[20] used an infrared fiber optic sensor to detect and identify petroleum contaminants. Ghodrati (1999)[18] employed a fiber optic miniprobe system consisted of a light source, input and output fiber optic bundles, mini-probe, and detector for *in-situ* and real-time characterization of contaminant transport in packed columns.

In this study, laboratory scale experiments were conducted to develop a sensor system using a fiber optic transflection dip probe (FOTDP) for *in-situ* monitoring of gaseous ozone simultaneously at multi-points within soil columns packed with variably saturated porous media.

MATERIALS AND METHODS

Fiber Optic Sensor System

The fiber optic transflection dip probe (FOTDP) system developed in this study is based on the transmission of ultra violet (UV) light through the input leg of a bifurcated fiber optic bundle to the end of a dip probe. UV light was selected since it can be absorbed by gaseous ozone in the short-UV wavelength range. The system works as follows: 1) incoming UV light is absorbed by gas phase ozone at the end of prove, 2) the transmitted light, which was not absorbed by ozone, is carried through the output leg of the bifurcated bundle to a spectrometer for quantification, and 3) a computer attached to the spectrometer records the intensity of the output signal as a function of time.

The FOTDP system developed in this study (Fig. 1) consists of 1) a deuterium light source (D-1000, Ocean Optics, Inc., FL, USA) that produces an intense and continuous spectral output from 200 to 400 nm, 2) a fiber optic transflection dip probe (T300-RT-UV/VIS, Ocean Optics, Inc., FL, USA), 3) a miniature fiber optic spectrometer (S2000, Ocean Optics, Inc., FL, USA) to monitors the light transmitted through the single-strand optical fiber, 4) an A/D converter with a serial port interface

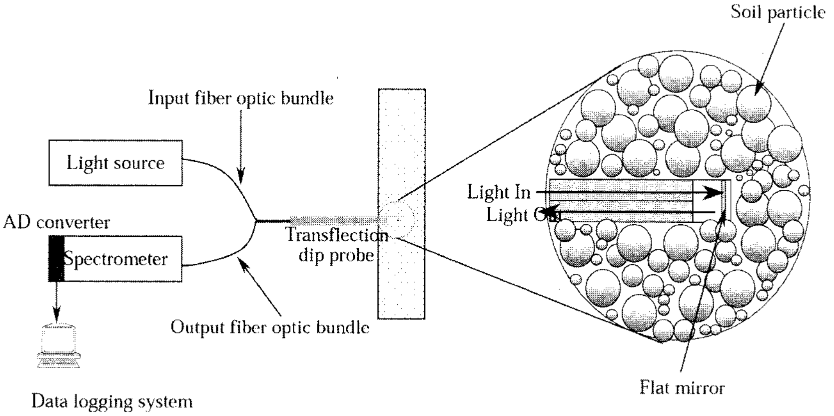

Figure 1. Schematic of fiber optic transflection dip probe (FOTDP) system and transflection dip probe for measurement of gas phase ozone in porous media.

(SAD500, Ocean Optics, Inc., FL, USA) and 5) a computer connected to the spectrometer to record the output data. The A/D converter was used to interface the spectrometer with the computer, which supports the RS-232 communication protocol. The signal transmitted through the fibers was logged by the computer and OOIBase32^{TM}, spectrometer operating software (Ocean Optics, Inc., FL, USA). A polyfurcated fiber optic bundle with a common end and 4 legs was used to divide the UV light from a single source into 4 channels to detect ozone concentrations at multiple points within the soil column. In the present study, ozone concentrations were measured at 3 points simultaneously.

The transflection dip probe consists of two bundles of optic fibers: one for light input and the other for light output. At one end of the dip probe, each leg is outfitted separately for connection to either the light source or a spectrometer. At the other end, the two bundles are meshed to form the common end of the bifurcated cable. The common end is encased in a stainless steel cylindrical tube to form the fiber optic transflection dip probe. The dip probe is cylindrical in shape with an outside diameter of 3.0 mm and a length of 10 cm. Screw-on, interchangeable probe tips, with a slit of path lengths of 1 mm, are attached to the end of the probe. The mirror is attached to the probe tip. The dip probe consists of two identical fibers with silica cores in a bifuricated assembly (one for illumination and one for reading). A plano-convex len is used to focus the light emitting from the illumination fiber, after which the light is transmitted through the sample, reflects off the mirror, and interacts with the sample again before being transmitted back through the probe via the read fiber, as shown in Figure 1. As the light travels through the sampling region twice, the optical path length is actually twice the length of the sample aperture, which is 2 mm.

Soil Column Experiments

A Pyrex glass of 5 cm in inner diameter and 30 cm in length was used for the soil column. To minimize reactions with ozone, Teflon and stainless steel were used for end caps and fittings of the columns, respectively. Three small holes were drilled into the side of the column at 7.5 cm, 15 cm, and 22.5 cm lengths from the bottom of the column. Before packing the column with porous media, three probes were inserted into the holes prepared on the column wall to locate the probe tips at the center of the column. Either glass beads (Aldrich Chemical Co.) or sands (Jumunjin, South Korea) were used for packing. Table 1 summarizes the characteristics of the two porous media. The results of the X-ray fluorescence analysis for the sands are reported elsewhere.[6)] The density and porosity of porous media packed in the column were estimated by measuring the mass of the column before and after packing. Desired water saturations were obtained by adding distilled water to the porous media. The soil columns were sealed at both ends and stored at room temperature for 24 hours to ensure homogeneous moisture distribution.

Table 1. Properties of the glass beads and sands used in the experiments

Property	Glass beads	Sand
Total Organic Carbon (wt.-%)	0.00	0.01
Porosity	0.53	0.52
Bulk Density (g/cm^3)	1.60	1.48
Specific Weight	2.60	2.51
Particle Size (μm)	425-600	425-600

The columns packed with porous media were placed in an experimental system as shown in Figure 2. The system consisted of an ozone generator (GL-1, PCI-100; NJ, USA), a mass flow controller (F201C-FAC-22-V, Bronkhorst Hi Tec; Netherlands), a gas-washing bottle and an UV/ VIS spectrophotometer (Smart Plus 1900, Youngwoo Instrument Corp.; Korea). The gaseous ozone was moisturized by passing it through the gas-washing bottle containing deionized water acidified to pH 2, and then injected into a UV/VIS spectrophotometer equipped with a flow

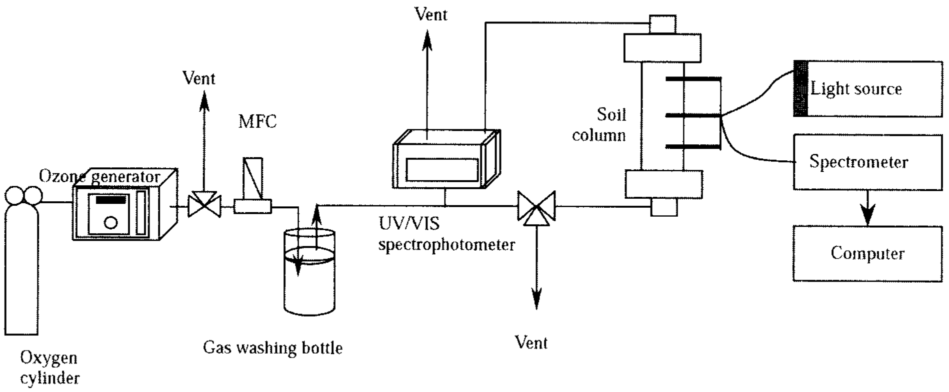

Figure 2. Schematic of the experimental setup for in-situ ozone monitoring.

cell for continuous monitoring of the concentration. The flow rate of the gaseous ozone was controlled using a mass flow controller. For all experiments, gaseous ozone was measured using a wavelength of 259 nm, and the results were recorded by a PC-based data acquisition system. Once ozone concentration stabilized, gaseous ozone was passed through the columns from bottom to top. Then, the ozone concentrations at the column outlets were determined using the UV/VIS spectrophotometer. The spectrometer operating software provides a function to display the light intensity into absorbance mode and transmittance mode. In the present study, the light intensity was recorded in the transmittance mode instead of the absorbance mode. Therefore, the light intensity was inversely proportional to the ozone concentration. Duplicate experiments were carried out at 25 ± 2°C for all experimental studies.

RESULTS AND DISCUSSION

General Performance of FOTDP

Changes in the light intensity were measured to evaluate the ability of the FOTDP system measurement when ozone was applied into the column packed with the glass beads in two different injection modes, a pulse injection and a step injection. Glass beads washed with HCl (1 M) solution were found to exert no significant ozone demand.[7] Figure 3 shows the intensity of the transmitted light, which was not absorbed by the ozone. The light intensity sharply decreased as gaseous ozone was injected into the column at two injection modes. With the step injection mode, a constant light intensity was observed by 100 sec (Fig. 3(a)), indicating a steady-state ozone concentration. With the pulse injection

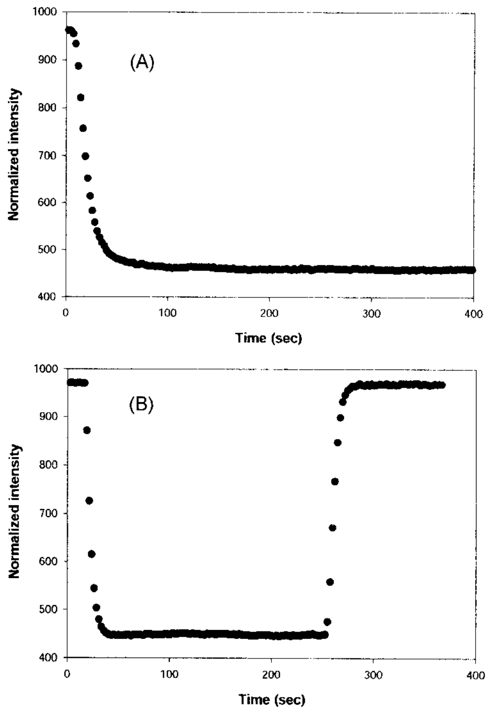

Figure 3. Output light intensity (Relative Transmittance): Ozone flow rate=300 mg/L: (A) step injection mode; (B) pulse injection mode.

mode, the light intensity rapidly returned to the initial value when ozone injection was stopped (Fig. 3(b)). The FOTDP system was not only sensitive to changes in the light intensity caused by ozone injection, but was also stable at the steady state ozone concentration. Therefore, it was concluded that the FOTDP system could be used to monitor gaseous ozone concentrations in columns packed with porous media.

The relationship between ozone concentration and normalized intensity is determined to convert normalized intensity into a formal breakthrough curve (BTC). For this purpose, normalized intensities of UV light were measured at various ozone concentrations ranging from 3.6 mg/L to 103.6 mg/L in a column packed with glass beads (Fig. 4(a)). The initial ozone concentration was 103.6 mg/L, and the concentration decreased step-wise to 3.6 mg/L. As shown in Fig. 4(b), a non-linear relationship was observed between the normalized intensity and the ozone concentration within the given concentration range. There is a nearly perfect polynomial fit between these two quantities (r^2= 0.999). Therefore, the normalized intensity determined during *in-situ* ozonation can be easily used to determine an ozone concentration.

The formation of small tail has been generally observed in the solute transport experiments with non-reactive tracers even in the column packed homogeneously. This is because immobile phase exists in the column. This tail can not be explained by the convective-dispersive equation due to the immobile phase. The resident concentration is referred to as the combined concentration of mobile-immobile phases in the column. Ghordrati et al. (2000) reported that they measured the resident concentration of solute in homogeneously paced columns using fiber optic probes. However, the FOTDP system designed in this paper measured the flux-averaged concentration of gaseous ozone due to the unique property of dip probe: the tip contained a slit of path, and gaseous ozone passed through the slit was monitored.

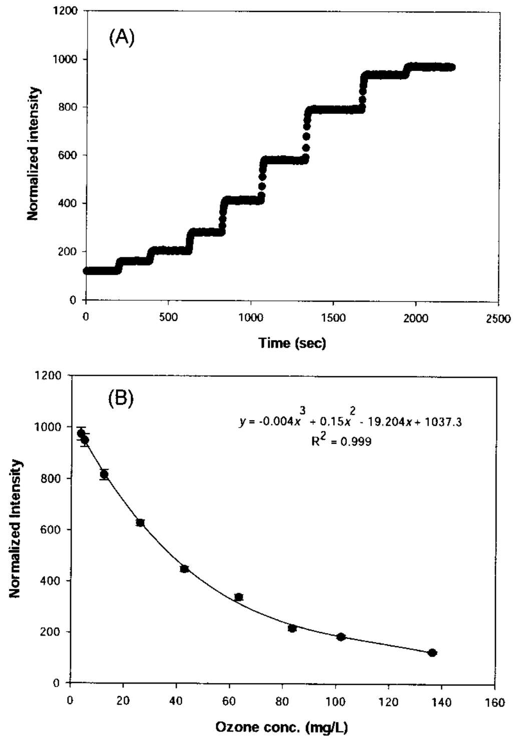

Figure 4. Calibration of the fiber optic transflection dip probe in the glass-bead packed column: (A) calibration fronts; (B) resulting calibration curve.

Measurement of the Breakthrough Curves (BTCs) in Dry Columns

The change in gaseous ozone concentrations were measured at three points within the column packed with glass beads. Figure 5 presents the normalized concentrations of gaseous ozone as a function of pore volume. The breakthrough time of the ozone was linearly proportional to the distance to the monitoring point. Accurate measurements of ozone concentrations at various flow rates are important in applying the FOTDP system for *in-situ* monitoring. To investigate the applicability and accuracy of the FOTDP system at various flow rates, the BTCs of the gaseous ozone were measured at three different flow rates of 200, 300 and 500 mL/min. Pore volumes required to reach C/C_o=0.5 are presented in Figure 6. Note that the pore volumes can be obtained by dividing the breakthrough time by the time required for 1 pore volume (1 replacement

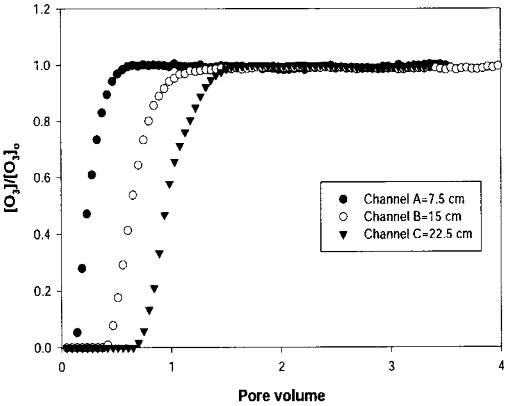

Figure 5. Measurement of ozone BTCs at the different monitoring points. The flow rate, ozone concentration, and water saturation were 500 mL/min, 50 mg/L, and 0%, respectively.

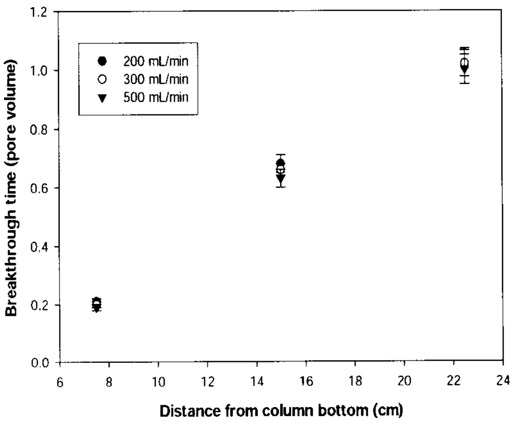

Figure 6. Breakthrough time of ozone measured at C/C_o=0.5 for the various flow rates.

of the entire column). The pore volumes required at C/C_o=0.5 for the three flow rates were not statistically different (t-test, α=0.05) at the three measurement points and were linearly proportional to the distance to the measurement points. These results indicate that the FOTDP system accurately measures gaseous ozone concentrations at various flow rates.

Measurement of Ozone BTCs Under Various Water Saturations

Soil water saturation is one of the most important factors to consider in characterizing the fate and transport of gaseous ozone in unsaturated porous media.[7,13] Thus, the ozone BTCs in the columns packed with sand were monitored under various water saturations using the FOTDP system. Figure 7 shows the ozone BTCs at various water saturations in columns packed with sands. Theoretically, the average linear gas velocity of a conservative gas at a fixed gas flux, proportionally increases as water saturation increases. This trend is a result of reduced gas pore volume in the soil column. However, as shown in Figure 7, the transport of gaseous ozone was retarded as water saturation was increased except for the case of 70% water saturation, resulting from increased dissolution of gaseous ozone into the pore water. In other words, the gaseous ozone injected into the column rapidly dissolves into the pore water until equilibrium is reached.

The soil organic matter (SOM) content in the sand was 0.01%. The fate and transport of ozone were expected to be influenced by the reactions of ozone with SOM and metal oxide. Choi et al.[6,7] reported that SOM and metal oxide on the soil surface enhance the decomposition of ozone during *in-situ* ozonation. The similar result was observed in this study. Gaseous ozone initially broke through several pore volumes slower than in the column packed with glass beads, which is attributed to ozone

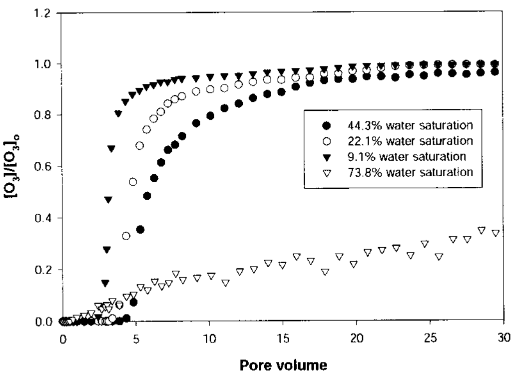

Figure 7. Effect of water saturation on the measurement of the ozone BTCs in the sand-packed column using the FOTDP system. The flow rate and ozone concentration were 300 mL/min and 50 mg/L, respectively.

reactions with SOM and metal oxide on sand surface. The water film, however, blocks the reaction between the gaseous ozone and SOM and metal oxide. Therefore, there was no significant effect of SOM on determining the concentration of gaseous ozone using the FOTDP.

Figure 7 clearly shows that the FOTDP system was not able to measure the ozone concentration precisely at 70% water saturation and may not measure the concentration over 70% of water saturation. This failure might have been caused by the foggy or wet transflection mirror caused by the pore water at high water saturations. However, water saturation may have no significant impact in field applications of the FOTDP system, since a well with small diameter should be constructed for insertion of the dip probe into the subsurface.

CONCLUSIONS

A new monitoring method using a fiber optic sensor has been successfully developed for *in-situ* real time measurement of ozone transport in unsaturated porous media. The system consists of light source, which produces intense and continuous UV light, a bifurcated optic fiber bundle, a transflection dip probe, a miniature fiber optic spectrometer, and a computer system for data aquisition. At the probe's tip, incoming light interacts with gas phase ozone and is partially reflected back into the probe. The reflected light is transmitted through the output leg to the spectrometer where it is quantified.

The calibration of the FOTDP system was successfully carried out for various ozone concentrations using a column of 30 cm length and 5 cm diameter packed with glass beads. The BTCs of the ozone were obtained by converting the normalized intensity into ozone concentrations. The FOTDP system reflected the ideal transport phenomena of gas phase ozone at various flow rates and worked well for *in-situ* monitoring of gaseous ozone under various water saturations and in the presence of soil organic matter (SOM). However, precaution should be exercised in measuring ozone concentrations if soil water saturations are too high.

REFERENCES

1. Hwang, S., Min, K.-S. and Curtright, C. J., "PAH biodegradation in soil-water suspensions contaminated with waste oil," *Environ. Eng. Res.*, **9**, 1-12 (2004).
2. Miller, C. M., Valentine, R. L., Roehl, M. E. and Alvarez, P. J. J., "Chemical and microbiological assessment of pendimethalin-contaminated soil after treatment with Fenton's reagent," *Water Res.*, **30**, 2579- 2586 (1996).
3. Hsu, I. and Masten, S. J., "The kinetics of the reaction of ozone with phenanthrene in unsaturated soils," *Environ. Eng. Science*, **14**, 207-217 (1997).
4. Masten, S. J. and Davies, S. H. R., "Efficacy of in-situ ozonation for the remediation of PAH-contaminated soils," *J. Contam. Hydrol.*, **28**, 327-335 (1997).
5. Nam, K. and Kukor, J. J., "Combined ozonation and biodegradation for remediation of mixtures of polycyclic aromatic hydrocarbons in soil," *Biodegradation*, **11**, 1-9 (2000).
6. Choi, H., Lim, H. N., Kim, J. Y. and Cho, J., "Oxidation of polycyclic aromatic hydrocarbons by ozone in the presence of sand," *Water Sci. Technol.*, **43**, 349-356 (2001).
7. Choi, H., Lim, H. N., Kim, J., Hwang, T. M. and Kang, J. W., "Transport characteristics of gas phase ozone in unsaturated porous media for in-situ chemical oxidation," *J. Contam. Hydrol.*, **57**, 81-98 (2002).
8. Kim, J. and Choi, H., "Modeling in situ ozonation for the remediation of nonvolatile PAH-contaminated soils," *J. Contam. Hydrol.*, **55**, 261-185 (2002).
9. Lim, H. N., Choi, H., Hwang, T. M. and Kang, J., "Characterization of ozone decomposition in a soil slurry: kinetics and mechanism," *Water Res.*, **36**, 219-229 (2002).
10. ESTCP, Technology status review, *in situ*

oxidation, DAC39-99-C-002, Environmental Security Technology Certification Program, U.S. Department of Defense, Washington D.C (1999).

11. Nimmer, M. A., Wayner, B. D. and Morr, A.A., "In-situ ozonation of contaminated groundwater," *Environmental Process,* **19**, 183-197 (2000).
12. Hsu, I. and Masten, S. J., "Mathematical modeling and column studies of gaseous ozone in unsaturated soil," *J. Environ. Eng.*, **127**, 546-554 (2001).
13. Jung, H., Kim, J. and Choi, H., "Reaction kinetics of ozone in variably saturated porous media," *J. Environ. Eng.*, **130**, 432-441 (2004).
14. Lee, B., "Review of the present status of optical fiber sensors," *Optical fiber technology,* **9**, 57-79 (2003).
15. Chudyk, W. A., Carraba, M. C., and Kenny, J. E., "Remote detection of groundwater contaminants using far-ultraviolet laser induced fluorescene," *Anal. Chem.*, **57**, 1237-1242 (1985).
16. Reichert, J., Sellien, W. and Ache, H. J., "Development of a fiber-optic sensor for the detection of ammonium in environmental waters," *Sens. Actuators, A,* **25**, 481-482 (1991).
17. Dybko, A., Maciejewski, J., Brzozka, Z., Wroblewski, W. and Romaniuk, R. S., "Application of optical fibres in oxidation-reduction titrations," *Sens. Actuators, B,* **29**, 374-377 (1995).
18. Ghodrati, M., "Point measurement of solute transport processes in soil using fiber optic sensors," *Soil Sci. Soc. Am. J.,* **63**, 471-479 (1999).
19. Ghodrati, M., Garrido, F., Campbell, C. G. and Chendorain, M., "A multiplexed fiber optic miniprobe system for measuring solute transport in soil," *J. Environ. Qual.*, **29**, 540-550 (2000).
20. Ge, Z., Brown, C. W. and Albert, J. J., "Infrared fiber optic sensor for petroleum," *Environ. Sci. Technol.*, **29**, 878-882 (1995).