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Photocatalytic Disinfection of *E. coli* in a Suspended TiO_2/UV Reactor

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Abstract−Disinfection capability using both TiO_2 and UV radiation was more than 27 times as that by using only the UV light. Optimal TiO_2 concentration and UV light intensity were 0.1 g TiO_2 l^{-1} and 50 W m^{-2} with which 100% reduction time was just 2-3 min in a batch-type slurry reactor.

Key words: Water Treatment, Disinfection, *E. coli*, Photocatalyst, TiO_2, UV

INTRODUCTION

Chlorine has been widely used to disinfect drinking water due to simple, cheap, and well-developed technology; however, toxic chlorine by-products are formed such as carcinogenic trihalomethanes (THMs). Furthermore, some pathogens such as viruses, certain bacteria *Campylobacter, Yersina, Mycobacteria,* or *Legionella,* and protozoans *Cryptosporidium or Giardia lamblia* cysts have been known to be resistant to chlorine disinfection [Regli, 1992; Pontius, 1990]. Certain coliform organisms, especially *Enterobacter cloacae, Citrobacter freundii, and Klebsiella pneumonia* and *oxytoca* can grow again in distribution pipe networks, utilizing assimilable organic chemicals [Moser, 1992].

Longer residence time of chlorine as well as higher dosage of chlorine in a reactor can increase the disinfection level, but it makes THM increase. Reduction of organic matters in influent water is needed to reduce chlorine dosage to prevent THM formation. In order to reduce organic pollutants and to increase disinfection efficiency, photocatalytic oxidation can be used as a pretreatment step of chlorine disinfection. Among photocatalysts such as TiO_2, ZnO, WO_3, CdS, and ZnS, TiO_2 has been mostly studied for the removal of xenobiotics [Ollis and Al-Ekabi, 1993; Halmann, 1996; Hoffmann et al., 1995; Legrini et al., 1993; Byrne et al., 1998; Anpo et al., 1997; Lee and Lee, 1998; Yamashita et al., 1998]. TiO_2 has been known as a chemical that is non-toxic, fairly inexpensive, and stable under UV radiation. When TiO_2 is illuminated with light of wavelength less than 400 nm, an electron is promoted from a valance band to a conduction band to give an electron/hole pair. The potential of the valance band is positive enough to generate hydroxyl radicals at the surface, and the potential of conduction band is negative to reduce molecular oxygen. The hydroxyl radical is used as a powerful oxidizing agent to convert organic pollutants into CO_2 or inactivate microorganisms.

TiO_2 has two common crystal structures, anatase and rutile. Several studies have noted that rutile is not an active photocatalyst [Davis, 1994; Mo et al., 1994]. The bandgap energy for rutile is 3.0 eV, as compared to 3.2 eV for anatase. Thus, the oxidation-reduction potentials are slightly less for the rutile phase and some reactions may not be favored with rutile, thermodynamically. An increase in TiO_2 specific surface area will enhance the photocatalytic activity due to increased area for adsorption of H_2O and OH·, and the subsequent generation of OH· radicals. UV radiation in inactivation of microorganisms is primarily active at 254 nm for the anatase type of TiO_2, whereas the longer wavelengths of solar UV are much less active as a germicide.

There have been a few reports that TiO_2 photocatalysis may be a viable process for disinfection of bacteria in water treatment systems. A UV lamp emitting a wavelength of 300-400 nm with coaxially wrapped TiO_2 (anatase form) fiber-glass mesh was used in a flowthrough water reactor [Ireland et al., 1993]. Tap water was dechlorinated with excess sodium thiosulfate to remove the scavenging effect of OH radicals, and then fed into the reactor with *E. coli* cultures of 2.7×10^7 colonies per 100 mL. A reduction in the concentration of viable organisms by 7 orders of magnitude was reported. Fouling effect of TiO_2 catalyst, which was dependent on feed water quality and scavenging effect of OH radicals due to chlorine, was pointed out as a potential problem. Matsunaga, et al. [1985] reported microbial disinfection by using TiO_2 (anatase) and Pt black mixtures under metal-halide lamp irradiation. Experiments were done in a batch culture of a slurry reactor. Survival ratios of *S. cerevisiae* were reported of 54% in 60 min and 0% in 120 min and those of *E. coli* were 20% in 60 min and 0% in 120 min. Block [1997] showed comparative results in a petri dish for the disinfection effect using UV light alone and using UV light and TiO_2. The time for 100% photocatalytic disinfection with 0.01% TiO_2 was reported as 8, 7, and 10 min for *Serratia marcescens, E. coli,* and *Straphylococcus aureus,* respectively. These works show that the time for 100% kill is somewhat long. Some experiments were done not in a large reactor, but in a petri dish only, which is not realistic for a field application. Furthermore, comparative results were not shown between only the UV and the UV/TiO_2 disinfections.

In this study, disinfection capabilities in a slurry reactor were estimated comparatively for both cases using only UV light and using UV light/TiO_2. Optimal TiO_2 concentration and UV light intensity need to be estimated for the application of photocatalytic disinfection using TiO_2. As TiO_2 concentration increases, the disinfection capability tends to increase. However, the capability decreases above a certain TiO_2 concentration, since the available UV intensity decreases due to light scattering and absorption by TiO_2 parti-

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cles themselves. Basic information which will be obtained in this work is needed in our continuing studies, where optical fibers immobilized by TiO_2 will be used to distribute UV light more effectively and uniformly. Costless solar light diffusing with optical fiers will be ultimately applied to disinfection in the future.

EXPERIMENTAL

1. Microorganism and TiO_2

E. coli MG-1655 (wild type) was used as a model microorganism for disinfection studies. Optimal pH and temperature for growth were found to be 7 and 37-40 °C in shaking-flask experiments and its specific growth rate was 1.36 h^{-1}. Luria-Bertani medium [Atlas, 1993] was used which consisted of bacto tryptone (10 g l^{-1}), bacto yeast extract (5 g l^{-1}), and NaCl (10 g l^{-1}).

TiO_2 (P-25, Degussa, Honau, Germany) was used as the photocatalyst in a batch-type slurry reactor. Average particle size was 21 nm, BET surface area was 50±15 m^2 g^{-1}, and the density was 3.89 g cm^{-3} at 20 °C.

2. Disinfection

E. coli was cultivated for 12 h at pH 7 and 37 °C. The cells were harvested by centrifugation at 15,000 rpm and washed three times with distilled water before being suspended as 10^4 ml^{-1} in 0.85% NaCl solution and used for the disinfection experiments.

In order to investigate the effect of UV intensity on the disinfection capabilities, UV was irradiated onto the cell suspensions including *E.coli* in a 1-*l* slurry reactor at 10, 20, 30, 40, 50, and 70 W m^{-2} (Fig. 1). Sampling was done at certain time intervals, and then cell number was determined as a colony forming unit after spreading sample solution on agar plate and incubating for 24 h at 37 °C.

3. UV Source and Light Intensity

A 100 W high-pressure mercury lamp (Dongsu Illumination Co., Seoul, Korea) was used as a UV light source. Its energy spectrum (Fig. 2) was measured with a monochromator (404VM, Acton Research Co., MA, U.S.A.). Radiometric light intensity was measured with a quantum meter (Model 1000, LI-COR, Inc., Nebraska, U.S.A.) and a radiometer (VLS3W, Cole-Parmer, Illinois, U.S.A.).

RESULTS AND DISCUSSION

Disinfection with UV light only was conducted by using a 100 W high-pressure UV lamp to find a reference disinfection capability. Since cells of different ages or physiological stages of growth exhibit differences in their susceptibility to UV irradiation, cells after 12 h cultivation in the same condition were inoculated into a 1-*l* batch-type slurry reactor which was irradiated with a 100 W UV lamp. The effect of UV intensity on the survival ratio is shown in Fig. 3. The UV intensity to which cells were exposed is shown above each graph line. As UV intensity increases from 10 to 70 W m^{-2}, survival ratio decreases considerably.

It is well known that disinfection by UV radiation is due primarily to damage of DNA, and 260 nm is the most effective wavelength of UV as a lethal agent. Purine and pyrimidine bases of the nucleic acids absorb ultraviolet radiation strongly, and the absorption maximum for DNA and RNA is at 260 nm. Proteins also absorb UV which has a peak at 280 nm. One well-established effect is the induction in DNA of pyrimidine dimers, a state in which two adjacent pyrimidine bases become covalently joined, so that during replication of the DNA the probability of DNA polymerase inserting an incorrect nucleotide at this position is greatly increased [Brock et al., 1994].

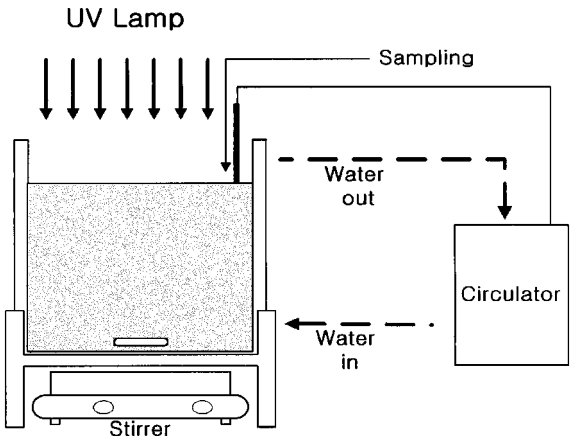

Fig. 1. Schematic diagram of a suspended TiO_2/UV reactor.

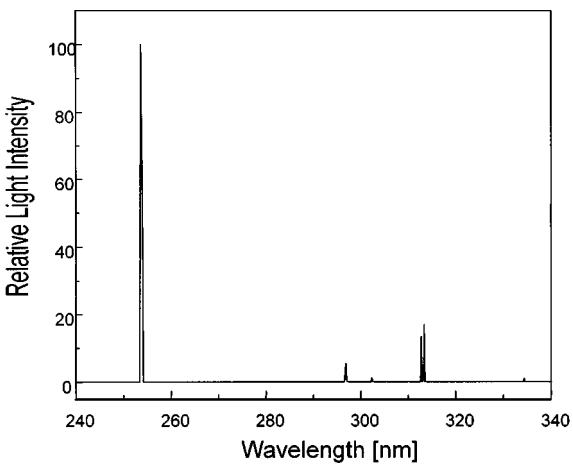

Fig. 2. Energy spectrum of a high-pressure mercury lamp.

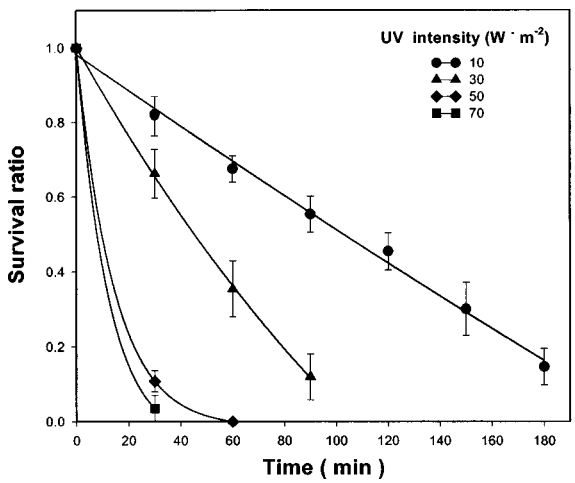

Fig. 3. Effect of UV intensity on survival ratio of *E. coli* in a batch reactor without TiO_2.

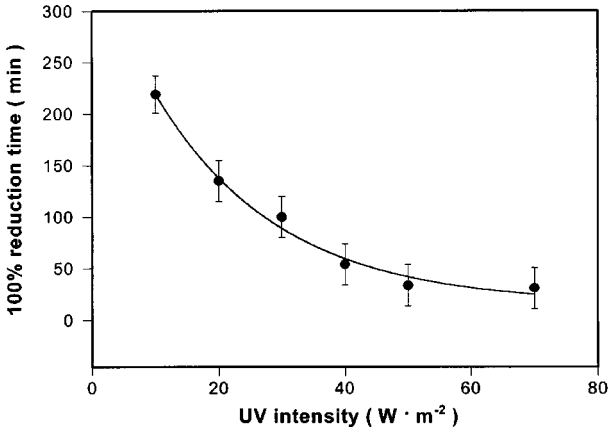

Fig. 4. Effect of UV intensity on 100% reduction time of *E. coli* in a batch reactor without TiO_2.

A 100% reduction time with respect to UV intensity is shown in Fig. 4, where 100% reduction time is defined as the time required for the complete disinfection of *E. coli* by UV light. It is 220, 34, and 31 min for UV intensities of 10, 50, and 70 W m^{-2}, respectively. The 100% reduction time - corresponding with the decrease of the cell concentration--decreased exponentially with the increase of UV light intensity, which means the disinfection capability increase exponentially with the UV intensity. However, the disinfection capability shows the pattern of saturation kinetics above 50 W m^{-2}.

Effect of TiO_2 concentration on the survival ratio of *E. coli* cells was determined at a constant UV light intensity of 10 W m^{-2}. As shown in Fig. 5, survival ratio with time decreased as TiO_2 concentration increased from 0 to 0.1 g l^{-1}, but it increased in the concentration above 0.1 g l^{-1} (Fig. 5). As explained in the introduction, hydroxyl radicals produced during photocatalytic reaction of TiO_2 react with and inactivate macromolecules in the cell, of which the most important is DNA. There are other recent reports. One of those is that lipid peroxidation reaction is the underlying mechanism of death of *E. coli* cells that are irradiated in the presence of the TiO_2 photocatalyst [Manners et al., 1999]. The other is that coenzyme A in the whole cells is photochemically oxidized and, as a result, the respiration of cells is inhibited which causes death of the cells [Matsunaga et al., 1985].

Since the key steps to TiO_2 photocatalytic oxidation occur at the TiO_2 surface, the reaction rate would be expected to increase linearly with available catalyst. At dilute TiO_2 concentrations, such a relationship is observed. However, above certain concentrations, the rate of oxidation does not increase and approach to a saturation level as the Langmuir-Hinshelwood kinetics [Davis, 1994]. In the case of TiO_2/UV disinfection, the photocatalytic disinfection capability, not the oxidation rate, increases also up to a certain level of TiO_2 like the Langmuir-Hinshelwood type. However, the disinfection capability decreases above a certain level due to the absorption and scattering of UV light by the suspended TiO_2 particles themselves. This effect was observed at 2.5 mg ml^{-1} TiO_2 concentration in a conventional optical fiber reactor [Matsunaga, 1995]. In this experiment, maximum disinfection capability occurred at 0.1 g TiO_2 l^{-1} (Fig. 6). Other factors that contribute to the rate independence of TiO_2 concentration include the reactor configuration and the light reflection [Davis, 1994].

Effects of UV light intensity and TiO_2 concentration on 100% reduction time of *E. coli* were investigated (Fig. 7). As UV light

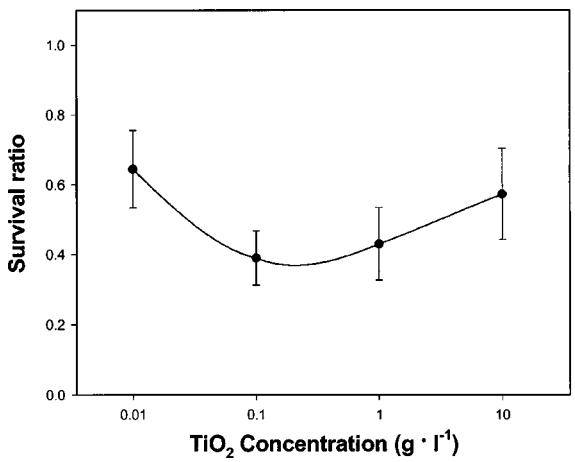

Fig. 6. Effect of TiO_2 concentration on survival ratios.

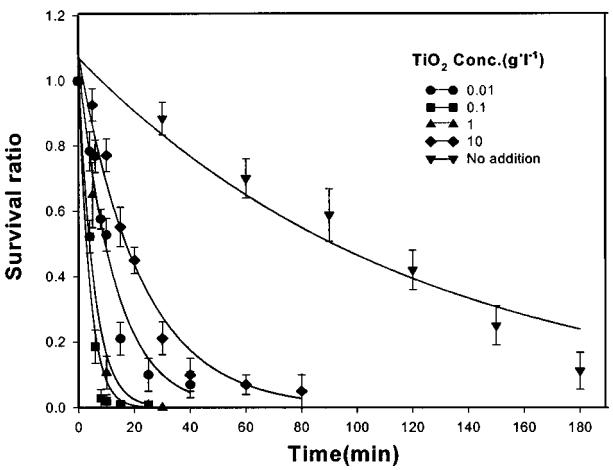

Fig. 5. Survival ratio of *E. coli* at UV intensity of 10 W · m^{-2} with TiO_2 concentration as suspended in a batch reactor.

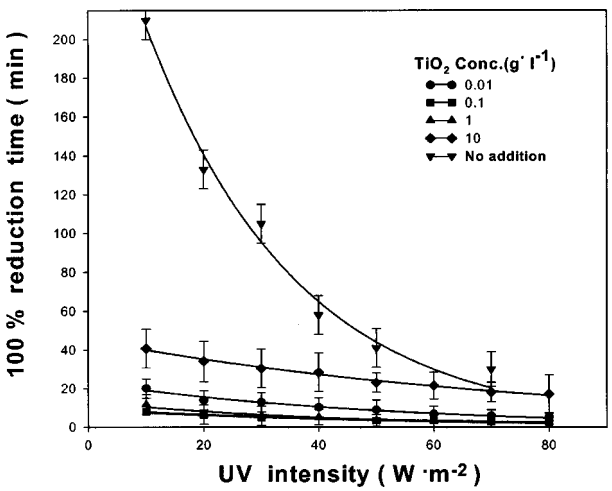

Fig. 7. Effect of UV intensity on 100% reduction time of *E. coli* in a batch with suspended TiO_2.

intensity and TiO_2 concentration increased, 100% reduction time corresponding to the disinfection capability decreased. Even though the maximum disinfection capability at the low light intensity of 10 W m^{-2} occurred at 0.1 g TiO_2 l^{-1} in Fig. 6, it was very similar for both 0.1 and 1 g TiO_2 l^{-1} as the light intensity increased. The reason may be that maximum available photon flux can be similar for both concentrations of TiO_2 as UV intensity increases above 70-80 W m^{-2}. The 100% reduction time at an optimal concentation of 0.1 g TiO_2 l^{-1} was 8 and 3 min at 10 and 50 W m^{-2}, respectively. The 100% reduction time using both TiO_2 and UV light was shorter than 27 times when compared with that using only the UV light. An effective method such as an optical-fiber reactor diffusing incident light intensity uniformly throughout the reactor can be applied to reduce electric energy required in the UV light energy. UV source can be obtained from sunlight, which has about 5% UV intensity.

The time was not considerably reduced in this experiment even though the light intensity increased above 50 W m^{-2}. In summary, optimal TiO_2 concentration and UV light intensity were 0.1 g TiO_2 l^{-1} and 50 W m^{-2} with which 100% reduction time was 2-3 min in a slurry reactor. Difficult separation of TiO_2 particles for the recycle should be overcome in a slurry reactor by applying an immobilization technique such as a sol-gel method in future studies.

Effect of initial cell concentration on 100% reduction time was also examined. Reduction time does not vary considerably with the initial cell concentration (Fig. 8). The reason may be that scattering and absorption effect of the incident UV light is not much different in these ranges of initial cell concentrations. As shown in Fig. 6, 100% reduction time was the shortest in the concentration of 0.1 g TiO_2 l^{-1}, but it was similar as that in the concentration of 1 g TiO_2 l^{-1}.

CONCLUSIONS

The 100% reduction time at a UV intensity of 10 W m^{-2} with 0.1 g TiO_2 l^{-1} was 8 min, while the time at 10 W m^{-2} without TiO_2 existence was 220 min. It can be concluded from these results that disinfection capability in the aspect of time using both TiO_2 and UV light was more than 27 times as that by using only the UV light.

Optimal TiO_2 concentration and UV light intensity were 0.1 g TiO_2 l^{-1} and 50 W m^{-2} with which 100% reduction time was 2-3 min in a slurry reactor. Separation problems of TiO_2 particles in a slurry reactor should be overcome by applying an immobilization technique using a sol-gel method in the future study.

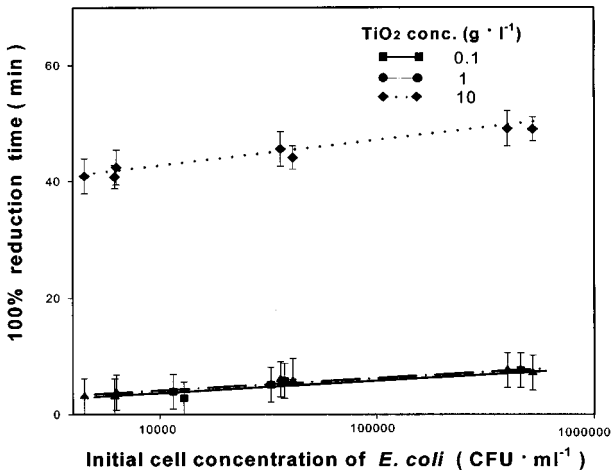

Fig. 8. Effect of initial cell concentration on 100% reduction time of *E. coli* in a batch reactor with suspended TiO_2.

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