DISINFECTION OF MUNICIPAL WASTEWATER BY SENSITIZED PHOTOOXIDATION

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ABSTRACT

To optimize the disinfection of treated municipal wastewater by sensitized photo-oxidation as a new alternative disinfection method, secondary unchlorinated activated-sludge-treated effluents from a sewage treatment plant were treated by semiconductor-sensitized photo-oxidation. Experiments of disinfection were performed in a photo-reactor system, which is a cylindrical borosilicon glass reactor with an effective volume of 1.1 litre. A NEC black light lamp (T10 20W) is placed at the centre of the reactor as an artificial light source to provide near UV irradiation with a maximum intensity at 350 nm. Hydraulic retention time (HRT) was used up to 60 minutes in this study. The effluents, after adding titanium dioxide as sensitizer, were exposed to the illumination of near UV light for various irradiation time and incident light intensities. Number of bacteria and coliforms were significantly declined from 35,000/100 ml to 59/100 ml after 60 minutes treatment, with existing of titanium dioxide, light irradiation and aeration. After the photo-oxidation process, the titanium dioxide in the treated effluent was separated by precipitation. The influence of light energy from 5.2 to 45 W/m^2, absorbed by the sensitizer in the visible range, on micro-organisms in secondary effluents was determined by testing for *Escherichia. coli (E. coli)* and total coliforms. An optimum titanium dioxide concentration found in the test is about 1 g/L. While the destruction rate of *E. coli* was affected by pH, dissolved oxygen (DO) and temperature (T), it was found that number of bacteria destroyed during disinfection mainly depends on incident light intensity (I_0) and irradiation time (t), which follows an exponential relationship. A kinetic model has been developed using the product of I_0 and t defined as a Dose Number (D) for this disinfection reaction.

KEYWORDS

Disinfection; photo-oxidation; sensitized; sensitizer; semi-conductor; titanium dioxide; wastewater; sewage; treatment; kinetics;

INTRODUCTION

Disinfection of water or wastewater by chlorine or ozone has now been done for about one hundred years. However some chlorine residuals in water are toxic to many aquatic organisms, and some by-products of chlorination in water such as trihalomethane (THM) may be carcinogenic. To avoid adding chemicals to the drinking water and wastewater, disinfection by UV rays, the specific photochemical reaction with the nucleic acids of the microorganisms, has been growing in recent years. UV disinfection is one of the alternatives which has generated considerable interest. There is little evidence to suggest that UV disinfection of water and wastewater produces potentially hazardous by-products. However, the cost of UV irradiation is relatively high when compared with chlorination.
Since the role of sunlight in modifying organic compounds in the environment has been recognised, a newly developed photochemical technology, called the sensitised photo-oxidation reaction, is based upon the wavelength range of irradiation close to sunlight, using a sensitizer and molecular oxygen system. (Li, et al., 1992; Matthews, 1986; Ollis, et al., 1990).

In the semiconductor-sensitised photo-oxidation process, metal chalocogenide semiconductors (TiO_2, Z_nO, C_dS, WO_3, and S_nO_2) have been utilised widely in photocatalytic processes destined for energy production (formation of chemical fuels) and degradation of environmental contaminants via light-induced redox reactions at the semiconductor/solution interface. These are light-induced redox reactions involving the generation of conduction band electrons and valence band holes by near UV illumination of the semiconductor material with suitable bandgap light energy. The TiO_2 is the most popularly used semiconductor for photo-oxidation purpose, due to its non-toxic, insoluble, comparatively cheap and high photoactivity (Matthews, 1991). Various studies on semiconductor sensitised photodegradation have been released since the mid 70's, in which titanium dioxide powder was used as the most popular sensitizer in slurry suspension or coated on the surface of reactors. In this heterogeneous reaction, titanium dioxide as sensitizer can be easily separated from treated wastewater by precipitation. This method has been intensively investigated for the degradation of many nonbiodegradable organics such as halogenated organics in synthetic aqueous solution and natural water systems (Matthews, 1986; Pruden and Ollis, 1983)
However, the disinfection capabilities of semiconductor-sensitised photo-oxidation have only been investigated by only limited studies. Ireland, et al. (1993) performed an experiment in which titanium dioxide in the anatase crystalline form was used as a photocatalyst to generate hydroxyl radicals in a flow-through water reactor and pure cultures of *E. coli* in dechlorinated tap water were tested. A rapid cell death was observed with both pure cultures and members of the indigenous flora in a natural water sample. A study using diffuse-light emitting optical fibbers (DLEOFs) was carried out for disinfection of *E. coli* indicated that the use of DLEOFs should provide a generally applicable method for photodisinfection of water supplies. (Matsunaga and Okochi, 1995).
This research project was designed to fully investigate the disinfection rates of semiconductor-sensitised photo-oxidation affected by operational parameters at a laboratory-scale with an aim of utilizing sunlight as a light source.

METHODOLOGY

Material and equipment

Secondary activated-sludge-treated effluents from a municipal wastewater treatment plant in Hong Kong were collected as wastewater samples and analysed for main characteristics including COD, BOD, pH, SS, number of *E. coli*, total coliforms and total bacteria, and stored at 4°C for use. To remove suspended solids prior to each experiment, the wastewater samples were filtered with filter papers of 1 μm, and *E. coli* and Total coliforms in the filtrate were counted as initial cell densities for tests. Titanium dioxide (TiO_2) was purchased from BDH with the grade of GPR and used as a sensitizer without any further purification. Concentrated slurries of TiO_2 was firstly prepared by

mixing TiO_2 powder with distilled water and sonicated for 15 minutes. Then the sonicated slurries were diluted with filtered wastewater samples before each run.
Experiments of disinfection were performed in a photo-reactor system, which is a cylindrical boro-silicon glass reactor with an effective volume of 1.1 litre. A NEC black light lamp (T10 20W) is placed at the centre of the reactor as an artificial light source to provide near UV irradiation with a maximum intensity at 350 nm. The wastewater slurry as influent was pumped into the reactor from an inlet at bottom and effluent was collected from an outlet at top. Hydraulic Retention Time (HRT) was used up to 60 minutes in this study.

Analyses

To determine the destruction of bacteria in the tests, total coliforms and *E. coli* were counted as main analytical parameters by Membrane Methods which are recommended methods by Environmental Protection Department of Hong Kong (HKEPD).

(Figure 1. Sketch of a continuous flow photo-reactor system)

For total coliforms tests, *m-Endo broth* was used as culture and samples were kept in an incubator at 35°C for 24 hours. For *E. coli* tests, membrane *laurel sulphate broth* was used as culture and samples were kept in an incubator at 44.5°C for 24 hours.

Experimental procedure

As the occurrence of *E. coli* in water is regarded as an important indicator of water pollution from the faeces of warm blooded animals, the survival of *E. coli* in the water exposed to the photo-oxidation reaction should be measured. Samples of effluent containing added sensitizer TiO_2 , were pumped into the photo-oxidation reactor and exposed to illumination of the UV lamp for different irradiation periods under continuous aeration. When the desired amount of irradiation was reached, the samples were collected from outlet of the reactor and examined for *E. coli* and total coliforms. Control samples were run simultaneously either in the dark in an incubator at 44°C with TiO_2, or exposed to illumination without a sensitizer,. After exposure, the TiO_2 was separated from the effluent by two hours precipitation.

RESULTS AND DISCUSSION

Preliminary study

For a feasibility test, the filtered effluent samples were pumped to the reactor from bottom and remained for a maximum period of 60 minutes. Reaction conditions were kept as pH = 6.9; temperature = 21°C, Concentration of TiO_2 = 2 g/L, incident light intensity = 45 W/m^2, DO = 8.34 mg/L. To determine essential conditions for an effective disinfection, tests were carried out in three different combinations of aeration only, aeration with UV irradiation, and aeration , UV irradiation with present of TiO_2. During the three runs, samples were collected at 0, 10, 20, 30, 40, 50, 60 minutes in each run and the remaining of *E. coli* were counted and shown in Figure 2 as below:
The results from first two tests indicate that the remaining of the *E. coli* was still more than 80 % of initial cell density after a 60 minutes treatment in the reaction with aeration only and there was a significant reduction of *E. coli* in the reaction with aeration plus UV irradiation in which number of *E. coli* was declined from 3500/100 ml to 200/100 ml (94.3% removal) after 60 minute treatment.

It is believed that the reduction of *E. coli* was mainly caused by a near UV irradiation such as dye-off of bacteria in maturation ponds. In third run, wastewater sample was aerated and irradiated by UV light with existing of TiO_2 for same period.

(Figure 2. Removal of E. coli in different reacting conditions)

The results show that the reduction rate of *E. coli* was significantly faster than that in the treatment without TiO_2, and the residue of *E. coli* was declined to 59/100 ml which can meet the HKEPD standard for discharged effluent. It implies that a mechanism of UV irradiation combined with photo-oxidation can significantly enhance the destruction of bacteria during the treatment. For the disinfection caused by UV irradiation, the efficiency mainly depends on the intensity and wavelength of UV light provided. For the disinfection caused by sensitized photo-oxidation reaction, the efficiency will depend on light intensity, sensitizer concentration, dissolved oxygen concentration, pH and temperature. A further investigation was performed in following tests to determine the optimum reacting conditions.

The optimum concentration of TiO_2

To find out the destruction rate of bacteria affected by the concentration of TiO_2 in the slurry, a set of runs were carried out in which the wastewater samples with same initial cell density were treated for 30 minutes with different TiO_2 concentrations from 0.1 g/L to 8 g/L. Both numbers of *E. coli* and total coliforms in the effluent from each run were counted as shown in Figure 3. It can be seen that increasing the concentration of TiO_2 slurry up to 2.0 g/L caused an increased die-off of the *E. coli* and total coliforms in the effluent. Over 89% destruction of E. coli organisms and 91% of total coliforms were achieved with 2.0 g/L of TiO_2 slurry after 30 minutes treatment. As the TiO_2 concentration increased further, the destruction of the *E. coli* and total coliforms in the effluent were less effective. It was implied that there is an optimum concentration of TiO_2 for the best results. The bactericidal effect was obtained by destructive oxidation and was not a mere TiO_2-sensitizer inhibition of coliforms growth. This fact was demonstrated when a sample of aerated effluent containing an *E. coli* concentration of 7200/100 ml and 2.0 g/L TiO_2 was incubated for 30 minutes at 44° C in the dark, and only insignificant changes in the *E. coli* density was observed.

(Figure 3. Destruction of E. coli and Total Coliforms affected by Concentration of TiO_2)

No. of *E. coli* remaining affected by incident light intensity

To determine the destruction rate of *E. coli* affected by light intensity, a set of runs were carried out in a beaker and incident light intensity was controlled by adjusting the distances between light source and the surface of the reaction solution in the beaker. From the experimental results, an exponential relationship between number of *E. coli* remaining and incident light intensity from 0 to 17 W/m^2 has been implied by a linear relationship between log (No. of E. coli remaining) and incident light intensity shown in Figure 4.

(Figure 4. Destruction of E. coli affected by incident light intensity)

Other tests were carried out in the continuous flow photo-reactor as shown in Figure 1 and the incident light intensity from the NEC blacklight lamp was 45 W/m^2 which is close to a direct sunlight intensity from 35 to 45 W/m^2 in a clear day between winter and summer in Hong Kong area. Generally speaking, higher light intensity will proportionally increase the rate of bacteria destruction in the sensitized photo-oxidation reaction.

E. coli remaining affected by dissolved oxygen concentration

(Figure 5. Destruction of E. coli affected by DO concentration)

To determine the *E. coli* removal affected by the concentration of dissolved oxygen, a series of constant DO concentrations during the reaction need to be carefully controlled, while the wastewater was intensively aerated with a mixed gas of N_2 and O_2 from nitrogen and oxygen cylinders and a saturated DO concentration proportional to O_2 partial pressure inside the reactor was always reached. When a flow radio of N_2 and O_2 in the mixed gas was adjusted with two gas flowmeters, the partial pressure inside the reactor was under control which means DO concentrations can be controlled as required. The mechanism of the destruction of bacteria in this reaction consists of two approaches including near UV (between 300 - 400 nm) irradiation and sensitized photo-reaction. The results in Figure 5 show when DO concentration is below 1 mg/L, inactivity of the bacteria is limited due to the only function of UV irradiation. When DO concentration is increased to 4 - 5 mg/L, the destruction rate of *E. coli* was significantly enhanced due to an addition of sensitized photo-oxidation reaction. However, it was found that the energy input in the aeration system is not proportional to the destruction efficiency when it exceeds a critical value such as 5 mg/L. No further increase of destruction rate of *E. coli* was found, which implied a critical range of 4 - 5 mg/L should be controlled as an optimum condition. It is worthwhile noting that an effective photo-oxidation process should be achieved with a carefully controlled aeration system. In addition, it is considered that the aeration process also improves the contact between light source and the wastewater surface by means of mixing.

E. coli remaining affected by initial cell density

Two samples with different initial cell densities ($4.0x10^3$/100 ml and $1.1x10^3$/100 ml) were tested and the number of *E. coli* remaining were counted at different exposure time as shown in Figure 6. The final destruction rates of *E. coli* in both samples were 99.7% and 99.9% after a 60 minutes treatment. The sample with the lower initial cell density only showed a slightly higher destruction rate.

(Figure 6. Destruction of E. coli affected by initial cell density)

Kinetic model of disinfection

When pH, aeration TiO_2 concentration are controlled within certain ranges, incident light intensity and exposure time become the most important parameters for this disinfection operation. To establish a kinetic model, the *E. coli* destruction is assumed to be a function of incident light intensity and the *E. coli* remaining in %, and follows a first order model as below:

(Equation 1)

where C is the number of *E. coli* remaining in the reaction, I_0 is the incident light intensity (W/m^2), and k is a constant

Hence, C can be expressed as follows;

(Equation 2)

where C_0 is initial number of E. coli and t is the exposure time (min)

It is necessary to define a Dose Number (D) with a unit of W/m^2.min as the product of I_0 and t, and the kinetic model will be expressed as follows:

(Equation 3)

(Figure 7. Fitting of experimental data by the kinetic model)

CONCLUSIONS

Secondary effluents from the municipal wastewater treatment plant in Hong Kong were successfully disinfected using TiO_2-sensitized photo-oxidation, and the number of *E. coli* and total coliforms were reduced to an acceptable level. An optimum concentration of TiO_2 found was about 2 g/L. Air aeration could enhance the rate of bacteria destruction in wastewater. It was found that number of bacteria destroyed during disinfection mainly depends on incident light intensity (I_0) and irradiation time (t), which follows an exponential relationship. A kinetic model has been developed using the product of I_0 and t defined as a Dose Number (D) for this disinfection reaction. A further study is being carried in an outdoor reactor in order to utilize sunshine directly as a light energy source.

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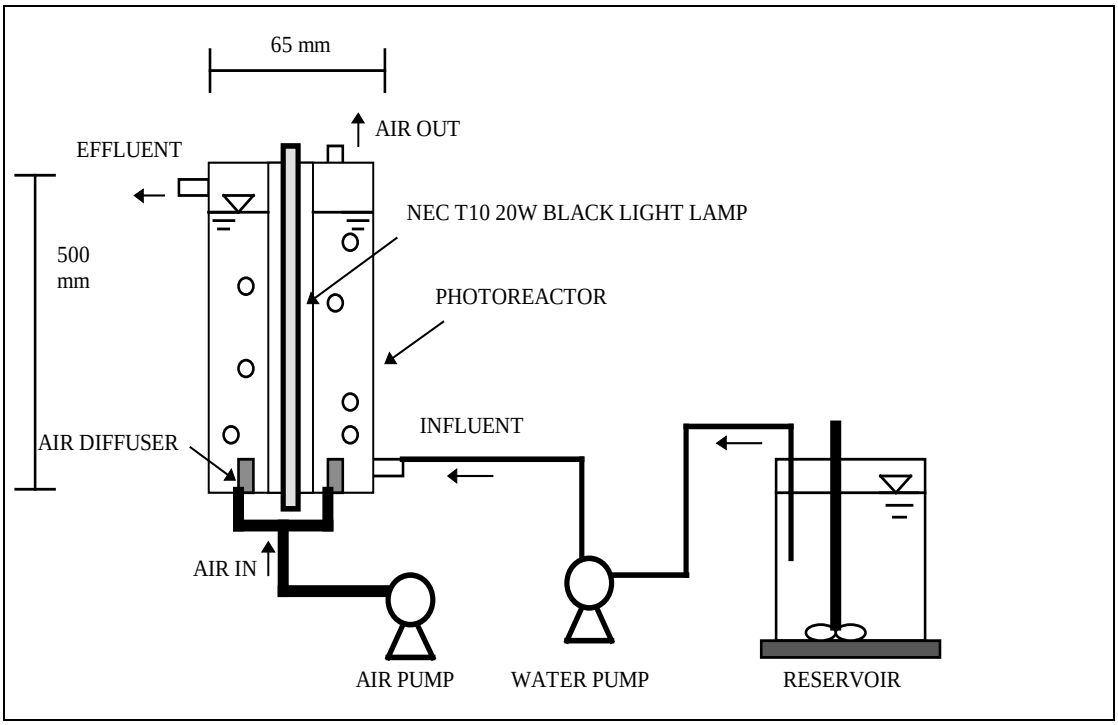

Figure 1. Sketch of a continuous flow photo-reactor system

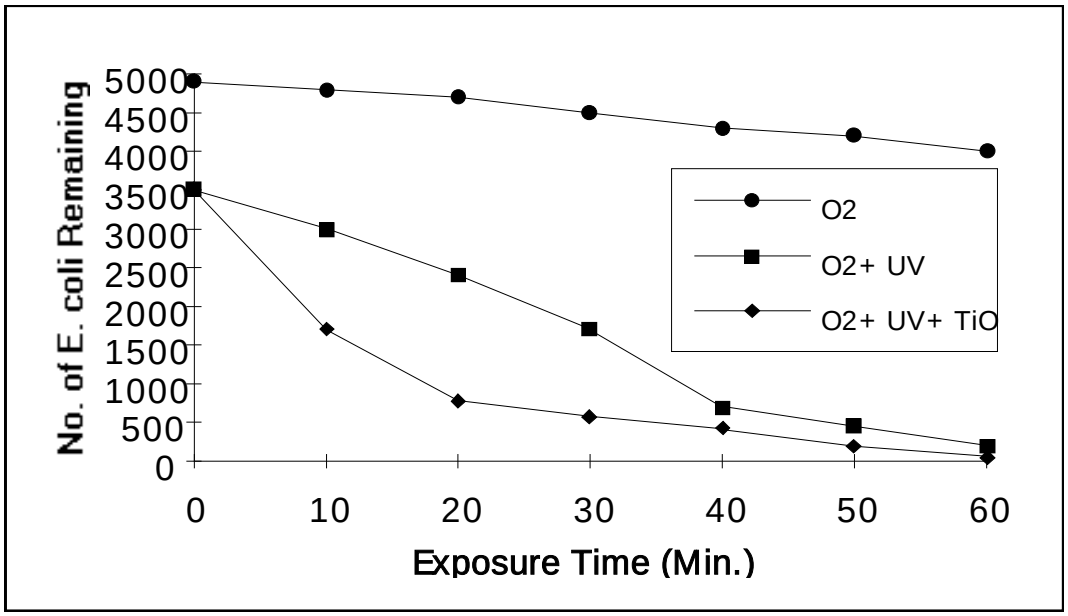

Figure 2. Removal of *E. coli* in different reacting conditions

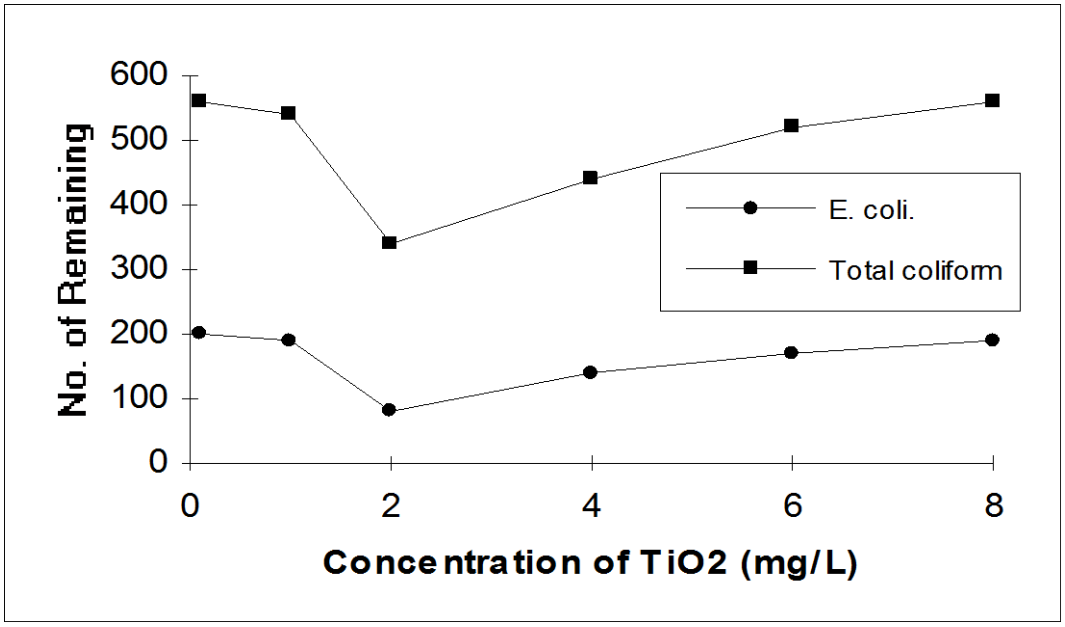

Figure 3. Destruction of *E. coli* and Total Coliforms affected by Concentration of TiO_2

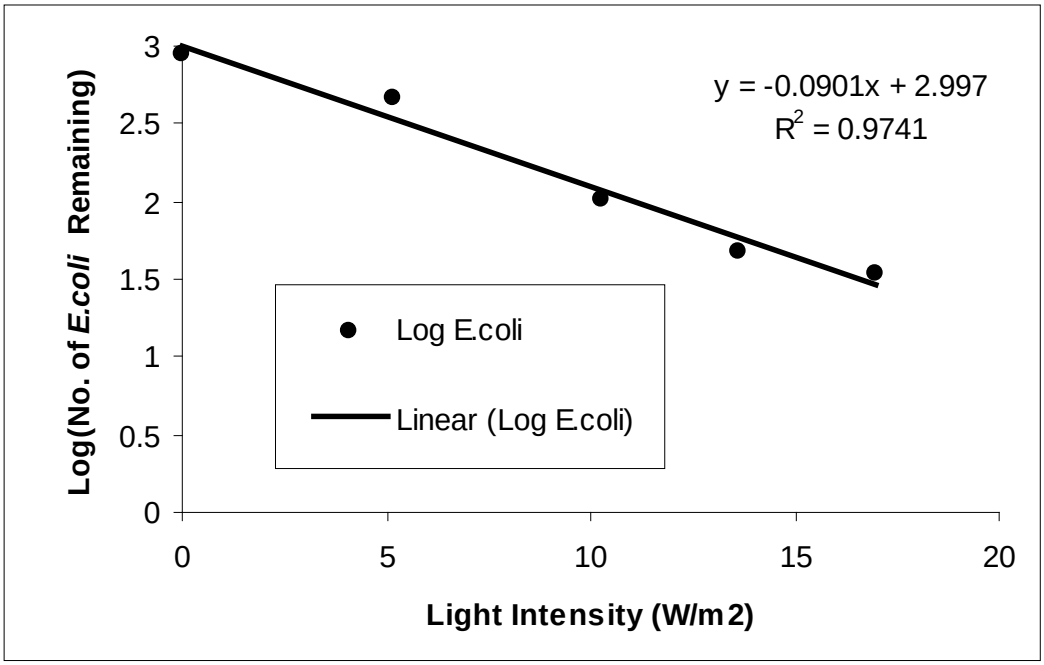

Figure 4. Destruction of *E. coli* affected by incident light intensity

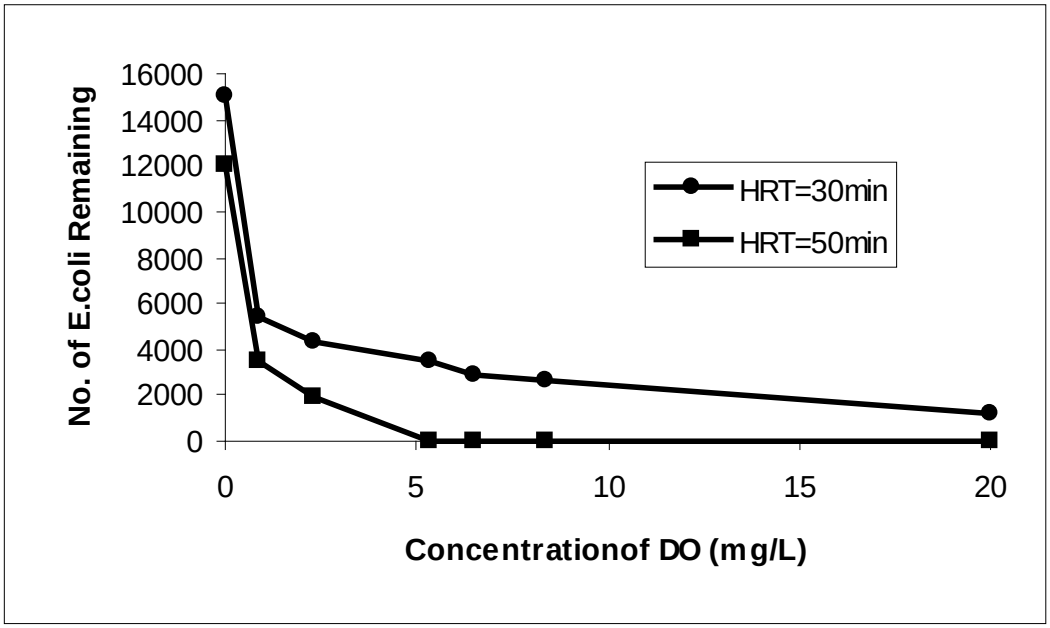

Figure 5. Destruction of *E. coli* affected by DO concentration

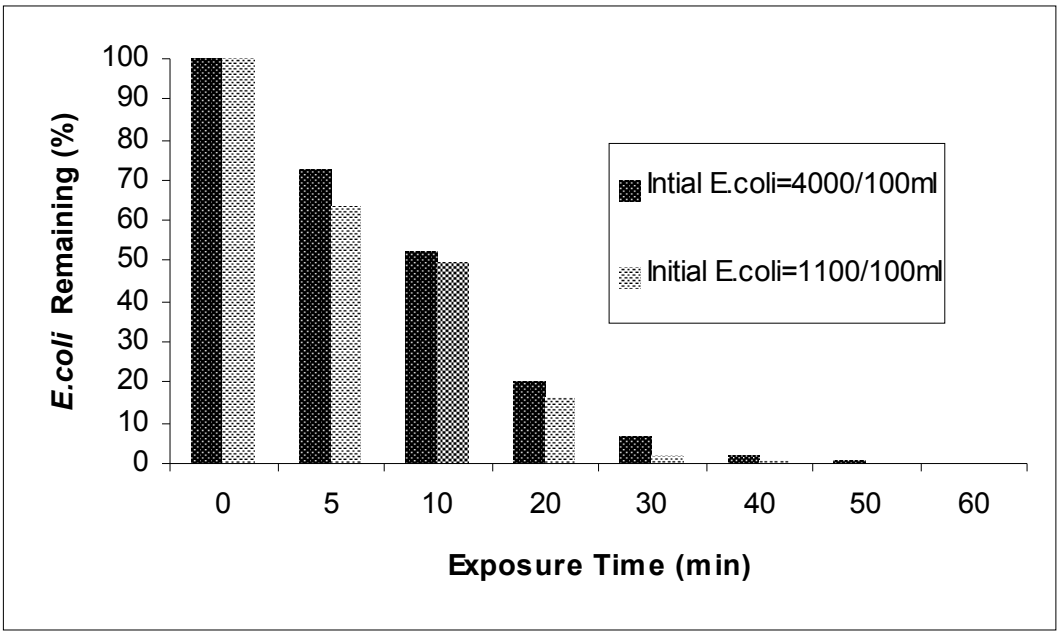

Figure 6. Destruction of *E. coli* affected by initial cell density

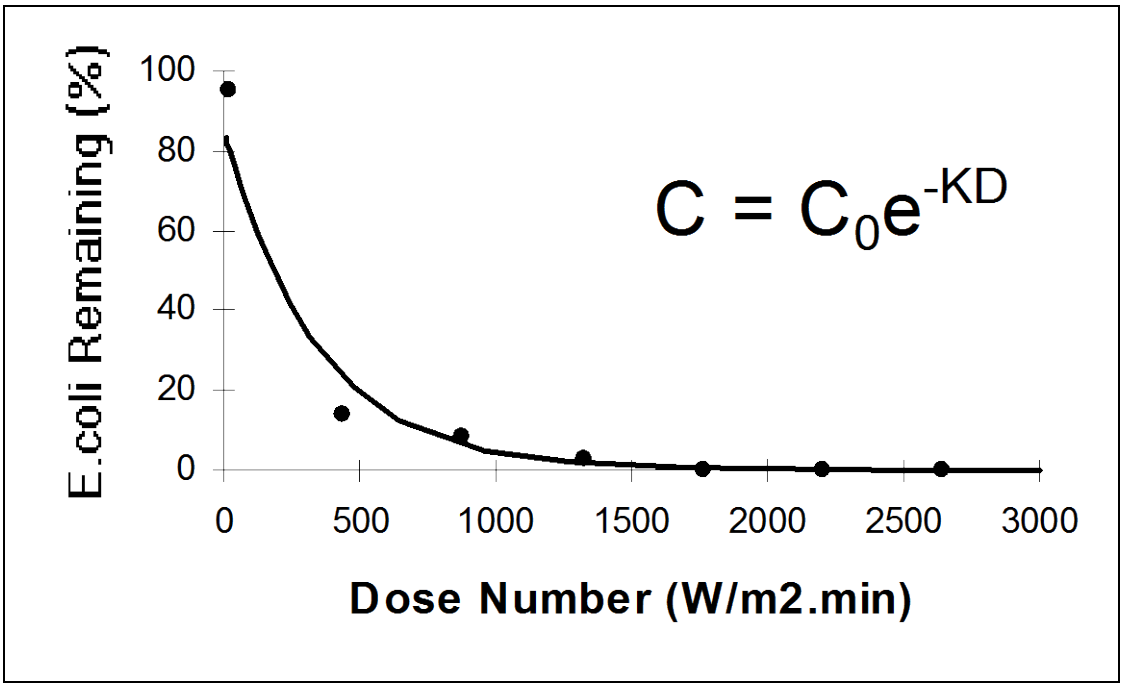

Figure 7. Fitting of experimental data by the kinetic model

Equation 1: $$\frac{dC}{dt} = -kI_0C$$

Equation 2: $$C = C_0e^{-KI_0t}$$

Equation 3: $$C = C_0e^{-KD}$$