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Solar photocatalytic disinfection of a group of bacteria and fungi aqueous suspensions with TiO_2, ZnO and Sahara desert dust

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Abstract

This photocatalytic method was aimed to destroy bacteria, to prevent fungi in some industrial products and to create desirable hygienic medium under solar irradiation. The efficiencies of disinfection with the photoactive metal oxides and the Sahara desert dust was investigated. We have studied photocatalytic disinfection of two-groups of microorganisms which are known as bacteria and fungus in pathogenic-organisms: *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Saccharomyces cerevisiae*, *Candida albicans*, *Aspergillius niger*. Aqueous suspension of the microorganisms (1.10^5 cfu/ml), in the presence of TiO_2, ZnO and Sahara desert dust were irradiated with a 400 W sodium lamp for various time periods in order to simulate solar radiation. Minimum catalyst concentration was used as 0.01 mg/ml. Sahara desert dust that contain some photoactive/inactive metal oxides (ZnO, Fe_2O_3, etc.) and some organics, is known as fertilizer of bioactivities in nature. In accordance with, no microbicidal effect of Sahara dust. Efficient microbicidal effects of TiO_2 and ZnO were detected under sodium light irradiations. Except for *A. niger*, all selected bacteria and fungus were disinfected in a short period by using 400 W sodium lamp in the presence of photocatalysts. Three strains of bacteria were destroyed in 40 min, two strains of fungi were also destroyed in 120 min at the same conditions. Photocatalytical method is an advantageous and an alternative one in comparison with former literatures.

Keywords: Photocatalytic disinfection; TiO_2; ZnO; Sahara desert dust; *Escherichia coli*; *Pseudomonas aeruginosa*; *Staphylococcus aureus*; *Saccharomyces cerevisiae*; *Candida albicans*; *Aspergillius niger*

1. Introduction

Water supply resources consist varieties of physical, chemical and biological constituents. Particularly, reclamation of wastewater is more and more widely practiced since the limitations of fresh water supply. Therefore, disinfection is mostly applied before usage of the fresh and reclamated wastewater [1].

Photocatalysis is a promising technology based on the interaction between light and solid semiconductor particles and is able to produce highly oxidative species that not only destroy bacteria, but also destroys a large variety of chemical contaminants in water [2]. Among the photoactive semiconductors are namely TiO_2, ZnO, Fe_2O_3, WO_3, and CdSe [3–5]. TiO_2 is most widely used in different media as photocatalyst, because of its lack of toxicity and its stability [3,6].

Matsunaga et al. [7] reported for the first time the microbiocidal effect of TiO_2 photocatalytic reactions. Since then, research work on TiO_2 photocatalytic killing has been intensively conducted on a wide spectrum of organisms including viruses, bacteria, fungi, algea, and cancer cells [8]. Most of these studies used the conventional powder photocatalyst, commonly the Degussa P25 TiO_2. Most work has been in aqueous phase [2,9–12], but transparent TiO_2 films [13], TiO_2 thin films prepared by sol–gel and reverse micelle methods [14], Ag-loaded TiO_2 [1], Al or Cu doped TiO_2 [15] have been tested and recommended to improve the application.

Advanced oxidation technologies (AOTs) have been investigated with the aim of developing methods to purify water and several results have been reported using TiO_2 powder as photocatalyst for varying waste materials [1].

A wealth of information has demonstrated the efficacy of the biological disinfectious actions of TiO_2 as photocatalyst. The aim of our study is to investigate the TiO_2, ZnO, and

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Sahara desert dust catalysts for the complete disinfection of some microorganism within a shorter illumination time with a solar simulating lamp. The results obtained from these two different semiconductors and Sahara desert dust which contain of ferric oxide, zinc oxide [16] were compared. In some literature, ferric oxide was alone used (as a photocatalyst) or with TiO_2 together.

Although TiO_2 is recognized as the choice for water treatment, some researchers have also investigated zinc oxide for photodegradation of organic compound [6]. Also photoreactivity of ZnO has been found as high as TiO_2 under concentrated sunlight [17].

When irradiated, TiO_2 particles are in direct contact with or close to microorganisms, the oxidative species hydroxyl radicals that are produced by the irradiation of the catalyst, will attack to the microbial surface [1].

Photocatalytic oxidation is a promising technology for the detoxification and disinfection of water and wastewater. When catalytic semiconductor powder, such as titanium dioxide and zinc oxide are suspended aqueous media and irradiated with near UV $\lambda < 385$ nm, $^{\bullet}OH$ radicals are generated. The $^{\bullet}OH$ radical is highly toxic towards microorganism and very reactive in the oxidation of organic substances. The photocatalytic degradation of various organic compounds by illuminated TiO_2 have been reported [12]. Photocatalytic inactivation of bacteria *Escherichia coli*, *Bacillus pumilus* and spores of *Clostridium perfringens*, as well as *virus Phage QB* have been investigated [12]. In these photocatalytic disinfection studies, UV (250–400 nm) or sunlight-emitting lamps were used as sources of light [12].

1.1. Reaction mechanism

Mechanisms for the primary events occurring at the surface of the catalyst have been described [12]. The irradiation of TiO_2 with photons of energy equal or greater than its band-gap (3.2 eV) resulted in the promotion of electrons from the valence band (vb) to the conduction band (cb) of the particle. The result of this process is region of positive change termed a hole (h^+) in the vb, and a free electron (e^-) in the cb.

$$TiO_2 + h\nu \rightarrow TiO_2 + e^-(cb) + h^+(vb)$$

At the TiO_2 particle surface, the holes react with surface hydroxl groups (OH^-) and adsorbed H_2O, to form $^{\bullet}OH$ radicals.

$$OH^- + h^+ \rightarrow {}^{\bullet}OH$$

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+$$

In the absence of electron acceptors the electron–hole recombination is possible. The presence of oxygen prevents this recombination by trapping electrons through the formation of superoxide ions. The final product of the reduction may also be radical.

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet -}$$

$$2O_2^{\bullet -} + H^+ \rightarrow 2{}^{\bullet}OH + O_2$$

Hydroxyl radicals can inactivate microorganisms [12].

$$\text{Bacteria} + {}^{\bullet}OH \rightarrow \text{bacterial inactivation}$$

2. Materials and methods

2.1. Materials

The photocatalysts were TiO_2 and ZnO and Sahara desert dust was supplied by Degussa P25, Merck and Professor Dr. A. Cemal Saydam (TUBITAK), respectively. All other reagents were at least of reagent grade and used without further purification. All solutions and materials were sterilized by autoclaving.

2.2. Culture of microorganisms

1. *E. coli* ATCC 35218
2. *S. aureus* ATCC 25923
3. *P. aeruginosa* ATCC 27853
4. *A. niger* (standard strain of laboratory)
5. *C. albicans* ATCC-90028
6. *S. cerevisiae* (standard strain of laboratory)

2.3. Photocatalytic reaction procedure

The amounts of the catalysts were varied 0.01 mg/ml. The illuminations were carried out using a 400 W sodium lamp located ~10 cm from the reaction vessel. The reaction was carried out in a pyrex reactor with water-cooling.

The microorganisms used in inactivation studies were *E. coli*, *P. aeruginosa*, *S. aureus*, *S. cerevisiae*, *C. albicans*, *A. niger*. The microorganisms solutions were prepared with saline solution (%0.9 NaCl). The microorganisms at initial concentrations of 1.105 colony forming units, cfu/ml. The solutions were irradiated for 4 h.

2.4. Cell viability

The number of viable cells in this suspension that were subjected to the photocatalyst-light or Sahara desert dust treatment or were not subjected to the photocatalyst-light or dust treatment were determined by plating 10 μl aliquots of serially diluted suspensions onto blood agar plates for bacteria cells, onto sabura dextrose agar plates for fungi spores. The blood agar plates were incubated at 37 °C for 24 h, and the sabura dextrose agar plates were incubated at 37 °C for 48 h. Then, the numbers of colonies on the plates were counted.

3. Results and discussion

It is well known that direct UV-A irradiation produces deleterious effect in bacteria cells, with different sensitivity to the radiation depending on the type of bacteria and amount of light doses [9].

Direct contact between TiO_2 and target cells to ensure the direct oxidation of cell components. TiO_2 photocatalytic killing studies have revealed that sensitivity of microorganisms to TiO_2 photocatalysis is likely in the following order: virus > bacterial cells > bacterial spores. This suggest that nonidentical microorganisms respond differently to TiO_2 photocatalyst due to their structural differences, particularly in the complexity and thickness of the cells envelope.

In this work, we have investigated the photocatalytic disinfection of *E. coli*, *P. aeruginosa*, *S. aureus*, *S. cerevisiae*, *C. albicans*, *A. niger* microorganisms by sodium light in the presence or absence of TiO_2 or ZnO.

The microbial inactivation except *A. niger* occur with TiO_2 or ZnO addition in a short time by sodium light. But direct microbicidal is not observed action in absence of TiO_2 or ZnO under sodium light. Also, the microbial inactivation do not occur in the dark and in presence of TiO_2 or ZnO. These results are consistent with the previous experiments reported in the literature showing that the TiO_2 itself do not act as a germicide in the dark [12].

In addition, we have studied the disinfection of selected microorganisms in presence of Sahara desert dust as photocatalyst which is known to contain photoactive metal oxides of zinc oxide and ferric oxide. A surprising fact is Sahara desert dust creates wonders in nature by fertilizing the bacterial life under solar light even in atmosphere, unlike any of the known desert dusts [16]. The cause of no microbicidal effect in presence of Sahara desert dust under photolysis may be attributed to inhibition of hydroxyl, superoxide anion radicals with the organic molecular structures (i.e. oxalates) in the dust particle cages and formation of carbon radicals which initiates photosynthesis. Sahara desert dust is found to be rich with organic materials unlikely of other desert dusts [16]. All selected microorganisms have continued on their life in presence of Sahara desert dust under sodium light at our investigations.

- The complete *E. coli* inactivation by sodium light irradiation over TiO_2 or ZnO suspension was reached in 40 min (Figs. 1 and 2).
- The complete *P. aeruginosa* inactivation by sodium light irradiation over TiO_2 or ZnO suspension was reached in 40 min (Figs. 3 and 4).
- The complete *S. aureus* inactivation by sodium light irradiation over TiO_2 or ZnO suspension was reached in 120 min (Figs. 5 and 6).
- The complete *C. albicans* inactivation by sodium light irradiation over TiO_2 or ZnO suspension was reached in 120 min. But with ZnO, the disinfection was reached in 180 min (Figs. 7 and 8).

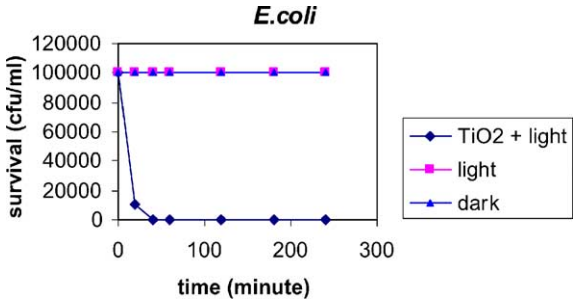

Fig. 1. Effect of TiO_2 (1 mg/ml) on *E. coli* survival. Initial concentration 10^5 cfu/ml. Inactivation of *E. coli* by sodium light with and without TiO_2 addition, and in the dark.

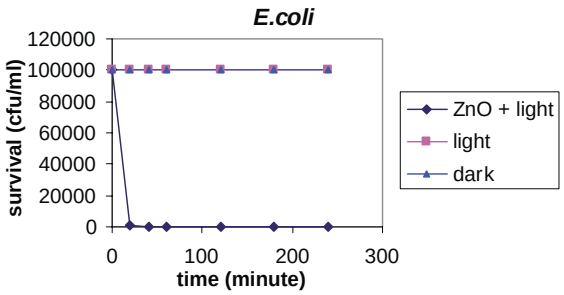

Fig. 2. Effect of ZnO (1 mg/ml) on *E. coli* survival. Initial concentration 10^5 cfu/ml. Inactivation of *E. coli* by sodium light with and without ZnO addition, and in the dark.

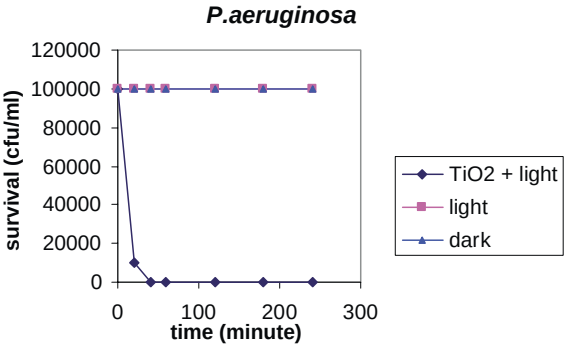

Fig. 3. Effect of TiO_2 (1 mg/ml) on *P. aeruginosa* survival. Initial concentration 10^5 cfu/ml. Inactivation of *P. aeruginosa* by sodium light with and without TiO_2 addition, and in the dark.

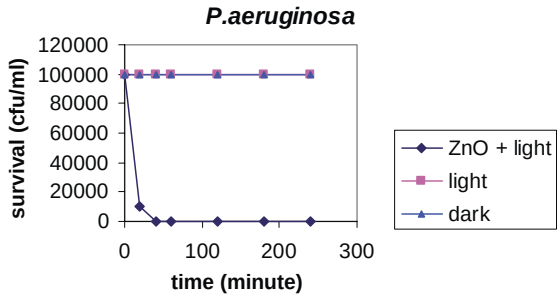

Fig. 4. Effect of ZnO (1 mg/ml) on *P. aeruginosa* survival. Initial concentration 10^5 cfu/ml. Inactivation of *P. aeruginosa* by sodium light with and without ZnO addition, and in the dark.

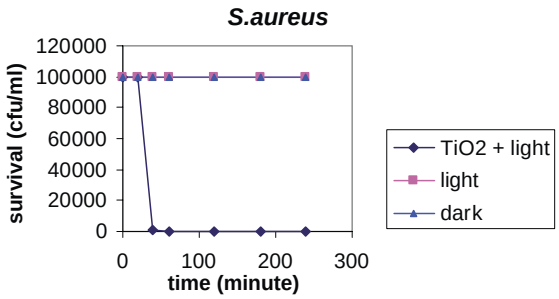

Fig. 5. Effect of TiO_2 (1 mg/ml) on *S. aureus* survival. Initial concentration 10^5 cfu/ml. Inactivation of *S. aureus* by sodium light with and without TiO_2 addition, and in the dark.

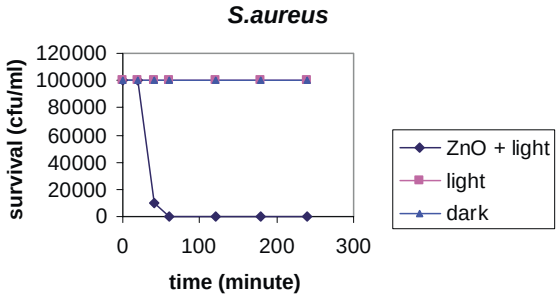

Fig. 6. Effect of ZnO (1 mg/ml) on *S. aureus* survival. Initial concentration 10^5 cfu/ml. Inactivation of *S. aureus* by sodium light with and without ZnO addition, and in the dark.

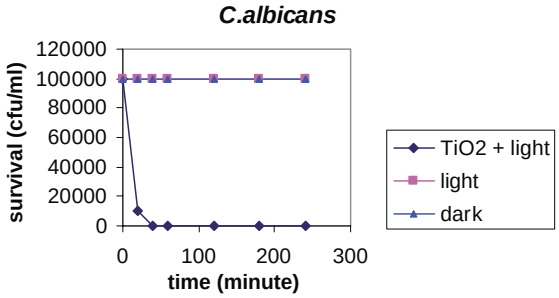

Fig. 7. Effect of TiO_2 (1 mg/ml) on *C. albicans* survival. Initial concentration 10^5 cfu/ml. Inactivation of *C. albicans* by sodium light with and without TiO_2 addition, and in the dark.

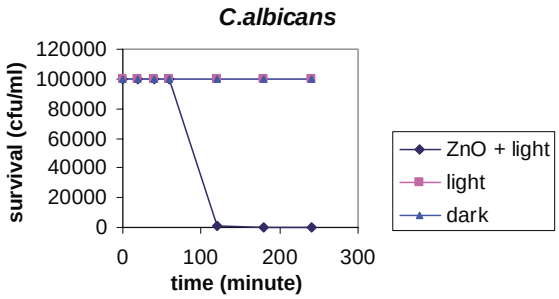

Fig. 8. Effect of ZnO (1 mg/ml) on *C. albicans* survival. Initial concentration 10^5 cfu/ml. Inactivation of *C. albicans* by sodium light with and without ZnO addition, and in the dark.

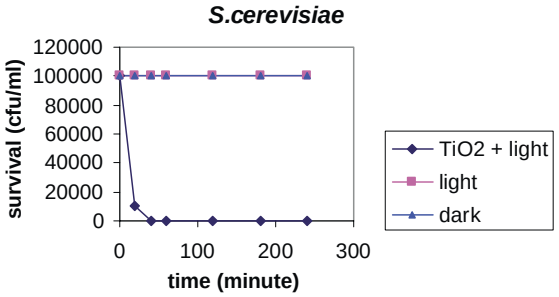

Fig. 9. Effect of TiO_2 (1 mg/ml) on *S. cerevisiae* survival. Initial concentration 10^5 cfu/ml. Inactivation of *S. cerevisiae* by sodium light with and without TiO_2 addition, and in the dark.

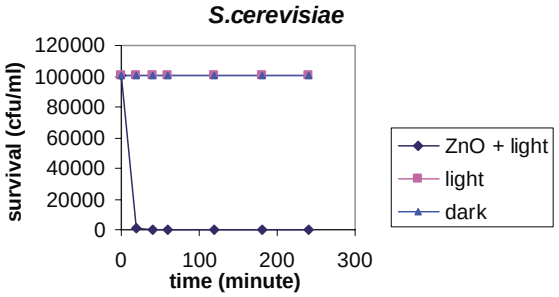

Fig. 10. Effect of ZnO (1 mg/ml) on *S. cerevisiae* survival. Initial concentration 10^5 cfu/ml. Inactivation of *S. cerevisiae* by sodium light with and without ZnO addition, and in the dark.

- The complete *S. cerevisiae* inactivation by sodium light irradiation over TiO_2 or ZnO suspension was reached in 120 min. But with ZnO, the disinfection was reached in 40 min (Figs. 9 and 10).

The inactivation of *A. niger* by sodium lamp did not occur with or without TiO_2 or ZnO addition during 240 min. Also in the dark with TiO2 or ZnO, the disinfection did not occur. *A. niger* is much resistant to TiO_2 or ZnO and some strong chemicals than other studied microorganisms. Because its structure is different and its cell envelope is more complex.

4. Conclusions

The photocatalytic inactivation of various microorganisms by sodium light was studied using semiconductors of TiO_2, ZnO. The complete inactivation has been found in the case the studied microorganism except *A. niger* which is more resistant. The microbial inactivation by light without TiO_2 or ZnO and in the dark with TiO_2 or ZnO did not occur. We have studied microbicidal effect of Sahara dust which contain ferric oxide. But we have found that Sahara desert dust do not have any microbicidal effect.

Solar disinfection with TiO_2 or ZnO is the consequence of the photocatalytic action of the excited TiO_2 or ZnO particles. On the other hand, photocatalytic inactivation has been explained by the attack of radicals photogenerated at the

surface of catalyst like $O_2^{\bullet -}$, $HO_2^{\bullet}$, and $OH^{\bullet}$ [12,17]. All three species have bactericidal characteristics, but the hydroxyl radical is the most potent. The mechanism of cell death has not been elucidated in our studies. There are some suggestions and evidences of the steps leading to cell inactivation. In the earliest reports, the bactericide activity was attributed to the inhibition of respiration by decrease of Coenzyme A and formation of its dimer [7]. The other suggestion, the hidroxyl radicals are not the only species responsible for the bactericidal effect, but that also the cooperative action to promoted peroxidation of phospholipid componenets of the lipid membrane, essential functions as respiratory activity and cell death [10].

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