Efficiency of solar water disinfection photocatalyzed by titanium dioxide of varying particle size
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ABSTRACT
Titanium dioxide photocatalyzed water disinfection is induced by the interaction of light with TiO₂, which generates highly reactive free hydroxyl radicals (OH⁻). These free radicals create lethal damage that leads to bacterial death. Normally, decreasing TiO₂ particle size increases the area of light interaction. This may possibly increase the concentration of OH⁻ generated and hence increases disinfection efficiency. Moreover, decreasing the particle size increases the force of attraction between the particles and cells, which could create aggregates that may contribute to the local OH⁻ concentration. In the present investigation cells of *Escherichia coli* were used as the test microorganism, TiO₂ as the photocatalyst and sunlight as the light source. Four different surface areas of TiO₂ particles corresponding to 10, 50, 80–100 and ≥ 300 m² g⁻¹ were tested at a concentration of 1 g l⁻¹. Disinfection efficiency increased with increasing the surface area producing a maximum between 80–100 m² g⁻¹ followed by a reduction at ≥ 300 m² g⁻¹. The reduction in the efficiency at this relatively high surface area was attributed to the increase in the local concentration of OH⁻. This increase may be high enough to initiate radical-radical interaction that would compete with bacterial cells and reduce the chance of bacterial cell-radical interaction taking place. Moreover, the phenomenon of TiO₂ aggregation with bacterial cells plays an important role, and the extent of aggregation increases with decreasing particle size. Such aggregation could augment the concentration of OH⁻ within the cell vicinity. This suggests that surface area is a key factor in determining the efficiency of disinfection, and that concentration is a vital factor.

Key words | disinfection, photocatalysis, sunlight, TiO₂, water

INTRODUCTION
About one third of the population of developing countries do not have safe drinking water (Wegelin *et al*. 1994) which is mainly due to unavailability of proper water purification procedures and sanitation. Water represents one of the main sources of disease transmission, particularly the gastrointestinal diseases, which contribute to about 6 million deaths per year in the form of diarrheal diseases (Thielsen & Guerrant 1996). This problem is becoming highly alarming and requires international input in order to minimize incidents of water transmitted diseases, and to develop clean water supplies by adopting cheap, efficient and accessible means of water purification. Intensive investigations have been conducted and a number of solutions have been put into effect. Particularly, this problem has been under serious consideration by both WHO and UNICEF in addition to many other institutions all over the world. Sunlight has been proposed as having a promising role in improving water quality particularly in those regions that enjoy a conducive climate (Ciochetti & Metcalf 1984; Davies-Colley *et al*. 1994; Conroy *et al*. 1996; McGuigan *et al*. 1998; Conroy *et al*. 1999; McGuigan *et al*. 1999; Reed *et al*. 2000). However, the solar disinfection
process is lengthy and its efficiency is very much affected by daily and seasonal changes (Salih 2001). Therefore, investigators are very keen to find a practical means that can increase the disinfection efficiency and promote the practicality of using solar disinfection. Accordingly a number of ways have been suggested including the use of the semiconductor, TiO₂.

Several studies have shown that TiO₂ suspended in water reduced the time of light exposure required to induce disinfection (Matsunaga et al. 1985; Martiny et al. 1988; Matsunaga et al. 1988; Watts et al. 1994; Herrera Melian et al. 2000). Similarly, immobilized TiO₂ was almost as effective as the powdered form (Matsunaga et al. 1988; Salih 2002). The effectiveness of semiconductors depends mainly on their concentration and light intensity (Matsunaga et al. 1988; Békbolet & Araz 1996) that provided the environment is devoid of inorganic radical scavengers (Ireland et al. 1995).

TiO₂ is thought to enhance solar disinfection by forming OH• which is produced by the interaction of light with the TiO₂ particle surface (Ireland et al. 1993; Békbolet & Araz 1996; Cho et al. 2004). This radical is believed to have a great damaging effect on irradiated biological systems at diffusion controlled rates (Dorfman & Adams 1973; Alpen 1998). Therefore, it could then be possible to increase the surface area of light interaction with TiO₂ which would enhance the production of OH• and thus increase disinfection efficiency. In addition, the cellular charge effect (Gilbert et al. 1991; Saito et al. 1992) may facilitate the adhesion of bacterial cells to TiO₂ particles (forming aggregates) thus giving OH• an immediate and a bigger chance to reach the cell wall/cell membrane and react with it. This aggregation could very well be promoted when a smaller particle size is used as influenced by the electrostatic attraction and therefore, more OH• is expected to be locally generated leading to increased disinfection. This potential effect prompted the present investigation, with the primary objective being to examine the influence of varying the particle size of TiO₂ on water solar disinfection.

MATERIALS AND METHODS

Cells of a wild type of Escherichia coli, obtained from the Sultan Qaboos University Hospital, were used as the microbiological indicator. The radiobiological characteristics of this bacterial strain was very well established in our laboratory (Salih 2003; Salih 2004). An exponentially growing culture was harvested, washed twice with sterile distilled water and re-suspended in distilled water. The use of distilled water was to exclude the effects which may be imposed by the components of other diluents. The total number of cells in the stock suspension was determined by using a platelet counting chamber (Gallenkamp, Loughborough, UK) and the actual viable count was performed using the plate dilution method. Viable counts were performed by appropriately diluting an aliquot of 0.1 ml of the washed cell suspension and plating out onto 5 nutrient agar plates (Oxoid, Hampshire, UK). Plates were incubated at 37°C for 24 hours and visible colonies were scored.

Sunlight intensity was regularly monitored on experimentation days using a Research Radiometer IL 1700 equipped with SED 623 detector with a wavelength range of 200–3,000 nm (International light, Newburyport, MA, USA). The average sunlight intensity was 5.69 × 10² W m⁻², which gives a rate of exposure of 34.14 kJ m⁻²min⁻¹. Solar exposure was usually made during a period extending from about 11:00 h to 14:00 h. The selection of this period was based on the sunlight intensity being at its highest and the rate being almost consistent over the entire exposure period. Exposure was performed so that sunlight fell almost perpendicular to the surface of the test tube; this required periodical rearrangement of the exposure geometry.

Photosensitive semiconductor, TiO₂, (Millennium Chemicals, Baltimore, MD, USA) was used as the photo-oxidizing agent. In order to test the effect of varying the particle size of TiO₂ powder on cellular solar response, four different surface areas of TiO₂ of 10, 50, 80–100 and ≥300 m² g⁻¹, corresponding to average particle sizes of 1,500, 25, 20, and 7.5 nm, were tested at a concentration of 1g l⁻¹ (particle sizes were certified by the manufacturer). For convenience these samples are denoted 1, 2, 3 and 4 respectively. The powder was first suspended in water and sonicated for 5 minutes to ensure reasonable dispersion. Prior to investigating the influence of suspended TiO₂ on the efficiency of solar disinfection, its optimum concentration was determined (Salih 2002). For each particle size a set of ten test tubes (internal diameter was 12 mm) containing suspensions of TiO₂ in distilled water were
prepared to give concentrations ranging from 0.25 to 3 mg ml$^{-1}$. A given number of bacterial cells were added to each test tube so that test tubes contained $5 \times 10^3$ cells ml$^{-1}$. Test tubes were exposed to sunlight for 10 minutes; this was an adequate time of exposure to reduce survival to about 10%. At the end of exposure the content of each test tube was well shaken to assure proper homogeneity and dispersion. Aliquots were withdrawn from each test tube, diluted properly, plated out and the number of visible colonies scored.

Another aspect of our work involved the effect of fixing the surface area at 0.01 m$^2$ ml$^{-1}$ (this value represented the surface area of 1 mg ml$^{-1}$ of sample 1 that produced the highest efficiency) and changing the concentration accordingly, to evaluate water disinfection efficiency. In order to obtain suitable suspensions using this surface area, 1, 0.2, 0.1 and 0.033 mg ml$^{-1}$ suspensions were prepared. Prior to sunlight exposure a given number of bacteria were added to each tube. After exposure aliquots were taken to assess the number of viable cells.

Toxicity of TiO$_2$ in the absence of light was studied by suspending a known number of cells in distilled water containing 1 mg ml$^{-1}$ TiO$_2$ for as long as the experimentation period. Viable cells were then assessed.

In order to measure light absorption of TiO$_2$ suspension, 0.5 mg ml$^{-1}$ TiO$_2$ suspensions were prepared in distilled water from each of TiO$_2$ samples. Absorption was measured spectrophotometrically (Helios $\alpha$ spectrophotometer, Thermo Spectronic, Cambridge, U.K.) using 10 mm quartz cuvette over a wavelength range of 200–1,000 nm.

**RESULTS**

The effect of varying the concentration of TiO$_2$ on solar water disinfection efficiency for the four particle sizes is shown in Figure 1. Increasing the concentration from 0.25 mg ml$^{-1}$ increased the efficiency up to 1 mg ml$^{-1}$ where the maximum efficiency was achieved for all samples except for sample 4, which gave its highest effect at 2 mg ml$^{-1}$. Further increases in the concentration caused reduction in efficiency. When 1 mg ml$^{-1}$ of each of the four samples was tested (Figure 2), the efficiency increased with increasing the surface area (decreasing the particle size) giving a maximum (96% increase in efficiency over that seen without TiO$_2$) at sample 3 then followed by a reduction to a level a little lower than that produced by sample 2 (63% increase in efficiency). It should be noted that no cytotoxic effect of TiO$_2$ was seen when bacterial cells were incubated in TiO$_2$ suspension in the absence of light for as long as the experimentation period.
When the surface area of suspended TiO$_2$ in a sample was fixed at 0.01 m$^2$ml$^{-1}$, the disinfection efficiency decreased with increasing the TiO$_2$ particle surface area (from 10 to 300 m$^2$g$^{-1}$) until it became close to zero for sample 4, as shown in Figure 3.

Spectrophotometric scanning of the four sample suspensions is shown in Figure 4. Absorptions were almost consistent between 280 to 1,000 nm except for sample 3 where the absorption showed a maximum (between 280 and 340 nm) and then flattened out. The existence of this maximum is not well understood, and could be the subject of future study. As shown in Figure 4, the magnitude of absorption rose with increasing surface area up to that of sample 3 then declined for sample 4 to almost that produced by sample 2.

**DISCUSSION**

The efficiency of solar water disinfection though promising is limited by a number of factors. Sunlight intensity, as a key element in determining the length of sunlight exposure required to produce disinfection, is affected by daily and seasonal changes (Salih 2001). Improvement of the efficiency of solar water disinfection became a necessity which has been well considered by a number of institutions in order to make potable water available for as many people as possible. Disinfection efficiency can be augmented by the addition of a photocatalyst such as TiO$_2$, which mainly reduces the time of exposure (Salih 2002; Cho et al. 2005).

TiO$_2$ produces its effect through the interaction of light with the surface of TiO$_2$ particles. Such interaction produces OH$^-$ that induces cellular lethal damage (Cho et al. 2004). Our primary objective was to demonstrate that if the surface area available for interaction increased, we should expect a corresponding increase in the efficiency. Increasing the surface area requires reducing the size of the particle. Smaller particle size enhances the electrostatic attraction generated by the cellular charge effect (Gilbert et al. 1991; Saito et al. 1992). This may further facilitate the adhesion of TiO$_2$ particles to bacterial cells (forming aggregates) thus increasing the local concentration of OH$^-$ which may further increase the efficiency.

Our objective was examined by testing four different surface areas (particle sizes) of TiO$_2$ corresponding to 10, 50, 80–100 and $\geq$300 m$^2$g$^{-1}$. Generally, increasing the concentration of TiO$_2$ increased the efficiency up to 1 mg ml$^{-1}$ followed by a reduction to almost that seen without an added agent. Deviating from this picture was sample 4 where the maximum efficiency was achieved at 2 mg ml$^{-1}$. These results do not fully agree with the previously held notion that increasing surface area would...
increase efficiency through increasing the local concentration of OH•. A possible explanation of this discrepancy comes from the fact that increasing the local concentration of OH• to a certain limit would increase the biological effect, and further increases in concentration above this limit would cause radical-radical interaction (Spinks & Woods 1990; Alpen 1998). The latter interaction may compete with the interaction of OH• with the biological targets thus reducing the effect.

When the surface area of suspended TiO2 was kept constant at 0.01 m² ml⁻¹ and the concentrations were changed accordingly, the efficiency decreased with increasing surface area (decreasing particle size) (Figure 3). This was attributed to the reduction in the concentration, which is an important factor that determines disinfection efficiency (Figure 1).

The reduction in the efficiency seen at 300 m² g⁻¹ (Figures 1 and 2) and the proposed radical-radical interaction are supported by the general theory of free-radical interactions (Spinks & Woods 1990; Alpen 1998). However, the spectrophotometric studies of TiO2 suspensions (Figure 4) indicate that light absorption increased with increasing TiO2 surface area up to 100 m² g⁻¹ followed by a reduction close to that seen with 50 m² g⁻¹. These findings agree with those seen with the efficiency experiments (Figures 1 and 2) but totally disagree with the previously held radical-radical notion. Such a phenomenon may imply that less light is intercepted by the smaller particles and therefore the light energy is not efficiently utilized. An important point is that the wavelength-range could contribute to the efficiency, which is a factor that is often disregarded in studies of this nature. The spectrophotometric study of TiO2 (Figure 4) shows clear characteristic TiO2 band-gap absorptions at wavelength less than 400 nm for sample 3, while it was unapparent for the other samples. However, there is still a reasonable extent of absorption (between 180 to 400 nm) seen with these three samples, which justifies the observed photocatalytic effects.

CONCLUSIONS

The concentration of TiO2 that gave highest efficiency of solar water disinfection was 1 mg ml⁻¹ for TiO2 particle surface areas 10, 50 and 100 m² g⁻¹. However, increasing the surface area to 300 m² g⁻¹ required 2 mg ml⁻¹ to achieve maximum efficiency. Furthermore, increasing the surface area of TiO2 particle per unit mass (i.e. decreasing particle size) up to 100 m² g⁻¹ increased the efficiency of disinfection followed by a reduction when the surface area was increased to 300 m² g⁻¹. When the surface area of suspended TiO2 in a sample was fixed, disinfection efficiency decreased with decreasing particle size.

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