Efficiency of solar water disinfection photocatalized by titanium dioxide of varying particle size

F. M. Salih and A. E. Pillay

ABSTRACT

Titanium dioxide photocatalysed water disinfection is induced by the interaction of light with TiO_2, which generates highly reactive free hydroxyl radicals ($OH^{\bullet}$). These free radicals create lethal damage that leads to bacterial death. Normally, decreasing TiO_2 particle size increases the area of light interaction. This may possibly increase the concentration of $OH^{\bullet}$ 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 $OH^{\bullet}$ concentration. In the present investigation cells of *Escherichia coli* were used as the test microorganism, TiO_2 as the photocatalyst and sunlight as the light source. Four different surface areas of TiO_2 particles corresponding to 10, 50, 80–100 and $\geq 300\,m^2\,g^{-1}$ were tested at a concentration of $1\,g\,l^{-1}$. Disinfection efficiency increased with increasing the surface area producing a maximum between 80–100 $m^2\,g^{-1}$ followed by a reduction at $\geq 300\,m^2\,g^{-1}$. The reduction in the efficiency at this relatively high surface area was attributed to the increase in the local concentration of $OH^{\bullet}$. 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 TiO_2 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 $OH^{\bullet}$ 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, TiO_2, water

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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 (Thielman & 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

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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, TiO_2.

Several studies have shown that TiO_2 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 TiO_2 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; Bekbölet & Araz 1996) provided that the environment is devoid of inorganic radical scavengers (Ireland *et al.* 1993).

TiO_2 is thought to enhance solar disinfection by forming $OH^{\bullet}$ which is produced by the interaction of light with the TiO_2 particle surface (Ireland *et al.* 1993; Bekbölet & 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 TiO_2 which would enhance the production of $OH^{\bullet}$ 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 TiO_2 particles (forming aggregates) thus giving $OH^{\bullet}$ 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 $OH^{\bullet}$ 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 TiO_2 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 $5.69 \times 10^2\,W\,m^{-2}$, which gives a rate of exposure of $34.14\,kJ\,m^{-2}\,min^{-1}$. 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, TiO_2, (Millennium Chemicals, Baltimore, MD, USA) was used as the photooxidizing agent. In order to test the effect of varying the particle size of TiO_2 powder on cellular solar response, four different surface areas of TiO_2 of 10, 50, 80–100 and $\geq 300\,m^2\,g^{-1}$, corresponding to average particle sizes of 1,500, 25, 20, and 7.5 nm, were tested at a concentration of $1\,g\,l^{-1}$ (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 TiO_2 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 TiO_2 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 5×10^3 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 experiment 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 α 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

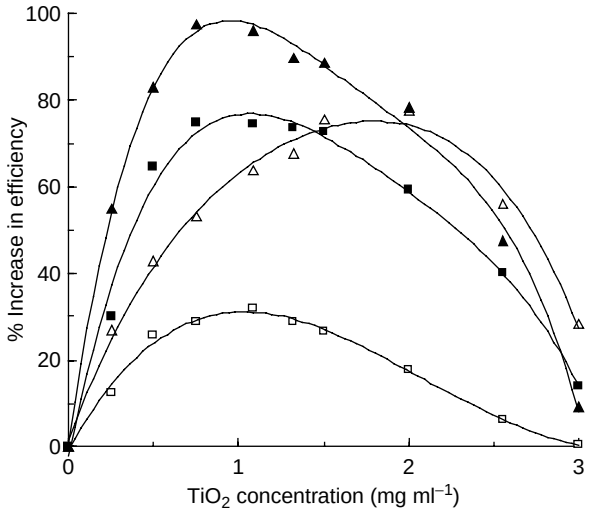

Figure 1 | Effect of changing TiO_2 concentration on the efficiency of solar water disinfection. Samples 1 (□); 2 (■); 3 (▲); 4 (Δ).

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.

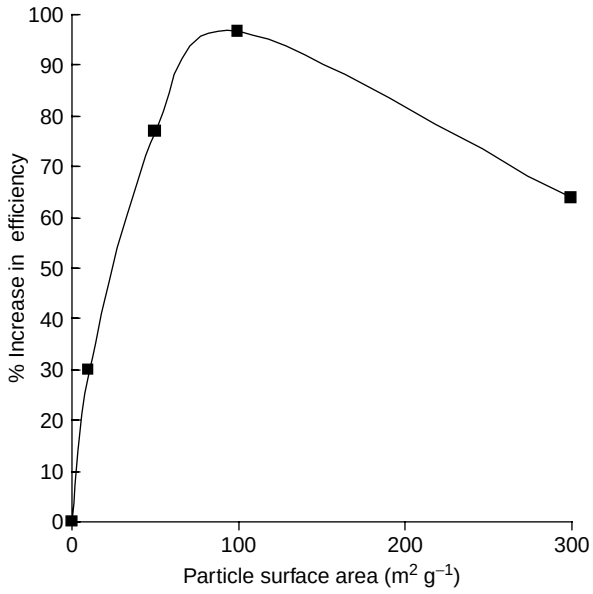

Figure 2 | Effect of surface area of TiO_2 particle, at a fixed concentration of 1 mg ml^{-1}, on the efficiency of solar water disinfection.

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.

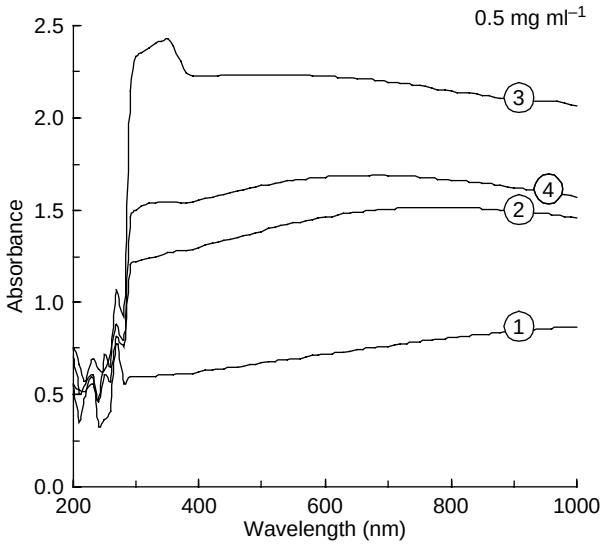

Figure 4 | Spectrophotometric absorption spectra of TiO_2 suspension containing $0.5\,mg\,ml^{-1}$ of samples 1, 2, 3, and 4.

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).

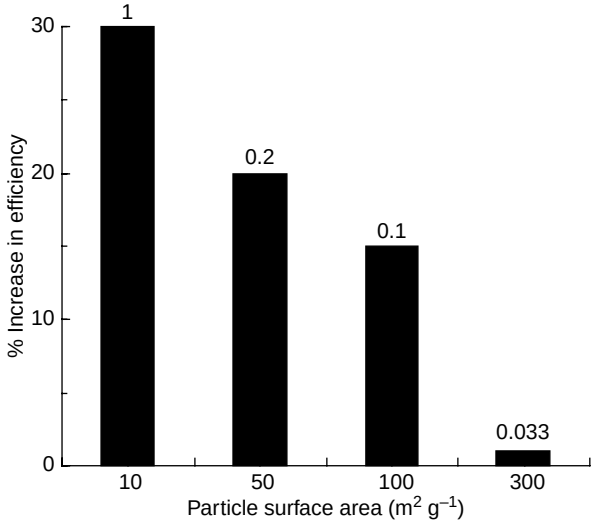

Figure 3 | Effect of changing concentration of TiO_2, at a fixed surface area of $0.01\,m^2\,ml^{-1}$, on the efficiency of solar water disinfection. Numbers on top of the bars represent the concentration of TiO_2 in $mg\,ml^{-1}$ of sample that gives the specified surface area.

TiO_2 produces its effect through the interaction of light with the surface of TiO_2 particles. Such interaction produces $OH^{\bullet}$ 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 $OH^{\bullet}$ which may further increase the efficiency.

Our objective was examined by testing four different surface areas (particle sizes) of TiO_2 corresponding to10, 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 $OH^{\bullet}$. A possible explanation of this discrepancy comes from the fact that increasing the local concentration of $OH^{\bullet}$ 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 $OH^{\bullet}$ with the biological targets thus reducing the effect.

When the surface area of suspended TiO_2 was kept constant at $0.01\,m^2\,ml^{-1}$ 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 $300\,m^2\,g^{-1}$ (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 TiO_2 suspensions (Figure 4) indicate that light absorption increased with increasing TiO_2 surface area up to $100\,m^2\,g^{-1}$ followed by a reduction close to that seen with $50\,m^2\,g^{-1}$. 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 spectrophotometic study of TiO_2 (Figure 4) shows clear characteristic TiO_2 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 TiO_2 that gave highest efficiency of solar water disinfection was $1\,mg\,ml^{-1}$ for TiO_2 particle surface areas 10, 50 and $100\,m^2\,g^{-1}$. However, increasing the surface area to $300\,m^2\,g^{-1}$ required $2\,mg\,ml^{-1}$ to achieve maximum efficiency. Furthermore, increasing the surface area of TiO_2 particle per unit mass (i.e. decreasing particle size) up to $100\,m^2\,g^{-1}$ increased the efficiency of disinfection followed by a reduction when the surface area was increased to $300\,m^2\,g^{-1}$. When the surface area of suspended TiO_2 in a sample was fixed, disinfection efficiency decreased with decreasing particle size.

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