Visible and solar light photocatalytic disinfection of bacteria by N-doped TiO_2

V. Arya and Ligy Philip

ABSTRACT

A water treatment system was developed based on a photocatalytic process, employing immobilized N-doped TiO_2, which worked under solar radiation. Batch reactor studies were conducted using an immobilized and suspended form of N-doped TiO_2. Activities of Degussa P-25 and N-doped TiO_2 were compared. Optimization of catalyst concentration was also carried out. Reaction rates under different working conditions were compared. The bacterial kill followed a pseudo first-order reaction. Continuous reactor studies were carried out using N-doped TiO_2 coated glass plates. Three-log inactivation of bacteria was obtained after a contact time of 40 min. The effects of turbidity, bicarbonate ions and organic matter were studied. It was found that the efficiency of the system decreased due to these components. Comparison of the performance of solar water-disinfection (SODIS) and solar photocatalytic treatment for disinfection of water was also carried out. The results showed that the suspended catalyst achieved complete inactivation in 1 h compared to SODIS which took 6 h. Bacterial regrowth was observed in the case of SODIS treatment whereas no bacterial growth was observed after solar photocatalytic treatment.

Key words | bacterial regrowth, continuous reactor, N-doped TiO_2, photocatalytic disinfection system, SODIS method, solar and visible light

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INTRODUCTION

Contamination of drinking water sources is a major problem faced by most countries. There is a need for a low-cost decentralized/point-of-use water disinfection system in a country like India where more than 700 million people reside in rural areas. Solar water disinfection (SODIS) is a simple and low-cost disinfection method which can remove bacteria and virus contamination (Sommer *et al.* 1997; Smith *et al.* 2000). The major drawback of SODIS is that the treated water should be consumed within 24 h as there is a chance of recontamination. Advanced oxidation processes are emerging as an alternative technology for water treatment. In these methods, highly reactive oxygen species such as hydroxyl radicals, hydrogen peroxide and superoxide are produced. Hydroxyl radicals have a very high oxidizing potential close to fluorine (Carp *et al.* 2004). As a result, the reaction rate is very high. Moreover, as these radicals are non-selective in nature, along with pathogens other components in the water will also get oxidized. Titanium dioxide is widely used as a photocatalyst because it is relatively inexpensive, chemically and biologically inert and stable against corrosion (Hoffmann *et al.* 1995).

There are numerous studies reporting the use of titanium dioxide in water purification. The use of UV light for excitation of TiO_2 makes the treatment process expensive. There are several methods to modify TiO_2 such as doping or using surface sensitizers so that TiO_2 can be excited under sunlight, which makes the system economical and sustainable. TiO_2 is doped with metal and non-metal dopants to enhance the efficiency of the catalyst in the visible region. Several studies have shown the photocatalytic properties of non-metal dopants such as nitrogen (Senthilnathan & Philip 2010; Lee *et al.* 2013), carbon (Lin *et al.* 2013; Wu *et al.* 2013) and sulphur (Jalalah *et al.* 2013). Band gap shifting towards the visible region enhances the

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performance of the catalyst under solar radiation. N-doped TiO_2 is widely studied. The advantages of N-doped TiO_2 are improved photocatalytic activity and ease of synthesis, compared to other non-metal doping (Yang *et al.* 2010; Dozzi & Selli 2013). The present study focused on the possibility of using N-doped TiO_2 for disinfection.

Studies on bacterial disinfection using photocatalysis started three decades ago (Matsunaga *et al.* 1985). During photocatalysis, electrons from the valence band of TiO_2 are excited to the conduction band, leading to the formation of holes in the valence band. These holes and excited electrons react with water and oxygen, respectively, to produce reactive species such as hydroxyl and superoxide radicals. These reactive species penetrate into the cell membrane of bacteria and the cell components are oxidized leading to complete destruction of the bacteria. The outer membrane is ruptured initially, followed by the inner membrane (Sunada *et al.* 2003). Most of the studies on disinfection employing photocatalyst were done under UV radiation. The effectiveness of solar photocatalytic disinfection has also been reported (Rincón & Pulgarin 2003; Gelover *et al.* 2006; Helali *et al.* 2013). The majority of the studies used suspended forms of catalyst, which in turn needs a catalyst removal system. Hence, slurry systems are not preferred in field-scale applications. There have been some studies conducted using an immobilized form of catalyst also (Salih 2002; Rincón & Pulgarin 2003). It has been reported that effective TiO_2 coatings can be made without using expensive laboratory equipment (Lonnen *et al.* 2005). However, not many studies have dealt with the development of a treatment system that can be employed in the field as a small-scale disinfection unit. The objective of the present study was to evaluate the potential of using immobilized N-doped TiO_2 in a continuous reactor for disinfection of drinking water, under solar radiation.

MATERIALS AND METHODS

Degussa P-25 TiO_2, supplied by Vicas Rane, India Limited, Bombay, India, was used for the studies. The catalyst consists of a mixture of 70% anatase and 30% rutile with an average crystalline size of 30 nm and a reactive surface area of 50 m^2/g. Analytical grade isopropanol (purity 99.7%) and ethyl alcohol (purity 99.9%) from Ranbaxy Chemicals, India, were used for coating nanoparticles. Analytical grade titanium isopropoxide and triethyl amine (Ranbaxy Chemicals, India) were used for preparing N-doped TiO_2.

The bacterial inactivation studies were carried out under UV and visible lights. Medium pressure mercury lamps (125 and 80 W), supplied by Haber Scientific, India, which emit predominantly UV radiation at a wavelength of 365 nm, were used for UV irradiation. High pressure tungsten visible lamps (500 and 125 W), which emit light with wavelengths longer than 400 nm, were used as the visible light source.

Microbes

Escherichia coli was used as the model organism for all bacterial inactivation studies. Single colonies were isolated from Luria Bertani agar plate cultures and inoculated to 200 mL of Luria Bertani liquid media in a 500 mL Erlenmeyer flask. The culture was incubated overnight at 30 °C on an orbital shaker at 200 rpm. The initial count of the prepared culture was measured by plating it on the tryptone bile glucuronic agar. The plates were incubated at 37 °C for 24 h. The colonies that appeared on the plates after 24 h were manually counted.

Before starting each experiment, the culture was refreshed by transferring 10 mL of culture to 100 mL of nutrient broth and keeping it on a shaker for 2–3 h to ensure maximum cell viability. After that, 50 mL of the culture was taken and centrifuged. The pellet was washed three times using physiological saline water to ensure that the broth was completely washed away. Then, the pellet was re-suspended in physiological saline water and diluted to get the desired initial concentrations.

Preparation of N-doped TiO_2

N-doped TiO_2 was prepared by the hydrolysis of titanium isopropoxide, as per the procedure described by Senthilnathan & Philip (2010); 2.4 mL of titanium isopropoxide was dissolved in 20 mL ethyl alcohol and the desired amount of nitrogen-containing organic compound (tri-ethylamine) was added to it followed by adding 20 mL of 0.1 M of HCl to the above solution and then stirring to get a clear liquid. The above solution was autoclaved at 80 °C for 12 h, the suspension was

centrifuged at 8,000 rpm and the residue was dried at 100 °C. The dried sample was calcined at 550 °C for 4 h.

Batch reactor studies

A cylindrical reactor with a volume of 400 mL, provided with a water circulation arrangement to maintain the temperature in the range of 25–30 °C, was used for the bacterial inactivation studies with a suspended photocatalytic system under UV radiation. The reactor had three chambers: the outer chamber contained the water to be treated and separate ports were provided in this chamber for sampling and air purging, the inner chamber held the lamp and coolant water was passed through the middle chamber. A diagram of the batch reactor is shown in Figure 1(a). The UV lamp was inserted into the inner chamber of the photoreactor; 200 mg/L of catalyst in suspension form was used in all studies. Before starting the experiments, the UV lamp was switched on for 15 min to attain stable energy output. The solution was stirred at 200 rpm throughout the experiment. Air purging was also carried out during the entire period of the experiment. Studies were conducted using visible light lamps in the same manner. Experiments were carried out using N-doped TiO_2 and Degussa P 25 under UV light and visible lights. In order to assess the effect of light sources alone on disinfection, experiments were also carried out using only UV and visible lights without TiO_2. Experiments were conducted by varying concentrations of doped TiO_2 under visible light to determine the optimum concentration to produce the maximum photocatalytic efficiency. An initial *E. coli* concentration of 1,000 CFU/mL was used in all the experiments.

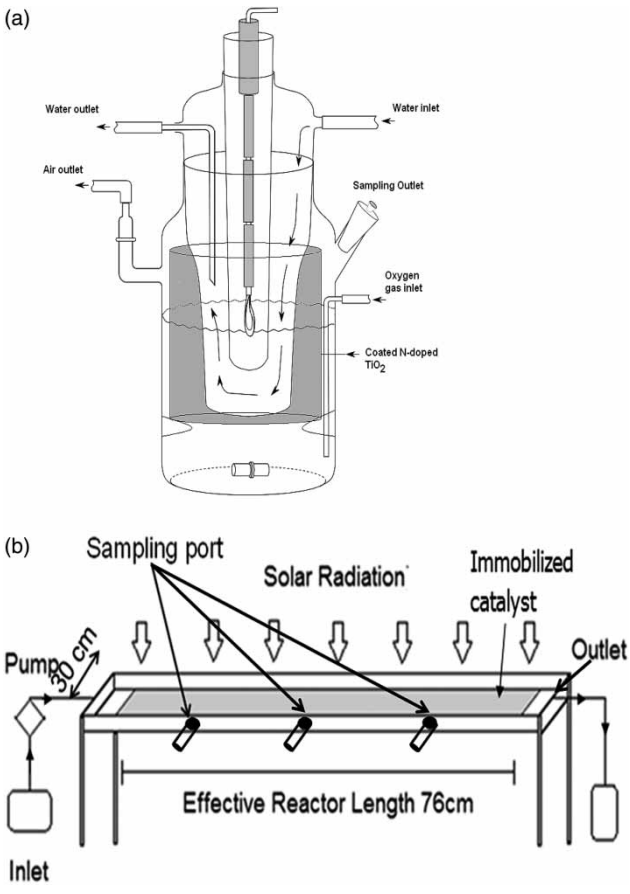

Figure 1 | Block diagrams of (a) batch reactor and (b) thin film continuous photo reactor.

Continuous reactor studies

A thin film fixed bed continuous reactor was used for the disinfection studies using N-doped TiO_2 under solar radiation. The total length and width of the continuous reactor used for these studies were 80 and 30 cm, respectively. The effective length of the reactor was 74 cm, which was separated by a glass plate barrier of 0.6 cm height and 0.5 cm thickness to maintain uniform thickness of the water film. The effective volume of the reactor was 1,332 cm^3 (74 cm × 30 cm × 0.6 cm), with a catalyst coated area of 1,220 cm^2. A schematic diagram of the reactor is shown in Figure 1(b). The desired flow rate was maintained using a peristaltic pump. Samples were collected from different ports along the length of the reactor. All the studies were carried out using 1,000 CFU/mL bacterial solution. The experiments were carried out under sunlight from 10.00 am to 4.00 pm. Solar irradiance data during the experiment were collected from the continuous air-quality monitoring station of the Central Pollution Control Board located 100 m away from the experimental setup. The average solar irradiance during the studies was found to be 200 W/m^2.

The main operational parameter in the case of the continuous reactor system is the contact time, which is affected by the flow rate. Hence, experiments on the optimization of contact time were carried out. Experiments were conducted at different flow rates of 20, 30, 40 and 50 mL/min. The corresponding contact times were 67.5, 45, 33.75 and 27 min, respectively. Samples were collected from various ports

placed at different lengths of the reactor and analysed for residual bacterial concentration.

It is well proven that the presence of anions, organic matter and turbidity will reduce photocatalytic efficiency (Ireland *et al.* 1993; Coleman *et al.* 2005; Alrousan *et al.* 2009). Natural surface water may contain organic matter which can compete for radicals in photocatalytic treatment. Humic acid is a dominating species, which reduces the efficiency of photocatalytic disinfection (Marugan *et al.* 2008; Alrousan *et al.* 2009). The effect of bicarbonate ions, organic matter and turbidity on photocatalytic disinfection needs to be studied to understand the working of such systems in field conditions. To correlate the results with actual surface water samples, an experiment was conducted using a water sample containing 1,000 CFU/mL *E. coli*, 10 NTU turbidity, 20 mg/L dextrose and 300 mg/L bicarbonate ions. Optimized contact time was maintained throughout the studies. Samples were collected at regular time intervals after providing sufficient contact time.

Comparison of SODIS and solar photocatalytic systems

SODIS is commonly used for treatment in many places where there is no municipal water treatment system. However, modification of SODIS using photocatalysts can enhance the reaction. Studies were carried out using immobilized and suspended forms of photocatalyst to evaluate the improvement in disinfection. Bacterial solutions were taken in polyethylene terephthalate (PET) bottles. A 200 mg/L suspension of TiO_2 was mixed with 1 L of water containing 1,000 CFU/mL of *E. coli*. The above solution was placed in the PET bottles and kept under sunlight. For the immobilized system, N-doped TiO_2 was coated on the sides of the PET bottles, and was used for disinfection studies under solar radiation. PET bottles were kept under sunlight for 6 h. Samples were collected from the PET bottles at different time intervals, after exposure to sunlight, and were analysed for remaining CFUs.

It is reported that the damage to cells caused by SODIS is reversible and bacteria can repair the cell damage and become viable if stored for longer periods (Marugan *et al.* 2008). In order to ensure that the damage caused by solar photocatalytic reaction is irreversible, bacterial regrowth studies were carried out. Water samples were collected after treatment using SODIS and a continuous photoreactor. The samples obtained from the continuous reactor after 120 min and samples obtained from SODIS-treated water after 6 h were preserved in incubators for 24 h and the viability of microbes was checked by the plate count method.

RESULTS AND DISCUSSION

Effect of light source and catalyst

From the experiments, the source of light which exhibited more efficiency for a particular catalyst was discovered. The results obtained from the experiments are shown in Figure 2. The bacterial degradation using Degussa P 25 under UV light showed the highest reaction rate. It is clear from Figure 2 that better bactericidal efficiency was achieved using N-doped TiO_2 under visible light, which confirms that the synthesized catalyst exhibited visible-light activity. UV light alone was able to reduce bacterial concentration to a considerable extent. The narrow range of UV radiation emitted by the tungsten lamp used in the study explains the removal rate under visible light alone. However, destruction time was reduced significantly in the photocatalytic system compared to UV disinfection. The rate of reaction also was higher for N-doped TiO_2 under UV light compared to UV light alone. It is also clear from the results that N-doped TiO_2 works better under visible

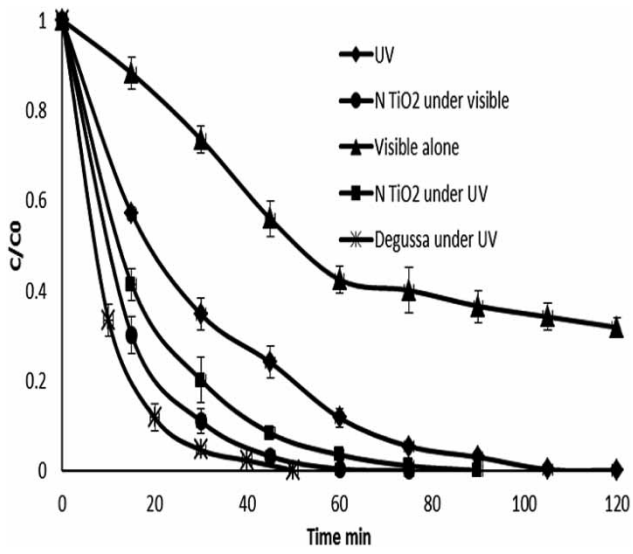

Figure 2 | Effect of photocatalyst and light source on bacterial inactivation.

light than UV light because doping with nitrogen reduced the band gap suitable for irradiation under visible light. Seventy per cent destruction occurred within 10 min. Lee *et al.* (2013) also reported the efficiency of N-doped TiO_2 under visible light for the inactivation of *E. coli*. Similar results were reported by Senthilnathan & Philip (2010) and Vereb *et al.* (2012). Livraghi *et al.* (2006) reported that the single-atom nitrogen centres in the bulk of N-doped TiO_2 prepared via the sol-gel route play a key role in photocatalytic activity. These nitrogen centres introduce intra energy states and thus reduce the band gap. Moreover, the nitrogen centres help in promoting electrons to the conduction band and in transferring the photo-induced electrons to the pollutants, leading to their disintegration. Experiments were also conducted using different initial bacterial concentrations. It was assumed that the degradation of bacteria is dependent only on the bacterial concentrations and all other factors are constant throughout the experiment. The reactions followed pseudo first order which was in accordance with earlier results (Alrousan *et al.* 2009).

Optimization of catalyst concentration

As the concentration of catalyst increased, efficiency increased up to a certain value due to the increase in available active sites, and then started decreasing. The optimum catalyst concentration was found to be 200 mg/L. It was found that efficiency increased initially with increase in catalyst concentration and after a particular value, it started decreasing. This is due to the increase in turbidity of the sample which reduces the optical penetration. At high catalyst concentration, the particles cause light scattering and shadowing effects which reduce the light penetration (Coleman *et al.* 2005). Malato *et al.* (2009) reported that radiation incident on the reactor, reactor configuration and the path lengths inside the reactor were crucial in determining optimum catalyst concentration. Depending on the methods adopted and the reactor configurations, a wide range of optimum loading rates of catalyst in photocatalytic disinfection systems are reported.

Optimization of contact time

It was observed from the results that the flow rates of 20, 30 and 40 mL/min were able to achieve almost 100% removal of bacteria at the outlet of the reactor. However, at a flow rate of 50 mL/min, the survival ratio increased, which indicates that the contact time should be more than 27 min. From the results, it is observed that a minimum of 30 min contact time is required to achieve efficient killing of bacteria. Based on the results, 40 mL/min was taken as the optimized flow rate and the corresponding contact time is 33.75 min. Gelover *et al.* (2006) reported that a contact time of 30 min was sufficient to reduce 1,000 CFU/mL of *E. coli* to non-detectable levels, while using a batch solar photocatalytic reactor employing TiO_2 as the catalyst.

Effects of influencing factors

The effects of influencing factors on the performance of the reactor are shown in Figure 3. It was found that the turbidity of water had a marginal effect on efficiency. After retention time, the percentage survival was almost identical to that obtained for non-turbid water samples. However, a large increase in turbidity may show an adverse effect on efficiency: as the turbidity of the sample increases, optical penetration decreases. The presence of bicarbonate decreased the photocatalytic efficiency and increased the pH of the solution. Similar results have been reported by Coleman *et al.* (2005) and Marugan *et al.* (2008). It is reported that bicarbonate ions decrease the efficiency by competing with oxidizing species and blocking the TiO_2

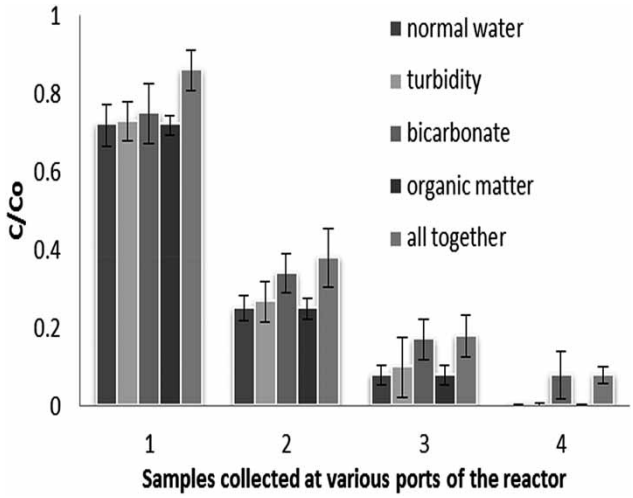

Figure 3 | Effect of inhibitory substances on survival ratio of *E. coli* during the continuous operation of the reactor (samples collected after contact time).

surface (Coleman *et al.* 2005). The results showed that the presence of low concentrations of dextrose did not have any adverse effect on the photocatalytic efficiency. Marugan *et al.* (2008) reported that even low concentrations of humic acid reduced the photocatalytic efficiency whereas the same experiment carried out using sucrose had negligible effect on the degradation. Hence, the study concluded that carbohydrates even at significant concentrations do not reduce the efficiency of the reaction whereas humic acid is an inhibitor. The present study results are in agreement with those results. The efficiency of the system was reduced by 20% when the study was conducted using water containing all the three factors. Hence, the quality of the water needs to be analysed and these factors controlling the efficiency of photocatalysis should be maintained at a lower concentration by adopting a suitable pretreatment.

Comparison of SODIS and solar photocatalytic treatments

There was 50% reduction of the bacterial concentration after 15 min in catalyst-suspended PET bottles. After 1 h, 100% inactivation was obtained. It took 3 h for the immobilized catalyst system to completely inactivate the bacteria. In the SODIS method, complete inactivation occurred after 6 h only. Results show that suspended catalyst has higher efficiency. The catalyst was coated on the inside wall of the PET bottles to make it immobilized. The decrease in efficiency of the immobilized form may be due to the reduction in surface area available for reaction and reduced contact between bacteria and catalyst. In the case of solar photocatalytic disinfection, the bacteria removal rate will be faster due to the synergistic effect of solar radiation and photocatalysis, leading to complete degradation of the bacteria (Helali *et al.* 2013). Gelover *et al.* (2006) also observed that bacterial inactivation time is less for solar photocatalysis compared to SODIS. From the studies, it is clear that N-doped TiO_2, synthesized using a simple process, possesses significant potential for disinfection under sunlight. The modification of SODIS by incorporating N-doped TiO_2 can be used as an alternative disinfection unit. Moreover, the system will be sustainable as it requires no power supply.

The samples were subjected to bacterial regrowth studies. SODIS-treated water samples containing plates showed viable colonies, however, no colonies were found in continuous reactor-treated water samples. Similar results have been reported by several other studies (Gelover *et al.* 2006; Rincón & Pulgarin 2007; Helali *et al.* 2013). During photocatalysis, the outer membrane of the cell wall is ruptured, followed by the inner membrane due to the penetration of the reactive species into the cell (Sunada *et al.* 2003). Hence, it is irreversible and bacteria cannot repair this damage. Thus, there is no chance of recontamination. The treated water from the continuous reactor can be stored and used when enough sunlight is not available, with no fear of contamination. This will be helpful during alternate cloudy or rainy days.

CONCLUSIONS

Batch and continuous reactor studies were carried out to assess the disinfection ability of N-doped TiO_2 as a photocatalyst. The efficiency of Degussa P-25 under UV radiation was greater compared to its efficiency under visible light. N-doped TiO_2 worked more efficiently under visible light than UV light. Moreover, N-doped TiO_2 performed better under solar radiation compared with visible light. Among the various ions commonly present in natural water, bicarbonate ions were found to reduce the reactor performance. The continuous reactor showed very good bacterial removal efficiency at a contact time of 40 min. Bicarbonate ions and turbidity affected the efficiency of the system. Simple organic compounds like dextrose had a negligible effect on the system. Solar photocatalytic disinfection is more efficient compared to the normal SODIS method. Photocatalysts exhibited better efficiency both in suspended and immobilized forms. There was no bacterial regrowth after photocatalytic treatment whereas bacterial regrowth occurred in SODIS-treated water. The efficiency of the system depended upon the quality of water to be treated. The presence of ions, organic matter, turbidity, etc. affect the efficiency of the system. When these components are present in excess amounts, a preliminary treatment system must be provided prior to photocatalytic treatment. The newly developed system seems to be a promising option for disinfecting water in rural areas of developing countries where an uninterrupted power supply is not available.

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