Disinfection of roof harvested rainwater for potable purpose using pilot-scale solar photocatalytic fixed bed tubular reactor

S. Saran, P. Arunkumar and S. P. Devipriya

ABSTRACT

The potable use of harvested rainwater is limited, mainly due to contamination with various pathogenic microorganisms. Disinfection of microorganisms by solar photocatalysis is emerging as a promising technique for drinking water treatment. The present study deals with the preparation of Ag-doped TiO$_2$ by the sol gel method, and its immobilization over the inner surface of the Pyrex glass pipes used in fabrication of pilot-scale reactors. The solar photocatalytic efficiency of the reactors was tested for the disinfection of microorganisms in tap water and roof harvested rainwater. The photocatalytic experiments under solar irradiation illustrate that doping with silver ions significantly increases the inactivation rate of all microorganisms compared with pure TiO$_2$ and direct photolysis. The inactivation efficiency against various microorganisms was found in the following decreasing order: *E. coli* > *MS-2 phage* > *Aspergillus* spores. The roof harvested rainwater was completely disinfected in addition to chemical oxygen demand (COD) removal, within 120 minutes of solar irradiation. The experimental cycle was repeated several times to study the stability of the reactor. The pilot-scale solar photocatalytic fixed bed tubular reactors were found to be very effective for the disinfection of rainwater for potable use.

Key words | catalyst immobilization, disinfection of rainwater, inactivation of microorganism, pilot-scale fixed bed tubular reactor, silver doped TiO$_2$, solar photocatalysis

INTRODUCTION

The presence of pathogenic microorganisms is a grave menace to the human population as it leads to 3.4 million deaths per year due to waterborne diseases. Nearly 768 million people do not have access to drinking water and as many as 185 million people rely on unsafe water to meet their daily drinking water requirements (Byrne et al. 2011). Treated rainwater can be used as an alternative source for drinking water. Rainwater harvesting (RWH) is receiving increased attention worldwide as an alternative practical solution to water shortage and for supplying freshwater at household and community levels especially in developing countries (Meera & Ahammed 2006). Recently, harvested rainwater has been used mostly for nonpotable purposes such as gardening and landscaping, toilet flushing, surface cleaning and laundering (Amin & Han 2009a, 2009b; Kabir et al. 2014). However, the potable usage of harvested rainwater is limited, mainly because the quality of stored rainwater is lower than the drinking water standards mainly due to contamination with pathogenic microorganisms (Amin et al. 2014). Apart from microbial contamination, roof harvested rainwater may also be contaminated with various organic pollutants as well as heavy metals, pesticides, PAH and emerging contaminants from surface wash-off from the roof catchment area (Bucheli et al. 1998; Sánchez et al. 2015).

RWH using roof catchment is a simple method consisting of a catchment area, a storage tank, a supply facility and
piping used to provide urban populations with potable water supplies in many parts of developing countries (Han & Mun 2007). This stored rainwater requires the minimum treatment to make it potable. The existing facilities available to disinfect rainwater are chlorination (Garrett et al. 2008), solar disinfection (SODIS) (Amin & Han 2009a, 2009b), UV light illumination (Jordan et al. 2008) and ozone treatment (Ha et al. 2013). But those conventional disinfection practices such as chlorination produce secondary toxic byproducts like chloramine, trihalomethane etc. which are potential carcinogenic agents (Dunlop et al. 2002), whereas UV and ozone treatment involve high energy and cost (Sharpless et al. 2003). SODIS can be used by harnessing solar energy for the disinfection of microorganisms present in rainwater. But it has certain limitations such as only small volumes being able to be treated (2–3 L) and it requires prolonged exposure, nearly 6–8 hours under strong sunlight for complete disinfection (Amin & Han 2011). Further, the efficiency of SODIS is dependent on a range of environmental parameters including the solar irradiance, initial water quality, organic loading, turbidity level and nature of the bacterial contamination (Byrne et al. 2011). To overcome these difficulties titanium dioxide (TiO2)-based photocatalysis is an alternative method for the disinfection of microorganisms present in rainwater, as it is nontoxic, environmentally stable, inexpensive, earth abundant and completely mineralizes the pollutants without producing any disinfection byproducts (Pagnout et al. 2012; Yang et al. 2014).

Typically, in photocatalytic experiments, when an aqueous solution (sample) along with catalyst (TiO2) is illuminated with light of the appropriate wavelength, this induces a charge separation process leading to the formation of various reactive oxygen species (ROS) which play a vital role in the disinfection of microorganisms (Alrousan et al. 2009; Patchaiyappan et al. 2016). Among the various noble metals, silver is widely used as dopant as it is cheaper, easily available and also acts as an antimicrobial agent (Chen et al. 2014). Most of the studies carried out so far are towards the disinfection of microorganisms by photocatalysis in small or laboratory-scale bench reactors under controlled conditions. But the disinfection of various microorganisms present in drinking water in pilot-scale reactors under sunlight is limited.

Hence the current study focuses on the solar photocatalytic disinfection of water by inactivating various microorganisms such as bacteria, virus and fungal species spiked in tap water using cost-effective pilot-scale fixed bed tubular photoreactors. Ag-doped TiO2 is prepared by modified sol gel synthesis and immobilized over the inner surface of Pyrex glass pipes. The pilot-scale reactors were fabricated locally with the catalyst-immobilized Pyrex glass pipes. The efficiency, stability and feasibility of the reactors were evaluated for the treatment of roof harvested rainwater. To the best of our knowledge, this is the first report on the disinfection of roof harvested rainwater by pilot-scale solar photocatalytic fixed bed tubular reactors.

**EXPERIMENTAL**

**Materials and method**

Titanium isopropoxide (TTIP), silver nitrate, absolute ethanol and other chemicals used in this study were purchased from Sigma Aldrich and used without further purification. All reagents and solutions required for the experiment were prepared with Millipore deionized water.

**Preparation and immobilization of Ag-doped TiO2**

For the preparation of Ag-doped TiO2, a modified sol gel method (Ghosh et al. 2016) was adopted by using TTIP (Ti[OCH(CH3)2]4), absolute ethanol (C2H6O), silver nitrate (AgNO3) and nitric acid (HNO3). In a typical process 5 ml of TTIP was used as titanium precursor dissolved in 75 ml of absolute ethanol followed by the addition of the required amount of AgNO3 and the solution was stirred for 30 min. Then 1.0 ml of 1 M HNO3 was added as peptizing agent and the resulting transparent sol was further stirred for
1 h. The synthesized sol was immobilized on the inner surface of the Pyrex glass pipes. An amount of 10 ml of Ag-doped TiO$_2$ sol was coated in each pipe and dried at 100 °C for 2 hours followed by calcination at 500 °C for 1 hour for the conversion of amorphous TiO$_2$ to crystalline form. The above process was repeated three times for even coating and for control experiments, in which glass pipes were prepared as mentioned above without catalyst and with TiO$_2$ sol alone.

**Design and fabrication of pilot-scale fixed bed tubular reactor**

The reactor consists of six Pyrex glass tubes immobilized with Ag-doped TiO$_2$ mounted on a fixed platform tilted 35° (local latitude) as shown in Figure 1. The tubes are connected in series so that the water flows directly from one to another and finally into a tank. A peristaltic pump powered by using solar photovoltaic cells was used to circulate the water from the tank to the reactor. The illuminated solar collector surface was 1.0 m$^2$. The outer diameter of the glass tubes was 50 mm and the illuminated volume of the whole system was 4.5 L out of a total reactor volume of 16 L. For control experiments, the same one immobilized with pure TiO$_2$ and another without photocatalyst coating were used.

**CHARACTERIZATION OF THIN FILM**

The surface morphology of the thin film was characterized using a scanning electron microscope (SEM, Hitachi, Model: S-3400N) accelerating with 15 kV. The phase formation and crystalline structure of the films were determined by the X-ray diffraction (XRD) technique. The X-ray diffraction patterns were measured using a PAN analytical X-ray diffractometer with Cu K-α radiation at an angle of 2θ from 20° to 70°. The optical adsorption properties of the films were determined with a UV-Vis NIR spectrophotometer (Varian Cary 5000). The photoluminance (PL) emission spectrum was measured in the wavelength range of 350–600 nm with a spectrofluorometer (JY Fluorolog – FL3-11) using a xenon lamp excited at 320 nm.

**Culture and analysis of microbes**

*Escherichia coli*

*E. coli* (strain ATCC-19853), the most common pathogenic indicator in drinking water, was selected as the representative of bacterial species. It was inoculated in soya casein digest medium and incubated at 37 °C overnight. This culture was harvested by centrifugation and the pellet was

![Figure 1] Picture of pilot-scale fixed bed tubular solar photocatalytic reactor.
suspended in 15 ml sterile saline. The bacterial population was enumerated using the membrane filtration technique (ISO 9308-1 2000).

**MS-2 phage**

Bacteriophage MS-2, a virus pathogenic indicator, was studied due to its similarity with waterborne viral pathogens in shape, size and morphology. The stock solution was prepared by infecting the host *E. coli* (ATCC-19853) with MS-2 phage (ATCC 15767) in tryptic soya broth and incubated at 37 °C overnight. The incubated culture was quantified using the single agar layer method (EPA 1602 2001).

**Aspergillus niger**

Most of the fungal spores are recalcitrant towards various treatment methods such as chlorination, UV treatment etc. (Gong et al. 2014). Hence, *Aspergillus niger* was chosen as the representative for fungal species in the experiments. The spores were maintained in Sabouraud dextrose medium overnight at 37 °C and enumerated using the spread plate technique.

**PHOTOCATALYTIC INACTIVATION STUDIES**

The photocatalytic disinfection experiments were performed on the catalyst-immobilized reactors operated with 20 L of sterilized tap water spiked with microorganisms such as *E. coli*, MS-2 phage and *Aspergillus niger* spores at neutral pH. The physicochemical parameters of the tap water were analyzed and are illustrated in Table 1. All glassware and samples were sterilized at 120 °C prior to experiments using an autoclave. All experiments were carried out under sunlight at Pondicherry University (India, local latitude 12.01 °N and longitude 79.85 °E) during the months of March to June 2016 between 10.00 a.m. and 2.00 p.m. The control experiments were performed in the dark by covering the reactor. The average solar intensity was measured using a handheld UVtech radiometer. The photocatalytic reactors were irradiated under sunlight for 120 minutes to check its photocatalytic disinfection efficiency. The samples were collected at specific time intervals and serially diluted in 0.85% NaCl solution and tested for their viable count by appropriate methods as mentioned above. All the experiments were conducted three times and the results were averaged.

**Solar photocatalytic disinfection of roof harvested rainwater**

In order to evaluate the efficiency of the reactor for the disinfection of roof harvested rainwater, the experiments were conducted with 20 L of rainwater. The physicochemical and microbial analysis of roof harvested rainwater is shown in Table 2. Samples were withdrawn at different time intervals for the evaluation of chemical oxygen demand (COD) and total bacterial and coliform count naturally present in the rainwater. Total bacterial count was checked by the standard plate count method whereas coliform bacteria were evaluated by using the membrane filtration technique and the COD was measured by using the closed reflux method using the Hach photometer. All the experiments were repeated three times and the results were averaged.

**RESULTS AND DISCUSSION**

**Characterization of thin film**

The XRD patterns of pure and Ag-doped TiO₂ thin film are shown in supplementary Figure S1 (available with the online version of this paper). It can be seen that the pure
TiO₂ films exhibited different diffraction peaks attributed to the anatase as well as rutile phase with sharp intensity, whereas the diffraction pattern of Ag-doped TiO₂ thin film exhibits the anatase phase alone, which shows that doping with silver will significantly retard the phase transformation from anatase to rutile as reported earlier by Malagutti et al. (2013) and Lei et al. (2017). Also no diffraction peaks appear for silver particles, which ensures that Ag particles were well dispersed into the TiO₂ matrix (Nasr-Esfahani & Habibi 2013).

The SEM micrographs of the undoped and Ag-doped TiO₂ thin films are illustrated in Figure S2(a) and S2(b) respectively. The SEM image of the films reveal that particles are more or less spherical in shape and are agglomerated with each other and there is no significant morphological difference between the undoped and the doped TiO₂. The EDAX spectra of both pure and Ag-doped thin films illustrated in Figure S3(a) and S3(b) have respectively confirmed the presence of TiO₂ by showing the corresponding peaks, which are in accordance with the XRD results.

The UV-visible diffuse reflectance spectra of the doped and undoped films are shown in Figure S4 and exhibit that both the samples have strong absorptions in the UV region, whereas the Ag-doped TiO₂ shows extended wavelength at 400–600 nm when compared to pure TiO₂, which might be attributed to the presence of Ag clusters or to the surface plasmon absorption of spatially confined electrons in the Ag nanoparticles (Kment et al. 2015). Therefore, the photocatalytic efficiency of the Ag-doped TiO₂ has been enhanced possibly by inducing a charge separation process under visible light (Ubonchonlakate et al. 2012). Silver may also act as an electron trap thereby inhibiting the electron–hole recombination rate, which in turn produces more ROS compared with pure TiO₂ (Bensouici et al. 2015).

Table 2 | Physical, chemical and microbial analysis of roof harvested rainwater

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.8</td>
</tr>
<tr>
<td>EC (µS/cm²)</td>
<td>55</td>
</tr>
<tr>
<td>TDS (ppm)</td>
<td>39</td>
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<tr>
<td>Turbidity (NTU)</td>
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</tr>
<tr>
<td>Total hardness (ppm)</td>
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<tr>
<td>Calcium (ppm)</td>
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</tr>
<tr>
<td>Magnesium (ppm)</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Sulphate (ppm)</td>
<td>2.4</td>
</tr>
<tr>
<td>Chloride (ppm)</td>
<td>4.5</td>
</tr>
<tr>
<td>Iron (ppm)</td>
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</tr>
<tr>
<td>Phosphate (ppm)</td>
<td>0.34</td>
</tr>
<tr>
<td>Nitrate (ppm)</td>
<td>0.67</td>
</tr>
<tr>
<td>COD (ppm)</td>
<td>74</td>
</tr>
<tr>
<td>Total bacterial count (CFU/ml)</td>
<td>3 × 10³</td>
</tr>
<tr>
<td>Total coliform count (CFU/ml)</td>
<td>4 × 10²</td>
</tr>
</tbody>
</table>

Solar photocatalytic inactivation of microorganisms

Photocatalytic inactivation of bacterial, viral and fungal species spiked in tap water under solar irradiation is illustrated in Figures 2–4 respectively. The mechanism of photocatalytic disinfection, when the surface of the TiO₂ photocatalyst is illuminated with energy equal to or higher than its band gap, induces the charge separation process which leads to the formation of conduction band electrons...
and valence band holes (h⁺) (Linsebigler et al. 1995; Kim & Choi 2010). These photogenerated electrons and holes may recombine in bulk or migrate towards the surface of the TiO₂, react with water molecules and produce ROS by redox reactions (Devipriya & Yesodharan 2005; Robertson et al. 2002). The surface migrated conduction band electrons react with molecular oxygen and reduce it to superoxide ions (O₂⁻), while the valence band holes react with the water molecules and generate hydroxyl radicals (·OH) (Dunlop et al. 2008; Liou & Chang 2012). These photogenerated ROS such as hydroxyl radicals (·OH) and superoxide ions (O₂⁻), hydroperoxy radicals (·OOH), hydrogen peroxide (H₂O₂) and hydroxyl ions (OH⁻) cause the disinfection of microbes.

The inactivation efficiency shown by the Ag-doped TiO₂ and pure TiO₂ catalyst is in this order, E. coli > MS-2 phage > Aspergillus niger. This is due to the complex nature of the cell membrane and also resistance towards various environmental factors, which is in close agreement with the results of Wolfrum et al. (2002) and Davies et al. (2009). The important findings of this experiment are as follows.

No significant inactivation of microorganisms was observed when the experiment was performed under dark conditions, which clearly shows that inactivation takes place only in the presence of light and catalyst. Nearly 44%, 28% and 19% inactivation of E. coli, MS-2 and Aspergillus niger respectively was observed after 2 hours by direct photolysis. In Ag-doped and pure TiO₂ immobilized photoreactors, complete inactivation of E. coli was observed at 30 minutes and 45 minutes of solar irradiation respectively. Similarly, complete inactivation of MS-2 phage was shown by Ag-doped TiO₂ at 45 minutes and 60 minutes in pure TiO₂, demonstrating that doping with silver ions relatively increased their photocatalytic inactivation efficiency. To the
best of our knowledge, this is the first report of the complete inactivation of *Aspergillus niger* spores within 90 minutes of solar irradiation using Ag-doped TiO₂, whereas 60% inactivation was observed with pure TiO₂ after 120 minutes of solar irradiation. Earlier reports showed that complete inactivation of *Aspergillus niger* spores was achieved only after 2 hours of solar irradiation (Mitoraj *et al.* 2007).

The solar photocatalytic inactivation of Ag-doped TiO₂ shows better inactivation efficiency than pristine TiO₂ and by direct solar irradiation, which was in close agreement with the results of Vohra *et al.* (2006) and Eswar *et al.* (2015). The increase in inactivation efficiency of the Ag-doped TiO₂ is due to silver, having Schottky barriers which act as electron traps, thus reducing electron-hole recombination and promoting the interfacial electron transfer process which leads to the highest generation of ROS (Saran *et al.* 2016). In addition to this, the surface plasmon resonance property of nanosized silver makes it work under the visible region (Iliev *et al.* 2006; Zheng *et al.* 2011).

The inactivation of the tested microorganisms is in the order *E. coli* < MS2 < *Aspergillus niger*. The results illustrate that inactivation of microorganisms is due to the complexity in their cellular membranes, which was previously discussed by Chen *et al.* (2009). *E. coli* shows less defense against photocatalysis because it is inactivated by ROS such as •OH, O₂⁻ and H₂O₂ formed during the photocatalysis. Moreover, it has a thin cell membrane when compared with MS-2 phage and spores (Hou *et al.* 2012). But MS-2 phage and Aspergillus spores were inactivated only by the •OH radical and also the cell wall of these microorganisms is highly resistant towards various environmental factors such as heat, light and chlorine disinfection, which was previously demonstrated by Cho *et al.* (2005) and Elahifard *et al.* (2007).

### Solar photocatalytic decontamination of roof harvested rainwater

Figures 5 and 6 illustrate the solar photocatalytic disinfection of total bacteria and coliform bacteria present in roof harvested rainwater respectively. The results reveal that the Ag-doped TiO₂ immobilized reactor shows maximum disinfection of microorganisms when compared with the pure TiO₂ immobilized and uncoated reactors as described in the preceding section. No significant reduction of total bacterial count and coliform bacteria were observed under dark experimental conditions, whereas complete disinfection of total bacteria was observed in both the Ag-doped and pure TiO₂ immobilized reactors after 90 and 120 minutes respectively. Nearly 22% reduction of bacteria was observed by direct photolysis. Similarly, complete inactivation of total coliform was observed within 60 and 90 minutes in the Ag-doped and pure TiO₂ immobilized
reactors respectively. Compared with laboratory-cultured spiked bacterial experiments (as explained in the preceding section), bacteria present naturally in roof harvested rainwater show more resistance towards inactivation. This may be due to the presence of organic matter in roof harvested rainwater which will compete for ROS and photon absorption in rainwater rather than spiked tap water (Alrousan et al. 2009).

Figure 7 illustrates the percentage reduction of COD in roof harvested rainwater at different time intervals, and shows that complete mineralization of organic contaminants was observed in the Ag-doped TiO₂ and nearly 90% removal of COD in the pure TiO₂ immobilized reactors after 120 minutes of solar irradiation. The contribution of COD in roof harvested rainwater is mainly from surface wash-off dust and dirt, animal droppings, moss, lichens and particulates from urban pollution (Le Nhung et al. 2014). The treated rainwater can be used as an alternative source of drinking water in water-deprived regions.

**Determination of silver ions released in the water**

To ensure the viability of the reactor, the amount of silver ions lixiviated during the photocatalytic inactivation experiments was monitored and compared with permissible standards. The silver ions lixiviated during the photocatalytic inactivation experiment were determined by using inductively coupled plasma atomic absorption spectroscopy (ICP-AAS). The samples were withdrawn at regular time intervals and were digested with nitric acid in a microwave digester. The concentration of silver in the sample was determined by aspirating the acid-digested sample in ICP-AAS. The results are shown in Figure 8, and indicate that there is a gradual increase in the silver ion concentration from 0 to 2 hours of solar irradiation. The total concentration of Ag ions released after 2 hours was about 0.009 mg/l, which is much less than the permissible standard level of 0.1 mg/l as per the regulation issued by the environmental protection agency.

**Post-disinfection regrowth potential**

From a practical point of view, it is important to monitor if there is any post-treatment bacterial regrowth while storing the samples under ambient conditions for a certain period of time. Potential regrowth of total bacterial count was studied by collecting the photocatalytic treated rainwater samples from the reactors after the complete inactivation, storing in aseptic conditions for 24 and 48 hours and plating. The results illustrated that there is no bacterial regrowth, when the samples were collected from both the pure TiO₂ and Ag/TiO₂ immobilized reactors (Chen et al. 2010). This may be due to the photocatalytically generated ROS like *OH, O₂⁻ and H₂O₂ damaging the cell wall followed by cytoplasmic membrane damage leading to a direct intracellular
attack which induces cell death that cannot be repaired during the post-treatment storage period (Huang et al. 2000). From this result, roof harvested rainwater treated with catalyst immobilized reactors can be stored and used for potable purposes.

**Reuse of the reactor**

Since Ag-doped TiO₂ shows maximum inactivation efficiency against all microorganisms, we selected the Ag TiO₂ immobilized reactor to check its ability for reuse by conducting the experiments in repeated cycles with roof harvested rainwater for the disinfection of the total bacteria count present in it. The results illustrated in Figure 9 show that there is a negligible reduction in the efficiency of the reactor even after ten cycles under solar irradiation. This slight reduction in efficiency might be the deposition of ions over the coating as well as the gradual leaching of Ag ions from the coating or it may be just the variation in the sunlight intensity. The reactor is found to be suitable for repeated reuse for the treatment of rainwater in areas with ample sunlight.

**CONCLUSION**

A simple, cost-effective pilot-scale solar photocatalytic fixed bed tubular reactor was fabricated locally for the treatment of roof harvested rainwater. Silver-doped TiO₂ was prepared by a sol gel method and was immobilized over the inner surface of the Pyrex tubes used in the reactors. The characterization results confirm that doping of TiO₂ with silver ions extends its wavelength response towards the visible light region and increases the production of ROS by reducing the e⁻ and h⁺ recombination rate. Further doping with Ag ions increases the photocatalytic efficiency for the inactivation of various microorganisms from water using solar irradiation. The roof harvested rainwater could be disinfected completely within 120 minutes in addition to COD removal under solar irradiation. No bacterial regrowth was observed even after 48 hours of storing under ambient conditions. The reactors were found to be suitable for repeated reuse. These reactors could serve as an efficient, cost-effective method for the disinfection of roof harvested rainwater for potable purpose.

**ACKNOWLEDGEMENTS**

We gratefully acknowledge the University Grants Commission (UGC), New Delhi, Govt. of India for funding the research project (F. No. 40/146/2010 (SR)). The authors also acknowledge the Central Instrumentation Facility and Centre for Nanoscience and Technology, Pondicherry University, for providing instrumentation facilities for the characterization of the thin films. The authors are thankful to Miss G. Manjari, Research Scholar, for her continuous support.

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First received 24 November 2016; accepted in revised form 11 May 2017. Available online 24 May 2017