Visible-Light Responsive Photocatalysis: A Novel sustainable water treatment technology in the inactivation of bacteria for drinking purpose

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Introduction

Safe drinking water supply is a vital issue regarding human health, and water disinfection has become an urgent need in present scenario due the microbial pathogenic contamination of water. According to World Health Organization (WHO), approximately more than one billion people throughout world are still not getting safe water for drinking, as well as around 3.4 million people, especially children are dying annually with diseases associated with intake of impure water. Pathogenic microorganisms, hazardous chemicals and inadequate water sanitation are the major factor of causing severe health related problems in human beings (Chong et al., 2011; Malato et al., 2009; Pigeot-Remy et al., 2011). Among the south-east Asian countries, ~48% acute respiratory infections and diarrheal diseases are reported, and consequently, around 3.07 million deaths are occurring every year. Five Asian countries including Bangladesh, India, Indonesia, Myanmar and Nepal are having highest incidences of the water born diarrhea diseases, which is causing about 60,000 deaths annually (Batabyal et al., 2013). Therefore, treatment of microbial pathogens present in water must be treated before human consumption. Some conventional techniques such as chlorination, ozonation, and chloramination have been very popular for water disinfection since several decades. However, these conventional techniques discharge some disinfection by-products (DBPs) in treated water, which are reported as potential carcinogens and mutagens. Due to these negative health effects of DBPs on human, these treatment techniques are not acceptable for the drinking water purification systems (Pigeot-Remy et al., 2011; Rincón et al., 2003; van Grieken et al., 2010). Therefore, need for the development of other novel disinfection technologies have arisen for providing safe drinking water to the human society. Now, world researches are focused to explore the alternative methods of water treatments like photocatalysis for water disinfection purpose (Paspaltsis et al. 2006, Prasad et al. 2009).

Heterogeneous photocatalysis has emerged as an alternative effective technique of bacterial inactivation especially sun light blessed areas where solar irradiation can be employed (Chen et al., 2007). Killing of Gram-negative, Gram-positive bacteria, yeast, and green algae using TiO-Pt photocatalyst was firstly reported by Matsunaga et al. (1985) in presence of UV light. After which, photocatalyst has widely been used in the purification and disinfection of pathogenic microorganism infected water, these microorganisms may be prions, coccidian, bacterial strains, mycobacteria, viruses, fungi, yeast etc. (Kazuhito et al., 2005; Malato et al., 2009; Pulgarin et al., 2012). Photocatalysis became renowned method for the disinfection of water, because it has many benefits such as high efficiency to kill the microorganisms without need of any extra chemical oxidant, chemical stability, negligible toxicity, saves energy and a cost-effective process (Pigeot-Remy et al., 2011). However, most of the photocatalysts are working in presence of UV light only, but TiO_2 modification can extend its application to visible light irradiation. Doing of TiO_2 with noble metals, oxides or non-metals are found to increase the photocatalytic activities of titanium dioxide (Markowska-Szczupak et al., 2011). Due to doping, the bactericidal inactivation mechanism of catalysts are able to work in presence of visible light in resemblance of

UV illumination (Markowska-Szczupak et al., 2011), and it appears that the future of photo-disinfection catalyst is bright and can be applied to disinfect the water for drinking purpose.

Water Supply Crisis

Water withdrawal (%) of total available water indicated a global situation of water (shortage) stress. Figure 1 depicts the situation of water crisis among world's countries in between the years 1995 and projected till 2025.

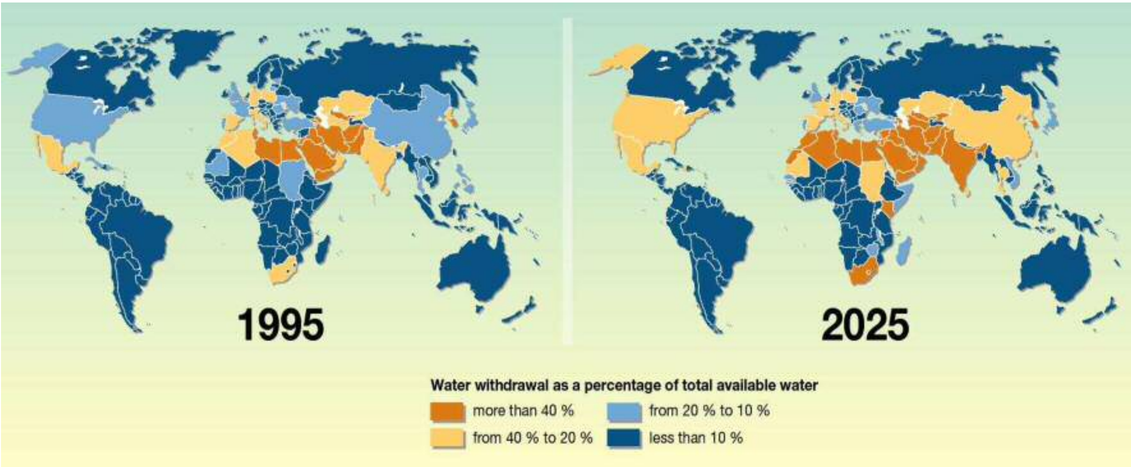

Figure 1. Water stress conditions around the world in between year 1995 and 2025.

(Source: Philippe Rekacewicz (Le Monde diplomatique), February 2006)

The areas of world experiencing water stress as defined by a high percentage of water withdrawal compared to total available water. People in these areas have lack of access to sufficient and clean water. As indicated in figure, water stress level in 19 countries were severe in 1995. According to an estimation, by 2025 more than 32 countries will face severe lack of water. The water withdrawal problem (more than 40%) of world will be increased up to 188% and water withdrawal percentage will also increase from 10-20% to 20-40%. The global water stress situation will become significantly more serious by 2025 than water stress level in 1995. In general, water stress is greatest in that areas where very low precipitation (major deserts) occurs or having large population density (Editors, 2013).

According to the human development report of the United Nations Development Programme (UNDP), 11% of the world's population (700 million people) lives under water stress with a per capita water supply below 1,700 m^3/year (Watkins, 2006). By 2025, more the 3 billion people (around 40% of the global population) will live in water stress areas, most of them will be from China and India, two big countries of Asia. The water crisis may also affect the food production and ability of feeding the ever-growing population. In future, global another conflict might be associated with water shortage as well as its pollution. Even at this time, some conflicts for river waters are reported among the countries like in middle east Asia (Euphrates and Tigris River conflict among Turkey, Syria, and Iraq; Jordan River conflict among Israel, Lebanon, Jordan, and the Palestinian territories), Africa (Nile River conflict among Egypt, Ethiopia, and Sudan), central Asia (Aral Sea conflict among Kazakhstan, Uzbekistan, Turkmenistan, Tajikistan, and Kyrgyzstan), and south Asia (Indus river conflict between India and Pakistan) (Editors, 2013).

From the Figure 2, the world map shows the direct normal irradiation among the countries and areas between southern and northern tropics

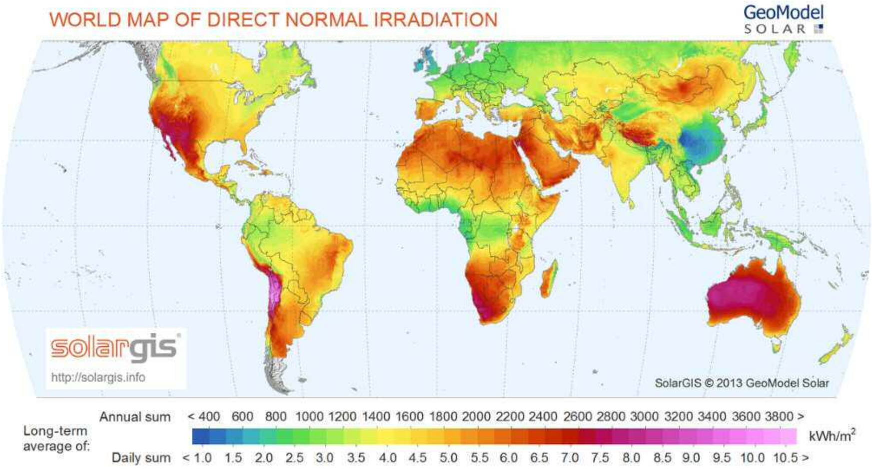

Figure 2. World map of direct normal irradiation.
(Source: SolarGIS © 2014 GeoModel Solar)

If compared with the water withdrawal percentage, Asia countries which are near to the northern tropic indicated both high water stress situations as well as the abundant availability of direct solar radiation. The highest quantity of annual solar radiation is equal to around 2600 kWh/m^2 (@around 7.2 kWh/m^2 daily). Therefore, the easy availability of solar light in Asian countries facilitates the well opportunities to use of novel visible light responsive photocatalytic water treatment technology.

Visible-Light Responsive Photocatalyst

Although, heterogeneous photocatalysis has been considered a novel and effective technique of water disinfection technology. Upon irradiation with photons of UV light ($\lambda \leq 385$ nm) on the photocatalyst (e.g. TiO_2), electron will be promoted from the valance band (VB) to conductive band (CB) and creates an electron-hole pair. These photogenerated electrons and holes react with oxygen molecules with water adsorbed on the TiO_2 surface to produce reactive oxygen species (ROS) (i.e. $^\bullet OH$, $O_2^{\bullet -}$, and H_2O_2). ROS can oxidize the organic substances and inactivate the bacteria as well as other pathogenic microorganisms present in water. However, the most of the pure form of photocatalyst can work only with UV light (λ < 400 nm), that is 4% of the total solar energy on the earth which limits the practical applications (Demeestere et al., 2005). Hence, visible-light responsive photocatalyst is more attractive and effective for disinfection as compared to UV light driven photocatalyst. Because, visible light accounts about 45% of the total sunlight spectrum (Wang et al., 2012). By doping non-metals element into the matrix of TiO_2 can expand its application to the spectrum of visible light, because doping reduces the stimulation band gap and increased the efficiency of titanium dioxide (Markowska-Szczupak et al., 2011). Authors have successfully synthesized a visible light responsive photocatalyst in laboratory conditions via doping of nitrogen in the structures of titanium dioxide and it is designated as nitrogen doped titanium dioxide (N-TiO_2). This visible light responsive N-TiO_2 photocatalyst has shown the significant potential for the disinfection of water and may be employed at a large scale of water treatment plants in the future. It can be especially applicable for the countries or areas which are near to the northern tropic and are facing water storage and supply of safe drinking water problem to their citizens. Because these countries are well blessed with plenty of solar radiation. This advantage of using visible light responsive N-TiO_2 photocatalyst reveals its economic feasibility for heterogeneous photocatalysis.

Photocatalytic disinfection of *E. coli* under visible light

In order to examine the efficiency of N-TiO_2 photocatalyst for disinfection of water, *Escherichia coli* (*E. coli*) was selected as the target microorganism, and causes diarrhea diseases in humans after taking *E. coli* infected water. *E. coli* excreted by all warm-blooded animals as well as some reptiles in their faeces (Ashbolt, 2004).

During the experimentations, the effect of N-TiO_2 dosages on the photocatalytic inactivation of *E. coli* were observed in the range from 0.6-1.0 g/L at three respective initial bacterial concentrations as 10^4 to 10^6 CFU/mL under 6.5 mW/cm^2 of light intensity. Maximum inactivation of *E. coli* was 97.2% within 240 min using 1.0 g/L N-TiO_2. *E. coli* inactivation was decreased with increase in the initial concentration of *E. coli* in water. 1.0 g/L N-TiO_2 dosage was found better for the killing of bacteria from water.

Atomic force microscopy (AFM) was used to get more detail information of microorganism regarding their structural damages during various time intervals of photocatalytic reactions. Because, AFM is able to monitoring the images of cellular surfaces, cell's characteristics and structure at very high resolution (Muller et al. 2009; Liu and Wang, 2010). Three dimensional (x and y, ~20 Å; z, ~1 Å) digital images of *E. coli* can be obtained by using AFM (Braga and Ricci, 1998). Therefore, AFM images of *E. coli* at various treatment stages were also acquired in present study to understand the effect of photocatalytic inactivation of N-TiO_2 on the Gram-negative bacteria (*E. coli*). In the beginning of photocatalytic experiment, the bacterial cells had shown a complete rod shape structure and cells were also found in healthy condition. However, within 30 min reaction period, the cells have shown some damages as seen in AFM images, but still rod shape was retained by the bacteria. In 180 min of reaction time, most of the bacterial shape were distorted.

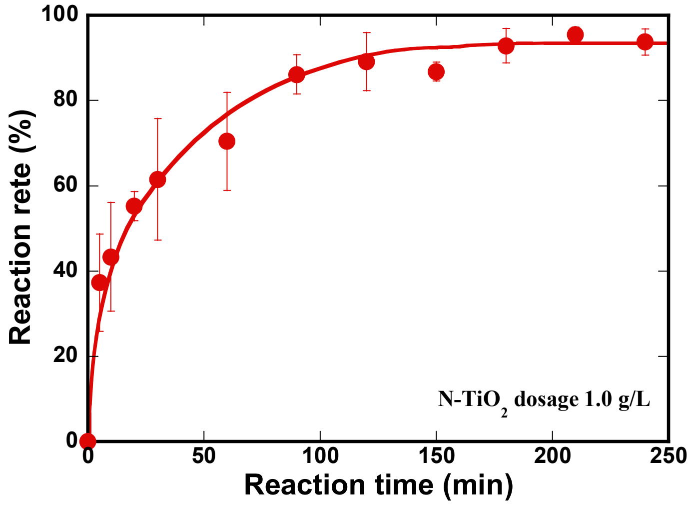

Figure 3. Inactivation of *E. coli* bacteria at 1.0 g/L N-TiO_2 dosage.

Three stages for *E. coli* inactivation by N-TiO_2

Normally, photocatalytic process of bacteria inactivation have three different profiles including, a log-linear inactivation region, and a tail region (Benabbou et al., 2007; Chong et al., 2011; Marugán et al., 2008). In which, shoulder region indicates a cumulative damage instead of any instant lethal effect (Benabbou et al., 2007; Gyürék et al., 1998). But, the log-linear region is most important part of the bacterial inactivation reactions and a continuous invasion effort keep pricking the bacteria outer membrane (Benabbou et al., 2007). In tail region, bacterial inactivation rate decreases because of competition like situations developed in between the organic products and intact cells or the more resistant bacteria against the disinfection process (Benabbou et al., 2007; Lambert et al., 2000).

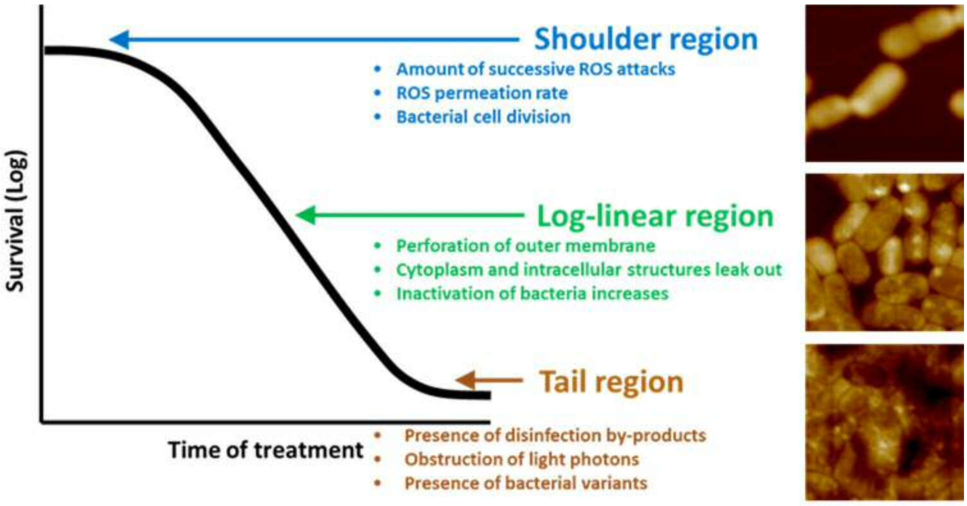

Figure 4. Three stages of inactivation process for *E. coli*.

Conclusions

In summary of present study, an effort has been made to develop a nitrogen doped titanium dioxide (N-TiO2) photocatalyst, which is able to work efficiently in presence of visible light irradiation. N-TiO_2 photocatalyst was synthesized in laboratory conditions and examined for the inactivation of *E. coli* bacteria from water using visible light. The global water stress areas are having sufficient sun light, hence this can be used over there very efficiently. Maximum inactivation was around 97.2% for *E. coli* with 1.0 g/L N-TiO_2 dosage under 6.5 mW/cm^2 visible light intensity in 240 min reaction time. AFM images showed that most of the bacterial shapes were destructed by N-TiO_2 photocatalyst within 180 min of reaction time. Based on the above experimental facts, it appears that N-TiO_2 photocatalyst has significant potentials to inactivate the *E. coli* bacteria from water. Authors are anticipated that the present novel N-TiO_2 photocatalyst can be used for water treatment technology and it would be a better option for the global community to overcome the water stress situation.

Acknowledgements

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References

Ashbolt, N. J. (2004). Microbial Contamination of Drinking Water and Disease Outcomes in Developing Regions. *Toxicology, 198*(1-3), 229-238. doi: 10.1016/j.tox.2004.01.030

Batabyal, P., Mookerjee, S., Sur, D., & Palit, A. (2013). Diarrheogenic Escherechia Coli in Potable Water Sources of West Bengal, India. *Acta Trop, 127*(3), 153-157. doi: 10.1016/j.actatropica.2013.04.015

Benabbou, A. K., Derriche, Z., Felix, C., Lejeune, P., & Guillard, C. (2007). Photocatalytic Inactivation of Escherischia Coli - Effect of Concentration of TiO2 and Microorganism, Nature, and Intensity of Uv Irradiation. *Applied Catalysis B-Environmental, 76*(3-4), 257-263. doi: 10.1016/j.apcatb.2007.05.026

Bolshakova, N., Azuaje, F., & Cunningham, P. (2005). A Knowledge-Driven Approach to Cluster Validity Assessment. *Bioinformatics, 21*(10), 2546-2547. doi: 10.1093/bioinformatics/bti317

Chen, X., & Mao, S. S. (2007). Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical Reviews, 107*(7), 2891-2959. doi: 10.1021/cr0500535

Chong, M. N., Jin, B., & Saint, C. P. (2011). Using H-Titanate Nanofiber Catalysts for Water Disinfection: Understanding and Modelling of the Inactivation Kinetics and Mechanisms. *Chemical Engineering Science, 66*(24), 6525-6535. doi: http://dx.doi.org/10.1016/j.ces.2011.09.020

Demeestere, K., Dewulf, J., Ohno, T., Salgado, P. H., & Van Langenhove, H. (2005). Visible Light Mediated Photocatalytic Degradation of Gaseous Trichloroethylene and Dimethyl Sulfide on Modified Titanium Dioxide. *Applied Catalysis B: Environmental, 61*(1–2), 140-149. doi: http://dx.doi.org/10.1016/j.apcatb.2005.04.017

Editors, U. (2013). Sustainability: A Comprehensive Foundation. Retrieved from the Openstax-Cnx Web Site: http://Cnx.Org/Content/Col11325/1.43/.

Gyürék, L., & Finch, G. (1998). Modeling Water Treatment Chemical Disinfection Kinetics. *Journal of Environmental Engineering, 124*(9), 783-793. doi: 10.1061/(ASCE)0733-9372(1998)124:9(783)

Kazuhito, H., Hiroshi, I., & Akira, F. (2005). Tio 2 Photocatalysis: A Historical Overview and Future Prospects. *Japanese Journal of Applied Physics, 44*(12R), 8269.

Lambert, R. J., & Johnston, M. D. (2000). Disinfection Kinetics: A New Hypothesis and Model for the Tailing of Log-Survivor/Time Curves. *J Appl Microbiol, 88*(5), 907-913.

Malato, S., Fernandez-Ibanez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Decontamination and Disinfection of Water by Solar Photocatalysis: Recent Overview and Trends. *Catalysis Today, 147*(1), 1-59. doi: 10.1016/j.cattod.2009.06.018

Markowska-Szczupak, A., Ulfig, K., & Morawski, A. W. (2011). The Application of Titanium Dioxide for Deactivation of Bioparticulates: An Overview. *Catalysis Today, 169*(1), 249-257. doi: 10.1016/j.cattod.2010.11.055

Marugán, J., van Grieken, R., Sordo, C., & Cruz, C. (2008). Kinetics of the Photocatalytic Disinfection of Escherichia Coli Suspensions. *Applied Catalysis B: Environmental, 82*(1–2), 27-36. doi: http://dx.doi.org/10.1016/j.apcatb.2008.01.002

Matsunaga, T., Tomoda, R., Nakajima, T., & Wake, H. (1985). Photoelectrochemical Sterilization of Microbial Cells by Semiconductor Powders. *Fems Microbiology Letters, 29*(1-2), 211-214. doi: 10.1111/j.1574-6968.1985.tb00864.x

Pigeot-Remy, S., Simonet, F., Errazuriz-Cerda, E., Lazzaroni, J. C., Atlan, D., & Guillard, C. (2011). Photocatalysis and Disinfection of Water: Identification of Potential Bacterial Targets. *Applied Catalysis B-Environmental, 104*(3-4), 390-398. doi: 10.1016/j.apcatb.2011.03.001

Pulgarin, C., Kiwi, J., & Nadtochenko, V. (2012). Mechanism of Photocatalytic Bacterial Inactivation on TiO2 Films Involving Cell-Wall Damage and Lysis. *Applied Catalysis B: Environmental, 128*(0), 179-183. doi: http://dx.doi.org/10.1016/j.apcatb.2012.01.036

Rincón, A. G., & Pulgarin, C. (2003). Photocatalytical Inactivation of E. Coli: Effect of (Continuous–Intermittent) Light Intensity and of (Suspended–Fixed) TiO2 Concentration. *Applied Catalysis B: Environmental, 44*(3), 263-284. doi: http://dx.doi.org/10.1016/S0926-3373(03)00076-6

van Grieken, R., Marugan, J., Pablos, C., Furones, L., & Lopez, A. (2010). Comparison between the Photocatalytic Inactivation of Gram-Positive E. Faecalis and Gram-Negative E. Coli Faecal Contamination Indicator Microorganisms. *Applied Catalysis B-Environmental, 100*(1-2), 212-220. doi: 10.1016/j.apcatb.2010.07.034

Watkins, K. (2006). Human Development Report.