Investigating Catalytic Effect of Titanium Dioxide on Solar Disinfection of Water

ANWAR RASHID SALEEMI, NAVEED RAMZAN* AND MUHAMMAD NAEEM HAFEEZ
Department of Chemical Engineering, University of Engineering and Technology, Lahore, Pakistan.

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Summary: In this paper the catalytic effect of titanium dioxide (photo-catalysis) on solar disinfection of water for inactivation of Fecal coliform bacteria is investigated. Coating of titanium dioxide crystals on glass are exposed to sunlight in two ways: mobilize and immobilize form. An experiment is conducted in consideration for household application. Coating of titanium dioxide on glass rods (immobilize) and rings (mobilize) are positioned in glass bottles filled with water. Inactivation of Fecal coliform is compared with the normal solar disinfection (SODIS) process. Experiment results shows that titanium dioxide enhances the inactivation efficiency of SODIS by 1:1.3:1.8 corresponding to immobilize and mobilize titanium dioxide, respectively. This development is intended for use by small communities, refugee camps, institutions, and during emergency and disaster situations.

Introduction

Poor quality of drinking water is a major health threat to human beings, especially in developing countries. Over one billion people each year, are exposed to unsafe drinking water [1]. Five out of every thousand of those exposed to unsafe drinking water will die from diseases carried by the contaminated water [2]. In developing countries, ground water and surface water such as rivers, streams and lakes are used for multiple activities including livestock watering, bathing and cooking. This water, which may be contaminated with pathogenic organisms, is also used as drinking water. People didn't get any option except drinking this poor quality water due to lack of water distribution infrastructure, lack of funding for installations of water treatment systems and high population growth.

Therefore, water disinfection methods that can be easily employed in developing countries are needed. Chemical disinfection options such as chlorine and ozone treatment *etc.* and physical treatment options such as filtering *etc.* require materials that may not be easily acquired or purchased. Solar Water Disinfection (SODIS) is a simple promising option and easily utilized. It has been recommended by several researchers for use in countries that receive abundant sunshine, specifically areas lies between latitudes 35°N and 35°S [3]. In SODIS, drinking water is exposed to solar radiation to inactivate pathogenic microorganisms mainly bacteria, virus, fungi, spore-forming organisms, cyst-forming protozoa and *Escherichia coli.* This disinfection is accomplished by exposing it to ultraviolet solar radiation especially near the UV range (320-400 nm) [4]. However, the sunlight only consists about 3 % of ultraviolet light, an alternate means to improve the efficiency of process is to use a semiconductor as a photo catalyst that is excitable by the energy of photons provided by sunlight [5]. In this paper, the catalytic effect of titanium dioxide on solar water disinfection both in immobilize and mobilize form is investigated. The effect is acknowledged by testing the presence of fecal coliform bacteria in samples taken from glass bottles with and without containing titanium dioxide.

Theoretical Fundamentals

SODIS uses the sun energy to provide an economically feasible means of providing safe drinking water and is included in the technologies reviewed by WHO for household water treatment and storage. It uses the destructive power of different bands of the electromagnetic spectrum to destroy pathogens. The most important bandwidths for SODIS are the UV-A, red, and infrared of the electromagnet spectrum. UV-A light is the main bandwidth involved in the eradication of microorganisms [3, 6, 7]. These radiations inactivate microorganisms by three different ways: DNA alteration, thermal pasteurization [8] and photo-oxidative destruction. UV-A effects directly DNA and forms highly destructive oxygen species as a secondary product. Red and infrared radiations are absorbed by water strongly resulting in thermal pasteurization. SODIS operates on the principle that

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*To whom all correspondence should be addressed.

sunlight-induced DNA alteration, photo-oxidative destruction, and thermal effects will inactivate microorganisms. For these parameters to be effective, the environment must be sunny and hot enough, the water must be clear enough to allow the light to penetrate, and the type of container being used must not substantially hinder these processes.

Sun light, consisting about 3 % of ultra-violet light, takes 5-6 hours of full sunshine to inactivate 99 % bacteria. This efficiency of SODIS process can be improved by using a semiconductor as a photocatalyst. This is called photo catalysis, an interesting non conventional method for removing organic species in the environment. A wide range of semiconductors can be used for photo catalysis, such as titanium dioxide, zinc oxide, magnesium oxide, ferric oxide, cadmium sulphate, calcium titanium (III) oxide, molybdenum oxide, *etc.* [9]. An ideal photo catalyst should possess the properties such as photoactivity, biological and chemical inertness, stability toward photo corrosion, suitability towards visible or near UV light, cheap availability and lack of toxicity. All of these properties exist in titanium dioxide at their best [5]. Titanium dioxide also have excellent pigmentary properties, high ultraviolet absorption and high stability, which makes it most suitable for the photo catalytic degradation of contaminants in water and air. It can be used in the form of a suspension, or a thin film in water treatment. Titanium dioxide exists in three types of crystal structures namely anatase, rutile and brookite. Among these crystal structures, the anatase type exhibits higher photo catalytic activity due to the difference in the position of conduction band. In anatase type crystals, conduction band is closer to negative position as compared to other crystal structures which makes its reducing power stronger than these crystals.

When light is absorbed by titanium dioxide, two carriers, electrons (e^-) and positive holes (h^+) are formed. In ordinary substances, electrons and positive holes recombine quickly; however, in titanium dioxide photocatalyst they recombine more slowly. The percentage of carrier recombination has a major effect on the photocatalytic efficiency. In Titanium dioxide, positive holes have the strong oxidative decomposing power, which is greater than the reducing power of electrons excited to the conduction band. The surface of a photocatalyst contains water, which is referred to as "absorbed water." When this water is oxidized by positive holes, hydroxyl radicals (^{-}OH), which have strong oxidative decomposing power, are formed. Then, the hydroxyl radicals react with organic matter. If oxygen is present at the time of occurrence of this process, the intermediate radicals in the organic compounds and oxygen molecules can undergo radical chain reactions and consume oxygen in some cases. In such a case, the organic matter eventually decomposes, ultimately becoming carbon dioxide and water. Under some conditions, organic compounds can react directly with the positive holes, resulting in oxidative decomposition. Meanwhile, the reduction of oxygen contained in the air occurs as a pairing reaction. As oxygen is an easily reducible substance, if oxygen is present, the reduction of oxygen takes place instead of hydrogen generation. The reduction of oxygen results in the generation of superoxide anions (O_2^-), superoxide anions attach to the intermediate product in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then to water. As reduction tends to occur more easily in organic matter, the possibility of positive holes being used in the oxidative reactions with organic matter increases, thus reducing the rate of carrier recombination. Under conditions in which positive holes are sufficiently consumed, the process of electrons transferring to oxygen molecules on the reduction side determines the reaction speed of the entire photo catalytic reaction. Thus, by enabling easier transfer of electrons to oxygen molecules, the efficiency of photo catalytic reactions can be improved. This photo catalysis mechanism of TiO_2 is given below.

Chemical Reactions

Electron-Hole Pair Formation

$$TiO_2 + h\upsilon \rightarrow TiO_2 + OH^- \text{ (or } TiO_2^+\text{)}$$

Electron Removal from the Conduction Band

$$TiO_2^- + O_2 + H^+ \rightarrow TiO_2 + HO_2^-$$
$$TiO_2^- + H_2O_2 + H^+ \rightarrow TiO_2 + H_2O + OH^-$$
$$TiO_2^- + H^+ \rightarrow TiO_2 + 2H_2$$

Oxidation of Organic Compounds

$$OH^- + O_2 + OM \rightarrow CO_2 + H_2O$$

Non-productive Radical Reactions

$$TiO_2^- + OH^- + H^+ \rightarrow TiO_2 + H_2O \text{ (recombination)}$$

Results and Discussion

Field measurements were made in the city of Lahore because according to meteorological station Lahore, it has 2909 hours of sunshine for year 2007 that makes it most favourable regions for SODIS of drinking water. Artificially contaminated water is exposed to sunlight in glass bottles containing coated titanium dioxide glass rods and rings. Initial readings of temperature and lux are recorded and samples are taken to enumerate the starting concentration of bacteria. Samples are collected at predetermined intervals to determine the Fecal coliform concentration in order to investigate the effect of TiO_2 on SODIS. During each sampling, time, sample temperature, climate conditions by measuring lux are measured.

Table-1 shows the experimental data obtained during month of August and September 2007. Average Extinction rate is calculated for SODIS without TiO_2 and with TiO_2 coated rods and rings is 0.75, 0.88 and 1.35 per minute respectively. It shows that for killing 100 fecal coliforms during SODIS without TiO_2 and with both TiO_2 coated rods and rings takes approximately 133, 112 and 73 minutes respectively. It is also apparent that increasing radiance decreases the concentration of fecal coliforms in the sample. The overall outcome demonstrates that adding titanium dioxide in infected water kills coliform bacteria more rapidly in the presence of sunlight. The rate of bacteria destruction depends on the exposure of Titanium dioxide particle to sunlight rays and radiance.

For all results, cumulative analysis is made and given in Table-2. Temperature behaviour remains consistent every day while lux fluctuates as it depends directly on the presence of sunlight. With the increase in radiance i.e. UV rays, the concentration of bacteria decrease correspondingly. Fig. 1 shows the cumulative graph between time and concentration of bacteria indicating that concentration of bacteria decreases as the duration of SODIS water disinfection increases.

Initial samples prior to SODIS shows significant variation in the bacteria level. In order to understand the effectiveness of SODIS a cumulative extinction rate of bacteria per minute is used. The cumulative extinction rate calculated for SODIS without TiO_2, with TiO_2 coated rods and rings is 0.8, 0.97 and 1.4 per minute respectively. It shows that for killing 100 fecal coliforms during SODIS without TiO_2, with TiO_2 coated rods and ring take approximately 125, 102 and 70 minutes respectively. This depicts that extinction rate is higher in rings or suspended form of titanium dioxide. This is because of the exposure of sunlight rays, is more in case of suspended rings than rod. Fig. 2 plotting radiance (W/m^2) and concentration of bacteria describe the effect of sunlight rays on the concentration of Fecal coliforms.

Table-1: Results of SODIS water disinfection during the month of August and September, 2007.

Sr. No.	Time [h]	Temperature [°C]	Lux	Radiance [w/m^2]	Concentration[!] MPN/ 100 ml		
					SODIS	Rods	Rings
				August 08, 2007			
1	09:00	30	700	840	180	160	163
2	10:00	40	780	936	84	42	24
3	11:00	43	840	1008	32	12	0
4	12:00	48	880	1056	10	0	---------
5	13:00	52	895	1074	0	-------	---------
				August 17, 2007			
1	09:00	30	722	866	240	220	230
2	10:00	40	860	1032	110	49	31
3	11:00	45	930	1116	31	4	0
4	12:00	55	980	1176	4	0	---------
5	13:00	58	1040	1248	0	-------	---------
				August 27, 2007			
1	09:00	30	720	864	170	165	140
2	10:00	40	830	996	69	37	17
3	11:00	45	950	1140	23	2	0
4	12:00	50	990	1188	5	0	---------
5	13:00	54	1050	1260	0	-------	---------
				September 01, 2007			
1	09:00	30	760	912	170	160	160
2	10:00	42	940	1128	64	32	5
3	11:00	48	1007	1208	17	0	0
4	12:00	58	1020	1224	0	--------	---------
5	13:00	60	1050	1260	---------	-------	---------
				September 16, 2007			
1	09:00	30	700	840	210	180	180
2	10:00	40	790	948	95	48	28
3	11:00	44	855	1026	36	14	2
4	12:00	48	923	1108	5	0	0
5	13:00	53	1020	1224	0	-------	---------
				September 26, 2007			
1	09:00	30	723	868	180	170	160
2	10:00	40	780	936	84	40	25
3	11:00	45	820	984	29	12	2
4	12:00	50	850	1020	4	0	0
5	13:00	55	925	1110	0	-------	---------

[!] Concentration of Fecal Coliforms during Solar disinfection of water without TiO_2 , With TiO_2 coatings on
Glass rods and rings in MPN (Most Probable Number)/100 ml

Table-2: Cumulative result of water solar disinfection experiment.

Sr. No.	Time [h]	Temperature [°C]	Lux	Radiance [w/m^2]	Concentration[!] MPN/ 100 ml		
					SODIS	Rods	Rings
1	09:00	30	721	865	200	176	172
2	10:00	40	830	996	120	41	23
3	11:00	45	900	1080	60	7	0
4	12:00	52	941	1129	25	0	---------
5	13:00	55	997	1196	0	-------	---------

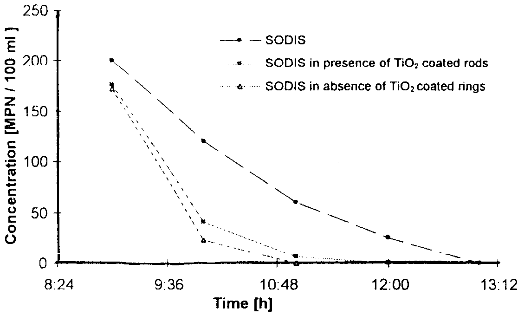

Fig. 1: Cumulative graph between concentration of Fecal coliforms and time.

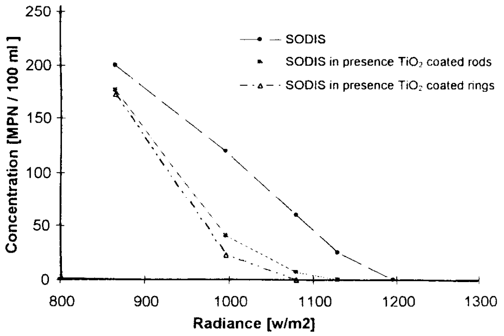

Fig. 2: Cumulative graph between concentration of Fecal coliforms vs. radiance.

Experimental

Catalytic effect of titanium dioxide on SODIS of water is studied by preparing titanium dioxide (anatase) in laboratory and coating it on glass rods and rings. Keeping in mind household application, experimentation methodology is adopted and experimentation is conducted on glass bottles.

In first step, titanium dioxide is prepared and coated on glass rods and rings. Titanium dioxide is prepared by carrying out exothermic reaction between titanium tetrachloride and 99 % pure ethanol. Ethanol is mixed with titanium tetrachloride by pouring it in a beaker and adding drop wise titanium tetrachloride in ethanol with a ratio of ethanol to $TiCl_4$ as 14:1. The solution is stirred continuously for approximately 30 min, until the solution become cold and thicker with yellowish colour. Then the solution is placed in oven at 60 ^{0}C for 5-6 hours to make it slurry. Dip coating technique is used for coating rods and rings. Two and fourty borosilicate glass rods and rings respectively are properly washed, dried and dipped for 5 minutes into the slurry of titanium dioxide and gently pulled out. Rods and rings are placed into the oven at 80 ^{0}C for 25 minutes to dry the solution. This process is repeated for 6 -7 times. Then these rods and rings are placed into the furnace at 550 ^{0}C for two hours, so that anatase crystals formed. Fig. 3 shows the titanium dioxide coated rods and rings.

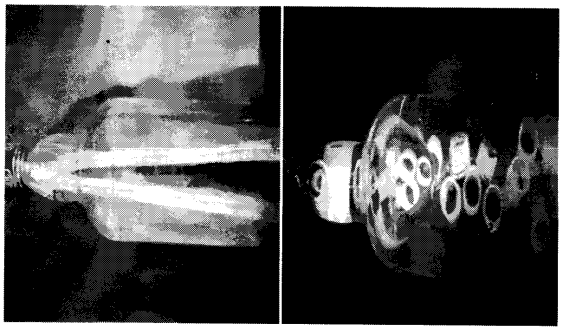
Coated Rods Coated Rings

Fig. 3: Titanium dioxide coated rods and rings in water.

In second step, a black insulated steel plate bottle stand is prepared on which water bottles are placed. To absorb the maximum radiations, bottle stand is prepared with the inclination angle equal to the latitude of Lahore facing the south direction approximately 34^0.

Three glass bottles of 1.25 litre of each is selected for experiment. One bottle is without any addition of titanium dioxide while the two other contains rings and rods. The rods are adjusted in bottle such that it appears in the centre of the bottle. Same testing, sampling, and enumeration methods for each experiment are used so that result can be compared. Contaminated water is artificially made by mixing 2 ml of sewage water into 1000 ml tap water. The sewage is filtered before use to make it free from suspended particles and thoroughly mixed with water to ensure homogeneity. Bottles are filled by mixing 100 ml contaminated water with tap water. Fig. 4 shows the filled bottles, placed on the stand.

The stand is placed open to sun light from sun rise to sun set. Fecal coliform bacteria is selected as test organism. To quantify the inactivation of Fecal coliform bacteria in each experiment, samples were taken after residence time of one hour. During each

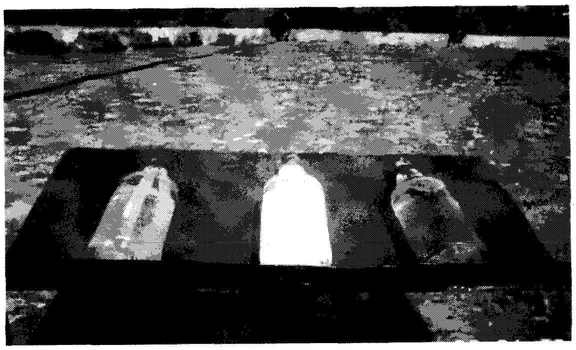

Fig. 4: Experimental setup.

sampling session, time, sample water temperature, lux, and sample volumes collected were recorded and brought to the laboratory. Initial sample is taken from each bottle before exposing them to sunlight. A dilution series was carried out and at least three appropriate dilutions were plated in order to determine the concentration of bacteria remaining in the sample bottles, and to calculate the inactivation off the bacteria in the treated water sample. The following standard test for Fecal coliform.

1. Multiple-tube Fermentation technique (MTF) (SM - 9221)

2. Membrane filter technique (MF) (SM-9222) are used.

Conclusions

Titanium dioxide can be used for the purification of drinking water because it is non-hazardous, high photo-activity or band gap value, stable towards photo corrosion and low cost than other semiconductors. Efficiency of water disinfection by solar radiation can be increased tremendously and the performance of results depends on ambient temperature, wind speed, ultraviolet radiation intensity, turbidity of contaminated water, residence time, geometry, initial concentration of bacteria.

Experimentation is conducted in bottles because of the availability concern of drinking water in rural areas. The experiment shows that by adding titanium dioxide in immobilize or mobilize form increases the efficiency of SODIS by 1:1.3:1.8 respectively.

Addition of titanium dioxide makes SODIS process more efficient and suitable for water treatment for household in urban and rural areas of Pakistan and other parts of the world. It is hoped that this disinfection method will produce an economically feasible technology to improve water quality and public health in Pakistan.

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References

1. UNICEF., Technical Report, Global water supply and sanitation assessment report, (2000).
2. WHO: The World Health Report: Making a Difference. Geneva, World Health Organization Geneva, (2000).
3. A. Acra, M. Jurdi, H. Muallem, Y. Karahagopian and Z. Raffoul, Water *Disinfection by Solar Radiation, Assessment and Applications, IDRC-TS66e. International Development Research Centre, Ottawa, Canada (1990).*
4. L. F. Caslake, J.C. Daniel, M. Vilas, M. D. Catriona, R. Ricardo and T. Javad, *Applied and Environmental Microbiology,* **70** (2), 1145 (2004).
5. P. R. Cecília, L. Z. Roberta and R. G. José, *Brazilian Journal of Chemical Society,* **18** (1), 126 (2007).
6. R. H. Reed, *Letters in Applied Microbiology,* **24**, 276 (1997).
7. K. G. McGuigan, T. M. Joyee, R. M. Conroy, J. B. Gillespie and M. Elmore-Meegan, *J. Appl. Microbiol.,* **84**, 1138 (1998).
8. M. Wegelin, S. Canonica, K. Mechner, T. Fleischmann, F. Pesaro and A. Metzler, *J. Water Ser. Res. Technol.-Aqua.,* **43**, 154 (1994).
9. R. A. Al-Rasheed, *Water Treatment by Heterogeneous Photocatalysis an Overview,* presented at 4th SWCC acquired Experience Symposium held in Jeddah, 2005.