Research Inventy: International Journal Of Engineering And Science
Vol.5, Issue 2 (February 2015), PP 50-55
Issn (e): 2278-4721, Issn (p):2319-6483, www.researchinventy.com

Investigation on the Effect of TiO_2 and H_2O_2 for the Treatment of Inorganic Carbon Present in Seawater

Hasna Al Jabri*[1], Alaa Al-Hudaifi[1], Shaik Feroz[1], Fouzul Ameer Marikar[2], Mahad Baawain[2]

[1]*Caledonian Center for Creativity and Innovation, Caledonian College of Engineering, Sultanate of Oman.*
[2]*College of Engineering, Sultan Qaboos University, Sultanate of Oman.*

ABSTRACT: *Sodium hypochlorite (NaClO) is regularly used as a disinfectant or a bleaching agent because of its high efficiency against many bacteria and viruses present in seawater along with its cheaper cost. Now a days, with the increase in the environmental concerns concerning the use of chlorination for the disinfection or bleaching of treated water related to the formation of potentially harmful chloro-organic by products through reactions with natural organic matter (NOM), it is preferred to implement a process with environmentally friendly chemicals for water treatment processes. About This report aim to study the possibility of reducing the inorganic carbon present in seawater by oxidization reaction of seawater with TiO_2 and H_2O_2. Investigated and a comparison between thin film method and suspension method with a reactor system in conjunction with a light concentrating system has been done.*

KEYWORDS: *Inorganic Carbon, H_2O_2, Nano photocatalysis, TiO_2, Seawater treatment, Solar Energy.*

I. INTRODUCTION

Throughout the last years several disinfection technologies have been investigated for drinking waters and waste waters, but seawater has only been tested recently. Since water quality is an important factor in the water treatment process, finding an alternative method which is environmentally friendly is important to avoid the production of toxic waste. Therefore more research is done on advanced oxidation technologies which are able to produce highly reactive OH radicals to accelerate the degradation rate of seawater contaminations.

Based on Oman Power and Water Procurement's 7-year statement from 2014 to 2020, water demand is expected to increase by 6% per year, from 238 million m^3 in 2013 to 349 million m^3 in 2020 in the northern region. Where 5.5% per year increase is expected in the Salalah System. Ad Duqm Zone is expecting a high increase of water demand of 32% for non-industrial and 76% for industrial uses. This high demand expectation is due to Ad Duqm projects including Ad Duqm airport and the industrial area. Expansion of a number of desalination plants and additional of new desalination plants to meet the high demand of water expected by 2020 was reported along with considering the potential of extending the contracts of a major supplying plant. [1]

Nano-scale Photocatalysts has more photocatalytic activity than the normal scale catalyst as it will be having larger surface area for contacting between the reactants and it's having a smaller size that will reduce the time needed for the carrier diffusing out of the photocatalyst pours to the photocatalysts surface. [2]

When light illuminate the surface of the photocatalysts with bandgap energy equal or higher than the semiconductors bandgap, the semiconductor gets activated by the absorption of photons then the electrons get excited from the valance bond to the conduction bond resulting in the formation of a positive hole (p+) in the valance band and an electron (e-) in the conduction band. The positive hole can oxidize the pollutant directly or oxidize water to form ($^{\cdot}HO$) radicals. At the same time, the electron reduces the oxygen adsorbed to the photocatalyst which prevents the combination of electrons and the positive hole. [3]

The reaction bellow explains the photocatalytic reaction mechanism:

$$\text{Photocatalyst} \longrightarrow e^- + p^+$$
$$e^- + O_2 \longrightarrow O_2^-$$
$$p^+ + \text{Organics} \longrightarrow CO_2$$
$$p^+ + H_2O \longrightarrow {}^{\cdot}HO + H^+$$
$${}^{\cdot}HO + \text{Organics} \longrightarrow CO_2 \text{ [4]}$$

There are several advantages and disadvantages of choosing suspension photocatalysis. Suspension process will be having a uniform photocatalyst distribution in the reactor system, higher efficiency because of it larger surface area and low pressure drop as the suspension particles are well mixed. The process will also minimize catalyst fouling because the catalyst is continuously removed. Where, the main disadvantage is the requirement of a Nano filter to separate the catalyst which will increase the cost of the unit. On the other hand, thin film method is a continuous operation and doesn't need a separation step after the reaction taking place. But it has lower light utilization efficiency because the surface area utilized is less than the suspension method. [5] It was reported that Titanium dioxide is having an energy bandgap of 3.2 eV which is activated by UV illumination with a wavelength up to 387.5 nm. At the ground level, solar irradiation starts at a wavelength of about 300 nm. Which results in utilizing 4 to 5% only the solar energy reaching the surface of the earth. [6]. A number of methods are available for producing hydroxyl radicals. It can be categorized into two categories: non-photochemical method and photochemical methods. Non-photochemical method includes: ozonation at elevated pH (> 8.5), Ozone and hydrogen peroxide (O_3/H_2O_2), Ozone and catalyst (O_3/CAT), Fenton system (H_2O_2/Fe^{2+}). Photochemical methods includes: ozone-UV radiation (O_3/UV), hydrogen peroxide-UV radiation (H_2O_2/UV), ozone-hydrogen peroxide-UV radiation (O_3/ H_2O_2/UV), Photo-Fenton and Fenton-like systems, and photocatalytic oxidation (UV/TiO_2). [7]

Table (1) shows Relative oxidation power of some oxidizing species. [7]

Oxidizing Species	**Relative oxidation power**
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, TiO_2^+	2.35

A comprehensive research was done on Milli-Q water, Leman Lake water and artificial seawater to observe the photo-inactivation and reactivation of E.coli. Along with studying the outcome of experimenting dissolved bicarbonates and NOM as these compounds affect the effectiveness of the treatment methods used. Milli-Q water should a higher decrease of the bacterial inactivation rate compared to Leman Lake water as a result of the absence of inorganic ions. Even though there is a high difference in salt concentration Leman Lake water and seawater but Inactivation rates were similar to each other. [8]

The advanced oxidation processes (AOPs) are presented as treatment of future in disinfection and removal of contaminants from water. [9] Advanced oxidation processes represent a group of techniques used for the treatment of water characterized by the generation of radicals, such as the hydroxyl radical (OH^o) and may be an alternative to chlorine disinfection. [10]

A Study of Hydrogen Peroxide electro-generation in seawater was done and the result showed that in the absence of a reducing substrate, the fast production rate of active chlorine leads to total depletion of H_2O_2. And the simultaneous anodic production of oxidizing species, mainly active chlorine, severely affects the stability of hydrogen peroxide due to the chemical reaction between these species. [11] It was found that in order to improve the elimination efficiency an oxidant could be added during UV irradiation which absorbs the UV light by itself and reacts with water to form a highly reactive OH radicals. Hydrogen peroxide (H_2O_2) and ozone are the commonly used oxidants. It was absorbed during the experiments that the absorbance efficiency of H_2O_2 is reliant on its concentration. The higher the concentration of H_2O_2, the better the performance of the water treatment system. [12] It was observed that the oxidation rate of nanomolar Fe(II) with H_2O_2 is a function of pH, temperature and the concentration of HCO_3^- and H_2O_2. And $FeOH^+$ is the most important iron species controlling the Fe(II) oxidation with H_2O_2 in the pH range of natural seawater systems. [13]

As shown in fig (1), using a concentrated light system that reflects the solar light onto the photocatalytic reactor by a reflecting surface is more desired because it will require a smaller reactor volume, it operates at a higher flow rate, better mass transfer rates, and it can be even operated under cloudy conditions. [14-15]

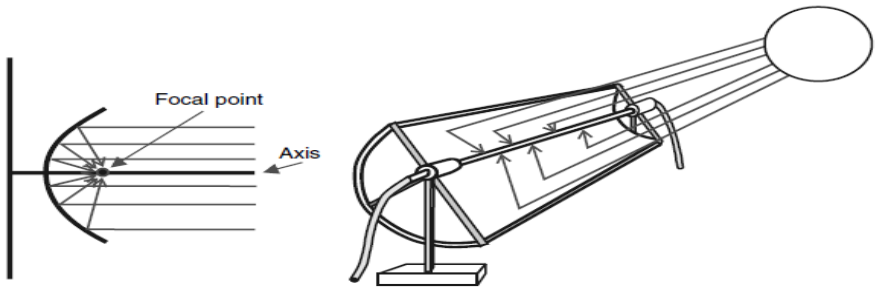

Figure 1: a parabolic shaped light reflecting

II. MATERIALS & METHODS

Thin Film Method

a- Material

Seawater was collected 1 km from Al Athibah Beach, Oman. Aeroxide P25 was obtained from Evonik Industries, 35% Hydrogen Peroxide from The Merck Group, and PVA from Oman Textile Mills Company L.L.C.

b- Preparation of Coating Solutions

Coating Solution: 5 grams of PVA and 2.2 grams of TiO_2 were dissolved in 60ml of water, 30ml of ethanol, 6ml of acetic acid and 4ml of ethylene glycol. The solution was left for stirring overnight.

c- Coating of Glass Tube

Glass tube is coated with TiO_2 thin film by passing the dispersed TiO_2 in the inner surface of the tube. The tube is allowed to dry and then calcinated at 400°C for about 1 hour.

Fig 2 represents the reactor system configuration. Seawater from the system tank was pumped to the thin film coated reactor using peristaltic pump, where the photo catalysis is activated by sunlight and oxidation reaction takes place.

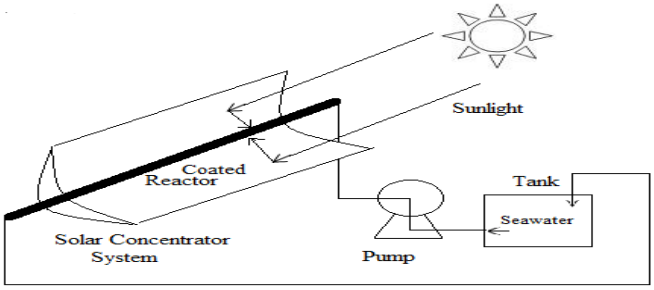

Figure 2: Schematic of the Thin Film Experimental Set-up

The tubular photo reactor is 1 meter long with an outer diameter of 2 cm. The system glass tank holds 1.5 litter of seawater water which is continuously re-circulated through the tubular reactor.

Suspension Method

Fig 3 represents the reactor system configuration. The seawater along with photo catalyst was fed to the reactor system using peristaltic pump, where the photocatalysis is activated by sunlight. Oxidation reaction takes places which lowers poisonousness inorganic matter in the contaminated seawater.

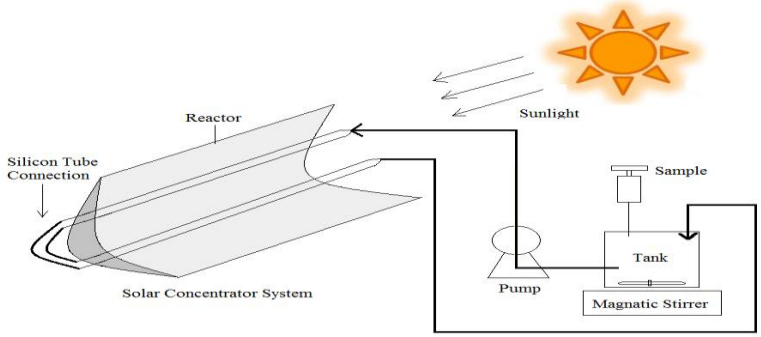

Figure 3: Schematic of the Suspension Experimental Set-up

Two tubular photo reactors were connected with a silicon tube. Each tube is 1 meter long with an outer diameter of 2 cm. The system glass tank holds 2 litter of seawater water along with 3 gram of the photo catalyst which is mixed by a magnetic stirrer. The solution is then continuously re-circulated through the tubular reactor.

III. RESULT AND DISCUSSION

Inorganic Carbon was measured with Total Organic Carbon Analyzer (TOC-L series) from Shimadzu Corporation.

a- Thin Film Method

Polyvinyl alcohol was used as a solution thickener and a binder to enhance the chemical bonding of TiO_2 to the inner surface of the glass tube. The transparent coated layers of TiO_2 was stable, very resistance and strongly stick on the inner surface of the tube after calcination.

The glass tubes were first illuminated under solar irradiation for 1 hour before it is fitted to the experimental setup. Then the photocatalytic reaction took place at a UV Index of 6 to 8.

Table (2) shows seawater analysis with coated tubular photoreactor with TiO_2. A slight decrease was noticed in the inorganic carbon value with time. And fig (4) shows the variation in inorganic carbon during photocatalytic reaction of TiO_2 with seawater.

TABLE (2): Seawater analysis with coated tubular photoreactor.

Time	0hr	1hr	2hr	3hr	4hr
UV Index	-	6	6	8	8
Temperature ºC	-	31	32	34	32
IC (ppm)	25.83	25.65	25.26	25.15	25.05

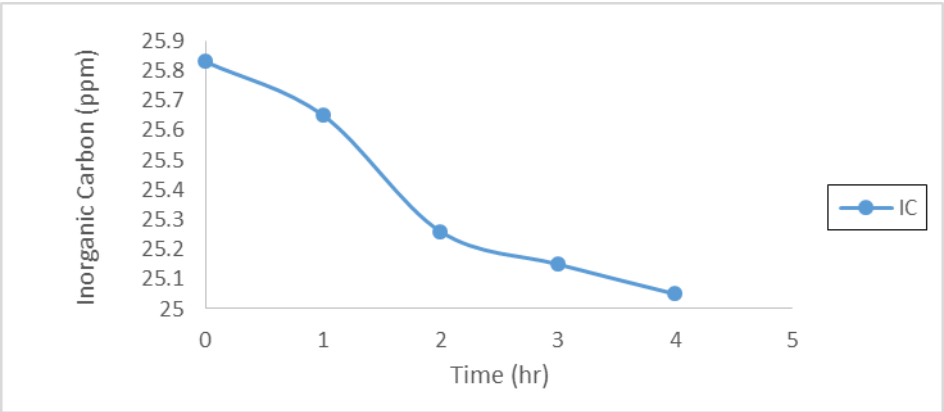

Figure (4): Variation in In-Organic Carbon during photocatalytic reaction of TiO_2 with seawater

Table (3) shows seawater analysis with coated tubular photoreactor with TiO_2 alone with H_2O_2. The decrease in inorganic carbon value is more when combining TiO_2 with H_2O_2 compared to TiO_2 coating alone. Fig (5) shows the variation in inorganic carbon during photocatalytic reaction of TiO_2 along with H_2O_2.

TABLE (3): Seawater analysis of coated tubular photoreactor with H_2O_2.

Time	0hr	1hr	2hr	3hr	4hr
UV Index	-	7	8	8	6
Temperature ºC	-	27	29	29	28
IC (ppm)	25.83	24.24	23.33	21.93	21.66

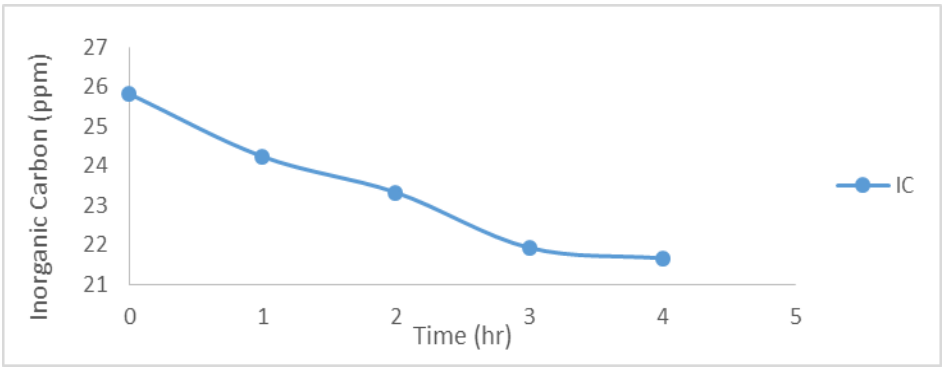

Figure (5): Variation in In-Organic Carbon during photocatalytic reaction of TiO_2 and H_2O_2 with seawater

b- Suspension Method

The reaction was carried out for 5 hours continuously and a sample of the treated water was collected every 60 min. The samples were not filtered but it was allowed to settle down overnight water analysis is done

Table (4) shows seawater analysis with suspended photocatalysis of TiO_2. It is observed that the decrease in inorganic carbon value is much more is suspension method compared to thin film method. And fig (6) shows the variation in inorganic carbon during photocatalytic reaction of TiO_2 in suspension.

TABLE (4): Seawater analysis with suspended photocatalysis.

Time	0hr	1hr	2hr	3hr	4hr	5hr
UV Index	-	5	6	7	6	5
Temperature ºC	-	23	23	23	23	23
IC (ppm)	26.2	23.02	22.5	22.14	22.14	21.43

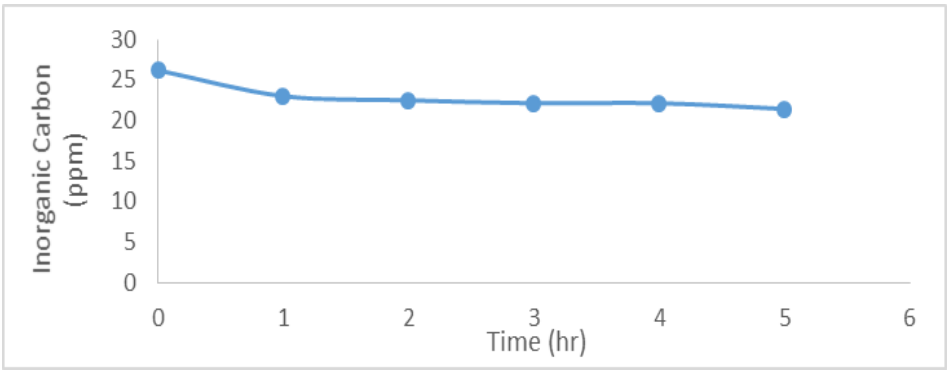

Figure (6): Variation in In-Organic Carbon during photocatalytic reaction of TiO_2 in suspension with seawater

Table (5) shows seawater analysis with suspended photocatalysis of TiO_2. It is spotted that there is a significant decrease in inorganic carbon value of seawater with time. Fig (7) shows the variation in inorganic carbon during photocatalytic reaction of TiO_2 in suspension.

TABLE (5): Seawater analysis of suspended photocatalysis with H_2O_2.

Time	0hr	1hr	2hr	3hr	4hr	5hr
UV Index	-	4	5	6	7	6
Temperature ºC	-	22	24	25	24	24
IC (ppm)	26.2	21.18	20.98	20.74	18.66	1.084

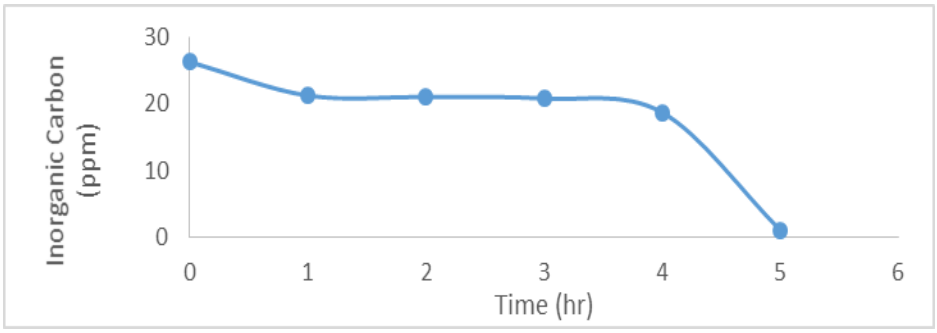

Figure (7): Variation in In-Organic Carbon during photocatalytic reaction of TiO_2 and H_2O_2 in suspension with seawater

IV. CONCLUSION

Oman is having high sunlight intensity which makes the utilization of solar photocatalysis an environmentally and sustainable process. Experimental investigations were carried out in an immobilized thin film Nano photo catalyst as well as suspension mode. The degradation of inorganic compounds present in seawater was studied. The following conclusions were drawn:

- Nano TiO_2 photo catalyst thin film inside the glass tube remains stable with a strong resistance.
- Reduction of Inorganic carbon present in seawater after photocatalytic reaction with TiO_2.
- Reduction of IC was slightly more in the presence of hydrogen peroxide.
- A significate reduction of IC was obtained in suspension method with the addition of hydrogen peroxide.

V. ACKNOWLEDGMENT

The authors would like to acknowledge the financial support received from The Research Council, Oman through grant number 83 (ORG/EI/12/003). The authors also wish to thank Ms. Shamsa Al Saadi for her support in the laboratory and Mr. Salim for his help in fabricating the experimental set-up in CCE's Workshop and finally Mr. Adil Azjoon from SQU Glass Glowing Workshop for sizing of glass tubes.

REFERENCE

[1]. Oman Power and Water Procurement Company (OPWP) 7-Year Statement (2014-2020).
[2]. Z. Meng, and Z. Juan, "*Wastewater Treatment by Photocatalytic Oxidization of Nano-ZnO*", *Global Environmental Policy*, *Japan*, No.12, p. 1-9, April, 2008.
[3]. Sarmad Ismail, "*Disinfection of wastewater using TiO_2 semiconductor photochemistry"*, Tampere University of Applied Sciences, 2013.
[4]. Radwan A.Al Rasheed, *Water Treatment by Heterogeneous Photocatalysis an Overview*, Saline Water Desalination Research Institute and Saline Water Conversion Corporation (SWCC), Saudi Arabia.
[5]. N. B. Mok, "*Photocatalytic Degradation of oily Wastewater: Effect of Catalyst Concentration Load, Irradiation Time and Temperature*", BSc thesis, Faculty of Chemical & Natural Resources Engineering, University Malaysia Pahang, 2009.
[6]. Bahnemann, D., Bockelmann, D. & Goslich, R. Mechanistic *"Studies of water detoxification in illuminated TiO2 suspensions"*, Sol. Energy Mater., 1991, 24, 564–583.
[7]. Melchor Gonzalez-Davila, J. Magdalena Santana-Casian, and Frank J. Millero, "*Oxidation of iron (II) nanomolar with H_2O_2 in seawater"*, Rosenstiel School of Marine and Atmospheric Science, University of Miami,, Geochimica et Cosmochimica Acta, Vol. 69, No. 1, pp. 83-93, 2005.
[8]. D. Rubio a ,b, E. Nebot b, J.F. Casanueva c, C. Pulgarin a, "*Comparative effect of simulated solar light, UV, UV/H_2O_2 and photo-Fenton treatment (UV-Vis/ H_2O_2 /Fe^{2+}, $^{3+}$) in the Escherichia coli inactivation in artificial seawater"*, Water Research 47 (2013) 6367 6379.
[9]. Holm, E.R., Stamper, D.M., Brizzolara, R.A., Barnes, L., Deamer, N.N., Burkholder, J.A., "*Sonication of bacteria, phytoplankton and zooplankton: application to treatment of ballast water"*, Marine Pollution Bulletin 56, 1201-1208.
[10]. De la Cruz, N., Gimenez, J., Esplugas, S., Grandjean, D., de Alencastro, L.F.,Pulgarin,C., :*Degradation of 32 emergent contaminants by UV and neutral photo-Fenton in domestic wastewater effluent previously treated by activated sludge*" Water Research 46, 1947 1957.
[11]. Elisabetta Petrucci, Daniele Montanaro, Luca Di Palma, "*A Feasibility Study of Hydrogen Peroxide Electrogeneration in Seawater for Environmental Remediation"*, The Italian Association of Chemical Engineering. ISBN 978-88-95608-19-8; ISSN 1974-9791.
[12]. Muriel Sona, Christine Baus, Heinz-Jürgen Brauch, *"UV Irradiation versus combined UV / Hydrogen Peroxide and UV / Ozone Treatment for the Removal of Persistent Organic Pollutants from Water"*, International Conference Ozone and UV, April 3rd 2006.
[13]. Melchor Gonzalez-Davila, J. Magdalena Santana-Casian, and Frank J. Millero, "*Oxidation of iron (II) nanomolar with H_2O_2 in seawater"*, Rosenstiel School of Marine and Atmospheric Science, University of Miami,, Geochimica et Cosmochimica Acta, Vol. 69, No. 1, pp. 83-93, 2005.
[14]. R. Thiruvenkatachari, S. Vigneswaran, Il Shik Moon, "*A Review on UV/TiO2 Photocatalytic Oxidation Process*", Korean j. chem. eng., 25(1), 64-72 2008, vol. 25, p. 64-72, 2008.
[15]. New Technology Demonstration Program, Parabolic-Trough Solar Water Heating. [Online] available: http://smartenergy.arch.uiuc.edu/pdf/Archive/ParabolicTroughSOlarWaterHeater.pdf