

# Studies on the Effect of TiO<sub>2</sub> Nano Photocatalysis in the Pretreatment of Seawater Reverse Osmosis Desalination

Hasna Al Jabri and S. Feroz

**Abstract**—Sultanate of Oman is experiencing rapid increase in water demand due industrialization and population growth. Desalination contributes for about 35% of water demand in Oman and almost all desalination plants are based on conventional energy source. Utilization of solar energy in desalination is good option due its abundance availability throughout the year in Sultanate of Oman. In this paper, the effect of titanium dioxide (TiO<sub>2</sub>) nano photocatalysis for the pretreatment step of reverse osmosis desalination has been studied. A tubular photo catalytic reactor was operated with TiO<sub>2</sub> thin film coating mode as well as in suspension mode in the presence of sun light. The effect of various parameters viz., Total Organic Carbon (TOC), Dissolved Oxygen (DO), Total Dissolved Solids (TDS), pH, and Salinity were studied.

**Index Terms**—Nano photocatalysis, TiO<sub>2</sub>, seawater treatment, solar desalination.

## I. INTRODUCTION

Oman and most of the countries in MENA region are having high potentials of utilizing sunlight in many processes including reverse osmosis desalination [1]. The reverse osmosis (RO) membrane is very sensitive to contaminations present in feed water which makes the pre-treatment step very important to ensure maximum efficiency of the RO process. There is scope to implement photo catalysis as a pre-treatment step in RO process. Photo catalytic reaction is relatively lower in cost as it only needs photons/light, catalyst, and air for the reaction to take place. Nano-scale photocatalyst has more photocatalytic activity than the normal scale catalyst due its larger surface area for contacting between the reactants and it's having a smaller size will reduce the time needed for the carrier diffusing out of the photocatalyst pours to the photocatalyst surface [2].

Using a concentrated light system that reflect the solar light onto the photocatalytic reactor by the use of a reflecting surface is more preferred because it requires smaller reactor volume, it operates at a higher flow rate, better mass transfer rates, and it can be even operated under cloudy conditions [2].

Photocatalyst in a form of a powder suspended in water can be used for water purification purpose. The powder can either coated on the reactor walls, surfaces of the reactor packing, outer surfaces of some exposure lamps or placed inside the reactors in the form of suspension. In case of suspension, an additional operation for solid-liquid

separation of the two phases will be required to remove the catalyst powder from water [3].

## II. REACTION MACHANISM

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 band to the conduction band resulting in the formation of a positive hole (p<sup>+</sup>) in the valance band and an electron (e<sup>-</sup>) in the conduction band.

The positive hole can oxidize the pollutant directly or oxidize water to form (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 [4].

The reaction below explains the mechanism: [4]

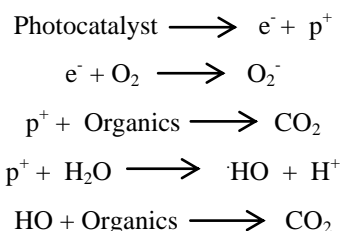


Photo catalytic reaction breaks down the pollutant molecules without any residue thereby eliminates the need of the removing sludge to landfill. The other advantage is that the catalyst lasts for long time and there is no need for adding chemicals in the process, which makes the operation simple and economical.

The process also increases the water production as the contaminant is attractive to the surface of the catalyst which will allow the process to work even at very low concentrations. Coated reactor system has the advantage of having a continuous process without the need of a separation/filtration step. Its disadvantage is its low efficiency caused by low light utilization because of immobilized photocatalyst which covers the reactor and a smaller surface area of the catalyst is utilized. On the other hand, photocatalyst in suspension is having a higher photocatalytic activity but it requires a separation step which is expensive [4]-[6]. The use of TiO<sub>2</sub> in suspension method increases the organic degradation efficiency by at least a factor of 10 when compared to using TiO<sub>2</sub> thin film method [5].

As shown in Fig. 1, a parabolic shaped light reflecting system is used to increase the transmission of sunlight to the photocatalysis either coated in the tubular reactor or in

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Hasna Al Jabri is with Caledonian Center for Creativity and Innovation, Caledonian College of Engineering, Sultanate of Oman (e-mail: h.k.jabri@gmail.com).

suspension [5].

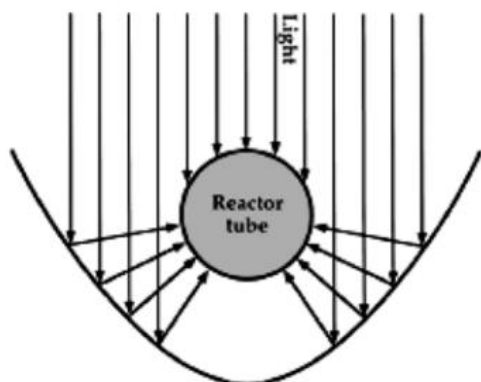


Fig. 1. A parabolic shaped light reflecting [5].

### III. TITANIUM DIOXIDE PHOTOCATALYSIS

Nano structured  $\text{TiO}_2$  photocatalyst has three crystal forms: anatase, rutile, and brookite. Anatase has a higher photocatalytic activity because the position of oxygen ions on the exposed crystal surface of anatase shows a triangular arrangement, allowing effective absorption of organics while, the position of titanium ions creates a favorable reaction condition with the absorbed organics. On the other hand, rutile phase has a wider pore size distribution which increases the photocatalytic activity. To achieve maximum photocatalytic efficiency the photocatalyst can be made of a mixture of anatase and rutile. P25 which consist of 70% anatase and 30% rutile was found to be having higher efficiency and it doesn't undergo photo-corrosion [5].

Titanium dioxide is mostly used because of its high photocatalytic activity, large stability to sunlight illumination, cheap price, resistance to chemicals, insoluble in water and it is nontoxic [7].

### IV. METHODOLOGY

#### A. Thin Film Method

##### 1) Material

Seawater was collected 1 km from Al Athibah Beach, Oman. Aeroxide P25 was obtained from Evonik Industries, and PVA from Oman Textile Mills Company L.L.C.

##### 2) Preparation of coating solutions

Coating Solution (1): 5 grams of PVA and 2.2 grams of  $\text{TiO}_2$  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.

##### 3) Coating of glass tube

Glass tube is coated with  $\text{TiO}_2$  thin film by passing the dispersed  $\text{TiO}_2$  in the inner surface of the tube. The tube is allowed to dry and then calcinated at  $400^\circ\text{C}$  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 photocatalysis is activated by sunlight and oxidation reaction takes places under UV index of 9 to 11.

The tubular photo reactor is 60cm long with an outer

diameter of 2 cm. The system tank holds 1.5 litter of seawater which is continuously re-circulated through the tubular reactor at constant flow rate with 170 rpm.

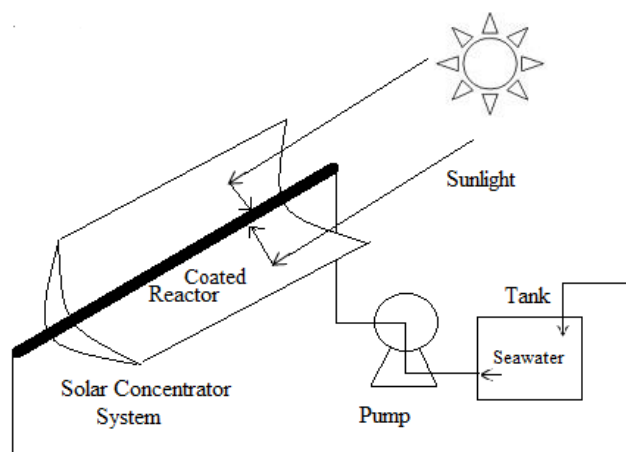


Fig. 2. Schematic of the thin film experimental set-up.

#### B. Suspension

##### 1) Material

Seawater was collected 1 km from Al Seeb Beach, Aeroxide P25 was obtained from Evonik Industries.

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 decompose organic matter into smaller compound and low poisonousness inorganic matter in the contaminated seawater at a UV index of 9 to 11.

The tubular photo reactor is 60cm long with an outer diameter of 2 cm. The system tank holds 1.5 litter of seawater along with 3 gram of the photo catalyst which is continuously re-circulated through the tubular reactor at constant flow rate with 170 rpm.

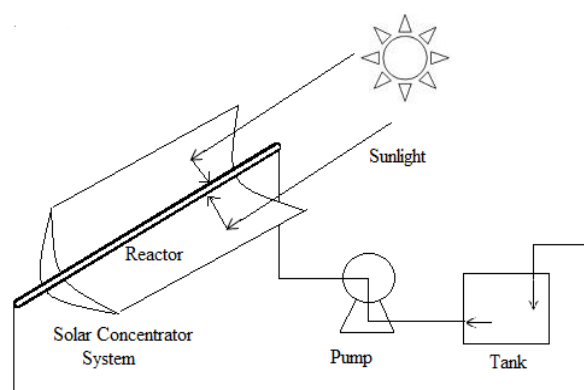


Fig. 3. Schematic of the experimental set-up.

### V. RESULT AND DISCUSSION

Sunlight was used because it's free, natural, sustainable source of energy and the concentrating system was used to increase the degradation rate by increasing the photonic efficiency for the desired photo catalytic reaction. Polyvinyl alcohol was used as a solution thickener and a binder to enhance the chemical bonding of  $\text{TiO}_2$  to the inner surface of

the glass tube. The coated layer of  $\text{TiO}_2$  was stable and strongly sticks on the inner surface of the tube after calcination.

The Table I shows the seawater analysis before and after the treatment with coated tubular photo reactor. It was found that the TDS and pH slightly decreases after catalytic reaction with  $\text{TiO}_2$  but more importantly there is slightly increase in TOC as well as Total Carbon (TC) as shown in Table II. Inorganic carbon seems to be marginally decreased.

TABLE I: SEAWATER ANALYSIS WITH COATED TUBULAR PHOTOREACTOR

	Raw Seawater	After Reaction
pH	7.99	7.85
TOC (ppm)	4.039	5.300
DO (mg/L)	0.11	0.11
TDS (ppt)	50.47	50.33
Salinity (ppt)	74.07	74.09

TABLE II: TOTAL ORGANIC CARBON VARIATIONS WITH TIME IN COATED TUBULAR REACTOR

Time (min)	0 min	15 min	45 min	75 min	135 min	195 min	285 min
UV Index	0	9	10	10	11	11	11
TOC	4.03	3.95	4.36	4.36	4.71	5.10	5.30
TC	30.25	30.34	30.58	30.50	30.63	31.35	31.91
IC	26.21	26.39	26.22	26.14	25.92	26.24	26.61

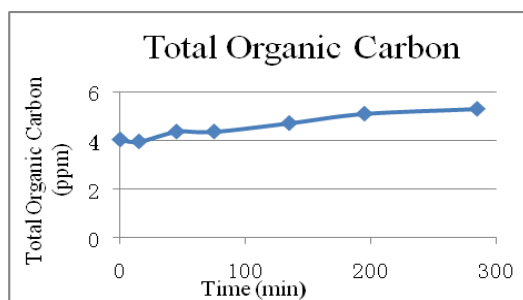


Fig. 4. Variation in Total Organic Carbon during solar photo catalysis.

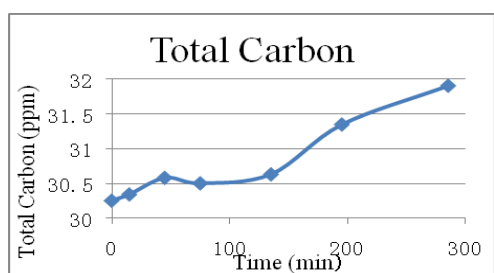


Fig. 5. Variation in Organic Carbon during solar photo catalysis.

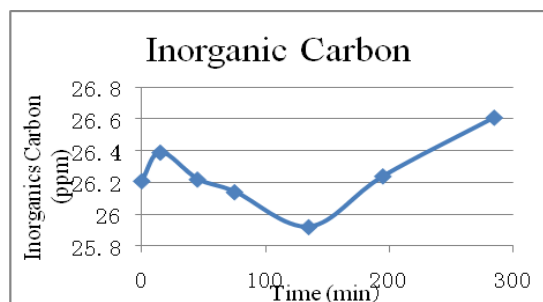


Fig. 6. Variation in Inorganic Carbon during solar photo catalysis.

Fig. 4 and Fig. 5 show the trend of increase in the total organic carbon and total carbon value in thin film coated

method. The possible reasons for increase in organic carbon might be due to presence of polyvinyl chloride in the thin film or formation of organic by-products. Fig. 6 shows the trend of total inorganic carbon which is gradually increasing from an initial dip. The composition of seawater is complex in nature which inferences with photo catalysis process. It seems to be there is a formation of by-product which results in the increase total organic carbon.

Table III shows the seawater analysis with suspended photocatalysis. It was observed that TDS and pH slightly decreases after photocatalytic reactions with  $\text{TiO}_2$  but the salinity increases to some extent.

TABLE III: SEAWATER ANALYSIS WITH SUSPENDED PHOTOCATALYSIS

	Raw Seawater	After Reaction
pH	8.10	7.90
TOC (ppm)	4.061	42.08
DO (mg/L)	0.08	0.09
TDS (ppt)	50.51	53.20
Salinity (ppt)	73.42	77.91

Table IV shows the total organic carbon variations with time in suspended photocatalysis. It was observed that the increase in suspension is much higher than the thin film method which is obvious due to availability of more catalytic surface area for the photo catalysis reaction.

TABLE IV: TOTAL ORGANIC CARBON VARIATIONS WITH TIME IN SUSPENSION PHOTOCATALYSIS

Time (min)	0 min	15 min	45 min	75 min	135 min	195 min	285 min
UV Index	0	9	10	10	11	11	11
TOC	4.061	28.14	36.92	38.96	46.42	35.88	42.08
TC	28.34	51.48	58.85	60.62	67.61	52.26	63.90
IC	24.27	23.33	21.93	21.66	21.19	20.38	21.82

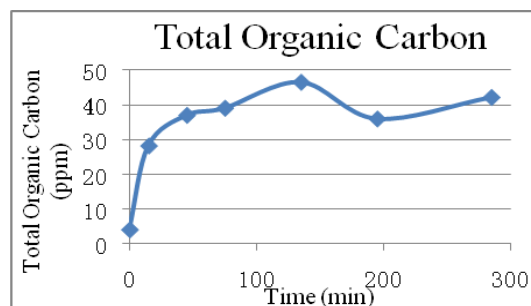


Fig. 7. Variation in Total Organic Carbon during solar photo catalysis.

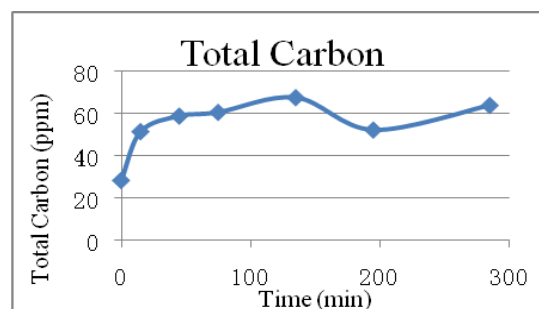


Fig. 8. Variation in Organic Carbon during solar photo catalysis.

Fig. 7 and Fig. 8 showed that there is a significant increase in the total organic carbon (TOC) as well as total carbon up to

150 min and thereby remains almost stable. This clearly follows the same trend of thin film coated reaction mechanism leading to the formation of organic by-products. Fig. 9 shows the decreasing trend of total inorganic carbon, which indicates the degradation of inorganic compounds present in the seawater.

Fig. 8 shows the formation of organic carbon after the reaction and the decrease in the inorganics in Fig. 9.

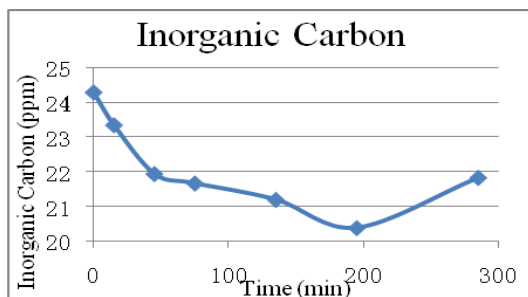


Fig. 9. Variation in Inorganic Carbon during solar photo catalysis.

## VI. CONCLUSION

Experimental investigations were carried out in an immobilized thin film Nano photo catalyst as well as suspension mode. The degradation of organic and inorganic compounds present in seawater was studied. The following inferences were drawn:

- Nano  $\text{TiO}_2$  photo catalyst thin film inside the glass tube remains stable.
- The total organic carbon and total carbon seems to be increasing in both catalyst thin film as well as in suspension mode. This may be due to formation of organic by-products during the photo catalytic reaction. The composition of seawater is complex in nature which inferences with photo catalysis process
- There is appreciable decrease in total inorganic carbon, which indicates the degradation of inorganic compounds present in seawater.
- The increase in TOC and TC seems to be high in suspension mode than in thin film reaction and the same trend was observed in case of decrease in total inorganic carbon. This is obvious because of more surface area availability in catalyst suspension mode.
- Since the chemical composition of seawater contains organics and inorganics with a wide variety of compounds, the formation of organics can occur in the reaction as a by-product or breakdown of organic matter in smaller molecules which might increase the total organic carbon (TOC) value.

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**Hasna Al Jabri** was born in Muscat, Oman on 19th September 1990. She has earned her BSc degree in chemical engineering in Caledonian College of Engineering, Oman in 2012. She had attended a two months training program in Oman Oil Refineries and Petrochemical Industries Company (ORPIC) from 28th to 24th August 2011 and a one week introduction of laboratory work at Petroleum Development of Oman (PDO) Mina Al Fahal (MAF) laboratory in Feb. 2011. She has also attended a five weeks training program on Nano Photocatalysis in Research lab, Leibniz University of Hannover, Germany in 2013. She is presently an MSc process engineering student at Caledonian College of Engineering, Oman and working on a research project on the application of nano photocatalysis in the Pretreatment of Seawater Reverse Osmosis Desalination that is sponsored by The Research Council.



**Shaik Feroz** is presently working as a research professor and the head (CCCCI) in Caledonian College of Engineering, Oman. He has obtained his doctorate in the field of chemical engineering from Andhra University, India. He has worked with various organizations for about 19 years and research experience. Professor Feroz has 76 publications to his credit in journals and conferences of international repute. He is one of the editors of the recent published text book by CRC press on wastewater treatment: Advanced processes and technologies. He is a life member of Indian Institute of Chemical Engineers and Institution of Engineers, India. He is also a member of Oman Society of Engineers and Environmental Society of Oman. Professor Feroz is associated as the principal investigator/co-investigator to a number of research projects and also involved as "Technology transfer agent" by Innovation Research Center, Sultanate of Oman. His has a significant contribution as a peer reviewer for various reputed international journals, as an editor of Caledonian Journal of Engineering and an advisory editor for International Journal of Pharma and BioScience. Professor Feroz developed research links with various international research centers and his research interest includes advance separation process, solar Nano-photo catalysis, reaction & environmental engineering.