

# The Effect of Combining TiO<sub>2</sub> and ZnO in the Pretreatment of Seawater Reverse Osmosis Process

Hasna Al Jabri and S. Feroz

**Abstract**—In Sultanate of Oman, the water demand is continuously increasing due to rapid industrialisation and population growth. Due to low average rainfall (100mm) and decline in ground water level, the demand is exceeding far by the supply. A number of desalination plants are coming up in Sultanate to counter the water crisis. Almost all the desalination plants are based on conventional energy sources and there is no large scale solar based desalination plant in Sultanate. The present research study is an attempt to develop a pre-treatment system using solar photo catalysis technique. A laboratory scale experimental set-up was put up at Caledonian college of engineering to study the effect of different Nano photo catalysts in degrading the organic pollutants in seawater. The sea water is continuously re-circulated in the presence of solar energy with Nano photo catalyst in suspension and thin film mode. The performance of the system was tested based on the various parameters, TOC, DO, TDS, pH, and Salinity.

**Index Terms**—Desalination, TiO<sub>2</sub>, total organic carbon, nano photocatalysis, solar, seawater, ZnO.

## I. INTRODUCTION

Oman lies on the Sunbelt region which is having high potentials in producing more energy as there is high sun radiation in MENA region. Utilization of solar energy in the pretreatment of RO system can be used to limit the use of chemicals which is expensive and reduce the environmental impact of these chemicals. As a result, photocatalyst can be used as it is relatively lower in cost as it only needs photons/light, catalyst, and air for the reaction to take place [1].

Desalination is a separation process used to reduce the dissolved salt content and some other chemicals of saline water to a usable level. The reverse osmosis desalination process consist of a membrane that separate the seawater into two streams; one with low concentration of dissolved salt which is the fresh water and the other stream is with the high concentration of salt and it's called the brine. [2]

The reverse osmosis membrane is very sensitive to contaminations in the coming feed water which makes the pre-treatment step very important to insure maximum efficiency of the RO process is achieved. After the feed water enters the filters, feed water enters a tubular reactor where it interacts with the photocatalysts which can be either coated on the base of the tube wall or in suspension with the seawater flowing into the reactor.

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## II. REACTION MECHANISM

As shown in Fig. 1, 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 (·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].

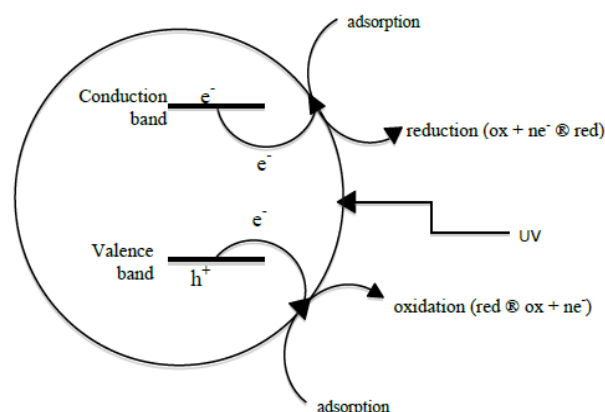
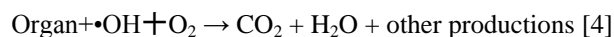
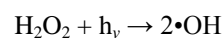
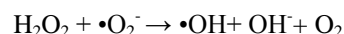
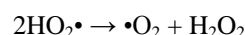
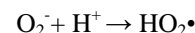
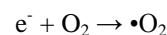
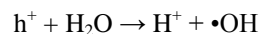
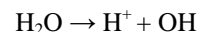
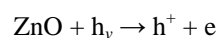


Fig. 1. Illustration of the principles of photocatalysis showing the energy band gap diagram of a TiO<sub>2</sub> spherical particle [3].

The reactions bellow explains the photocatalytic reaction taking place with ZnO:



Semiconductors Photocatalysts are used to oxidize contaminated seawater. It can decompose organic matter into smaller compound and low poisonousness inorganic matter. The reaction takes place between dissolved oxygen and water

and produce hydroxyls with high chemical activity which can oxidize the organic pollutants into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  [4].

### III. NANO PHOTOCATALYSIS

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 [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]-[8].

Although ZnO are having higher activity of a bandgap energy of 3.436 eV compared to  $\text{TiO}_2$  with a bandgap energy of 3.03 eV in Table I,  $\text{TiO}_2$  is more stable in aqueous media and that's why is it mostly used in water purification processes [7].

TABLE I: BANDGAP ENERGIES FOR SOME COMMON SEMICONDUCTOR MATERIALS AT 0 K [7]

Semiconductors	Bandgap energy (eV)	Semiconductors	Bandgap energy (eV)
Diamond	5.4	$\text{WO}_3$	2.76
CdS	2.42	Si	1.17
ZnS	3.6	Ge	0.744
ZnO	3.436	$\text{Fe}_2\text{O}_3$	2.3
$\text{TiO}_2$	3.03	PbS	0.286
CdS	2.582	PbSe	0.165
$\text{SnO}_2$	3.54	$\text{ZrO}_2$	3.87
CdSe	1.7	$\text{Cu}_2\text{O}$	2.172

### IV. PHOTOCATALYSIS IN DESALINATION

Using a concentrated light system that reflect the solar light onto the photocatalytic reactor by 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 [7].

Through experiments, it was observed that metal oxides along with sulphides and dyes are effective in increasing the production rate of desalted water. But metal oxides are more effective among them [9].

It was found from different studies that photocatalysis improve the solar desalination process of conventional basin solar still as it improves the water quality and increase the production rate of desalinated water. It was also reported from water analysis that solar desalination by the use of

photocatalysis decreases of pH level, conductivity, TDS, total alkalinity, chloride, sulphate, total hardness, calcium, magnesium and nitrate [9]-[11].

### V. METHODOLOGY

#### A. Thin Film Method

##### 1) Material

Seawater was collected 1 km from Al Athibah Beach, Oman. Aeroxide P25 was obtained from Evonik Industries, ZnO from Mknano, and Polyvinyl alcohol A 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.

Coating Solution (2): 5 grams of PVA and 2.2 grams of ZnO were dissolved in 100ml of water and left for stirring overnight.

##### 3) Coating of tubes

The inner surface of the tube was coated layer by layer with  $\text{TiO}_2$  and then ZnO. The tubes are then allowed to dry then calcined at 400 °C for about 1 hour.

##### 4) Reactor system configuration and operation

Seawater was collected and fed to the system tank. Using a peristaltic pump, seawater is pumped at a rate of 170 rpm to the tubular reactor where the photocatalysis are activated by sunlight and oxidation reaction takes places which decompose organic matter into smaller compound and low poisonousness inorganic matter in contaminated seawater.

The tubular photo reactor is 1 m long, 1.8 cm inner diameter and 2 cm outer diameter and the tank is containing 1.5 litter of water and operated at a UV-index from 9 to 11.

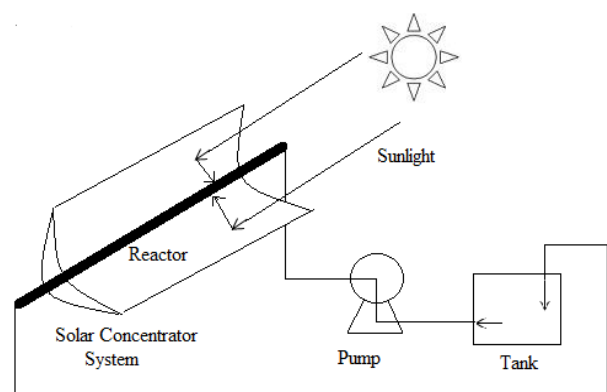


Fig. 2. Schematic of the experimental set-up.

#### B. Suspension Method

1.5 grams of  $\text{TiO}_2$  and 1.5 gram of ZnO were mixed with seawater in the tank. Using a peristaltic pump, seawater along with the photocatalysis is pumped a rate of 170 rpm to the tubular reactor where the photocatalytic reaction takes place as shown in Fig. 2. The tubular photo reactor is 1 m long, 1.8 cm inner diameter and 2 cm outer diameter and the tank is containing 1.5 litter of water and operated at a UV-index

from 8 to 11.

## VI. RESULT AND DISCUSSION

0.5 grams of photocatalyst in 1 liter of seawater were mixed in a batch-suspension process to study the effect of different photocatalysis and their combination. Table II shows the result after 1 hour of photocatalytic reaction under UV index of 10.

TABLE II: TOTAL ORGANIC CARBON IN BATCH-SUSPENSION PROCESS

	Total Organic Carbon	Total Carbon	Inorganic Carbon
Seawater	3.438	26.64	23.20
TiO <sub>2</sub>	6.193	29.14	22.95
ZnO	4.669	28.00	23.33
TiO <sub>2</sub> + ZnO	4.957	27.57	22.61

According to the result shown in Table II, both TiO<sub>2</sub> and ZnO increases the total organic value but the use of TiO<sub>2</sub> produces more organics and inorganics compared to ZnO. The combination of both TiO<sub>2</sub> and ZnO gives a value in between the two.

Table III shows various seawater parameters before and after treatment with photocatalysis. It was found that with the use of ZnO, TDS and salinity value increases with time and pH slightly decrease.

TABLE III: SEAWATER ANALYSIS WITH AND WITHOUT PHOTOCATALYSIS

	Raw Seawater	Treated Seawater With Coated Reactor	Treated Seawater With Catalyst in Suspension
pH	8.05	8.00	7.97
DO (mg/L)	0.11	0.11	0.11
TDS (ppt)	50.31	51.96	57.75
Salinity (ppt)	73.89	74.66	74.95

Table IV shows the total organic carbon variations with time in suspension photocatalysis. There is a slight decrease in pH value and a slight increase in salinity after the photocatalytic reaction.

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

	0 hour	1 hour	2 hour	3 hour	4 hour
UV Index	0	9	10	11	11
TOC	4.891	30.36	35.75	36.75	36.95
TC	26.71	54.13	59.09	60.86	67.68
IC	21.81	23.77	23.34	23.92	25.44

It was found from the experiments that the photocatalytic reactions increase the total organic carbon value with time as illustrated in Fig. 3, the possible reasons might be the reaction oxidize pollutants and produce CO<sub>2</sub> which reacts with other components in seawater to form organics that increases total organic carbon value.

CO<sub>2</sub> is considered inorganic and it can be seen from Fig. 4 that inorganics are produced and consumed. It can then react with other components to produce organics as shown in Fig. 5. The variation occurring in the results found might be because ZnO is not very stable in aqueous media compared to TiO<sub>2</sub> stability.

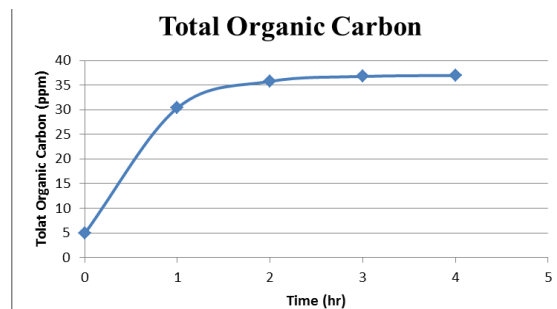


Fig. 3. Variation in total organic carbon during solar photo catalysis in suspension.

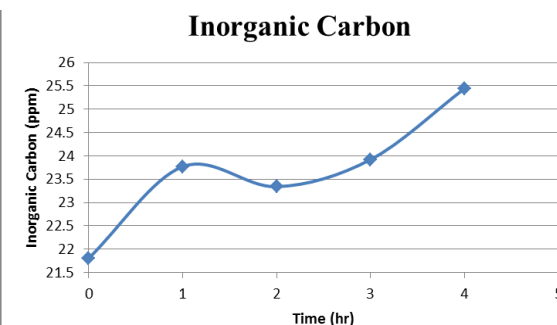


Fig. 4. Variation in inorganics carbon during solar photo catalysis in suspension.

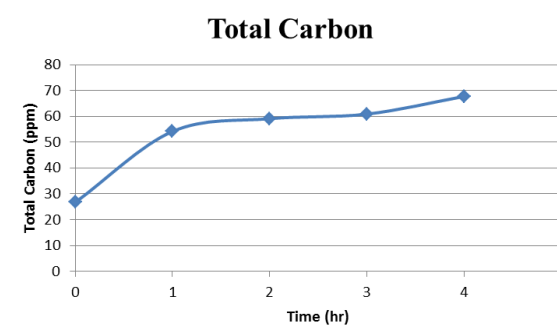


Fig. 5. Variation in total carbon during solar photo catalysis in suspension.

TABLE V: TOTAL ORGANIC CARBON VARIATIONS WITH TIME IN THIN FILM METHOD

	0 hour	1 hour	2 hour	3 hour	4 hour
UV Index	0	9	10	11	11
TOC	4.96	28.63	23.19	19.67	16.54
TC	28.4	52.12	46.77	43.21	40.00
IC	23.44	23.49	23.58	23.54	23.46

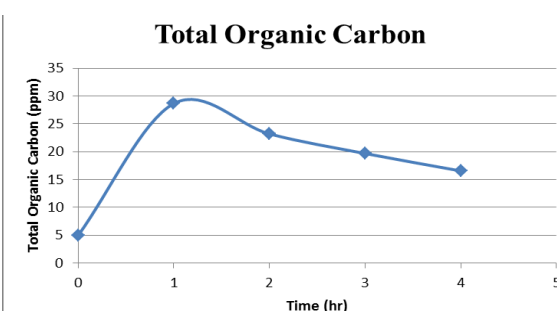


Fig. 6. Variation in total organic carbon during solar photo catalysis in thin film method.

Polyvinyl alcohol was used as a solution thickener and a binder to enhance the chemical bonding of TiO<sub>2</sub> and ZnO to the inner surface of the glass tube. The coated layers of TiO<sub>2</sub> and ZnO were stable, very resistance and strongly stick on the inner surface of the tube after calcination.

Table V shows the total organic carbon variations with time in thin film method. It was found that in thin film method the Total Organic Carbon value also increases but it is much less than the suspension method as it is also shown in Fig. 6.

In the coated tubular reactor, the inorganic carbon slightly increases then decreases as illustrated in Fig. 7. Where the organic carbon in Fig. 8 first significantly increases then decreases with time.

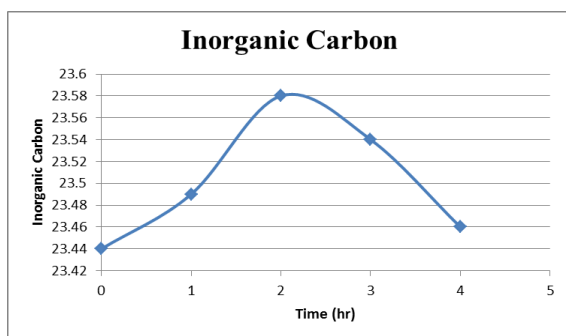


Fig. 7. Variation in total organic carbon during solar photo catalysis in thin film method.

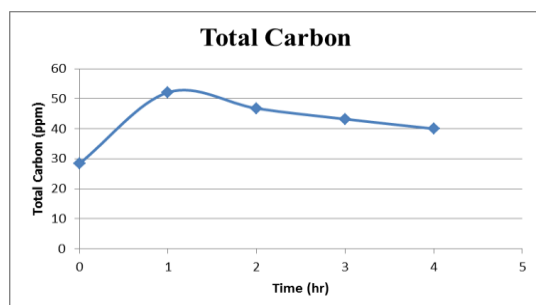


Fig. 8. Variation in total organic carbon during solar photo catalysis in thin film method.

## VII. CONCLUSION

Oman is having high sunlight intensity which makes the utilization of solar photocatalysis an environmentally and sustainable process.

It was found in this study that the concentration of photocatalyst, illumination time, and intensity of sunlight illumination affects the photocatalytic reaction.

According to the results, the total organic carbon (TOC) increases after photocatalytic reaction of  $\text{TiO}_2$  and  $\text{ZnO}$  with seawater.

Since seawater is a complicated mixture that contains various organics and inorganics components which might result in the formation of organic by products which might cause the increase in the total organic carbon.

The increase in TOC value in suspension was much higher than in the thin film method which is because of the photocatalyst concentration and surface area exposed to seawater is higher.

## ACKNOWLEDGMENT

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