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# Application of Solar Nano Photocatalysis in Treatment of Seawater

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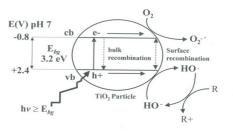
Abstract— Experimental investigations were carried out in a batch reactor system for the treatment of pollutants in seawater by solar nano photo catalysis. The degradation of pollutants was evaluated in terms of percentage decrease in Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS) and pH. Nano titanium dioxide (TiO<sub>2</sub>) particles were used as photo catalyst with and without the presence of poly amide (PA), to study the effect of degradation of pollutants present in the seawater.

Keywords— Desalination, Photocatalysis, Solar Energy, Sea water, Sultanate of Oman Introduction

#### I INTRODUCTION

Photocatalysis has an extensive application in water treatment. It can be utilized for the decomposition of organic and inorganic compounds, removal of trace metals as well as for the destruction of viruses and bacteria. It can be used to decompose natural organic matter (Humic and Felvic substances), which impact the environment and industries in many ways especially reverse osmosis desalination process. Nano- photo catalysts are more effective than conventional because they yield a tremendous surface area-to-volume ratio and posses' uniform and controlled particle size, composition and structure. Sultanate of Oman is considered among countries having highest solar energy density in the world and can theoretically cover all energy demand of Oman and it is in the world's arid belt with limited ground water resources. The per capita demand for fresh water is high (~500 m<sup>3</sup>, extreme stress) and water demand for various purposes: domestic, agriculture, industry has increased dramatically along with the improvement and rising living standards. Oman depends on ground water and its limited rainfall (annual average 100mm) for around 65% of its water supplies and the demand for water continues to rise, with desalinated water making up the remaining 35%. Almost all desalination plants run on conventional energy source in Oman but the policy makers are now encouraging to implement renewable energy based desalination plants. Photo catalysis is an advanced oxidation process widely used for the removal of trace pollutants present in water streams and TiO2 is the most commonly used semiconducting photo catalyst since it is highly photoactive, photo stable, biologically and chemically inert, nontoxic and relatively inexpensive. Polyamide (PA) material resists the Mahad Baawain<sup>2</sup> <sup>2</sup>College of Engineering, Sultan Qaboos University, Sultanate of Oman e-mail: msab@squ.edu.om

bacterial growth on its surface [1] and hence a combination of  $TiO_2$  and PA is considered in the present research work to study the effect of degradation of pollutants present in seawater with an aim to further develop solar nano photo catalysis treatment system for pre and post treatment in small scale reverse osmosis desalination process.  $TiO_2$  acts as a semiconductor, which turns to a high-energy state by receiving specific wavelengths of UV light energy, thus releasing the electrons from its illuminated surface. If the energy received at this stage is high enough, electrons that were initially located in the so-called 'valance band' all jump to the 'conduction band' as shown in the Figure 1[2]



R = organic pollutant Fig 1: Solar Photo Catalysis Mechanism

 $TiO_2 + hv \rightarrow electron(cb) + h^+(vb)$  (1) Thus, the energy that makes the electrons migrate is provided by light, and an electron hole will be generated on the  $TiO_2$ surface. The electron hole in the valance band (h<sup>+</sup>vb) will react with the water (H<sub>2</sub>O) or the ions of hydroxide (OH<sup>-</sup>) to produce hydroxyl radicals (OH<sup>-</sup>).

$$h^{+}vb + OH^{-} \rightarrow OH^{-}$$
(2)  
 
$$h^{+}vb + H_{2}O \rightarrow OH^{-} + H^{+}$$
(3)

In equations 1 to 3,  $h^+vb$  represents the 'valance-band' holes, and electron (cb) represents the 'conduction band' electrons. With oxygen acting as an electron acceptor as shown in equation (4), electron trapping prevents the photo-corrosion of the catalyst. Thus, TiO<sub>2</sub> has the property of resistance to photo-catalyst corrosion.

$$electron(cb) + O_2 \rightarrow O_2^-$$
 (4)

where 
$$O_2^-$$
 represents the super-oxide ion.  
electron (cb) +  $h^+vb \rightarrow heat$  (5)

The result is that the organic contaminant was destroyed and the hydroxyl radical was terminated by the recombining of the hole and electron that created heat as a product [3-4].

Seawater contains high-molecular weight organic matter (humic substances), suspended solids, bacteria and algae, and volatile halogenated carbons, etc. As these substances are traditionally considered hazardous for the membrane in reverse osmosis process, they should be removed from the feed water before they enter the membrane systems. The organic acids (humic substances) build adsorption layers on the membrane surface that reduce membrane flux and rejection [5-6]. Solar energy is abundant in Middle East countries like Oman and it can be effectively used in reverse osmosis pre-treatment processes. An ultraviolet driven photocatalytic pre-treatment can be employed for the degradation of humic substances (higher molecular organics) & microorganisms present in the feed water. The energy generated from the photo catalytic reaction breaks down the humic substances and also kills microorganisms, thereby eliminating the primary source for membrane fouling. An attempt is being made through the present research work on solar energy driven nano-photocatalysis as an ideal technology to be implemented in Oman small scale desalination plants particularly on pre and post treatment processes. In this paper, the research outcomes based on experimental batch studies on degradation of pollutants in raw seawater taken from Oman coast was presented.

#### **II MATERIALS AND METHODS**

Seawater was collected 1 km from Al Qantab Beach, Sultanate of Oman; Aeroxide P25  $TiO_2$  was obtained from Evonik Industries, Germany and PA from Carl Roth GmbH Company, Germany. Shimadzu, Japan make saline water TOC analyzer was used for analysis of TOC; COD was analysed by making use of Chemetrics Analyzer; TDS, pH and conductivity were analyzed by Eutech make water analysis kit.

A batch reactor of capacity 0.002m<sup>3</sup> was utilized in the experimental studies and a variomagmagnetic plate was used to stir the reactor contents as shown in Figure2. All the photoreaction experiments were performed under ambient conditions at Caledonian College of Engineering campus, located in Sultanate of Oman from 10.00AM to 3 PM. In most parts of Oman, clear sunny weather is experienced 250 to 300 days a year, this makes Oman a suitable site for the solar-based treatment processes. The solar radiation intensity was 650 W/m<sup>2</sup> during maximum experimental runs.

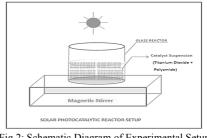


Fig 2: Schematic Diagram of Experimental Setup

### **III RESULTS AND DISCUSSIONS**

The reactants were charged into the batch reactor, well mixed, and are left to react for a certain period (Fig 2). Samples collected at every hour and the parameters TOC, COD, TDS and pH were analyzed. The percentage decrease in the parameters was evaluated and data was plotted. In the first set of experiments,  $TiO_2$  catalyst dosage was varied from 1g to 5g in  $0.002m^3$  of seawater and in second set of experiments the dosage of PA was varied from 0.5g to 1.5g with 5g  $TiO_2$  in  $0.002m^3$  of seawater.

Fig 3 shows the percentage decrease in TOC at different dosages of  $TiO_2$ . It was observed that there is a sharp decrease in TOC up to 3 hr of reaction time and thereafter it was stable, this may be due to increase in the availability of photonic energy from 10.00 AM to 1 PM. It was also observed that the degradation of pollutants seems to be on higher side at higher dosage of  $TiO_2$ , which may be due to availability of more active sites on photo catalyst. The amount of  $TiO_2$  is directly proportional to the overall photo catalytic reaction rate and a linear dependency holds until certain extent when the reaction rate to aggravate and becomes independent of  $TiO_2$  concentration [7]. A similar trend was observed in the present study as shown in Figure3.

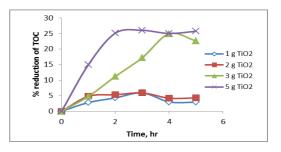


Fig 3: Percentage reduction of TOC at different dosage of TiO<sub>2</sub>

Fig 4 shows the percentage decrease in COD for various dosages of  $TiO_2$ . COD decreases sharply up to 30 min and there after it was stable. COD removal is low at 1 g  $TiO_2$  dosage and appreciable increase at higher dosage. Compare to TOC, the drop in COD is faster in the initial hour of reaction time.

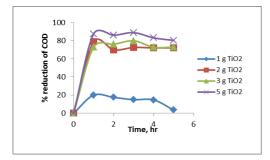


Fig 4: Percentage reduction of COD at different dosage of TiO<sub>2</sub>

Fig 5 shows the percentage reduction in TDS. It was observed that there is a sharp reduction in TDS up to 1 hour and thereafter it was stable. The reduction in TDS seems to be independent of  $TiO_2$  dosage.

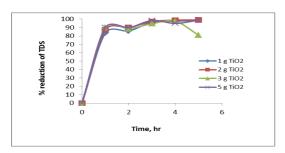


Fig 5: Percentage reduction of TDS at different dosage of TiO<sub>2</sub>

Fig 6 shows the percentage reduction of pH at various dosages of  $TiO_2$ , there is a continues reduction of pH which may be due to formation of multitude intermediate by products that may pose different chemical functional groups and effect the water pH indifferently [7].

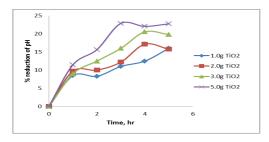


Fig 6: Percentage reduction of pH at different dosage of TiO<sub>2</sub>

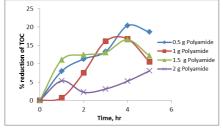


Fig 7: Percentage reduction of TOC at different dosage of Polyamide (5 g TiO<sub>2</sub> fixed)

The percentage reduction in TOC with fixed  $TiO_2$  and varied dosage of polyamide was shown in Figure 8. It was observed that the decrease in TOC was almost linear and found to be higher at lower concentration of polyamide. It was evident that the photo catalysis seems to be hindered by the presence of PA because it reduces the diffusional rate of pollutants on to TiO<sub>2</sub> catalyst surface.

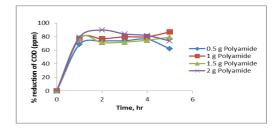


Fig 8: Percentage reduction of COD at different dosage of Polyamide (5 g TiO<sub>2</sub> fixed)

Fig 8 shows the percentage decrease of COD at various dosage of PA. As in the case of  $TiO_2$  alone, in the presence of PA also there is a sharp reduction of COD in the initial hour of reaction time and thereafter it is stable. It was observed that the presence of PA has minimum impact in the reduction of COD.

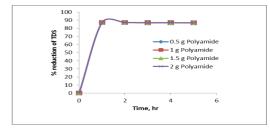


Fig 9: Percentage reduction of TDS at different dosage of Polyamide  $(5 \text{ g TiO}_2 \text{ fixed})$ 

Fig 9 shows the percentage reduction of TDS at various dosages of PA. It was observed that the presence of PA has minimum impact on the reduction of TDS. Figure 10 shows the percentage reduction in pH at various dosages of PA and it was observed that with increase in PA there is an higher decrease in pH.

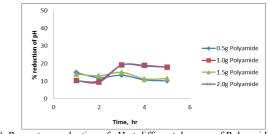


Fig 10: Percentage reduction of pH at different dosages of Polyamide (5 g TiO<sub>2</sub> fixed)

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## Conclusions

The seawater from Oman coastal line was subjected to solar photocatalysis using nano  $TiO_2$  particles with and without the presence of PA. The following conclusions are drawn from the present research study:

- Though there is an inference of chloride ions and scavenging of hydroxyl radicals, still substantial decrease in reduction of pollutants was observed and hence this technique solar photo catalysis can be applied for treatment of seawater.
- The decrease in TOC and COD is higher in the absence of PA, the presence of PA seems to hinder the diffusional rate of pollutants towards photo catalyst surface.
- pH decreases with solar photo catalysis reaction due to formation of intermediates and it was observed the reduction in pH is on higher side at higher dosage of PA.
- TDS reduces sharply in the initial hour of reaction time and there is minimal effect of variation in TiO<sub>2</sub> and PA concentrations on reduction of TDS.

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