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Application of solar nanophotocatalysis in reverse osmosis pretreatment processes

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CHAPTER 3

Application of solar nanophotocatalysis in reverse osmosis pretreatment processes

Shaik Feroz

3.1 INTRODUCTION

The demand for freshwater is growing rapidly and water scarcity is a major issue in many parts of the world, especially in developing countries (Ghaffour et al., 2015; Goosen et al., 2014). The earth is rich in saline water resources; seawater and brackish water together account for up to 97% of the total water available in the world. Efforts are being made to desalinate them and supply freshwater for human needs. However, desalination is an energy-intensive process and meeting the associated energy requirements from declining conventional sources is a major worldwide challenge. There is now rapid development towards linkage of desalination processes with renewable energy sources such as solar and wind. This will not only reduce the burden on conventional energy sources but will also protect the environment through lower emissions (Brand and Würzburg, 2015).

Reverse osmosis (RO) is a major technique employed to produce freshwater (Ghaffour et al., 2015; Goosen et al., 2014). This process, wherein water from a salt solution is forced through a membrane in the opposite direction by the application of pressure, requires pretreatment to remove substances from the feed water that would interfere with the desalting process. Suspended solids and other particles in the feed water must be removed to reduce fouling of the membranes, which lose their performance with time due to such fouling (Al-Rasheed et al., 2003a). One of the major causes for the loss of RO performance are the substances that become deposited on the membrane surface. Examples are silica, oil, clay, iron, sulfur and humic acids, which may be present in the feed water in a very fine or colloidal form. Even the typical five-micron cartridge filters used in the upstream of a RO system may not completely remove these foulants. Furthermore, surface water contains high-molecular weight organic matter (e.g. humic substances), suspended solids, bacteria and algae, and volatile halogenated carbons. As these substances are traditionally considered hazardous for the membrane, they should be removed from the feed water before they enter membrane systems. Organic acids (i.e. humic substances) build adsorption layers on the membrane surface that reduce membrane flux and rejection. A number of laboratory studies have reported that these biofilms consist of about 50% organic matter, of which about 40% will be organic acids (Al-Rasheed et al., 2003a).

Solar energy is abundant in many parts of world, especially in Middle East countries where desalination plays a major role in the supply of freshwater, and it can be effectively used in reverse osmosis pretreatment processes (Ghaffour et al., 2015). An ultraviolet-driven photocatalytic pretreatment can be employed for the degradation of humic substances (higher molecular weight organics) and microorganisms present in the feed water. The energy generated from the photocatalytic reaction breaks down the humic substances and also kills microorganisms, thereby effectively eliminating the primary source for membrane fouling. Ultraviolet (UV) photo-oxidation uses UV light to activate a catalyst to physically decompose the organic matter into non-toxic components. The degradation of organic compounds in the presence of UV light is a too slow a process (reaction rates are low) but may be considered for large-scale industrial applications. To enhance the reaction rates, several catalysts, such as hydrogen peroxide, ozone,
Fe (II) and titanium dioxide, are used in these types of reactions. Titanium dioxide is probably the best choice due to its low cost, low toxicity, resistance to photo-corrosion and catalytic efficiency (Kwak et al., 2001).

Kim et al. (2003) have fabricated hybrid polyamide thin-film composite/titanium dioxide (TiO₂) membranes possessing photocatalytic properties that reduce biofouling and enhance RO performance. Preliminary feasibility studies were carried out as a part of a project (08-AS-002) sponsored by the Middle East Desalination Research Centre (MEDRC). In addition, detailed examinations were carried out as part of a project (ORG/E1/12003/Grant83) sponsored by the Research Council of Oman. The experimental investigations were carried out using solar nanophotocatalysis in a laboratory-scale batch, as well as in a continuous reactor system, to assess the degradation of pollutants present in seawater. Positive results were reported, with substantial decreases in total organic carbon (TOC). Hence it was demonstrated that solar nanophotocatalysis could be implemented in the pretreatment for the RO desalination process, and could also be applied to any saline or industrial wastewater including oil-produced water, where the trace pollutants are difficult to remove with conventional treatment methods. However, due to the complex nature of seawater and the possible scavenging of oxidative agents by chloride ions, the photocatalytic technique still has challenges to overcome for seawater application.

The aim of the current investigation was to show that the solar nanophotocatalysis technique can be directly employed to effectively degrade pollutants in seawater, and to assess whether this technique can be successfully implemented at the commercial level. A case study was also performed to assess the influence of chloride ions and the scavenging of hydroxyl radicals on TOC levels.

3.2 REVERSE OSMOSIS AND FEEDWATER PRETREATMENT PROCESSES

RO membranes are used worldwide for saline water desalination, producing water for drinking and other industrial and agricultural purposes. Seawater RO desalination has become cost-effective when compared to thermal desalination due to recent developments in membrane technology and pressure exchangers (Ghaffour et al., 2015; Goosen et al., 2014). However, challenges remain with respect to fouling of membranes by the organic contents of shallow seawater feeds (Amjad, 1996; Goosen et al., 2014).

A typical RO system consists of a pretreatment system, cartridge filters, RO membrane, and post-treatment system. Pretreatment systems are classified as either conventional or membrane pretreatment. The conventional pretreatment of an RO system involves a clarifier, sand filters and multi-media filters (Amjad, 1996; Goosen et al., 2014). The purpose of pretreatment is to protect the RO membranes from being damaged by foulants and scalants. There is generally a cartridge filter upstream of the high-pressure pump. This filter serves the dual role of protecting the pump from particles that may damage the impellers and protecting the membranes from becoming fouled. Post-treatment includes mineralization, and sterilization with chloramines or UV light. Adjustment of pH or the addition of other chemicals in the post-treatment used will depend on the quality of water required for the end application.

The heart of the system is the RO membrane. All membranes are prone to fouling and therefore great care must be taken in selecting appropriate membranes, designing and building the RO system, and operating the system to avoid membrane fouling. Adequate pretreatment is, therefore, critical in RO plants. Furthermore, the economics of desalination suggest that the greater the percentage of pure water that can be recovered from the feed, the higher the efficiency of the RO process. However, as the concentration of the salts in the brine (i.e. leftover water on the feed stream side of the membrane) increases, the potential for fouling also increases, resulting in the precipitation of scale-forming salts from the brine (Amjad, 1996). The density of a colloidal material may also be increased on the feed side of the membrane during desalination, allowing for coagulation and deposition of colloidal matter from the brine. Concentration polarization further contributes to fouling (Goosen et al., 2004).
Commonly encountered foulants in desalination processes are scales, suspended/colloidal material and biological material (Amjad, 1996). The major fouling problems in the RO process are due to biofouling and fouling by CaCO₃, Mg(OH)₂, silica and iron products. Different types of fouling can be distinguished, viz. fouling by particulates (silt), bacteria (biofouling), organics (e.g. oil) and scaling (precipitated inorganic salts). Colloidal impurities, inorganic precipitates, macro-molecules and biological contaminants are the main type of foulants (Characklis, 1981). Pretreatment steps widely employed in seawater RO plants include disinfection, coagulation-flocculation, filtration and anti-scalant dosing. The types and doses of disinfectants, coagulants and/or anti-scalants, and the types of filtration systems used in these plants, are not the same. The quantity of chemical doses and the point of dosing also differ from one plant to another depending on the site-specific characteristics of the feed water. Organics can be successfully removed by filtration or active carbon adsorption. In practice, a combination of different pretreatments often has to be carried out to guarantee a steady process operation. Thus, the pretreatment train often requires a lot more space and attention than the main reverse osmosis system itself (Dudley et al., 1995; Sieburth and Jensen, 1968, 1969).

Experimental studies have reported on coupling photocatalytic oxidation processes and membrane separation for the reuse of dye wastewater (Ou et al., 2015). Prevention of organic fouling and biofouling can be achieved by coating membranes with photocatalysts that are non-toxic (Feroz and Jesil, 2012). Microorganisms are inactivated and organic material from cells is oxidized by photocatalysis. A UV-driven photocatalytic pretreatment technique can be employed, for instance, for the degradation of humic acids and microorganisms.

### 3.3 PHOTOCATALYSIS AND OXIDATION OF POLLUTANTS

Heterogeneous photocatalysis is a rapidly expanding technology for water and air treatment (Ibhadon and Fitzpatrick, 2013). The initial interest began when Fujishima and Honda (1972) discovered the photochemical splitting of water into hydrogen and oxygen with TiO₂. Photocatalytic oxidation reactions have the potential to totally degrade organic compounds to carbon dioxide. This provides a clean and energy-saving technology for treatment of polluted water and air.

Most of the semiconductors that have been investigated for the treatment of polluted water are metal oxides (e.g. TiO₂, ZnO, SnO₂ and WO₃) or chalcogenides (CdS, ZnS and CdSe) (Dunlop, 2001). The effectiveness of the process for the photo-oxidation of organics in water depends upon the reduction potentials of the valence band and conduction band. The TiO₂ conduction band potential is sufficiently negative for the reduction of O₂ and the valence band is sufficiently positive for the oxidation of OH⁻. Given the reduction potentials of the bands, SrTiO₃, ZnO, WO₃ and ZnS could also be used for the photocatalytic oxidation of organic pollutants. However, it is usually found that TiO₂ is the most efficient semiconductor for the treatment of water containing organic pollutants. ZnO is a suitable alternative to TiO₂ and has similar band gap energy. However, it is unstable with respect to incongruous dissolution.

Although ZnO has a higher activity than TiO₂, having bandgap energies of 3.436 eV and 3.03 eV respectively, TiO₂ is more stable in aqueous media and that is why it is mostly used in water purification processes. Nano-structured TiO₂ photocatalysts have 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 the titanium ions creates favorable reaction conditions with the absorbed organics. On the other hand, the rutile phase has a wider pore size distribution which increases the photocatalytic activity. To achieve maximum photocatalytic efficiency, the photocatalyst can be formed from a mixture of anatase and rutile (Dunlop, 2001).

Many researchers have reported on the photocatalytic degradation of pollutants in aqueous solution (Ibhadon and Fitzpatrick, 2013). The photocatalytic mechanism of TiO₂ is described here and it is similar to other photocatalytic processes. TiO₂ is insoluble in water and effectively...
Figure 3.1. Photocatalytic process on TiO$_2$ particle (Dunlop, 2001).

non-toxic. The photocatalytic process does not require the addition of consumable chemicals and a waste sludge is not produced. TiO$_2$ photocatalysis has been reported to degrade many aqueous chemical pollutants, including pesticides, herbicides, crude oil, surfactants and dyes (Dunlop, 2001; Ibhadon and Fitzpatrick, 2013). Irradiation of TiO$_2$ particles with photons of energy equal to, or greater than, the band gap energy results in the promotion of an electron from the valence band (vb) to the conduction band (cb) of the particle. The outcome of this process is the region of positive charge, termed a hole (h$^+$) in the vb and a free electron (e$^-$) in the cb:

$$\text{TiO}_2 + hv \rightarrow \text{TiO}_2 (e^-_{\text{cb}} + h^+_{\text{vb}})$$  \hspace{1cm} (3.1)

At the TiO$_2$ particle surface, the holes can react with surface-bound hydroxyl groups (OH$^-$) and absorbed water molecules to form hydroxyl radicals (•HO):

$$h^+ + (\text{vb}) + \text{OH}^- \rightarrow \text{•HO}$$  \hspace{1cm} (3.2)

$$h^+ + (\text{vb}) + \text{H}_2\text{O} \rightarrow \text{•HO} + \text{H}^+$$  \hspace{1cm} (3.3)

In the absence of electron acceptors, electron-hole recombination is a possibility. The presence of oxygen prevents recombination by trapping electrons through the formation of superoxide ions according to Equation (3.4). The final product of the reduction may also be hydroxyl radicals and the hydroxyl radical HO$_2$:

$$\text{electron (cb)} + \text{O}_2 \rightarrow \text{O}_2^-$$  \hspace{1cm} (3.4)

where O$_2^-$ represents the superoxide ion:

$$2\text{O}_2^- + 2\text{H}^+ \rightarrow 2\text{•OH} + \text{O}_2$$  \hspace{1cm} (3.5)

$$2\text{O}_2^- + \text{H}^+ \rightarrow \text{•HO}_2$$  \hspace{1cm} (3.6)

The photocatalysis mechanism reaction is shown in Figure 3.1 (Dunlop, 2001).

Hydroxyl radicals are known to be powerful, indiscriminate oxidizing agents. During the photocatalytic process the radicals can react with organic compounds and bacterial species adsorbed onto, or very close to, the semiconductor surface resulting in degradation. Similarly, the surface interaction of microorganisms with catalysts used during the photo-disinfection is essential for enhancing the inactivation rate. When the generated radicals make close contact with the microorganisms, the lipopolysaccharide layer of the external cell wall is the initial site attacked by the photo-induced radicals.
Hydroxyl radicals are known to be powerful, indiscriminate oxidizing agents (Chong et al., 2010). During the photocatalytic process the radicals can react with organic compounds and bacterial species adsorbed onto, or very close to, the semiconductor surface resulting in degradation. The surface interaction of microorganisms with a catalyst during the photo-disinfection is essential for enhancing the inactivation rate. The lipopolysaccharide layer of the external cell wall is the initial site attacked by the photo-induced radicals. This is followed by site attack on the peptidoglycan layer, peroxidation of the membrane lipids and eventual oxidation of the membrane proteins. All of these will cause a rapid leakage of potassium ions from the bacterial cells, resulting in direct reduction of cell viability. The decrease in cell viability is usually linked to the peroxidation of polyunsaturated phospholipid components in the cell membrane (i.e. loss of essential cell functions) and eventually leads to cell death. The transfer of a bacterial cell into the close vicinity of the surface-generated radical site is recognized to be the rate-limiting step in the photo-disinfection reaction (Chong et al., 2010).

The UV radiation required for photocatalytic processes may come from an artificial source or the sun. The artificial generation of UV radiation contributes to a large proportion of the operating capital and maintenance costs of a photocatalytic reaction system because of the utility consumption and periodic replacement of the UV lamps (Dunlop, 2001). There is, therefore, a significant economic incentive to develop solar-powered photocatalytic reactors. In addition, the environmental impact induced by the use of solar energy is minimal and this renders the photocatalytic process environmentally attractive. The application of solar-powered photocatalytic reactors to treat water contaminated with organic pollutants holds promise for regions receiving strong sunlight throughout the year, such as the Middle East North Africa (MENA) and the Arabian Gulf regions.

3.4 SOLAR PHOTO CATALYTIC PROCESSES AND REMOVAL OF ORGANIC AND INORGANIC COMPOUNDS FROM WATER AND AIR

Over the past three decades research in the photocatalytic field has been extensive, covering the removal of organic and inorganic compounds from contaminated water and air (Mehrjouei et al., 2015). The artificial generation of photons required for the detoxification of polluted water is the primary operational cost in photocatalytic wastewater treatment plants. This suggests that the sun may be employed as an economically and ecologically sensible light source. With a typical UV flux near the surface of the earth of 20–30 W m$^{-2}$, the sun puts out 0.2–0.3 mol photons per m$^2$ per hour in the 300–400 nm range. In principle, these photons are suitable for destroying water pollutants in photocatalytic reactors.

Extensive research work has been performed at various research centers/institutions on the application of solar photocatalysis to the treatment of pollutants in industrial wastewater (Malato et al., 2002; Mehrjouei et al., 2015). Despite its obvious potential for the detoxification of polluted water, there has been very little commercial or industrial use of solar photocatalysis as a technology so far. The published literature shows only a few engineering-scale demonstrations of the solar photocatalytic treatment of polluted groundwater, landfill leachates and industrial wastewater in the US and in Europe. The first engineering-scale field experiments were conducted in 1991 by the National Renewable Energy Laboratory (NREL) and the Sandia National Laboratories at a California Superfund Site, located at Lawrence Livermore National Laboratory (LLNL), treating groundwater contaminated with chlorinated solvents, mainly trichloroethylene (TCE) (Mehos and Turchi, 1993).

Parallel to the work performed in the US under the direction of the NREL and Sandia National Laboratories, several research groups from different European countries, funded by the European Community, have tested the solar detoxification loop with the use of parabolic trough reactors installed at the Plataforma Solar de Almería (PSA) in Spain since 1991 (Malato et al., 2002). Engineering-scale demonstrations of the non-concentrating solar reactor technology were conducted at Tyndall Air Force Base, Florida (US) in 1992 (Goswami et al., 1993), treating
groundwater contaminated with fuel, oil and lubricants that were leaking from underground storage tanks. Furthermore, Freudenhammer et al. (1997) reported their results from a pilot study using thin-film-fixed bed reactors (TFFBR), which was performed in various Mediterranean countries. Their results showed that biologically pretreated textile wastewater can be cleaned by solar photocatalysis. Likewise, highly polluted olive mill wastewater (OMW) from the olive oil industry, was treated by solar photocatalysis and a solar photo-Fenton process (Gernjak et al., 2004).

Although photocatalysis has been extensively applied to the treatment of industrial wastewater, very few researchers have actually tried this technique for saline water because seawater consists of a complex mixture and there is also the danger of chloride ion interference. In one of the first reports, Al-Rasheed and Cardin (2003b) have shown that humic acids (HA) can be effectively removed from high-saline waters using photocatalysis with titanium dioxide catalysts. The oxidative nature of these reactions was established by the requirements for oxygen, and the optimum conditions have been established (i.e. high temperature, low pH, high oxygen concentration and a TiO₂ concentration in the range 2.0–2.5 g L⁻¹). Photocatalytic degradation of HA was also observed in low-saline water, where it occurs more rapidly than in seawater. The activation energy was determined in seawater as 17 kJ mol⁻¹.

Thin films of TiO₂ might be more suitable for use with highly saline waters, in view of the instability of suspended TiO₂ in this medium, and the requirement for continuous agitation. The catalytic oxidation process does not conform closely with the Langmuir-Hinshelwood kinetic model, probably owing to competing reactions involving sulfate and bicarbonate ions (Kim et al., 2010). TiO₂ (Degussa P25), TiO₂ (anatase), TiO₂ (rutile), TiO₂ (mesoporous) and ZnO dispersions were used as catalysts, employing a medium mercury lamp to study the effectiveness of photocatalytic oxidation of HA in the increasingly important highly saline water. The effect of platinum loading on P25 and ZnO was also investigated and it was found that ZnO with 0.3% platinum loading was the most efficient catalyst. The preferred medium for the degradation of HA using ZnO is alkaline, whereas for TiO₂ it is acidic. Kim et al. (2010) focused on the photocatalytic membrane reactor treatment of seawater. The turbidity removal was significant and stable without any membrane fouling. Although TiO₂-mediated photocatalysis achieved a high degradation of the natural organic matter (NOM) present in freshwater (80% of lake NOM was removed within four hours), unexpectedly, it was found that no seawater organic matter (SOM) was decomposed by the same system. The authors argued that the reason behind this was that the salt level of seawater was altered by electrodialysis.

Kim et al. (2010) investigated the effects of seawater sources on photocatalytic microfiltration treatment with respect to the removal of particulate and organic matter, as well as control of membrane permeability. It was observed that photocatalytic degradation of SOM was marginal but it was enhanced significantly when sea salts were removed by electrodialysis. Likewise, Kim et al. (2003) designed a hybrid thin-film composite (TFC) membrane consisting of a self-assembly of TiO₂ nanoparticles with photocatalytic destructive capability on microorganisms as a novel means to reduce membrane biofouling. The photocatalytic bactericidal effect of the hybrid TFC membrane was examined by determining the survival ratios of the Escherichia coli (E. coli) cell with and without UV light illumination. The group demonstrated that the photocatalytic bactericidal efficiency was remarkably higher for the hybrid TFC membrane under UV light illumination. In addition, Rahimpour et al. (2011) reported on the antibacterial and antifouling properties of TiO₂-entrapped nanocomposite polyvinylidene fluoride (PVDF)/sulfonated polyethersulfone membranes. They observed a dramatic increase in anti-bacterial effect on E. coli. Shinde et al. (2011) studied the photocatalytic activity of seawater under solar light using a photoelectrochemical reactor module consisting of nine photoelectrochemical cells equipped with a spray-deposited TiO₂ catalyst and observed complete mineralization of organic compounds.

Very few researchers have attempted the treatment of seawater using solar photocatalysis and hence the work reported in this chapter provides an impetus for the development of technology that can be helpful to the desalination sector, especially in MENA countries.

Solar photocatalytic reactors can be distinguished according to whether the catalyst is applied in suspension or in thin-film form. There are several advantages and disadvantages of choosing
suspension photocatalysis. The suspension process results in a uniform photocatalyst distribution in the reactor system. It has higher efficiency because of its larger surface area and a low pressure drop because the suspension particles are well-mixed. The process also minimizes catalyst fouling because the catalyst is continuously removed. The main disadvantage is the requirement for a nano filter to separate the catalyst: this will increase the cost of the unit. In comparison, the thin-film method is a continuous operation and does not need a separation step after the reaction takes place. However, it has low efficiency as a result of low light utilization due to the immobilization of the photocatalyst, which results in a smaller surface area for reaction. The key elements affecting the photocatalytic system are the type of catalyst, the light source and the reactor configuration.

A concentrated light system (Fig. 3.2) that reflects the solar light onto the photocatalytic reactor via a reflecting surface is preferred because it requires a smaller reactor volume. It also operates at a higher flow rate, has better mass transfer rates and can be operated under cloudy conditions (Thiruvenkatachari et al., 2008). Tubular photo reactors are simple in their operation, can be designed easily, and light can be concentrated by the use of reflectors which will increase the photoreaction.

Thiruvenkatachari et al. (2008) showed that the photocatalytic reaction is affected by the dosage of the catalyst, the original concentration of reactants, the illumination time, the intensity of illumination, the pH value and the oxygen flow. It was also found that nano-scale photocatalysts have more activity as they have a larger surface area which reduces the time needed for the carrier to diffuse out of the photocatalyst pores to the photocatalyst surface (Bhattacharya et al., 2013).

The elimination potential of UV irradiation and advanced oxidation processes have been studied for UV/hydrogen peroxide and UV/ozone systems (Sona et al., 2006). 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 highly reactive hydroxyl radicals. Hydrogen peroxide ($\text{H}_2\text{O}_2$) and ozone are the commonly used oxidants. It was observed during the experiments that the absorbance efficiency of $\text{H}_2\text{O}_2$ was dependent on its concentration; the higher the concentration the better the performance of the water treatment system (Sona et al., 2006).

The solar photocatalytic reaction of TiO$_2$ in the presence of inorganic salts results in the deposition of a double layer of the salts on the catalyst surface leading to a reduction in the photocatalyst adsorption and its photocatalytic activity by scavenging of hydroxyl radicals (Guillard et al., 2003). Figure 3.3 shows an illustration of possible scavenging reactions of radicals by Cl$^-$ ions during seawater photocatalysis during which hydroxyl radicals and valence band holes oxidize organic matter (OM). Chloride ions show a negative effect on the photocatalytic oxidation reaction as 50% removal of total organic carbon (TOC) was obtained in the absence of chloride ions created by the addition of excess AgNO$_3$ prior to the photocatalytic reaction of TiO$_2$ in the presence of seawater (Kim et al., 2010; Surolia et al., 2007).
Table 3.1. Seawater composition analysis from case study area.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.96</td>
</tr>
<tr>
<td>Conductivity [mS]</td>
<td>54.22</td>
</tr>
<tr>
<td>Salinity [mg kg(^{-1})]</td>
<td>34200</td>
</tr>
<tr>
<td>Turbidity [NTU]</td>
<td>1.60</td>
</tr>
<tr>
<td>Dissolved oxygen [mg L(^{-1})]</td>
<td>5.38</td>
</tr>
<tr>
<td>Total dissolved solids [mg kg(^{-1})]</td>
<td>53200</td>
</tr>
<tr>
<td>Chemical oxygen demand [mg L(^{-1})]</td>
<td>5.0</td>
</tr>
<tr>
<td>Biological oxygen demand [mg L(^{-1})]</td>
<td>2.0</td>
</tr>
<tr>
<td>Total organic carbon [mg L(^{-1})]</td>
<td>2.94</td>
</tr>
<tr>
<td>E. coli</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

3.5 OMANI CASE STUDY OF REVERSE OSMOSIS PRETREATMENT USING SOLAR NANOPHOTOCATALYSIS

A case study was performed to assess the effect of chloride ions and the scavenging of hydroxyl radicals on total organic carbon (TOC), and thus whether solar nanophotocatalysis can be applied for RO treatment of seawater pollutants. Experimental studies were conducted in a batch recirculation reactor system and in a continuous thin-film reactor system. The seawater was taken from the Al Athibha beach area on the coast of the Sultanate of Oman and stored at normal temperature, 25°C. The seawater was collected 1 km offshore because seawater collected near the shore contains up to 50 mg L\(^{-1}\) total organic carbon (TOC), whereas water collected from 1 km offshore had TOC in the range 4–7 mg L\(^{-1}\). In general, the inlet for any desalination plant is placed 1 km away from the shore, hence the samples used in the present study. The seawater samples were analyzed at the Caledonian College of Engineering solar water research laboratory (Oman). Conductivity, pH, salinity, turbidity, dissolved oxygen (DO), total dissolved solids (TDS), chemical oxygen demand (COD), biological oxygen demand (BOD), TOC and E. coli levels were analyzed (Table 3.1). Experimental investigations were carried out with batch as well as continuous reactor systems (Fig. 3.4a through to Fig. 3.4d).

A 2 L glass beaker with magnetic stirrer was used as the batch reactor (Fig. 3.4a). The batch recirculation reactor (Fig. 3.4b) consisted of a 2 L glass tube of diameter 8 cm and length 100 cm fixed to a stand at an angle of 20°C. A small glass tube of diameter 1.2 cm and length 70 cm
was fixed inside the glass tube at the exact center and was connected to a peristaltic pump. Glass tubes 60 cm in length with an outer diameter of 2 cm and connected with a peristaltic pump were used for continuous reactor systems with the catalyst in suspension (Fig. 3.4c) or in a thin film (Fig. 3.4d).
3.5.1 Batch reactor studies with TiO$_2$

Figure 3.5 shows the percentage decrease in TOC at different dosages of TiO$_2$. It was observed that there was a sharp decrease in TOC over the first two hours of reaction time and thereafter the decline was stable. This may have been due to an increase in the availability of photonic energy. It was also seen that the degradation of pollutants seemed to be on the higher side at higher dosages of TiO$_2$, which may be as a result of availability of additional active sites on the photocatalyst. The amount of TiO$_2$ is directly proportional to the overall photocatalytic reaction rate and a linear dependency exists with TiO$_2$ concentration. A reduction of more than 50% in TOC was observed for 3 g TiO$_2$ dosage within a 5 h reaction time. This suggests that the technique can be applied to the treatment of seawater pollutants.

3.5.2 Batch reactor studies with TiO$_2$ recirculation

In the case of a batch reactor with recirculation, when the TiO$_2$ concentration was varied from 0.5 g to 3.5 g, a reduction in TOC of more than 45% was observed at the highest TiO$_2$ dosage (Fig. 3.6). With an increase in concentration of TiO$_2$ P25, the reduction in TOC was enhanced. This was probably due to the availability of more active sites on the catalyst surface. Seawater collected from the foreshore/beach had a high initial concentration of TOC, whereas seawater collected from 1 km offshore had a lower TOC concentration. It was observed that only glass reactors gave accurate results in these experiments; the use of any other material gave erratic results, possibly because of induced carbon content from reactor materials entering the seawater.

3.5.3 Continuous reactor studies with TiO$_2$ in suspension and in thin film

With TiO$_2$ in suspension in a continuous reactor, a substantial decrease in the TOC concentration was observed, especially at the lower TiO$_2$ dosage (Fig. 3.7). A sharp reduction in TOC was observed in the first two hours of exposure time and after that it was stable. A reduction in TOC of more than 35% was observed at 0.5 g TiO$_2$ dosage exposed to 5 h of irradiation. With an increase in catalyst dosage the percentage reduction in TOC declined, which may have been as a result of the agglomeration of catalyst particles, thereby inhibiting the generation of hydroxyl radicals.

With TiO$_2$ immobilized in a thin film in a continuous reactor, slightly different results were observed. Polyvinyl alcohol (PVA) was used as a solution thickener and a binder to enhance the chemical bonding of TiO$_2$ to the inner surface of the glass reactor tube. The coated layer of the nanophotocatalyst was stable and strongly bonded to the inner surface of the tube after calcination.
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Time [h]  
3.5 g TiO₂  
2.0 g TiO₂  
1.0 g TiO₂  
0.5 g TiO₂

% Reduction of TOC

0 5 10 15 20

Figure 3.6. Percentage reduction in TOC at various TiO₂ dosages in batch reactor with recirculation.

Figure 3.7. Continuous reactor studies with TiO₂ in suspension in 0.002 m³ of seawater, using a peristaltic pumping rate of 170 rpm to a tubular reactor where photocatalytic reaction took place.

It was found that there was a slight increase in TOC (Fig. 3.8), possibly due to the presence of polyvinyl chloride in the thin film or the formation of organic byproducts. The composition of seawater is complex in nature, which may interfere with the photocatalytic process. Though the TOC increased in the initial stages (perhaps due to the presence of PVA), after a certain amount of time it declined again, which shows that even in a thin-film coating the degradation of pollutants takes place. As a possible future study, an inorganic binder may be a better option than PVA to create the thin film.

3.5.4 Effectiveness of combination of photocatalysts and photo-Fenton reagent in reduction of TOC in reactor studies

Batch experimental studies were carried out with a combination of photocatalysts in a 0.002 m³ reactor system. The combinations used were: 3.0 g TiO₂ + 5 mL H₂O₂; 3.0 g TiO₂ + 5 mL H₂O₂ + 1.0 g Fe₂O₂S₃·5H₂O; 3.0 g TiO₂ + 1.0 g ZnO. The maximum reduction in TOC was observed with the TiO₂ + ZnO combination, as shown in Figure 3.9.
3.6 CONCLUDING REMARKS

Organic fouling and biofouling of reverse osmosis (RO) membranes requires conventional and/or membrane pretreatment of the feed water. Prevention of biofouling can be achieved by coating the reactor system with a nanophotocatalyst that is non-toxic. Photocatalytic coating is very effective against humic substances and microorganisms. If this technique can be successfully implemented at the commercial level, then solar energy can be utilized in a feasible manner for desalination, especially in RO pretreatment processes. From the case study, it was concluded that although there is interference by chloride ions and scavenging of hydroxyl radicals, substantial decreases in total organic content (TOC) were still observed and hence this technique can be applied to treatment of seawater pollutants. Experimental studies conducted in a batch recirculation reactor system have shown similar reductions in pollutants to those in a normal mixing batch-type reactor system. In a continuous reactor suspension system, a substantial decrease in TOC was observed. However, to apply suspension systems commercially, additional filtration systems...
are needed to separate nanophotocatalyst particles, which will increase both the capital and the operational costs, and this is one of the challenges that needs to be overcome for commercial exploitation.

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