

# Application of Modified Micro-Scaled Titanium Dioxide for Photocatalytic Degradation of *E. Coli* and Total Coliform in Seawater Using UV-Light

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**Abstract**—Water is one of the earth's most fundamental resources which plays an essential role for all living organisms on the planet. Although the earth contains approximately 1.386 billion km<sup>3</sup> of water, an immense 97% of it lies in oceanic form, and only about 1% available as freshwater resources. It is estimated that by the year 2040, 33 countries will face severe water-stress with an overall 167 countries experiencing low to high withdrawals of their water supply. Herein, using photocatalysis as a pre-treatment process of seawater as an alternative water source in South Africa comes in handy. Therefore, this study explored the potential of an integrated photocatalyst (IPCA) for photocatalytic degradation of bacteria in sea water under a UV-light source. The IPCA was synthesized by impregnating nanoparticle carbon-modified titanium dioxide (CM-n-TiO<sub>2</sub>) with activated carbon (AC). Three operating conditions investigated included the catalyst load (0.25; 1.375 and 2.5 g/L), pH (3; 7.8 and 10) and reaction time (10; 20 and 30 minutes). At an optimum catalyst load of 2.5g/L, pH of 10 and a reaction time of 30 minutes, a minimum of 93.06% degradation of total coliform and 97.97% degradation of *E. coli* was achieved. It was deduced, the characterised high surface area (357.824 m<sup>2</sup>/g) of the AC-CM-n-TiO<sub>2</sub> enhanced its agglomeration and photocatalytic efficiency of the treated seawater, as compared to CM-n-TiO<sub>2</sub> with surface area of 87.077 m<sup>2</sup>/g.

**Keywords**—Activated carbon, bacteria, *E. coli*, TiO<sub>2</sub>, seawater, photocatalyst.

## I. INTRODUCTION

Water is without question, one of the earth's most fundamental resources. It plays an essential role for all living organisms on the planet, especially for that of mankind. Although the earth contains approximately 1.386 billion km<sup>3</sup> of water, the entirety of it is unevenly distributed across the globe in various forms and with varying levels of accessibility. Of this approximate total, an immense 97% of it lies in oceanic form, with the remaining 2% found in glaciers and ice caps, and only about 1% available as freshwater resources [1]. The UN estimates that of the 7.8 billion world

population, at least 2.3 billion people currently reside in water-stressed countries. Furthermore, two-thirds of the worldwide population will experience extreme water scarcity for a period of at least one month per year [2]. The availability of safe drinking-water resources is a major health and development issue across the globe. Many coastal countries such as South Africa are perfectly suited for utilizing the process of desalination to produce treated seawater as an alternative to fresh water sources that are quickly depleting. The desalination process involves the formation of fresh water from seawater by removing the dissolved salts from the recovered water [3]. Reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED) are among the membrane-based technologies that are currently dominating the market for water desalination [4, 5]. However, most desalination plants across the globe now predominately use RO membranes in their operations. The overall performance of an RO desalination process depends heavily on the pre-treatment method utilized to control fouling and minimize the pollutant load [6]. The formation of a biofilm on the RO membrane is caused by microbial organisms such as fungi and bacteria, secreting polymers that stick to the surface of the membrane and accelerate the decomposition of the membrane which negatively impacts the operation of the RO desalination plant [7]. Therefore, the removal of microbial contaminants from seawater in RO desalination systems are of paramount importance to improve overall efficiency and cost-effectiveness.

In this context, advanced oxidation processes (AOP's) come in handy as a viable solution to mitigate membrane fouling caused by biofilms. AOPs such as photocatalysis coupled with suitable catalyst method can result in the degradation of various microbial contaminants in desalination of seawater [8]. The photocatalytic degradation process has generated widespread interest amongst researchers, with numerous studies done on the degradation and mineralization of recalcitrant organic compounds using the photocatalytic process [9]. Generally, the photocatalytic process occurs via the illumination of semi-conductor and the movement of electrons to the conduction band of the semi-conductor from the valence band. The movement of the excited electrons

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occurs under the illumination of a light source with the specific required wavelength needed to move the electrons from one band to another. These excited electrons then react with water molecules (hydrogen and oxygen) to generate hydroxide radicals and superoxide anions, which then degrades the organic pollutants [10]. Notwithstanding, there are several factors that can influence photocatalytic efficiency in the photocatalytic degradation process. Apart from catalyst load, pH, reaction time, wavelength and pollutant concentration all influence the overall performance of the photocatalyst [11]. The application of titanium dioxide ( $\text{TiO}_2$ ) to various absorbent materials such as activated carbon (AC) alumina silicates and carbon nanotubes can significantly increase the photocatalytic degradation of hazardous organic materials in water. Amongst these various absorbent materials, a great amount of attention has been focused on the use of AC due to its high porosity and adsorption capabilities [12, 13]. In this context, this study explores the potential of an integrated photocatalyst (IPCA) for photocatalytic degradation of bacteria in seawater under a UV-light source. Experimental conditions such as catalyst load, reaction time and pH were also investigated to determine the optimal operating conditions for percentage degradation.

## II. MATERIALS AND METHODS

### A. Chemicals Used

The CM-n- $\text{TiO}_2$  was synthesized using Titanium (IV) isopropoxide 97% from Sigma-Aldrich, Ethanol from Romachem Supplies, Hydrochloric Acid 1N from Minema Chemicals, and Sodium Hydroxide 0.1N from Lichro Chemical and Laboratory Supplies. An integrated photocatalyst (IPCA) was then synthesized by impregnating the CM-n- $\text{TiO}_2$  with powdered activated carbon (AC) to form AC-CM-n- $\text{TiO}_2$ .

### B. Catalyst Preparation

The first stage of catalyst preparation involved the synthesis of a nanoparticle carbon-modified titanium dioxide (CM-n- $\text{TiO}_2$ ) via the sonicated sol-gel method [14]. Titanium (IV) isopropoxide was slowly added to ethanol under ultrasonication. Deionized water was then slowly added into the mixture and left under sonification for 30 minutes. The pH of the solution was then adjusted between 3 and 3.5 using HCl and NaOH. The solution was then aged at ambient temperature for 24 hours before being filtered. The remaining catalyst was then washed several times with ethanol and deionized water before being allowed to dry at  $80^\circ\text{C}$  for 12 hours. CM-n- $\text{TiO}_2$  was then formed after being calcined at  $500^\circ\text{C}$  for 2 hours in a muffle furnace. Activated carbon and CM-n- $\text{TiO}_2$  in a 3:1 ratio was then added to deionized water and sonicated for an hour before being filtered and dried overnight at  $100^\circ\text{C}$ . The resulting composite was then washed with deionized water, filtered, and allowed to dry for 1 hour at  $110^\circ\text{C}$  to remove impurities. The final composite was then calcined at  $600^\circ\text{C}$  for 1 hour to form AC-CM-n- $\text{TiO}_2$ .

### C. Catalyst Characterization

To characterize the resulting catalyst, Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were utilized. The morphology of the catalyst was determined via SEM analysis (Tescan MIRA3). BET analysis was performed to determine the resulting surface area of the modified catalyst and EDS analysis was utilized to determine the elemental composition of the catalyst.

### D. Experimental Procedure

Fresh seawater samples used in this study was collected from Amanzimtoti beach in Kwa-Zulu Natal Province, South Africa. The raw seawater was fractionated into 3 equal quantities, two of which were dosed with varying amounts of Sodium Hydroxide (NaOH) and Hydrochloric acid to achieve a pH of 10 and 3 respectively. The third quantity was kept at its initial pH of 7.8. Before experimental runs could occur, a sample of each quantity of feedwater was taken for analysis to determine the initial quantity of *E.coli* present prior to experimental runs. Photocatalytic degradation experimental runs were then carried out at lab scale under the presence of UV light using the AC-CM-n- $\text{TiO}_2$  catalyst. The effects of catalyst load, reaction time and pH were investigated by altering the catalyst load between 0.25; 1.375 and 2.5 g/L, the reaction time between 10; 20 and 30 minutes, and the pH between 3; 7.8 and 10. Experimental analysis was carried out with the use of an Eins Sci E-MSH-MC 10 magnetic stirrer and 1L glass beakers as batch reactors. Each beaker was placed on the magnetic stirrer which was illuminated on either side with two 18W UV light bulbs.

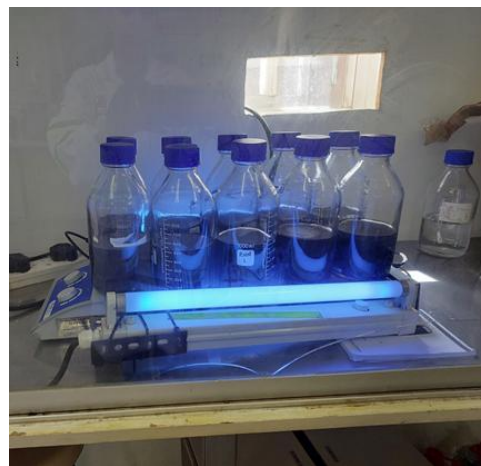


Fig. 1- Pictorial view of photocatalytic process in section

### E. Analysis

Once treated, seawater samples were filtered to remove all catalyst particles present before undergoing analysis. The IDEXX Colilert test kit was used to determine the amount of *E.coli* and total coliform present in both feedwater samples as well as treated samples. This was achieved by the addition of IDEXX Colilert-18 indicator to a 100 mL quantity of each sample. The sample containing the dissolved indicator was

then transferred to a Quanti-tray/2000 and the tray was then sealed using a Quanti-tray sealer. The sealed tray was then incubated for a period of 18 hours at a constant temperature of 35°C. Upon completion of incubation, the trays were then removed from the incubator and the number of positive wells (wells that have turned yellow) were counted. The trays were then placed under UV light to determine the number of fluoresced wells. The observed yellow wells were an indication of metabolized coliforms, whereas the fluoresced wells indicated metabolized *E.coli*. The number of yellow wells and fluoresced wells were then input in the IDEXX MPN generator program which then quantified the *E.coli* and total coliforms in terms of most probable number (MPN) per 100 mL. The percentage degradation (D%) was then calculated by using the following equations:

$$D\% = \frac{E.coli_{initial} - E.coli_{final}}{E.coli_{initial}} \times 100 \quad (1)$$

$$D\% = \frac{Total\ coliform_{initial} - Total\ coliform_{final}}{Total\ coliform_{initial}} \times 100 \quad (2)$$

Where  $E.coli_{initial}$  and  $Total\ coliform_{initial}$  represent the MPN of bacteria before treatment and  $E.coli_{final}$  and  $Total\ coliform_{final}$  represent the MPN of bacteria after treatment.

### III. RESULTS AND DISCUSSION

#### A. Catalyst Characterization

##### BET results

BET analysis of the CM-n-TiO<sub>2</sub> and AC-CM-n-TiO<sub>2</sub> revealed significant differences in their surface areas, pore volume and size. This demonstrated the impregnating of CM-n-TiO<sub>2</sub> with AC was successful. Table 1 summarizes the pore volume, pore size and surface area of each resulting catalyst. As can be seen, the incorporation of activated carbon resulted in the surface area of the catalyst increasing from 87.08 m<sup>2</sup>/g to 357.82 m<sup>2</sup>/g. Therefore, due to the high surface ability to enhanced agglomeration and photocatalytic efficiency of the treated seawater. The applicability of the AC-CM-n-TiO<sub>2</sub> was considered.

##### SEM results

The morphology of the synthesized CM-n-TiO<sub>2</sub> and AC-CM-n-TiO<sub>2</sub> is shown in Figure 2 and Figure 3 respectively with compactible and porous structured crystals.

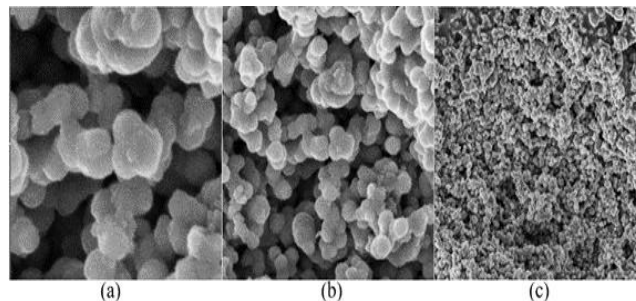


Fig 2- SEM images of CM-n-TiO<sub>2</sub> at a view filed of (a) 2.08μm, (b) 4.15μm and (c) 20.8 μm.

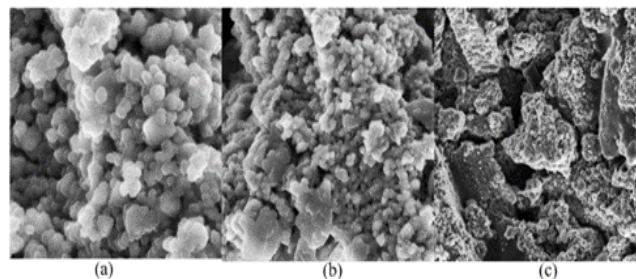


Fig 3- SEM images of AC-CM-n-TiO<sub>2</sub> at a view filed of (a) 2.08μm, (b) 4.15μm and (c) 20.8 μm.

##### EDS results

The EDS images (Figure 4a and b) and spectrum (Figure 5a and b) , affirms the compatibility and porosity of the CM-n-TiO<sub>2</sub> and AC-CM-n-TiO<sub>2</sub> respectively. Table 2 presents the elemental compositions of the the CM-n-TiO<sub>2</sub> and AC-CM-n-TiO<sub>2</sub> obtained from the EDS results,

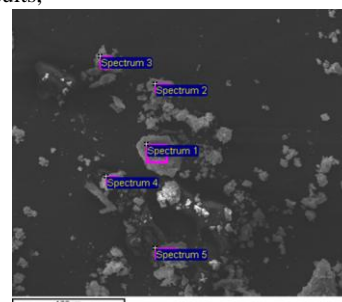


Fig. 4a- Site of interest for CM-n-TiO<sub>2</sub>

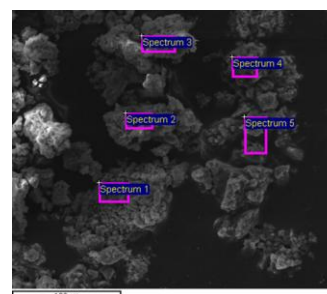


Fig 4b- Site of interest for AC-CM-n-TiO<sub>2</sub>

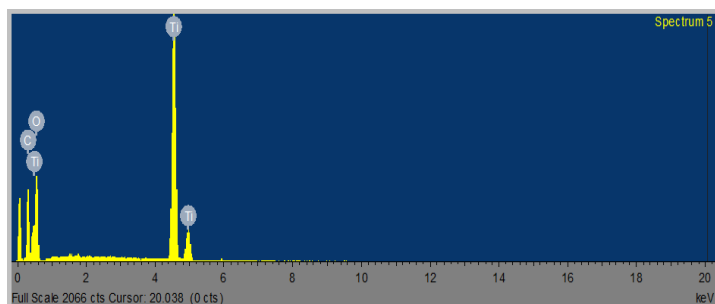
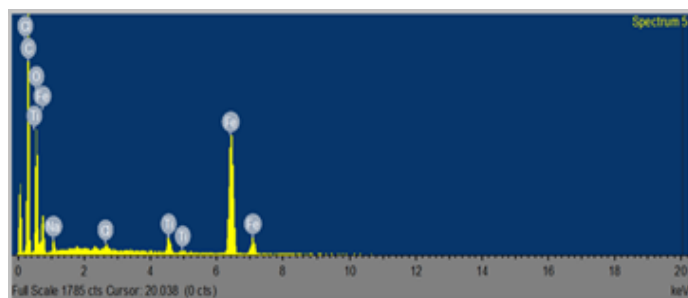
TABLE 1  
BET ANALYSIS RESULTS OF CATALYST

Sample	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	Surface area (m <sup>2</sup> /g)
CM-n-TiO <sub>2</sub>	0.022344	1.0844	87.0765
IPCA or (AC-CM-n-TiO <sub>2</sub> )	0.113827	2.0502	357.8237

TABLE II

## EDS ANALYSIS RESULTS OF CATALYST

Sample	Spectrum	Atomic %				
		O	Ti	Na	Cl	C
CM-n-TiO <sub>2</sub>	1	53.41	46.59	-	-	-
	2	63.42	36.58	-	-	-
	3	58.42	41.58	-	-	-
	4	57.95	42.05	-	-	-
	5	55.94	44.06	-	-	-
	Mean	57.83	42.17	-	-	-
IPCA or (AC-CM-n-TiO <sub>2</sub> )	1	36.07	4.74	2.78	0.49	55.91
	2	29.30	4.25	2.18	0.79	63.49
	3	30.67	3.70	2.81	1.23	61.59
	4	33.20	3.50	4.41	0.93	57.96
	5	33.90	3.21	4.35	0.76	57.78
	Mean	32.63	3.88	3.31	0.84	59.35

Fig 5a- EDS spectrum of CM-n-TiO<sub>2</sub>Fig 5b- EDS spectrum of AC-CM-n-TiO<sub>2</sub>

### B. Effect of Catalyst Load

The effect of AC-CM-n-TiO<sub>2</sub> load on the percentage degradation of *E.coli* and total coliform in seawater under UV light illumination was investigated to determine the optimum catalyst load. It can be noted that the increase in catalyst load from 0.25g/L to 2.5g/L subsequently increased the percentage degradation of both *E.coli* and total coliform due to the increased number of hydroxyl radicals formed. The optimum catalyst load was found to be 2.5g/L which resulted in 97.97% degradation of *E.coli* and 93.06% degradation of total coliforms as can be seen in figure 6.

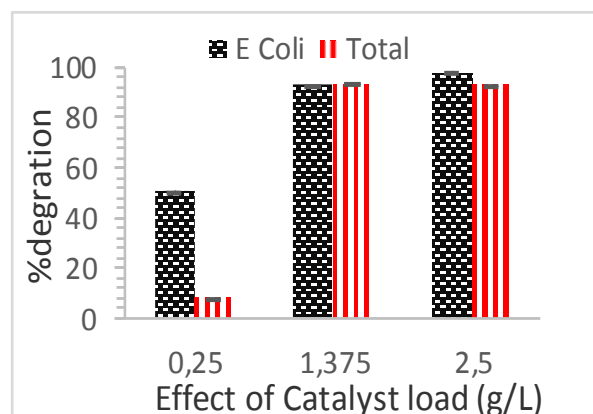


Fig 6- Effect of catalyst load on percentage degradation of *E.coli* and total coliform in seawater under UV light illumination at a constant pH of 7.8 and reaction time of 20 minutes.

### C. Effect of pH

The effect of pH on the photodegradation of *E.coli* and total coliform in seawater under UV light illumination was investigated at 3 different pH levels 3, 7.8 and 10. It should be noted that at a pH of 3, 100% degradation occurred for both *E.coli* and total coliform in the initial feed sample. This was found to be due to the addition of hydrochloric acid for accommodation of the pH change. This however will not be a viable solution for the pretreatment of seawater due to the amount of chemical alteration it will require to correct the pH once water treatment has occurred. As can be seen in figures 10 and 11, an increase in pH from 7.8 to 10 increased the overall percentage degradation of *E.coli* and total coliform in seawater under UV light illumination. The optimum pH level was determined to be a pH of 10 which achieved an overall percentage degradation of 100% *E.coli* and 94.99% total coliform.

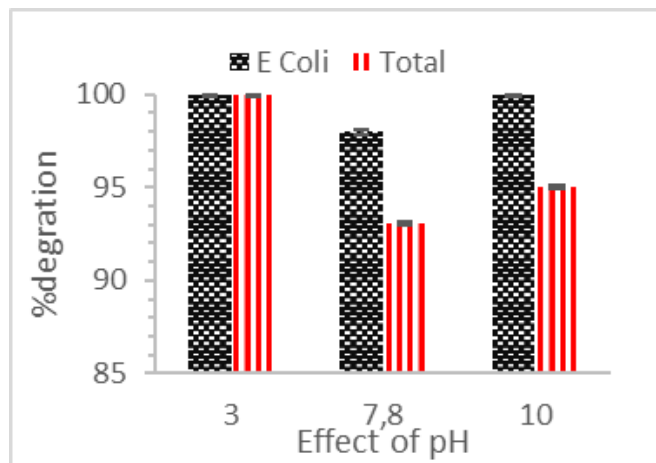


Fig. 7- Effect of pH on percentage degradation of E.coli and total coliform in seawater under UV light illumination at a constant catalyst load of 2.5g/L and reaction time of 20 minutes.

#### D. Effect of Reaction Time

The effect of reaction time on the photocatalytic degradation of E.coli and total coliform under UV light was investigated at 3 different reaction time intervals of 10 min, 20min and 30 min. As can be seen in figure 8, the highest percentage degradation of both E.coli and total coliform was achieved at a total reaction time of 30 minutes which yielded a 100% degradation of E.coli and 97.49% degradation in total coliform.

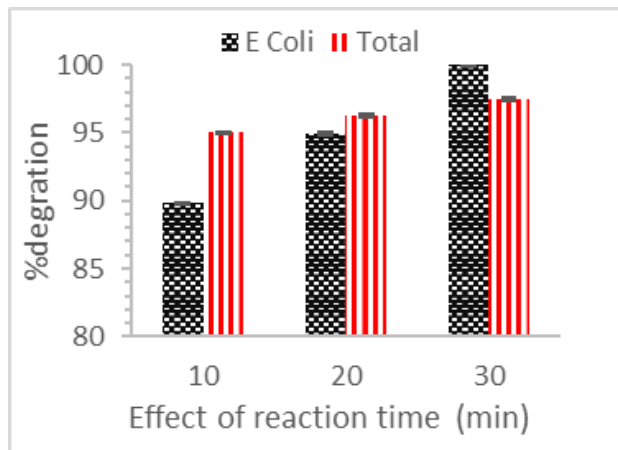


Fig 8- Effect of reaction time on percentage degradation of E.coli and total coliform in seawater under UV light illumination at a constant catalyst load of 1.375g/L and pH of 10.

#### CONCLUSION

This study presents the use of an integrated photocatalyst (IPCA) or (AC-CM-n-TiO<sub>2</sub>) for the effective photocatalytic degradation of bacteria in seawater under UV light. The characterization of AC-CM-n-TiO<sub>2</sub> such as BET, SEM and EDS revealed it was successfully synthesized. AC-CM-n-TiO<sub>2</sub> with a high surface area of 357.82 m<sup>2</sup>/g; was therefore considered and tested for *E.coli* and total coliforms in seawater under the presence of UV light. It was found that at a pH of 7.8, catalyst load 2.5g/L and reaction time of 30

minutes, over 95% *E.coli* and total coliforms were removed from the seawater. This suggests, the adoption of photocatalytic process as pre-treatment of desalination technology is viable to mitigate biofilms fouling.

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