

The effect of light wavelength on water quality in photocatalytic seawater pre-treatment

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Abstract— Alternative pre-treatment of seawater via photocatalytic reaction is not well explored. Although titanium oxide (TiO₂) is widely used in photocatalytic reaction, the application of other material especially from biomass ash is rare. In this research, the effect of light wavelength for seawater treatment and the degradation of organic pollutants by using hybrid TiO₂ photocatalyst supported by oil palm fiber ash (biomass ash) are studied. The photocatalyst which consisted of TiO₂ and oil palm fiber ash weight ratio of 1:1 (i.e Ti:Ash 50:50) was synthesized via wet impregnation method. The Ti:Ash 50:50 photocatalyst was calcined at 500°C in the presence of air. The experiment was performed in a one litre borosilicate photocatalytic reactor. The percentage weight ratio of 1:400 for catalyst to seawater sample was set. The mixture of photocatalyst and water sample was stirred at 400 rpm to have homogenized distribution of the photocatalyst in the water. The investigation was carried out for two hours by exposing the reactor with either 365 nm or 420 nm mercury light. The photocatalyst was characterized by using N₂ adsorption (BET) and UV/Vis/Nir to determine the specific surface area, pore volume and pore size and band gap energy of the catalyst respectively. The Ti:Ash 50:50 band gap energy was obtained at 3.1 eV. This indicates that the catalyst was reactive when less than 385 nm light wavelength was used. The quality of initial and product seawater was analyzed via pH, conductivity, turbidity and chemical oxygen demand (COD). The small reduction of conductivity and COD obtained when using Ti:Ash 50:50 without light present shows the system was dominant by adsorption without no reaction. Higher reduction of conductivity, pH, turbidity and COD was achieved when the Ti:Ash 50:50 photocatalyst was exposed to 365 nm light wavelength than the Ti:Ash 50:50 photocatalyst that was exposed to 420 nm light wavelength. In addition, significant increment of water temperature (from 25°C to 100°C) was observed when 420 nm light wavelength was used. This leads to distillation dominated the process rather than photocatalytic reaction. It can be deduced that hybrid photocatalyst of Ti:Ash 50:50 has remarkable capabilities in pre-treatment and purify the seawater. The light wavelength also plays important role in adsorption behavior and photocatalytic activity of the catalyst.

Keywords—*photocatalyst; pre-treatment; light wavelength; seawater; band gap energy*

1. INTRODUCTION

Seawater had become very hot issues nowadays. Seawater contains large amount of chloride (Cl⁻) and sodium (Na⁺) ions which conquering the world over 97% and left the small percentage amount of fresh water [1]. The lack of fresh water supply had become a reason to develop the desalination process. Desalination is a technique in removing the salt concentration and minerals from the seawater or saline water by some processes to produce (potable) fresh water fit for human consumption. In the last two decades, desalination industry has become the important sources of producing fresh water. For example, countries such as Middle East area especially in Saudi Arabia, Kuwait and etc and Singapore relied on the desalination technologies to supply the fresh water for utilizing in households, industries, agricultures and etc. These countries force to depend on the desalination technologies conjunction with the increasing of the population. Approximately 75 million and might be increase people worldwide obtain fresh water from desalination of seawater and brackish water [1].

Nowadays, photocatalyst technology have been investigate that can be used to degrade the contamination in the water and also have been used as an alternative methods to purify the waste water and seawater. Photocatalyst based TiO₂ have been used widely because of its effectiveness in purifying the water. TiO₂ is belongs to the family of transition metal oxides. In photocatalysis, (TiO₂) will generate hydroxyl radicals in the presence of ultraviolet (UV) light (photons) and attack organic matter present as pollutants in water and wastewater [2]. Photo-induces redox reactions of adsorbed substances and hydrophilic conversion of TiO₂ itself are two types of photochemical reaction occur on a TiO₂ surface [3]. TiO₂ is commonly utilized for

industrial now and in future because of its efficiency photoactivity and highest stability catalyst if compared to others catalyst used for photocatalyst. TiO_2 is inertness to chemical environment and its long term photo stability has made TiO_2 catalyst become the vital materials in many applications [4].

The initial innovation of photocatalyst studied was started by Fujishima and Honda in 1972 [5] where they were succeeded to prove about possibility of hydrogen production through water decomposition by photocatalyst and solar energy. Then, the researches were continued by some researchers in the same field and some of them also had implemented the photocatalyst by using TiO_2 catalyst to treat the seawater. For example, the application of TiO_2 was continued to investigate by Al-Rasheed and Cardin [6] by using the TiO_2 as an agent to degrade the humic acid contain in the seawater. Rather than that, Shinde et al. [7] was reported that the photoelectrochemical (PEC) reactor have potential in degrading the physicochemical and bacteriological in seawater. The wide application of TiO_2 also can be used to remove oil-emulsion contain in seawater up to 43% and for water up to 90% reduction [8]. Thus, the development of TiO_2 based photocatalyst application were still had been interested by some other researchers.

Energy from the light is needed to generate the catalyst based photocatalyst activity to excite the conduction and valence band to produce electron and hole pair. The electron and hole pair will be formed when the catalyst is absorbing the photon energy from the light and excite the band gap of catalyst [9]. The increasing of the rate of electron hole pair on the catalyst active site is increasing together with increasing of light and pollution will be fully oxidized by photocatalytic system [10]. The usual band gap energy of catalyst using in photocatalytic reaction should be between 0.7 to 3.5 eV. Sobczynski and Dobosz [11] had reported that the energy band gap of TiO_2 (anatase) is 3.2 eV. The same statement was reported by Ibhaden and Fitzpatrick [4] that the active phase of TiO_2 (anatase) is 3.2 eV and requires less than 387 nm of light wavelength. In addition, another investigation states that the TiO_2 (anatase) catalyst is having 3.3 eV of band gap energy and stable at the light wavelength under 387 nm [12]. Reddy et al. [13] reported that the synthesise catalyst will have energy band gap estimation from 3.3 eV to 3.4 eV and commercial samples will have band gap energy of 3.2 eV.

The innovative ways need to be improving in photoreaction technology to be applied in the desalination process due to the limited utilizing of photocatalyst in aspect of salt decomposition. Most of researches were focusing only for using the photocatalyst technology to improve the quality of water and seawater. To fulfil the improvement along with the desalination technology, the photoreaction technology also need to develop. Thus, this investigation is mainly to investigate the compatibility of hybrid catalyst TiO_2 that supported by oil palm fiber ash in reducing the salt concentration in the seawater and contamination degradation by varying the light wavelength of 365 nm and 420 nm in photocatalytic seawater pretreatment. This investigation is alternative technology and expected to overcome the water problem faced by world nowadays by improving the desalination technology to produce the fresh water, reducing of cost production and energy consumption in seawater purification.

2. EXPERIMENTAL PROCEDURES

A. Materials Preparation

Oil palm fiber ash was obtained from Felda Lepar Hilir 3 Palm Oil Mill, Gambang, Kuantan, Pahang, Malaysia. The TiO_2 was purchased from Sigma Aldrich contain 99% of purity. The seawater was obtained from Teluk Cempedak, Kuantan, Malaysia (Latitude: 3.815 Longitude: 103.363).

B. Catalyst Preparation and Characterization

The catalyst that consists of oil palm fiber ash and TiO_2 at a weight ratio of 1:1 was prepared by wet impregnation method. The mixture of was mixed with deionized water and stirred for four hours at 80°C temperature and slurry mixture was formed. The catalyst was dried for overnight in the oven at 100°C. The catalyst was then calcined at 500°C. The hybrid catalyst was crushed and sieved to the size of < 100 μm to have homogenized catalyst size. The catalyst is named as Ti:Ash 50:50.

The fresh and spent catalysts were analyzed for their specific surface area, pore volume and pore size by using nitrogen adsorption (Micromeritics ASAP2020). The fresh catalyst band gap energy was determined via Shimadzu, UV-2600 UV/Vis/Nir.

C. Photocatalytic Reactor and Procedures

The photocatalytic reactor set up is illustrated in Fig.1. The hybrid catalyst Ti:Ash 50:50 was tested in a one litre borosilicate glass photoreactor. The photocatalytic reactor system consists of vacuum pump, water container and condenser system to collect the vaporize water released from the reactor. The system also contains three regulator fans to control the temperature of the black box to prolong the life span of the light bulb. About 800 mL of seawater was used. The catalyst to seawater weight ratio was set at 1:400. The magnetic stirrer was used and set at 400 rpm to have well mix the catalyst Ti:Ash 50:50 and

seawater sample. The investigation was carried out for two hours by exposing the reactor with either 365 nm or 420 nm mercury light. A 47 mm diameter of mesh filter paper (1.5 μm) was used to filter out the catalyst from product seawater.

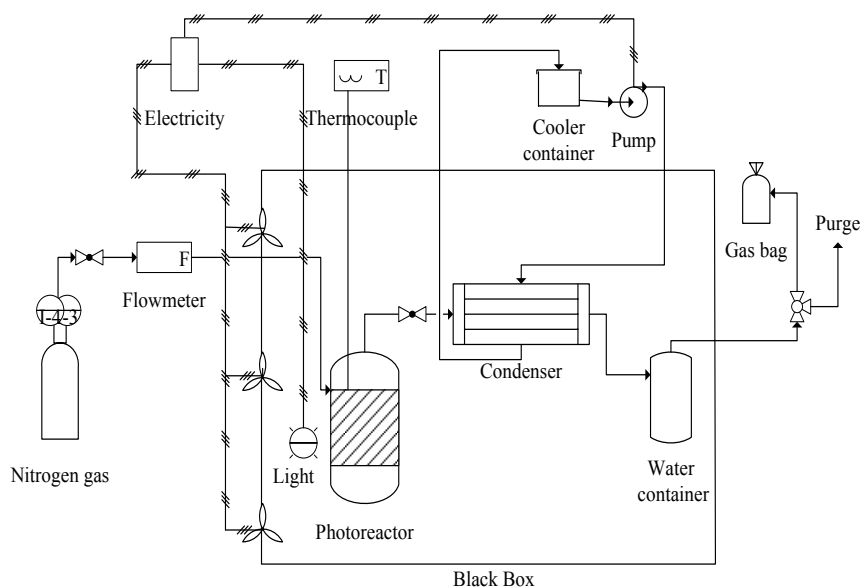


Figure 1: Schematic diagram of reactor set up.

The quality of filtered seawater was determined prior and after testing. The pH, chemical oxygen demand (COD), conductivity and turbidity of the seawater was determined. Hach Sension+ 150 mm was used to determine the pH and conductivity of the seawater. The turbidity of seawater was analyzed via Turbidity Meter Hach 2100 model. Meanwhile, the COD of the water was determined by using COD Digestion Reagent Vial High Range (435 COD HR).

3. RESULT AND DISCUSSION

A. Catalyst Characteristic

The hybrid Ti:Ash 50:50 catalyst was synthesized via wet impregnation method. The fresh and spent catalysts were characterized by using N_2 adsorption to determine their specific surface area, pore size and pore volume. Meanwhile, the fresh TiO_2 and Ti:Ash 50:50 catalyst band gap was determined by using UV/Vis/Nir spectroscopy.

Table 1 tabulates the specific surface area, pore size and pore volume of the fresh and spent Ti:Ash 50:50 catalysts. The catalyst was calcined at 500°C and tested with either 365 nm or 420 nm light. N_2 adsorption indicates that the catalyst was in the range of 2 nm to 50 nm. This result indicates that the catalysts are mesoporous. It can be seen in Table 1 that the specific surface area for both spent catalysts; tested with 365 nm and 420 nm, decreased from $9.15 \text{ m}^2/\text{g}$ to $6.67 \text{ m}^2/\text{g}$ for spent Ti:Ash 50:50 catalyst tested with 365 nm and $5.96 \text{ m}^2/\text{g}$ for spent Ti:Ash 50:50 catalyst tested with 420 nm. In addition, the same trend of pore volume is also observed for both catalysts. The pore volume of Ti:Ash 50:50 tested with 365 nm reduced from $3.49 \times 10^{-2} \text{ cm}^3/\text{g}$ to $2.29 \times 10^{-2} \text{ cm}^3/\text{g}$. And, the pore volume of Ti:Ash 50:50 tested with 420 nm also decreased from $3.49 \times 10^{-2} \text{ cm}^3/\text{g}$ to $2.94 \times 10^{-2} \text{ cm}^3/\text{g}$. However, pore size demonstrates different reading for both spent catalysts. The pore size of Ti:Ash 50:50 tested with 365 nm decreased from 18.63 nm to 15.54 nm. The pore volume of Ti:Ash 50:50 that tested with 365 nm reduced after testing. It might be caused by the reaction occur on the catalyst surface to degrade the contaminants and adsorption of the salt components had deposited onto the catalyst surface. But, the spent Ti:Ash 50:50 that tested with 420 nm light shows different results. The pore size of Ti:Ash 50:50 tested with 420 nm increased from 18.63 nm to 19.64 nm. It might be because of the catalyst do not reactive at 420 nm. The condition resulted the catalyst become fluffy and the catalyst pore cracked after prolong contact with the water.

Furthermore, UV/Vis/Nir spectroscopy indicates that the band gap energy of Ti:Ash 50:50 was 3.1 eV. And, the absorption of light wavelength was less than 385 nm. In addition, the TiO_2 alone also shows that the band gap energy value is equal to 3.1 eV and requires light wavelength of less than 385 nm. Thus, the result suggests that the band gap energy of TiO_2 catalyst had unchanged after synthesizing process. Hence, it can be deduced that the addition of support like oil palm fiber ash in the catalyst does not influence the band gap energy of TiO_2 .

B. Effect of Light Wavelength to Seawater Desalination Process

The quality of the fresh and product seawater was analyzed. The pH, conductivity, turbidity and COD of the seawater that reacted with different light wavelength are tabulated in Table 2.

Table 1: N₂ adsorption of Ti:Ash 50:50 that calcined at 500 °C.

Catalyst weight ratio, %	Specific surface area (m ² /g)			Pore volume x 10 ² (cm ³ /g)			Pore size (nm)		
	Fresh	Spent, 365 nm	Spent, 420 nm	Fresh	Spent, 365 nm	Spent, 420 nm	Fresh	Spent, 365 nm	Spent, 420 nm
Ti:Ash 50:50	9.15	6.67	5.96	3.49	2.29	2.94	18.63	15.54	19.64

Table 2: Seawater properties before and after the testing.

Seawater sample Analytical test	Seawater sample (initial)	Ti:Ash 50:50, 0 nm	Seawater sample (Initial)	Ti:Ash 50:50, 365 nm	Ti:Ash 50:50, 420 nm
Temperature (°C)	25.0	25.0	25.0	55.7	100.0
Conductivity (mS/cm)	49.2	48.1	48.7	44.3	49.2
COD (mg/L)	717	682	770	580	780
pH	8.08	7.87	8.17	7.57	8.13
Turbidity (NTU)	2.80	0.11	2.78	0.11	0.17

Table 2 tabulated that the conductivity of seawater treated with Ti:Ash 50:50 managed to reduce from 49.2 mS/cm to 48.1 mS/cm (2.24%) when no light was used in the system. In addition, the COD value of seawater reduced slightly from 717 mg/L to 682 mg/L (4.88%). Meanwhile, the pH and turbidity of seawater also decreased after treated with Ti:Ash 50:50 when no light was used. It can be seen that no significant change was observed when no light was used. The turbidity improvement was due to the effective filtration process after the testing. When no light was used, no photocatalytic occurred. The little improvement of conductivity, COD and pH might mainly due to adsorption. Therefore, adsorption dominated the process when no light was used and no significant improvement was achieved.

Table 2 also indicates that the conductivity of seawater that treated with Ti:Ash 50:50 and 365 nm light reduced from 48.7 mS/cm to 44.3 mS/cm, approximately 9% reduction was achieved. The COD value also decreased from 770 mg/L to 580 mg/L which indicates of up to 24% reduction. Meanwhile, the pH of seawater reduced from 8.17 to 7.57 (~ 7% reduction) after treating with Ti:Ash 50:50 and 365 nm light. The turbidity reduced more than 90% reduction which stated from 2.78 NTU to 0.11 NTU. However, it can be seen that the conductivity and COD of seawater increased from 48.7 mS/cm to 49.2 mS/cm and 770 mg/L to 780 mg/L respectively after treating with Ti:Ash 50:50 and 420 nm light. The pH, on the other hands, slightly reduced from 8.17 to 8.13. The turbidity of seawater significantly decreased from 2.78 NTU to 0.17 NTU after treated with Ti:Ash 50:50 and 420 nm light. The reduction of turbidity and cloudiness of the water causes by filtration process that was carried out to separate the catalyst from seawater.

The COD value of water tested with 420 nm light increased compare to the COD value for water tested with 365 nm. The result shows that Ti:Ash 50:50 tested with 365 nm has more capabilities in reducing the salt components and contaminants in the seawater compared to the Ti:Ash 50:50 tested with 420 nm. The increased of catalyst efficiency is influenced by the increment of the efficiency of electron and hole generation effect by the shorter wavelength irradiation [14]. The result of UV/Vis/Nir is in line with this statement as the hybrid catalyst Ti:Ash 50:50, which has the band gap energy equal to the 3.1 eV requires less than 385 nm wavelength of light for the photon energy to excite the catalyst. Hence, by using of 420 nm wavelength of light in the photocatalytic reactor, the reaction was not effectively occurred. Thus, the using of light wavelength at 365 nm was considered most suitable light source for seawater pre-treatment via photocatalytic reaction system. Although most of the researchers suggested that TiO₂ (anatase) had band gap energy equal to 3.2 eV [4, 11, 15], Valencia et al. [16] reported that the band gap energy less than 3.5 eV can be utilized in the photocatalyst system. In addition, the band gap energy of TiO₂ is in the range of 2.86 eV to 3.34 eV for anatase phase [17].

The light wavelength of 420 nm was ineffective in the photoreduction. It might because of the increasing of wavelength i.e. decrease irradiation energy cause the reduction of the electron and generated hole [14]. Thus, the energy of the electrons and hole excited by 420 nm was too low for photocatalytic reduction. Besides, by using 420 nm wavelength of light, the light gave high energy causing the temperature of seawater reach water boiling point (100°C). It is observed that the temperature of seawater increased from 25°C to 100°C when 420 nm of light was used. This condition leads to production of 20 ml of distillate water (2.5% yields) via distillation, not photocatalytic reaction. The distillate water property is tabulated in Table 3. It can be seen in the Table 3 that the distillate water has a conductivity of 20.7 µS/cm, a turbidity of 0.11 NTU, a COD of 4 mg/L and a pH at 7.16. In comparison to standard A of drinking water specification, the distillate water that produced via distillation

was complied with the standard specification (Table 3). However, the application of 365 nm light resulted to an increment of seawater temperature, from 25.0°C to 55.7°C. No fresh water was obtained at this condition. It can be concluded that the hybrid Ti:Ash 50:50 photocatalyst are reactive catalyst for degrading the contaminant when 365 nm light was exposed, while distillation dominated the process when 420 nm light was applied.

Table 3: Analyzed data of distillate water by using 420 nm light wavelength.

Seawater sample Analytical test	Distillate water, 420 nm	Standard A (Drinking water)*
Conductivity ($\mu\text{S}/\text{cm}$)	20.7	< 1000
COD (mg/L)	4	< 10
pH	7.16	6.5 – 8.5
Turbidity (NTU)	0.11 NTU	< 5

*Standard water from Interim National Water Quality Standards for Malaysia (INWQS) [18]

4. CONCLUSION

The effectiveness of Ti:Ash 50:50 to treat the seawater by using 365 nm, 420 nm and without light present in the photocatalytic reactor was investigated. The hybrid catalyst was prepared by using wet impregnation method and tested in the photocatalyst reactor scheme. It is found that Ti:Ash 50:50 is totally influenced by the wavelength of light. It indicates that the reaction on the surface of catalyst significantly depended on the light's wavelength. Without light present, the system was dominated by absorbance without reaction due to small increment obtained. The result indicates that Ti:Ash 50:50 strongly requires 365 nm wavelength of light to excite the band gap energy of TiO_2 (3.1 eV) and causes the photocatalytic activity occur on the catalyst surface. The application of 420 nm in photocatalytic reactor to treat the seawater by using Ti:Ash 50:50 is not an efficient light to cause the reaction on contaminant degrading. But, the high energy generated by the 420 nm light leads to cause the temperature of seawater increases and distillate water was produced. The salinity of seawater also increases as the increment of the seawater conductivity is observed. Better quality of seawater that treated with Ti:Ash 50:50 and 365 nm light as reduction of conductivity, pH, COD and turbidity were achieved as the reaction was occur in the system. It can be deduced that the light wavelength effect the photoreduction activity of the hybrid Ti:Ash 50:50 catalyst.

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