Hybrid TiO_2 in photocatalytic seawater desalination: Effect of operating time

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Abstract. Titanium dioxide (TiO_2) is excellently used in various applications including wastewater treatment. It is known to have superb pigmentary properties, high adsorption in the ultraviolet (UV) region, and high stability. The objective of this paper is to study the effect of contact time of seawater desalination in the photocatalytic reaction. The hybrid TiO_2 catalysts, a mixture of TiO_2 and biomass ash, was synthesized via wet impregnation and calcined at 800 °C. The photocatalyst was then characterized by using Scanning Electron Microscopy (SEM) and Braunauer-Emmett-Teller (BET). The investigation was carried out in a photoreactor equipped with UV light operated for up to 6 hours with catalyst to seawater weight ratio of 1:400 and stirring speed of 600 rpm. The salt concentration, turbidity and pH of the water were determined prior and after the investigation. The result indicates that the salt concentration gradually decreased as the contact time increased. However, there is no significant change on pH value of the water. It can be concluded that the hybrid TiO_2 is able to reduce the seawater salinity effectively.

Introduction

Nowadays, the scarcity of clean and fresh water resources and the need for additional water supplies is already critical and will be increasingly important in the near future. Recently in Malaysia, the clean water supply becomes a major concern by the government because of the shortage in clean water supply especially during long drought period. Only 2.5% of all water sources are fresh water, with 80% of this amount being frozen in the icecaps or combined as soil moisture, whereas about 97.5% of water source is salt water [1]. Seawater is the main source of water and can be found abundantly around the world. Unfortunately, seawater was poorly utilized and treated to become clean water source [2].

Desalination process is among the oldest mankind's technology used to treat seawater. It is a process to remove dissolve salt in salt water. However, one of the most sensitive and critical aspects of any water project is cost and the conventional desalination process is very costly [3]. Thus it has become pertinent to do further research in this field to improve the desalination process. In spite of technological advancement in the desalination technology with the passage of time, significant efforts in this field would lead to continuous decrease in the cost of water desalination [4]. The most expensive part in any of the desalination process is the price of energy involved. Many researchers like Garcia-Rodriguez [5] investigate seawater desalination driven by various renewable energies. However, solar desalination is an emerging and promising renewable energy powered technology for producing fresh water [6].

A photocatalyst is defined as a substance that is activated by the absorption of a photon and helps to accelerate a reaction, without being consumed [7]. It is widely used for desalination process by using solar energy [8-10]. Nevertheless, the photocatalytic of seawater desalination is not well explored yet. Photocatalysis has recently become a common word and various products using photocatalytic function have been commercialized. Among photocatalyst, TiO_2 is almost the only material suitable for industrial used at present and probably in the future too. This is because TiO_2 has the most efficient photoactivity, the highest stability and the lowest cost [11]. TiO_2 has special properties and is most frequently used as photocatalyst in water purification. Previous studies by Abhang *et. al.* [7] succeeded in purifying dirty water by using TiO_2 photocatalyst.

In this study, an alternative low cost photocatalyst by implementing biomass ash is developed for seawater desalination. Biomass ash is waste product from the palm oil fiber ash and extremely low in cost. It is converted from the waste product into a valuable product and worth to be used as a supporter for photocatalyst [12]. It is also abundance and has a potential to be good pollution absorber for water purification [13]. The used of biomass leads to significant reduce of the cost of the hybrid catalyst. Biomass ash is richer in calcium, silicon, alkaline minerals and micronutrient that is excellent for adsorption of the pollution and cleans the water significantly [14]. The influence of operating time to the catalyst performance in seawater desalination by purifying and salt removing of the seawater is investigated.

Experimental

Material

The seawater sample was obtained from Teluk Cempedak, Kuantan Pahang. Meanwhile, the biomass ash/palm oil fiber ash was collected from palm oil mill boiler in Felda Lepar Hilir 3, Kuantan Pahang. Titanium dioxide (TiO_2) with purity of 99% was obtained from Sigma Aldrich Malaysia.

Catalyst preparation

The catalyst was synthesized by using wet impregnated method. A mixture of 50 wt% titanium dioxide and 50 wt% biomass ash was stirred for 4 hours at 80 °C. The catalyst was dried in oven at 100 °C overnight. It was then calcined for 4 hours at 800 °C. The synthesized catalyst was cooled in the desiccator. Finally, it was crushed and sieved to the size of <100 μm.

Photocatalytic reaction procedure

A photocatalytic reactor was set up for the reaction process. It was a batch photoreactor consists of one liter of borosilicate-made reactor with eight centimeter (cm) in diameter and 30 cm in height. An UV light with 365 nm of wavelength was placed about three cm from the reactor. A thermocouple was used to monitor the reactor temperature.

A mixture of catalyst and seawater with a weight ratio of 1:400 was placed in the reactor. The mixture was then stirred at 600 rpm as the UV light was on. The investigation was carried out at operating time of 120, 240 and 360 minutes. All the experiment setup was done inside a black box to prevent UV light exposure out of the box.

Water analysis

The conductivity, pH and turbidity of the seawater were determined prior and after the investigations. The conductivity of seawater was tested to determine the salt concentration by using conductivity meter. Meanwhile, the pH was measured by using METTLER TOLEDO pH meter, and the turbidity was determined by using HACH 21000 portable turbidity meters.

Photocatalyst characterization

The fresh and spent catalysts were analyzed to determine the property change due to the investigation. The surface morphology of catalyst was analyzed by using an EVO 50 ZEISS, Scanning Electron Microscopy (SEM). The catalyst was observed throughout lower resolution to the higher resolution to get the best surface morphology of the catalyst. Meanwhile, the surface area, pore volume and pore size were determined via Nitrogen Adsorption of BET analyzer. The sample was degased for 6 hours at 200 °C to remove all moisture of the sample prior to analysis.

Result and Discussion

The performance of the catalyst in the photocatalytic reactor for seawater desalination was investigated at various operating times. The weight ratio of catalyst to seawater and the mixing rotation were constant at 1:400 and 600 rpm, respectively. The result of the investigation is tabulated in Table 1.

Table 1. Hybrid catalyst performance at various operating time

Catalyst	Operating time [min]	Conductivity [m/S]	Total salinity reduction (%)	Turbidity [NTU]	pH
TiO_2	0	53.3	0	1.86	8.10
TiO_2	120	42.8	19.7	0.10	7.32
TiO_2	240	41.8	21.6	0.12	7.27
TiO_2	360	41.6	22.0	0.16	7.22
Hybrid TiO_2	0	53.3	0	1.86	8.10
Hybrid TiO_2	120	44.9	15.8	0.14	7.69
Hybrid TiO_2	240	40.5	24.0	0.13	7.68
Hybrid TiO_2	360	39.7	25.5	0.14	7.60

In desalination process, the conductivity value of the water is parallel to the salt concentration of the seawater i.e. salinity of water. It can be seen in Table 1 that the salinity of water reduced as longer operating times were used. The initial value of seawater conductivity was 53.3 m/S. There is a drastic reduction of conductivity after 120 minutes for both TiO_2 and Hybrid TiO_2 catalyst which were reduced to 42.8 m/S and 44.9 m/S, respectively. Nevertheless, less significant difference was observed after 240 minutes as the conductivity value remained close to 41.8 m/S and 40.5 m/S.

After 120 minutes, the total salinity reduced significantly for both TiO_2 and Hybrid TiO_2 catalyst to 19.7 % and 15.8 %, respectively. This trend continued until 360 minutes of operating time was done for Hybrid TiO_2. About 24.0% reduction after 240 minutes and 25.5% reduction after 360 minutes were observed for Hybrid TiO_2. It also can be seen that less reduction were obtained for the next 240 minutes which were 21.6% after 240 minutes and 22.0% after 360 minutes for TiO_2.

The salinity reduction of seawater was significantly affected by the operating time. It is because salinity reduction depends on the contact time of seawater was being exposed to the UV light irradiation. The UV light exposure allows the excitation of electrons to the conduction band and generates holes in the valence band of semiconductor catalyst. Holes react with water to produce $\cdot OH$ free radicals from oxidizing the organic compounds. Hence, increasing the exposure time, more pairs of electrons and holes are formed to produce more hydroxyl OH for oxidizing the organic compounds [15].

The turbidity of the seawater improved to <1 NTU after 120 minutes of the investigation. It showed that the photocatalytic reaction was able to remove particles by sedimentation of the particle. Furthermore, the initial pH of the seawater was 8.10 then was reduced about 7.22 and 7.60 for TiO_2 and Hybrid TiO_2 at the end of operating time, respectively. In photocatalysis, UV light irradiation on semiconductor powder with energy more than its band-gap energy produces electrons (e^-) and holes (h^+) in conduction band and valence band, and they have abilities to reduce and oxidize the molecules at the surface, respectively [16]. The desalination process occurs due to the reduction of the salt concentration in seawater. Seawater contains Chloride ions (Cl^-). During the photocatalytic reaction of seawater, the water molecules excited to form $\cdot OH$ free radicals. The $\cdot OH$ radical might react with chlorine ion (Cl^-) to produce Hypochlorous acid ($HClO$). This reaction might also cause the reduction of pH from alkaline to slightly neutral pH (Table 1).

The morphology for fresh and spent of TiO_2 and for fresh and spent of Hybrid TiO_2 are illustrate in Figure 1a-1d, respectively. The SEM shows that the fresh Hybrid TiO_2 catalyst consist of large amount of mono dispersed particulate while fresh TiO_2 catalyst shows more agglomeration which is parallel to the result obtained by Lin *et.al* [17] in their work. The morphology of fresh TiO_2 was hard-grained aggregate and nearly spherical nanoparticles and porous in nature. Fresh TiO_2 has many shadow regions indicating that the nanoparticles have agglomerated [18]. It indicates that particles of fresh TiO_2 congregate together so densely that few gaps exist between the pores. In contrast, the particles of fresh Hybrid TiO_2 congregate loosely. It might lead to better surface area for the reaction process occurs [19]. The agglomeration of fresh TiO_2 particles resulted to low surface area and pore volume [18]. After 360 minutes of operating time, both spent TiO_2 and Hybrid TiO_2 particles are well distributed and maintain their original size and shape. Most part of the surface returned back to initial condition after photodegradation process. This gives an opportunity to use the catalyst repeatedly.

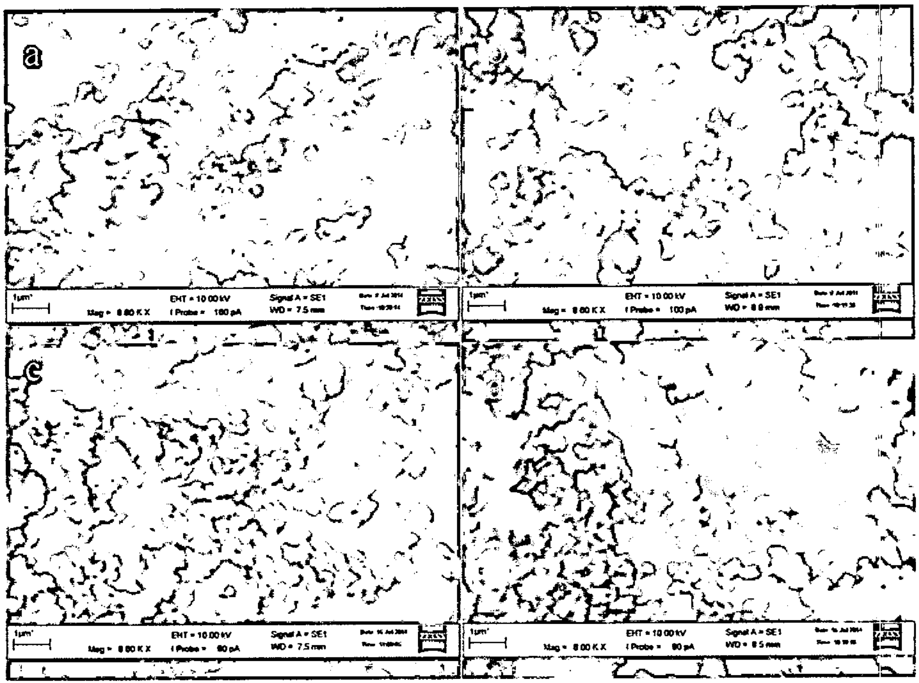

Figure 1: Catalyst morphology for (a) TiO_2 fresh (b) TiO_2 spent (c) Hybrid TiO_2 fresh (b) Hybrid TiO_2 spent catalysts.

Table 2. BET analysis for the titanium dioxide and biomass ash

BET analysis	Calcined temperature (°C)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
TiO_2	0	11.94	0.03	89.91
Biomass ash	0	34.85	0.02	26.40
Fresh TiO_2	800	12.22	0.04	88.02
Spent TiO_2	800	3.58	0.03	218.05
Fresh Hybrid TiO_2	800	4.00	0.01	127.07
Spent Hybrid TiO_2	800	6.42	0.02	101.98

The BET test was done to determine the surface area, pore volume and pore size of the fresh and spent of both catalysts. The result is tabulated in Table 2. It shows that by adding the biomass ash as a supporter for Hybrid TiO_2 increased the surface area during and after the reaction occurs. BET surface area has no effect on the phase of the TiO_2 nano particles [20] but they do have an effect on the photocatalytic reaction. Larger surface area increased adsorption/desorption capacity, consequently good photocatalytic activity [21]. The catalysts reacted faster for the reaction process occurs when having the higher surfaces areas. The initial pore size of the TiO_2 was bigger (89.91Å) than biomass ash (26.40 Å). The porous structure showed to be very important for the photocatalytic activity of TiO_2 due to its enhanced surface area [22]. The pore structure of TiO_2 influenced the adsorption of photoelectrons, reagents and products on the surface site. As the result, the photocatalytic activity of TiO_2 changed with its pore structure [18]. It can be seen that the pore size of spent TiO_2 increase to 218.05 Å after the reaction. Meanwhile, the spent hybrid TiO_2 do not show much difference than its initial value. However, the surface area of TiO_2 catalyst decreased drastically from 12.22 m^2/g to 3.58 m^2/g after the reaction. The surface area of hybrid TiO_2, in contrast, increased to 6.42 m^2/g from 4.00 m^2/g. This might be the reason why hybrid TiO_2 performed better than TiO_2 alone.

Conclusion

The biomass ash can be used as a supporter for the Hybrid TiO_2 photocatalyst as it can reduce the catalyst cost. The salt concentration of the seawater was gradually decreased as the contact time increased in the photoreactor of seawater desalination. The highest total salinity reductions after 360 minutes of operating time are 22.0% for TiO_2 and 25.5% for Hybrid TiO_2. The turbidity improved to <1 NTU after 120 minutes of the investigation but there was not much change on turbidity value by increasing the reaction time. The pH value of the water was about 7.22 and 7.60 after the reaction for TiO_2 and hybrid TiO_2, respectively. It can be deduced that the Hybrid TiO_2 is an alternative potential catalyst that able to reduce the seawater salinity effectively.

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