Photocatalysis of Sago Wastewater using Sago Starch-TiO_2 Films

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Abstract
This work is about wastewater treatment using sago starch-TiO_2 hybrid film. The surface morphology of the films was evaluated using Scanning Electron Microscopy (SEM), and the analysis of the sago wastewater treatment films was in terms of the Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Suspended Solid (TSS). Pseudo first order kinetic model was also included in the analysis. Findings show that the TiO_2 particles were embedded well within the starch matrix. White spots were observed on the SEM images indicating the distribution of TiO2 particles on the surface of the films. The ability of the films to treat sago wastewater was observed by the percentage reduction of BOD, COD and TSS, which were estimated to be about 80% and 60% for the photocatalysis under controlled UV light of 40 watts and under the sunlight, respectively. The Pseudo First Order kinetic model fit well onto the experimental data with mean square error of 2.3- 2.5 indicating the suitabilty of this model to predict the changes of BOD, COD and TSS with time. The constant, k, was estimated to be 0.0074.
Keywords: Sago starch, film, titanium oxide, photocatalysis, wastewater treatment

1. Introduction

Sago starch is a low cost and renewable resource with gel-forming ability, making it an attractive material for various applications such as thin film. Starch contains of amylose and amylopectin. Amylose consists of a linear chain of d-glucose units that are linked by α-1, 4 glycosidic linkage, which allows for tighter packing enhancing film strength. Sago starch composed of 34% amylose and 66% amylopectin (Sondari et al, 2020). Starch in heated water causes amylose to swell and form a gel-like matrix, an essential property that allows the formation of a coherent film upon cooling. The presence of amylose create strong intermolecular bonds contributes to the mechanical strength of the film, making it more resistant to tearing and puncturing. On the other hand, amylopectin is a highly branched polymer, consisting of glucose units linked by both α-1,4 and α-1,6 glycosidic bonds (Ogori and Taofeek, 2022), which contributes to its solubility and viscosity. The branched structure of amylopectin produces flexible films that can be important when some stretchability is required. Amylopectin retains moisture, which can be beneficial for maintaining film integrity. Modification of starch is necessary to achieve certain desired functionality such as adding plasticizers like glycerol or sorbitol to reduce the intermolecular forces, making the film more pliable. Cross-linking agents like epoxy compounds can also be added to improve the thermal stability and mechanical properties of the film, addressing the limitation of starch films to water sensitivity.

Several studies have reported on the development of film produced using starch [Zuzanna et al., 2021; Hooman et al., 2015; Arifa et al., 2020; Anitha et al., 2024). These work use varieties of starch including from maize, potato, oat, rice and tapioca. Findings from these work show that starch film has strength up to 12 MPa. The use of sago starch to produce film has also been studied [Dutta et al., 2024; Xue Mei et al., 2020; Layuk et al., 2019; Sondari et al., 2019; Jiang et al., 2020) and sago starch was also used in this work due to its abundance availability locally. Titanium dioxide is a common catalyst used in photocatalysis, but it often comes in powder form due to its nanosize (less than 100 nm). Immobilization of TiO_2 powder such as within film making it easier for reuse. Sago starch films reinforced withtitanium dioxide films applied in wastewater treatment has not been studied widely. Other studies on starch films reinforced with nanoparticles such as titanium dioxide are those made from corn (Hejri et al., 2013; Picolotto et al, 2023) andfrom yam (Chemiru and Gonfa, 2023).

Photocatalytic activities degrade pollutants into harmless byproducts such as carbon dioxide and water. In addition, this method has the advantage to reduce the generation of sludge, reducing the need for its handling and disposal. The use of sunlight in photocatalysis reducing the use of energy as well. Studies found in the literature on photocatalysis show the potential of this method for wastewater treatment with high percentage of pollutant removal of up to 100% [Ren et al., 2021; Shumaila et al., 2023; Tanzifi et al., 2016; Rostami et al., 2021; Koohestani et al., 2021; Ernawati et al., 2019). These work reported on pollutants removal of up to 64% for para nitro Toluene, of up to 99% for Congo red, of up to 90% for metanil yellow and of up to 90% for toluene. Findings from these work proved the capability of photocatalysis to treat wastewater, and in this work it was used for sago wastewater. Sago processing is one of the important industry in Southeast Asia, and it is associated with a huge amount of wastewater. Malaysia is one of the main sago exporters in the world with export of more than 40,000 tons of sago starch since 2004, and this export has been increasing 15-20% per year (Jenol et al., 2014; Mohamad et al., 2011). It is reported that one sago processing mill produces about 30 L/min of wastewater, which is about 21,600 L for an operation of 12 hours, daily(Wee et al., 2017). The wastewater is usually discharged to the nearby river, which is not good for the environmental sustainability in a long term. The search of low cost and efficient method to treat the huge amount of the wastewater is essential.

The objective of this work is to produce film using sago starch, and glycerol was used to modify the properties of the starch. The sago starch film was meant to immobilize TiO_2 particles, and the hybrid starch-TiO_2 film was used to treat sago wastewater.

Immobilization of TiO_2 helps to keep the particles in place, preventing it from being washed away during the wastewater treatment process, and also it can be reused, making the treatment process more cost effective and sustainable. In addition, reducing the risk of fine TiO_2 particles being released into the environment helps mitigate potential health risks associated with nanoparticle exposure. In this work, the characteristics of the film and the capability of the hybrid film to treat sago wastewater were analysed.

2. Methodology

40 mL of distilled water in 100 mL beaker was heated until the temperature reached around 70°C. Then, 2g of sago starch, 0.01 ml glycerol and. 0.01g of TiO_2 were added into the beaker, and the mix was stirred well for 30 minutes. Sago starch used here was those purchased from nearby supermarket in Kota Samarahan, Sarawak. Casting method was used to mold the thin film by putting the mixture in a petri dish, which was then put in a drying oven at temperature of 60°C 24 hours. After that, the film was cooled down at room temperature and kept in storage for further analysis. These steps were repeated using 0.01-0.03 g of Titanium Oxide. The surface morphology of the films was characterised using Surface Morphology Scanning Electron Microscopy (SEM) at 1000x magnification. The performance of the films to treat sago waste water was analysed based on the reading measured for BOD, COD and TSS. Here, the film was immersed in the sago wastewater contained in a beaker and exposed to UV light from a 40 Watts bulb. The beaker was wrapped with aluminium foil to retain the UV light within the beaker. Experiments were also done under the sunlight. The temperature recorded in Malaysia usually ranging from 27-33°C and the average solar radiation of 4-6kWh/m2 during clear days (Azhari et al, 2008).

3. Results and Discussion

Sago starch sample was subjected to SEM with magnification of500x for the granules morphology analysis, and the result is shown in Figure 1. The sago starch granules shown here are in round and oval shape with some chipped granules maybe due to the processing. The particle analysis shown that the granules are within 1 – 100 μm, as shown in Figure 2.

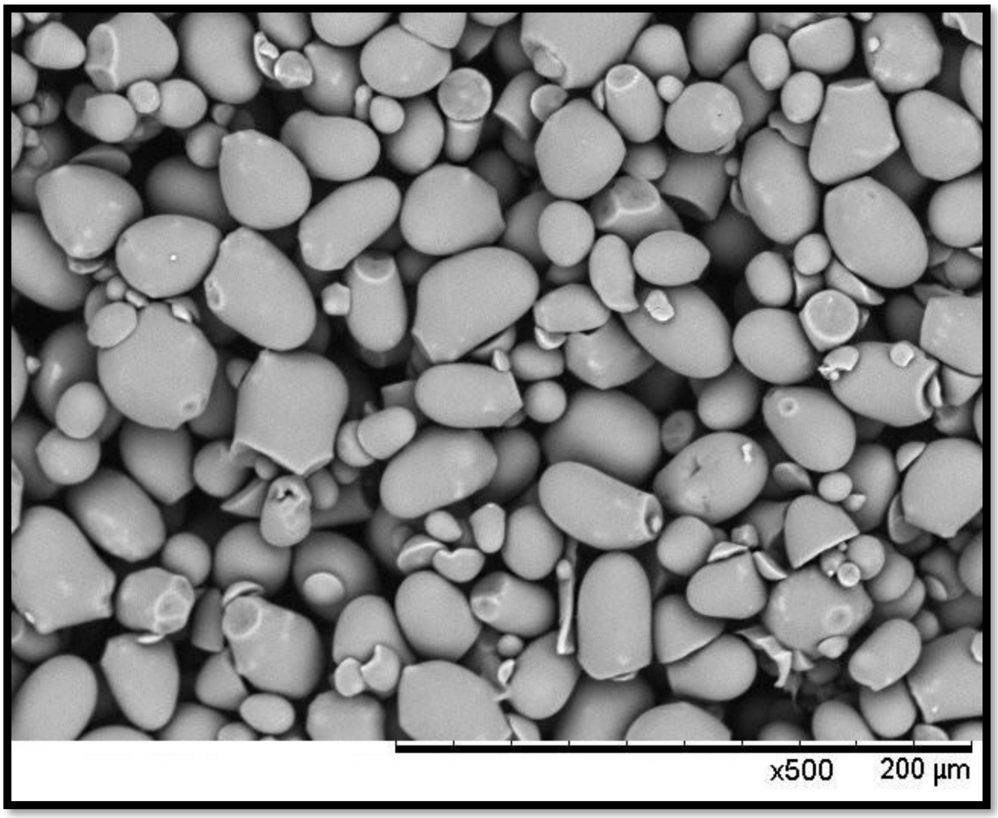


Figure 1: Sago starch granules with magnification of 500x

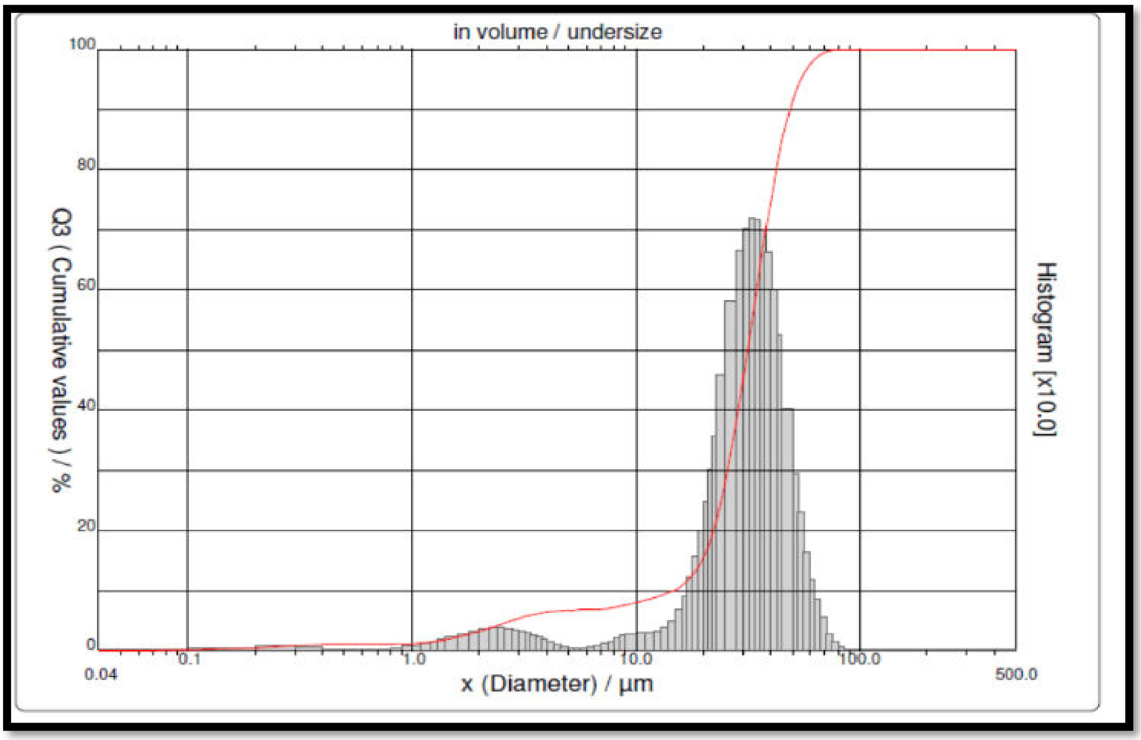


Figure 2: Sago starch granules' size distribution

3.1 Fourier transform infrared spectroscopy

The chemical properties of the sago starch film are analysed using FTIR as shown in Figure 3. Strong intensity is shown for the peaks observed at 3200 – 3400 cm^{-1} represent the O-H stretching of the alcohol group in starch-based film with the addition of additive, glycerol. The absorption peaksat 1338 cm^{-1} and 2927cm^{-1}could indicate the C-H stretching vibration from methylene and methyl groups indicating the glucose units in the sago starch. The peaks at 1078.21 cm^{-1} and 1149.57 cm^{-1} may associate with the C-O stretching vibrations of the glycosidic linkages between the glucose units in starch. Region with peaks around 500 – 800 cm^{-1} may likely corresponds to the Ti-O stretching vibration in the titanium dioxide.

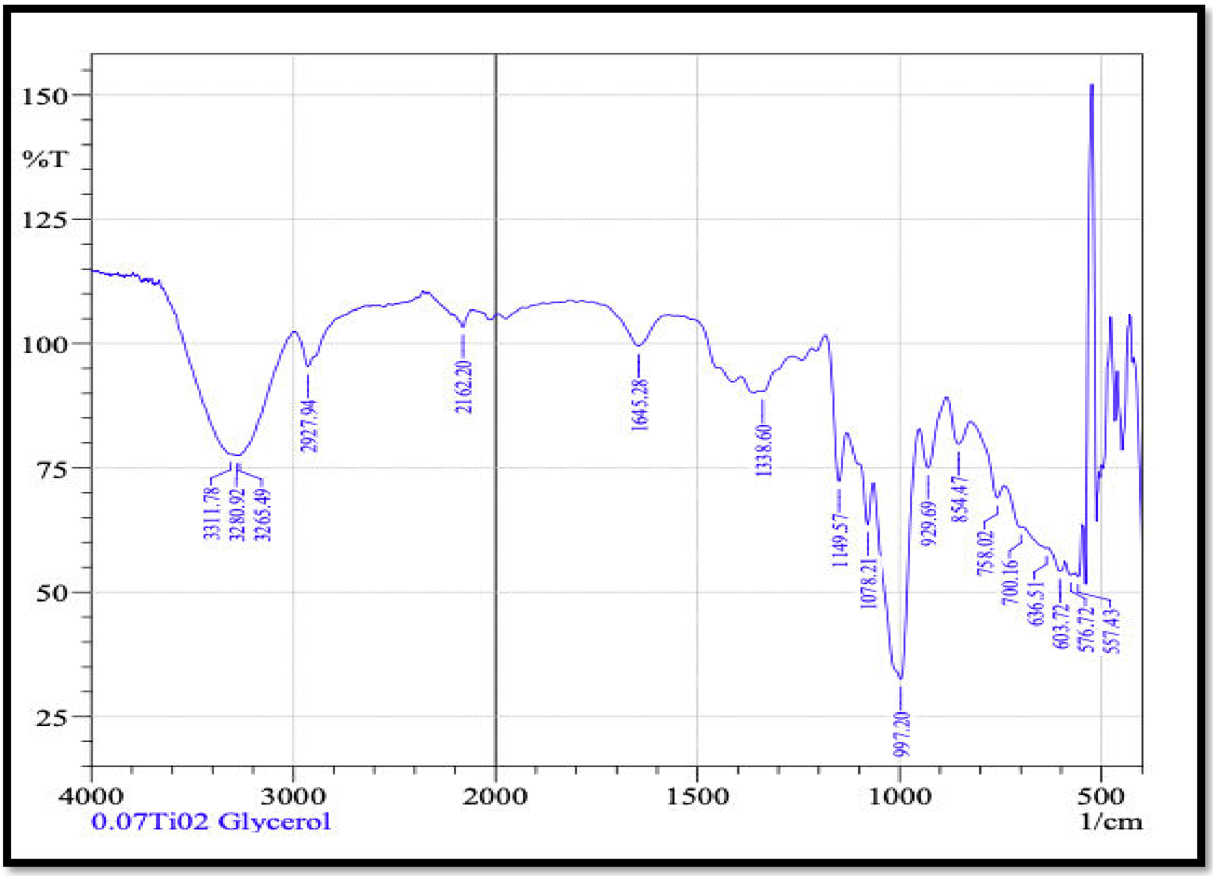


Figure 3: FTIR of the sago starch titanium dioxide film

3.2 SEM analysis

The hybrid sago starch-TiO_2 film formed is transparent as shown in Figure 4(a), making it a good support material for catalyst in photocatalysis that requires exposure of light to trigger the reaction. The addition of TiO_2particles makes the film becomes opaque as shown in Figure 4(b) -1(d). The morphology of the films with magnifications of 1000x are shown in Figure 5. The film with TiO_2 show white spots, expected to be TiO_2 particles that seems distributed onto the films' surface. Large white spots observed here could indicate accumulation of TiO_2 particles at certain area, which could be due to nonuniform particle distribution within the starch gel. The mixing time of 30 minutes may not be sufficient to allow the well distribution of the particles within the starch gel. It was also observed that the film produced using 0.01g TiO_2 shows cracks, but smoother films were obtained for films using 0.02-0.03 g of TiO_2. Results show here indicate that the starch matrix can provide stable support for nanoparticles like TiO_2, enhancing its usability in photocatalytic process such as wastewater treatment.

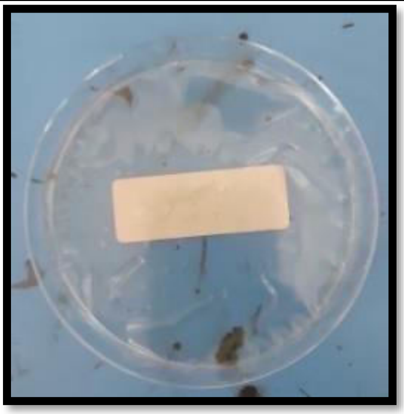
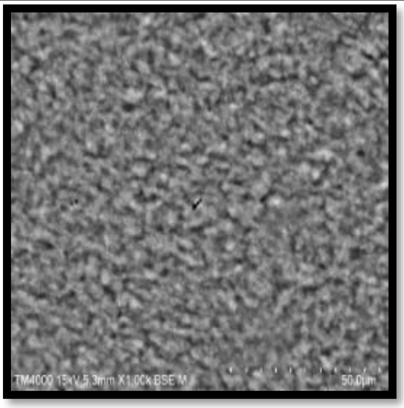
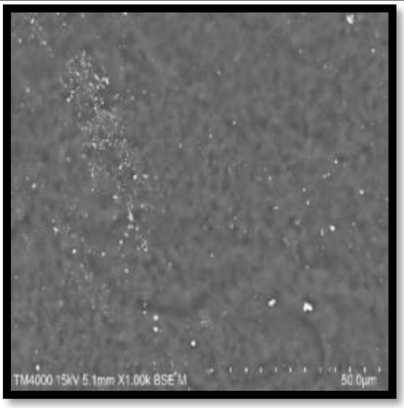
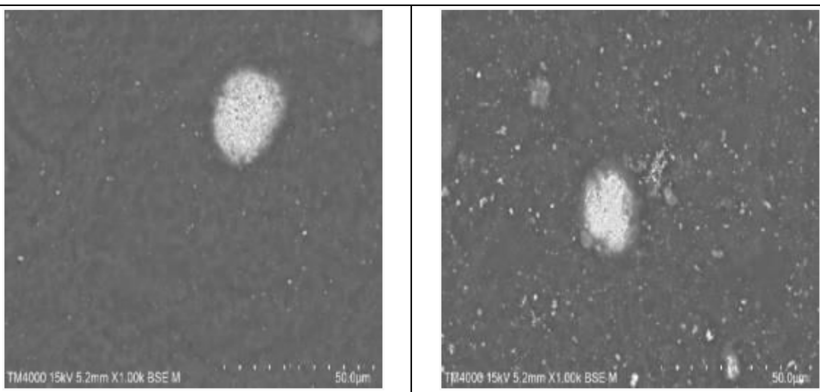
	
a) without TiO_2	(b) with 0.01g TiO_2
	
(c) with 0.02g TiO_2	(d) with 0.03g TiO_2

Figure 4: Sago starch-TiO_2 films

	
a) without TiO_2	(b) with 0.01g TiO_2



c) with 0.02g TiO_2 | (d) with 0.03g TiO_2

Figure 5: SEM images of sago starch-TiO_2 films

The stability of the films was tested by immersing the films in distilled water for 3 days. The percentages of change in the BOD, COD and TSS were below than 1% indicating low leachate from the films to the water.

3.3 Wastewater treatment analysis

The wastewater treatment analysis analysed in terms of percentage reduction of BOD, COD and TSS is shown in Tables 1 and 2. The data are plotted and shown in Figures 6-8. It is shown here that the photocatalysis under controlled UV light in the laboratory treated the wastewater better compared to those done under the sunlight. Maximum pollutants removal was estimated about 80% for the wastewater exposed to controlled UV light, and about 60% for those put under the sunlight for a period of 210 minutes (3.5 hours). For practical reason, wastewater treatment can be done just under the sunlight, but for a longer period of time.

Table 1. Results for photocatalysis under UV light

Time (minutes)	% Reduction (Under UV light)		
	BOD	COD	TSS
30	20.6	22.4	21.3
60	34.5	35.2	37.8
90	49.2	49.9	48.2
120	56.5	57.4	57.6
150	65.1	66.9	66.9
180	72.3	72.6	75.2
210	83.6	84.0	83.6

Table 2. Results for photocatalysis under sunlight

Time (minutes)	% Reduction (Under Sunlight)		
	BOD	COD	TSS
30	15.8	17.4	17.5
60	22.3	29.6	27.8
90	29.6	34.1	36.9
120	36.1	40.5	43.9
150	41.6	46.1	49.7
180	50.7	53.9	58.0
210	60.1	61.6	64.0

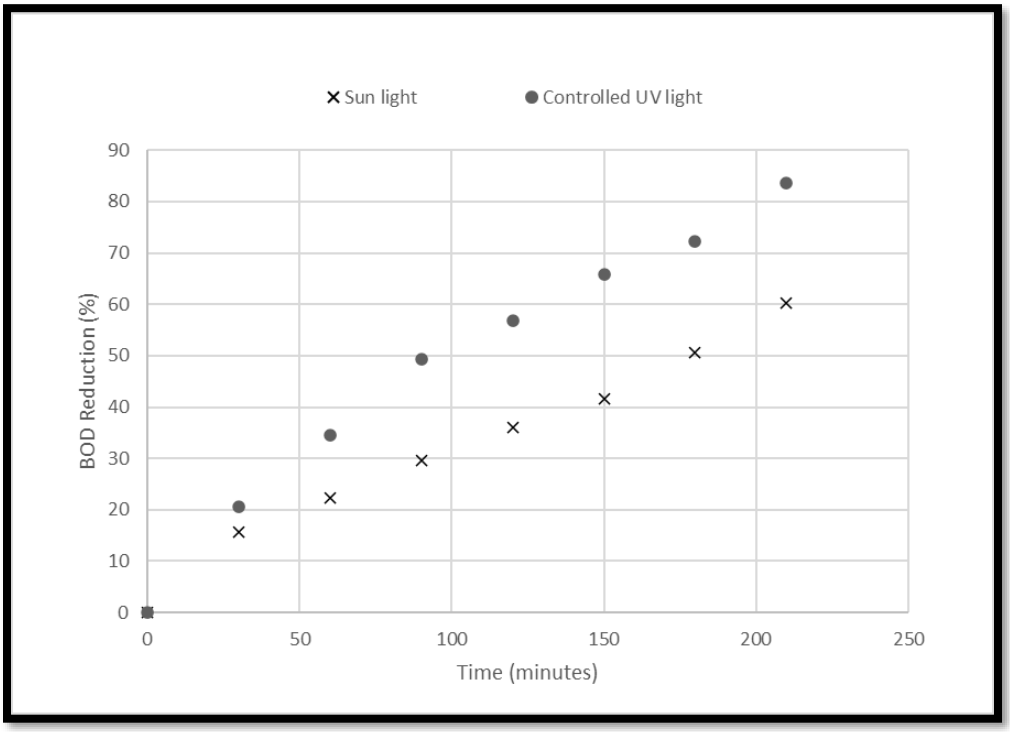


Figure 3. BOD versus Time

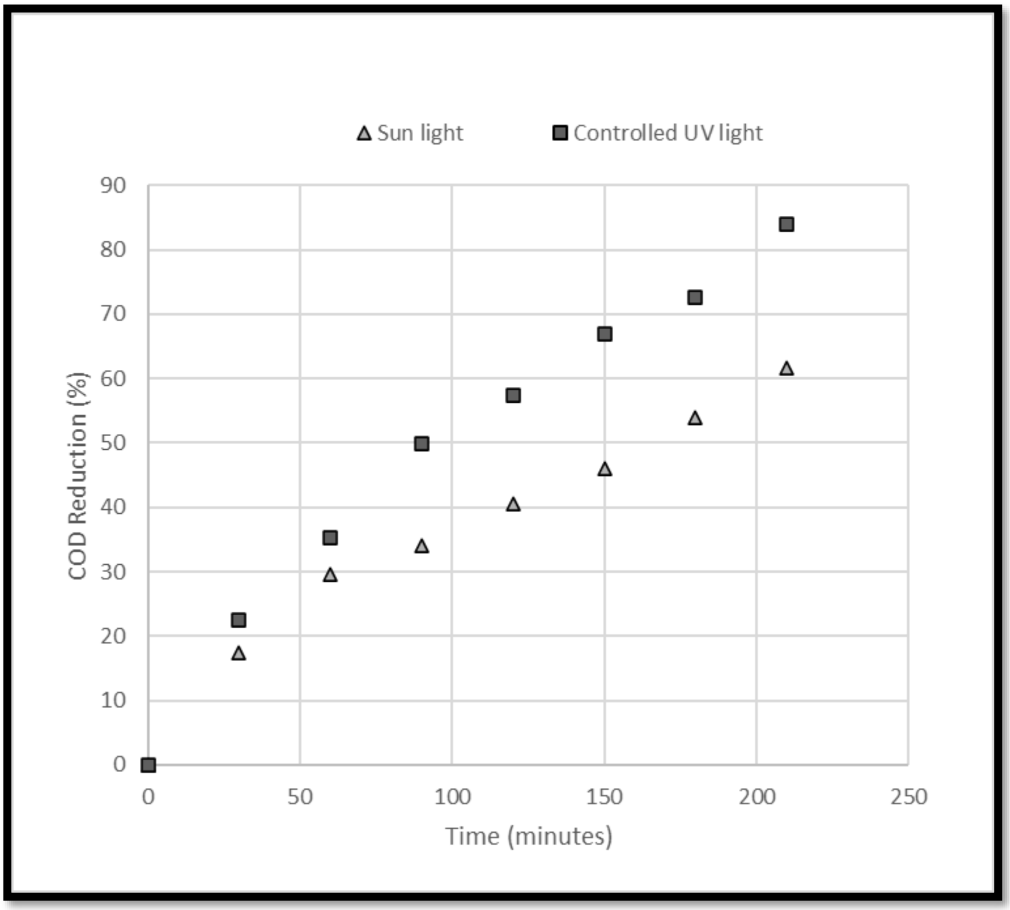


Figure 3. COD versus Time

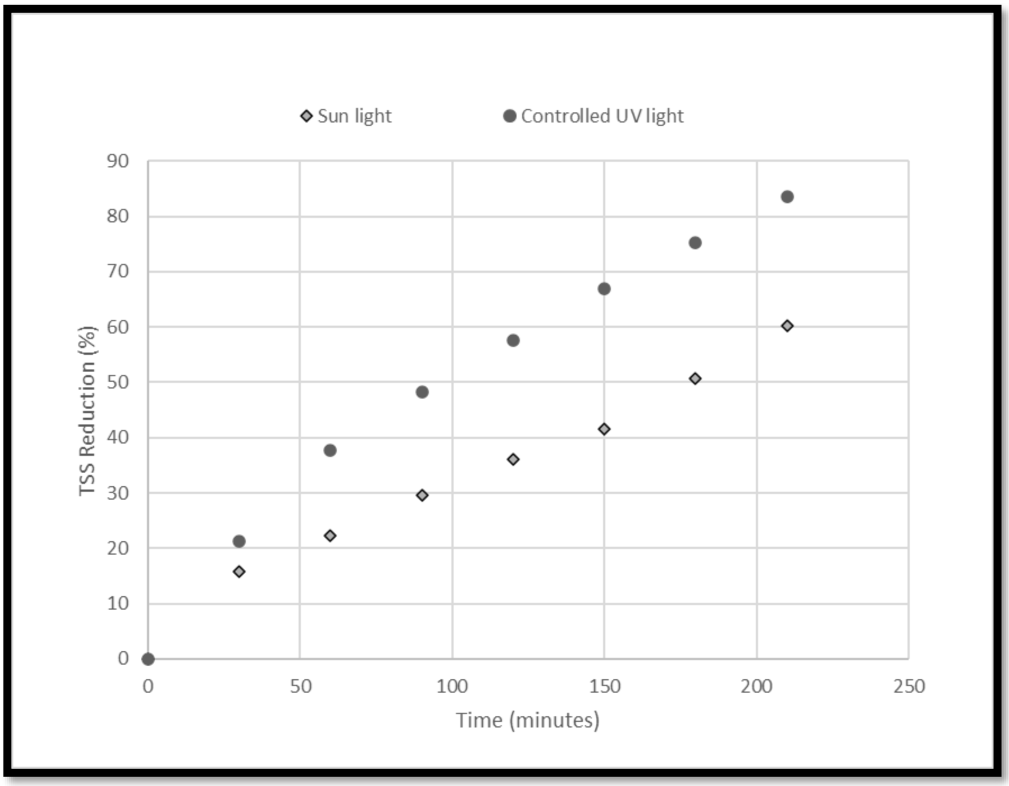


Figure 4: TSS versus Time (under UV light)

4. Conclusion

In this study, TiO_2 particles were immobilized successfully into the sago starch matrix forming thin films. The sago starch films without the titanium dioxide were originally transparent, and the films become opaque after the addition of titanium dioxide particles. The films show stability in water, and the surface morphology of the films produced was evaluated using SEM, while its capability to treat sago wastewater was analysed based on the reduction of BOD, COD and TSS. The SEM results showed white spots distributed on the surface of the films, which could be the titanium dioxide particles. The films were immersed in sagowater with UV exposure, and photocatalysis of sago wastewater gives reduction of BOD, COD and TSS up to 80%.

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