Faculty of Engineering

STUDY ON STARCH-TiO_2 HYBRID MATERIAL FOR SAGO WASTEWATER TREATMENT

Mohamad Danial Ashraf Bin Cairul Nafidz

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(Chemical Engineering)

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MOHAMAD DANIAL

Current Address:

DEPT. OF CHEMICAL ENGINEERING, FACULTY OF ENGINEERING, 94300 KOTA SAMARAHAN, SARAWAK.

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Rubiyah

AP DR RUBIYAH BAINI
(Final Year Project Supervisor)

Date
2nd June 2022

STUDY ON STARCH-TiO_2 HYBRID MATERIAL FOR SAGO WASTEWATER TREATMENT

MOHAMAD DANIAL ASHRAF BIN CAIRUL NAFIDZ

A thesis is submitted in partial fulfilment

of requirement for the degree of

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Dedicated to my beloved family and friends who continuously bless me with endless love and encouragements

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ABSTRACT

Metroxylon Sagu or also known as Sago starch, is one of local materials found in abundant in Sarawak. In this study of developing the sago starch-based thin film, Titanium Oxide (TiO_2) as the main catalyst to be infused within the thin film, and was used to treat sago wastewater The developed films were characterised using surface morphology scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) to analyse the pattern or image developed by the film under the beam light. Based on the characterisation of SEM, the structures formed on the surface of the film are nearly identical for each sample and the distribution of Titanium Oxide (TiO_2) are uniform. For FTIR analysis, both of the plasticizers have the same functional groups and compound only that glycerol contain higher intensity in the hydroxyl group due to stronger and wider hydrogen bond between the molecules. Analysis of wastewater in terms of Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS) against the function of time were also completed. The photocatalysis reaction between UV light with power of 40 watts and Sunlight were compared and it shows that the reaction under UV light showed better photocatalysis reaction compared to Sunlight due to the different intensity. For the comparison between plasticizers, sorbitol showed better photocatalysis reaction compared to glycerol. For the reaction of Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS) against the function of time with sorbitol, the readings of the degradation are 2% better compared to glycerol as the plasticizers. Overall, it shows that sorbitol are slightly better as the plasticizers to be used in order to treat sago wastewater via photocatalysis reaction.

Keywords: *Sago Starch, Titanium Oxide, Photocatalysis, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Biological Oxygen Demand (BOD)*

ABSTRAK

Metroxylon Sagu atau juga dikenali sebagai pati Sagu, merupakan salah satu bahan tempatan yang banyak terdapat di Sarawak. Dalam kajian membangunkan filem nipis berasaskan kanji sagu, Titanium Oxide (TiO_2) sebagai pemangkin utama untuk diselitkan dalam filem nipis, dan digunakan untuk merawat air sisa sagu Filem yang dibangunkan telah dicirikan menggunakan mikroskop elektron pengimbasan morfologi permukaan (SEM) dan Fourier Transform Infrared Spectroscopy (FTIR) untuk menganalisis corak atau imej yang dibangunkan oleh filem di bawah cahaya pancaran. Berdasarkan pencirian SEM, struktur yang terbentuk pada permukaan filem adalah hampir sama bagi setiap sampel dan taburan Titanium Oxide (TiO_2) adalah seragam. Untuk analisis FTIR, kedua-dua pemplastis mempunyai kumpulan berfungsi dan sebatian yang sama hanya gliserol yang mengandungi keamatan yang lebih tinggi dalam kumpulan hidroksil disebabkan oleh ikatan hidrogen yang lebih kuat dan lebih luas antara molekul. Analisis air sisa dari segi Permintaan Oksigen Biologi (BOD), Permintaan Oksigen Kimia (COD) dan Jumlah Pepejal Terampai (TSS) terhadap fungsi masa juga telah selesai. Tindak balas fotokatalisis antara cahaya UV dengan kuasa 40 watt dan Cahaya Matahari telah dibandingkan dan ia menunjukkan bahawa tindak balas di bawah cahaya UV menunjukkan tindak balas fotokatalisis yang lebih baik berbanding Cahaya Matahari kerana keamatan yang berbeza. Untuk perbandingan antara pemplastis, sorbitol menunjukkan tindak balas fotokatalisis yang lebih baik berbanding gliserol. Bagi tindak balas Permintaan Oksigen Biologi (BOD), Permintaan Oksigen Kimia (COD) dan Jumlah Pepejal Terampai (TSS) terhadap fungsi masa dengan sorbitol, bacaan degradasi adalah 2% lebih baik berbanding gliserol sebagai pemplastis. Secara keseluruhan, ia menunjukkan bahawa sorbitol adalah lebih baik sedikit sebagai pemplastis yang akan digunakan untuk merawat air sisa sagu melalui tindak balas fotokatalisis.

Kata Kunci: *Kanji Sagu, Titanium Oksida, Fotokatalisis, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), permintaan oksigen biokimia (BOD)*

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LIST OF ABBREVIATION

PEG	:	Polyethylene Glycol
TiO_2	:	Titanium Oxide
DSAT	:	Double Sided Adhesive Tape
MW	:	Molecular Weight
FTIR	:	Fourier Transform Infrared Spectroscopy
SEM		Scanning Electron Microscopy
SSA	:	Specific Surface Area
BOD	:	Biological Oxygen Demand
COD	:	Chemical Oxygen Demand
TSS	:	Total Suspended Solid
O_2	:	Oxygen
NP	:	Nanoparticles
ROS	:	Reactive Oxygen Species
OH	:	Hydroxide Radicals
$(Ca(OH)_2$	:	Lime
(Na_2CO_3)	:	Soda Ash
AOP	:	Advanced Oxidation Process
ROS	:	Reactive Oxygen Species

NOMENCLATURE

°C	:	Degree Celsius
%	:	Percentage
g	:	Gram
km	:	Kilometres
min	:	Minutes
hr	:	Hour
mg	:	Milligram
L	:	Litre
Kg	:	Kilogram

CHAPTER 1
INTRODUCTION

1.1 Background of Starch-Based Thin Film

Sago starch is derived from the pith of the Metroxylon sago palm. It is produced and exported mostly in Southeast Asia, particularly Malaysia. Malaysia exports around 44,000 tonnes of sago starch per year to a variety of nations, including Japan and Europe, according to Othman et al., 2015. Malaysia's largest sago production areas are located in the Sarawak states of Mukah and Dalat. Prior to the 1980s, the majority of sago was manufactured in traditional tiny mills, with the starch dried in the sun. In several of these mills, less than one metric tonne of dry starch per day was produced from just a few palms every day. During the mid-1980s, there were more than 40 factories that made sago along the Mukah and Dalat Rivers. There were also a few more modern mills that made refined sago starch, as well. Some of the traditional mills conveyed their crude wet starch to these larger mills for refinement. As of 2015, approximately ten contemporary sago plants remained operational in Sarawak, generating approximately 47,000 mt of refined sago per month. Sago starch processing processes were primarily adapted from cassava processing in Malaysia's larger factories, with changes to account for the structural variations among sago and cassava starch. Over the last three decades, constant upgrades and innovative equipment have been developed by specific firms or small technical workshops. The physicochemical qualities of sago starch have been improved through research. As is the case with other starches such as maize starch, alteration of sago starch is necessary to enhance its characteristics and usability. According to Jiang et al., (2019), As a natural polymer with inherent biodegradability, abundant supply, and annual renewal, starch is among the most suitable alternatives. Because of their low raw material prices and potential to be produced with conventional plastic processing equipment, starches provide a very appealing low cost base for new biodegradable polymers. Since the well-known challenges of oil scarcity and growing interest in reducing the environmental burden caused by the widespread usage of petrochemically-derived polymers, the development and applications of biodegradable starch-based materials have received increased attention. Apart from its benefits in the food industry and textile. Starch-based film are widely used in the wastewater treatment industry to clean the contaminated water. Starch wastewater is characterised by a high content of starch and a lack of toxicity. The biochemical approach, as well as flocculation and sedimentation, are the most extensively used methods for starch wastewater treatment. The type, dosage, and sedimentation time of coagulant were investigated in order to improve the efficacy of wastewater treatment. Hence, In this work, the potential of producing hybrid starch material is explored, and here, sago starch is chosen to immobilized TiO_2, a catalyst used in the wastewater treatment via the photocatalysis reaction to reduce organic pollutants such as those found in sago wastewater. TiO_2 has been found to be effective in reducing organic pollutants, but it usually comes in powder form making it difficult for recovery process. Modification of starch properties leads to the formation of starch based thin film. Although thin film can be produced using combination of chemicals only, the use of large amount of chemicals may be destructive to the environment. Sago starch, a sustainable and environmental friendly material can be a good option as hybrid material; in this study, hybrid material using sago starch and TiO_2 will be studied. An increasing number of countries have enacted legislation and policies prohibiting the use of throwaway plastics. **Figure 1** depicts images of various commercialised starch-based goods that are not only entirely biodegradable but can also be used to feed animals or even eaten.

Figure 1: Commercialized starch-based products Jiang et al., (2019)

On the other hand, the investigation of the distinct microstructures of different starches, as well as their multiphase transitions during thermal processing, has contributed to the advancement of fundamental knowledge in polymeric science, particularly in the understanding of the structure processing property relationships in polymers. Because of its overwhelming biodegradability, large abundance, and cost-effective nature, starch, a biologically essential macromolecule, is regarded as the most promising polymer of natural origin. There are numerous industrial uses for starch because of its easy availability and year-round regenerative nature. Due to the wide range of uses starch provides in the food business (such as thickening agents and water retention qualities), there is a growing demand for the product. Industrially, edible films and coatings are getting a lot of attention because they can help solve problems with pollution that are getting worse. Starch possesses extraordinary qualities, including biodegradability, sustainability, and abundance, and it may be changed or combined with other polymers. Food packaging uses for a variety of starches have been examined, including those derived from cereals, millet, and pulse grains. Starch could be utilised as a foundation ingredient in the formulation of eco-friendly packing materials. Other key attributes of biopolymers include low temperature, seal ability, air permeability, availability and low cost. Chemical modification of starch is necessary to enhance its properties to suit its applicability for certain function. The filmogenic characteristics of starch materials have garnered much attention. In comparison to other biopolymers, starch is abundant, inexpensive, biodegradable, and edible, as well as possessing an excellent filmogenic capacity. Starch-based films and composites have significant potential for use as a matrix, binder, or filler in the food, pharmaceutical, cosmetic, and paper sectors. This is because starch-based films can be utilised to generate antibacterial and antioxidant packaging. Natural starch's disadvantages, such as its insolubility in cold water, preclude its widespread use. However, starch processing, such as chemical, enzymatic, or physical modification, can alter these qualities, generating considerable interest from potential customers. For example, the hybrid starch-TiO_2 is meant for treating wastewater treatment, meaning the material has to have long durability when it is immersed in liquid form. However, the study on this hybrid material has not been studied widely yet making it difficult to select the appropriate method, which not only for lab study purpose, but also for potential commercialization purpose.

In order to increase the mechanical qualities of coatings and packaging, biopolymers such as starch, chitosan, whey and gums (such as alginate and carrageenan, which are derived from seaweed), plant gums (such as mastic gum), and microbial gums (such as xanthan gum and cellulose) are recommended.

1.2 Film Casting

In the process of casting thin films, there are few possible ways to cast the thin film following the method which suits the composition and also depending on the situation. For example, most of the industrial process, casting thin film by using the drum is most suitable as they mainly focus on the mass production of the film. For research purpose which will be conducted in a lab, the traditional casting method is the easiest way to produce a thin film. Simply by using a sterile glass rod and a clean glass plate, a thin film can be produced.

For industrial purpose, the method of producing a thin film differ from the thin film for research purpose. A web of thin film is extruded onto a cooled, highly polished, spinning roll during the film-casting process. The speed of the roll determines the draw-down ratio and the thickness of the film. After that, the film is pulled by a stripping roll that rotates in the opposite direction as the casting roll. Finally, the film is wound onto a roller after passing through a set of slitting rolls.

In this particular study, film casting is conducted by using starch as the main active ingredient to develop the thin film. This is due to that because starch is composed of distinct particles called granules, it is unique among carbohydrates. Starch granules are insoluble in water and only partially hydrate when exposed to cold water. As a result, they disperse quickly in water, forming low-viscosity slurries that are easily mixed and pumped, even at concentrations more than 35%. The viscosity-increasing or thickening properties of starch are apparent only after the granular slurry is cooled. Among renewable sources capable of film formation, starch meets all of the fundamental requirements for edible coatings/films, including ease of availability, high extraction yield, biodegradability, and biocompatibility, making it a potential product for edible coatings/films. One of the most remarkable properties of starch is its capacity to form films. Unlike conventional plastics, starch is not soluble in cold water because the degradation temperature of starch is lower than the melting point. However, when starch is exposed to stress, heat, or plasticizers, the granules lose their semi-crystalline characteristic and become a continuous matrix. This feature of starch is exploited to produce biodegradable films. Solution casting and extrusion processing are the two most prevalent methods for transforming starch into films.

1.3 Problem Statement

Some wastewater treatment produce slurry that require additional treatment. For example, prior to filtering or sedimentation, chemical coagulation and flocculation using lime, soda ash and polyelectrolytes to produce settleable flocs. As for the biological method, it incorporates microorganisms, fungi, bacteria, yeasts, and algae to breakdown the pollutants leaving sludge behind. Treatments involving photocatalytic reaction using catalyst such as TiO_2 is an alternative method to eliminate the problem of slurry production. However, there is a problem to reuse TiO_2 that usually comes in powder form. This is due to the brittle powder form that will disintegrate in the water when it is used once for the treatment process. Therefore, further research is to study the method to immobilise TiO_2; In this work, thin film incorporating starch, a sustainable material which is starch as the main component is chosen as it is cost effective and abundantly available in Sarawak will be developed and tested for sago wastewater treatment. Sago processing is one of the main industries in Sarawak producing a huge amount of sago wastewater that require proper treatment, for future environmental sustainability.

1.4 Research Question

The research questions that arise from the project study are discussed in this research paper are listed as follows:-

i. Does sago has the potential to be infused with Titanium Oxide (TiO_2) to develop a thin film for wastewater treatment?
ii. Will the starch-based film infused with Titanium Oxide (TiO_2) disintegrate in water?
iii. What are the effects of plasticizers towards the developed thin film?
iv. What are the characteristics of the developed thin film under the Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy
v. How the Starch-TiO_2 film with Plasticizers able to degrade and reduce the BOD, COD and TSS in the Sago wastewater

1.5 Research Gap

A number of related study are found in the literature discussed on the development of hybrid material for TiO_2 including those study on starch film such as those summarized in **Table 1**. Different formulation of thin film with chemicals were studied, but less study on the photocatalytic performance of starch-TiO_2 thin film. Starch wastewater is characterised by a high content of starch and a lack of toxicity. The biochemical approach, as well as flocculation and sedimentation, are the most extensively used methods for starch wastewater treatment. The type, dosage, and sedimentation time of coagulant were investigated in order to improve the efficacy of wastewater treatment. It was found that most of the developed starch-based thin film has been proved to helped the process in the wastewater treatment but had not been marketable globally or in a huge industry. Nevertheless, this small progress of developing thin film for the usage of industry slowly showing a positive impact towards the environment and also to the wastewater industries. Although it has been useful to treat effluent, Starch is a potential material for thin film making, but its hybrid properties require further analysis to ensure it is durable enough to withstand the long period in the water, and related findings found in the literature is very limited. Therefore, few studies on articles and journals regarding the development of starch-based thin film incorporated with Titanium Oxide (TiO_2) had been done in order to improve the efficiency of the film. Based on this table, it shows that lack of study related to the development of starch-TiO_2 hybrid material in particular for treating sago wastewater, which relate to the gap of research/knowledge for this project. Further study on the appropriate method, and on the evaluation of factors affecting the quality of the starch-TiO_2 hybrid material for sago wastewater will be explored.