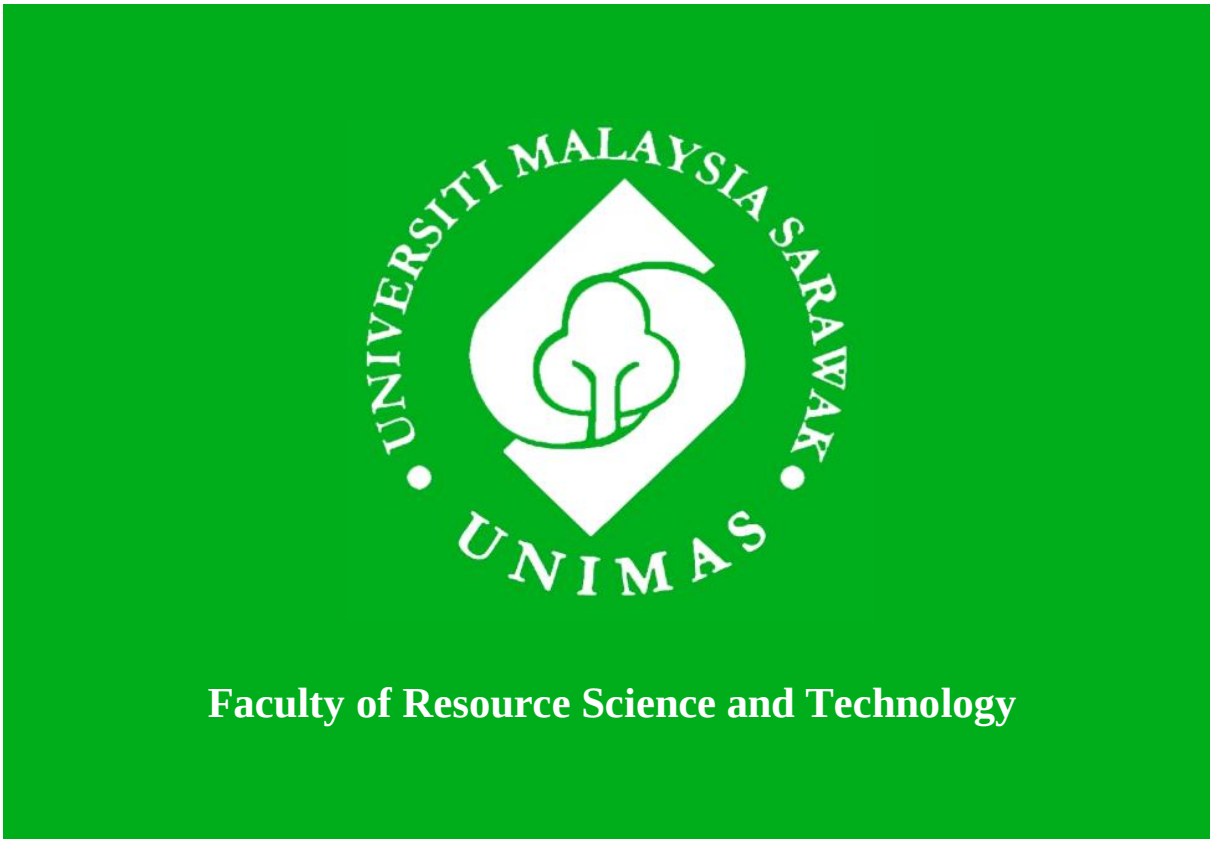

TiO_2/MSB Photocatalysis and Photo-Fenton for the Degradation of Sago Wastewater

Wong Soon Pang

Master of Science
2018

UNIVERSITI MALAYSIA SARAWAK

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TiO_2/MSB Photocatalysis and Photo-Fenton for the Degradation of Sago Wastewater

Wong Soon Pang

A thesis submitted

In fulfillment of the requirements for the degree of Master of Science

(Environmental Chemistry)

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK
2018

DECLARATION

I hereby declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. It is original and is the result of my work, unless otherwise indicated or acknowledged as referenced work. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Wong Soon Pang (15020369)

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ABSTRACT

The direct discharge of improperly treated sago effluent poses a great threat to water bodies due to the high amount of organic matter. Advanced Oxidation Processes, namely titanium dioxide (TiO_2)-mediated photocatalysis and photo-Fenton have emerged as state-of-the-art treatment tools for water purification. This work investigated the efficiency of TiO_2 photocatalysis and photo-Fenton treatment as possible means for the degradation of sago wastewater, particularly in removing chemical oxygen demand (COD) by employing Response Surface Methodology (RSM). In the case of TiO_2 photocatalysis, sago bark (SB), a solid waste material generated from sago industry was acid treated prior to the preparation of TiO_2/modified sago bark (TiO_2/MSB) mixture. To prepare the TiO_2/MSB mixtures, concentrations of TiO_2 and MSB was varied from 0.2 g/L to 0.8 g/L and 1 w/w% to 3 w/w%, respectively. Among six TiO_2/MSB mixtures, sample prepared by combining 0.2 g/L TiO_2 and 1 w/w% MSB demonstrated the highest COD removal 64.92%. Given that the highest removal was produced using this mixture sample, further optimisation of sago wastewater treatment was carried out by varying the independent variables, dosage and contact time. Under optimum condition, 0.10 g of 0.2 g/L TiO_2/1% MSB reduced 52.83% COD in 120 min contact time. Characterisations in term of surface morphology, functional groups, and elemental analysis supported the ability of TiO_2/MSB mixture to remove COD. For photo-Fenton treatment, three operating parameters namely, initial pH, H_2O_2 and Fe^{2+} ion concentrations were fixed for optimisation. A maximum COD removal of 90.00% was obtained when sago wastewater sample was treated at pH 2.66 in the presence of 4.01 g/L of H_2O_2 and 5.07 g/L Fe^{2+} ion. Photo-Fenton treatment resulted in better COD removal compared to dark Fenton which only produced 56.25%. Despite the high COD removal, the total organic carbon (TOC) removal under the same optimised condition was considerably low, 48.00% only suggesting incomplete mineralisation of stable intermediates or

degradation products present in the treatment solution. Toxicity assessment on the photo-Fenton treated sago wastewater solution revealed that the mortality of *Artemia salina* was less than 50%. This evidence concluded the non-toxic nature of the treated sago wastewater. The regression value (R^2 >0.99) of the polynomial models for both TiO_2 photocatalytic and photo-Fenton treatments indicated a high degree of correlation between the parameters evaluated. The findings obtained signify the feasibility of TiO_2 photocatalysis and photo-Fenton as appealing alternative protocols for sago wastewater treatment.

Keywords: Chemical oxygen demand, photo-Fenton, response surface methodology, sago wastewater, titanium dioxide

Fotopemangkinan TiO_2/KST dan Foto-Fenton ke atas Degradasi Air Sisa Sagu

ABSTRAK

Pembuangan efluen sagu tanpa rawatan yang sesuai boleh membawa kepada ancaman kepersekitaran air disebabkan oleh kandungan bahan organik yang ketara. Proses Pengoksidaan Termaju, iaitu fotopemangkinan berasaskan titanium dioksida (TiO_2) dan foto-Fenton merupakan teknik olahan air sisa terkini. Dalam kajian ini, tahap kecekapan fotopemangkinan TiO_2 dan rawatan foto-Fenton telah dikaji untuk degradasi sisa sagu, terutamanya untuk menyingkirkan tahap permintaan oksigen kimia (POK) dengan menggunakan kaedah Gerak Balas Permukaan (GBP). Bagi fotopemangkinan TiO_2, kulit sagu (KS), iaitu sisa bahan pepejal yang dihasilkan oleh industri sagu telah diprarawat dengan menggunakan asid sebelum digunakan untuk penyediaan campuran TiO_2/kulit sagu terubahsuai (TiO_2/KST). Bagi menyediakan campuran TiO_2/KST, kepekatan TiO_2 dan KST masing-masing telah dipelbagaikan dari 0.2 g/L hingga 0.8 g/L dan 1 w/w% hingga 3 w/w%. Daripada enam campuran TiO_2/KST yang disintesis, sampel yang disediakan dengan komposisi 0.2 g/L TiO_2 dan 1 w/w% KST mencatatkan tahap penyingkiran POK yang tertinggi iaitu 64.92%. Berdasarkan keputusan penyingkiran POK tertinggi yang diperolehi, sampel campuran tersebut telah digunakan untuk pengoptimuman lanjut olahan air sisa sagu dengan memilih dua pembolehubah bebas iaitu dos dan masa sentuhan. Di bawah keadaan optimum, 0.10 g 0.2 g/L TiO_2/1% KST dapat mengurangkan sebanyak 52.83% POK dalam masa sentuhan 120 minit. Keupayaan TiO_2/KST untuk penyingkiran POK telah diperkukuhkan oleh ciri-cirinya dari segi morfologi permukaan, kumpulan berfungsi, dan analisis unsur. Untuk degradasi foto-Fenton, tiga parameter operasi iaitu, pH awal, kepekatan H_2O_2 dan Fe^{2+} telah ditetapkan untuk proses pengoptimuman. Penyingkiran POK maksimum sebanyak 90.00% telah diperolehi apabila sampel air sisa sagu dirawat pada pH 2.66 dengan kehadiran 4.01 g/L

H_2O_2 dan 5.07 g/L ion Fe^{2+}. Rawatan foto-Fenton didapati lebih berkesan dalam mengurangkan kandungan POK berbanding dengan degradasi Fenton yang hanya menghasilkan 56.25%. Walaupun penyingkiran POK daripada air sisa sagu adalah ketara, namun penyingkiran karbon organik jumlah di bawah keadaan optimum yang sama adalah sangat rendah, hanya 48.00% mencadangkan tahap mineralisasi yang tidak lengkap bagi perantaraan yang stabil atau produk degradasian yang terdapat dalam larutan rawatan. Penilaian tahap ketoksikan terhadap air sisa sagu yang dirawat dengan foto-Fenton menunjukkan bahawa kadar mortaliti atau kematian Artemia salina *adalah kurang daripada 50%. Oleh itu, air sisa sagu yang dirawat oleh degradasi foto-Fenton boleh dirumuskan sebagai tidak toksik. Nilai regresi (R^2>0.99) model polinomial bagi kedua-dua rawatan fotopemangkinan TiO_2 dan foto-Fenton menunjukkan tahap korelasi yang tinggi di antara semua parameter yang telah dikaji. Dapatan daripada kajian ini menunjukkan teknik fotopemangkinan TiO_2 dan foto-Fenton boleh diaplikasikan sebagai protokol alternatif yang menarik bagi rawatan air sisa sagu.*

***Kata kunci**: Permintaan oksigen kimia, foto-Fenton, gerak balas permukaan, air sisa sagu, titanium dioksida*

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LIST OF ABBREVIATIONS

λ	Wavelength
ads	Adsorbed
ANOVA	Analysis of Variance
AOPs	Advanced Oxidation Processes
BBD	Box-Behnken Design
BOD	Biochemical Oxygen Demand
CB	Conduction Band
CCD	Central Composite Design
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOE	Department of Environment
e^-	Electron
EDX	Energy-Dispersive X-ray Spectroscopy
Fe^{2+}	Iron (II) or Ferrous ion
Fe^{3+}	Iron (III) or Ferric ion
FTIR	Fourier Transform Infra-Red Spectroscopy
H_2O	Water
H_2O_2	Hydrogen Peroxide
$HO_2^{\bullet}$ or HOO•	Hydroperoxyl radical
h^+	hole

$h\nu$	Photon energy
MSB	Modified Sago Bark
•OH	Hydroxyl radicals
$O_2^{\bullet -}$	Superoxides radical
POME	Palm Oil Mill Effluent
PZC	Point of Zero Charge
R^2	Coefficient of Determination
rpm	Revolutions per Minute
RSM	Response Surface Methodology
SB	Sago Bark
SEM	Scanning Electron Microscope
TiO_2	Titanium dioxide
TOC	Total Organic Carbon
TSS	Total Suspended Solid
UV	Ultraviolet
UV-VIS	Ultraviolet Visible
VB	Valence Band

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Solid or liquid wastes derived from a series of post-processing steps in agricultural industry could impose significant impacts on environmental degradation if not properly treated or managed. Agro-based industries contribute significantly to economic growth and development of countries around the globe. Nevertheless, from the environmental point of view, this industry also inevitably tends to increase the accumulation of wastes which demand considerable attention. One of the most important crops for starch production is sago palm (*Metroxylon sagu*). Sago palm, known as the highest starch-producing crop at 25/t/ha/year are mainly concentrated in the State of Sarawak, Malaysia with more than 90% of the total planting areas (Singhal *et al*., 2008; Bujang, 2015). The sago residues from sago starch processing mills are abundant and readily available. Wastewater effluent generated during sago debarking and sago processing is generally discharged into nearby rivers (Awg-Adeni *et al*., 2010). A study reported that approximately 400 tons of effluents are generated from a sago mill which typically consumes about 1,000 logs/day (Bujang, 2008). About 94-97% of the bulk of the sago wastewater is liquid, while the remaining portion is solid waste referred as roughage or 'hampas'. Sago bark (SB) is another solid waste generated during the debarking step of starch extraction process. SB degrades slowly due to its woody nature (Wahi *et al.,* 2014). Deposition or dumping of SB on land is the most common practice among most of the mill operators to address the disposal problem of this solid waste. Although such practice provides a short term solution, potential environmental problems could however emerge in the long term.

Sago effluent is complex and acidic in nature and typically characterised by elevated chemical oxygen demand (COD), 780-5130 mg/L, biochemical oxygen demand (BOD), 910-1300 mg/L and total suspended solids (TSS) 19-20,000 mg/L (Ibrahim *et al*., 2006; Rashid *et al*., 2010) and emits obnoxious odour. As the direct discharge of sago wastewater effluent may cause issues related to environmental deterioration, its treatment for either re-using or improving its discharged water quality has been the main interest of the sago mill operators.

Thus far, biological methods which have been widely used to treat sago wastewater include high-rate anaerobic treatment such as anaerobic fluidized beds and filters (Saravanane *et al*., 2001), anaerobic tapered fluidized bed reactor (Parthiban *et al*., 2008), three-phase fluidized bed bioreactor (Rajasimman & Karthikeyan, 2007), and hybrid upflow anaerobic sludge blanket reactor (Banu *et al*., 2006). Also, bio-management methods using bacteria and fungi have been utilised to treat sago wastewater (Ayyasamy *et al*., 2008; Savitha *et al*., 2009). These biological methods although known for their efficiency, are unable to completely degrade the effluent and therefore require other alternative treatments (Sangeetha *et al*., 2015). In this viewpoint, Advanced Oxidation Processes (AOPs), a non-biological method could be a desirable alternative to degrade organics present in the sago effluent as this treatment has emerged as an effective method for the degradation of various biorecalcitrant compounds in water and wastewater (Day, 2014).

AOPs which are chemical oxidation processes have been proven as highly effective for the oxidation of industrial wastewater containing toxic and organic materials (Yazdanbakhsh *et al*., 2014). AOPs involves *in situ* generation of reactive oxygen species (ROS) such as hydroxyl radicals (HO•), O_3, H_2O_2 and superoxide anion radical ($O_2^{\bullet-}$). These ROS act as a strong oxidant to oxidise organic compounds into biodegradable form and simpler end products such as CO_2 and H_2O (Abdulah *et al*., 2011; Kanakaraju *et al*., 2014). Among numerous AOPs, titanium