



Faculty of Resource Science and Technology

TiO₂/MSB Photocatalysis and Photo-Fenton for the Degradation of Sago Wastewater

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TiO₂/MSB Photocatalysis and Photo-Fenton for the Degradation of Sago Wastewater

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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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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 TiO₂ photocatalytic and photo-Fenton treatments indicated a high degree of correlation between the parameters evaluated. The findings obtained signify the feasibility of TiO₂ 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 TiO₂/KST dan Foto-Fenton ke atas Degradasi Air Sisa Sagu

ABSTRAK

Pembuangan efluen sagu tanpa rawatan yang sesuai boleh membawa kepada ancaman persekitaran air disebabkan oleh kandungan bahan organik yang ketara. Proses Pengoksidaan Termaju, iaitu fotopemangkinan berasaskan titanium dioksida (TiO₂) dan foto-Fenton merupakan teknik olahan air sisa terkini. Dalam kajian ini, tahap kecekapan fotopemangkinan TiO₂ 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 TiO₂, kulit sagu (KS), iaitu sisa bahan pepejal yang dihasilkan oleh industri sagu telah diprarawat dengan menggunakan asid sebelum digunakan untuk penyediaan campuran TiO₂/kulit sagu terubahsuai (TiO₂/KST). Bagi menyediakan campuran TiO₂/KST, kepekatan TiO₂ 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 TiO₂/KST yang disintesis, sampel yang disediakan dengan komposisi 0.2 g/L TiO₂ 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 TiO₂/1% KST dapat mengurangkan sebanyak 52.83% POK dalam masa sentuhan 120 minit. Keupayaan TiO₂/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 H₂O₂ dan Fe²⁺ 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 ₂ O	Water
H ₂ O ₂	Hydrogen Peroxide
HO ₂ [•] or HOO [•]	Hydroperoxyl radical
h ⁺	hole

$h\nu$	Photon energy
MSB	Modified Sago Bark
$\bullet\text{OH}$	Hydroxyl radicals
$\text{O}_2^{\bullet-}$	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 ($\text{HO}\cdot$), O_3 , H_2O_2 and superoxide anion radical ($\text{O}_2^{\cdot-}$). 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

dioxide (TiO₂) photocatalysis and photo-Fenton have been known for its potential to effectively treat wastewater. TiO₂ appears to be one of the most widely used photocatalysts owing to its biological and chemical inertness, inexpensiveness, photostability and non-corrosive (Kumar *et al.*, 2011). The application of TiO₂ in large scale water treatment is rather restrictive due to its limitations. Two major constraints of TiO₂ which limits its photocatalytic activity include (1) the large band gap (3.2 eV for anatase phase) limits its absorption only in UV region, in which only 3-5% of the solar spectrum can be utilised for its activation, and (2) fast recombination of photogenerated electron-hole pairs occurs during TiO₂ photocatalysis. In addition, nanosized TiO₂ tends to produce slurry (suspension) during treatment which makes recovery and recycling particularly difficult. Hence, to increase the photocatalytic activity of TiO₂, several methods have been proposed such as doping with non-metals and transition metals, noble metals or metal ions incorporation, fabrication of TiO₂ composite with other materials, surface sensitization and inclusion of inert support (Fujishima *et al.*, 2008; Chong *et al.*, 2010; Ngamsopasiriskun *et al.*, 2010; Gupta & Tripathi, 2011; Dong *et al.*, 2015; Fagan *et al.*, 2016). In this study, TiO₂ was combined with SB, a sago residue generated during sago processing, to prepare a novel mixture material which was then further assessed for the degradation of sago effluent. Although TiO₂-based composites or mixtures have been widely applied in various wastewater treatments and degradation of organic pollutants, there is no study thus far has been performed on sago wastewater effluent by TiO₂-based composites or mixtures.

Factors that affect TiO₂ photocatalysis include the amount of catalyst, irradiation time, temperature, pH, initial concentration of organic load, light intensity, design of photoreactor and the presence of ionic species (Krzeminska *et al.*, 2015). Existing studies have recognised the critical roles played by these intrinsic parameters in determining the removal or degradation efficiency of photocatalytic processes (Kumar *et al.*, 2011; Aljuboury *et al.*, 2016b; Liu *et al.*,

2016). As such, optimisation of TiO₂ photocatalytic parameters are often incorporated in related studies with the objective to maximise the degradation efficiency.

Fenton and photo-Fenton processes also appear as an attractive option in wastewater remediation owing to the short reaction time and high efficiency (Expósito *et al.*, 2016; Novoa-Luna *et al.*, 2016). Classical Fenton process utilises the Fenton's reagent (hydrogen peroxide (H₂O₂) and ferrous (Fe²⁺) ion) to generate HO• radicals to oxidise the organic compounds (Aljuboury *et al.*, 2014). Photo-Fenton process can be initiated either by artificial light source or solar irradiation (Romero *et al.*, 2016a). When H₂O₂ reacts with Fe²⁺ ions in the presence of ultra violet (UV) light, HO• radicals are generated by the decomposition of H₂O₂ (Elmolla & Chaudhuri, 2009). The generated HO• radicals will attack the organic compounds and eventually mineralise them into CO₂ and H₂O via the formation and decomposition of intermediates (Tokumura *et al.*, 2013). In photo-Fenton process, factors such as amount of Fe²⁺ ions and H₂O₂ and also initial pH greatly affect its overall efficiency (Tony & Bedri, 2014). Although photo-Fenton treatment has been extensively studied in literature, the application of this treatment on sago wastewater effluent has not been investigated.

In this study, the experimental design using a statistical-based technique, known as response surface methodology (RSM), was used to study the optimisation of both TiO₂ photocatalysis and photo-Fenton treatment processes. RSM is generally applied to optimise the individual parameters to maximise the degradation efficiency and also to reduce the number of experiments to be conducted (Muthukumar & Muthuchamy, 2014). Process optimisation by RSM is more economical and much faster for obtaining experimental results than the full-factorial or time-consuming one-factor-at-a-time approach (Alim *et al.*, 2008). Photo-Fenton using RSM approach has been applied in numerous wastewater degradation studies (Savitha *et al.*, 2009; Saber *et al.*, 2014; Aljuboury *et al.*, 2016a). Likewise, studies on TiO₂ photocatalysis

employing RSM in different wastewater treatment such as petroleum wastewater (Aljuboury *et al.*, 2015; Aljuboury *et al.*, 2016b), textile wastewater (Hosseini *et al.*, 2016), and olive mill wastewater (Costa & Alves, 2013) are also available.

To the best of our knowledge, no studies have been performed on sago effluent by means of TiO₂ photocatalysis and photo-Fenton. As RSM is known for its superiority in optimising chemical reactions, this study was designed to apply this statistical tool to determine the optimal conditions for the degradation sago wastewater effluent primarily focusing on COD as the target parameter.

1.2 Problem Statements

Many countries including Malaysia are struggling with water deterioration or depletion issue. One of the major sectors which have been contributing to water pollution as well as accumulation of solid wastes is agricultural. In Sarawak, heavy consumption of water by sago starch production industries resulted in the generation of large volumes of sago effluent. Besides sago effluent, sago 'hampas' and SB generated during sago starch production processes have been also causing environmental issues. Direct release of sago wastewater effluent into water bodies may be inappropriate due to the high amount of organic material, BOD, COD, and TSS. Continuous accumulation of SB on land also signifies issues related to its disposal. The existing biological treatments such as high rate anaerobic treatments and the use of bacteria and fungi to treat sago wastewater were ineffective as they are unable to completely degrade the effluent. Hence, the search for alternative methods or protocols becomes necessary to tackle these issues. Based on the existing literature, there remains a paucity of evidence of sago wastewater effluent degradation over TiO₂ photocatalysis and photo-Fenton despite the growing developments in

these fields of AOPs. The application of TiO₂ photocatalysis using a novel composite catalyst and photo-Fenton in degradation of sago wastewater effluent can be regarded as sufficient novel. In this study, TiO₂ photocatalysis and photo-Fenton processes were investigated as possible treatment methods to degrade sago effluent. SB, the solid waste was also assessed as a potential support or adsorbent for the preparation of TiO₂-based mixture. This study basically attempted to utilise solid waste for the degradation of liquid waste.

1.3 Research Question

Can water quality of sago wastewater effluent be sustainably and efficiently improved by the application of TiO₂/MSB photocatalysis and photo-Fenton treatments?

1.4 Objectives

The main objective of this study was to assess the efficiency of self-synthesised TiO₂/modified SB (TiO₂/MSB) mixture and the photo-Fenton treatment for the degradation of sago wastewater effluent. The specific objectives of this study were to:

- a. characterise sago wastewater effluent for water quality parameters
- b. prepare and characterise TiO₂/MSB mixture
- c. optimise the operational parameters of TiO₂ photocatalytic oxidation using TiO₂/MSB mixture for the degradation of sago wastewater effluent by employing RSM, and
- d. optimise the parameters of photo-Fenton treatment for the degradation of sago wastewater effluent by using RSM.

CHAPTER 2

LITERATURE REVIEW

2.1 Sago Palm

Sago palm is the species of the genus of *Metroxylon* which belongs to the Palmae family (Awg-Adeni *et al.*, 2010). At present, this species of sago palm is grown commercially in Malaysia, New Guinea, Philippines and Indonesia. The importance of this species includes for the production of sago starch and conversion to fuel ethanol or animal food (Awg-Adeni *et al.*, 2010). The state of Sarawak besides being the world's biggest exporter of sago also possesses the largest sago growing areas in Malaysia. Figure 2.1 shows the sago palms in Pusa, Sarawak. About 44,700 tons of sago starch were exported to Peninsular Malaysia, Singapore, Taiwan, Hong Kong and other countries in 2007 (Awg-Adeni *et al.*, 2010). In Sarawak, the total export earnings between US\$ 3.4 million to US\$ 10.8 million were generated from annual export of pure sago starch, which typically fluctuates between 30,000 to 50,000 tons (Bujang, 2014).

For countries in Southeast Asia, sago starch is an important ingredient in the preparation of various delicacies such as sago pearls, noodle, puddings, biscuit, soups, jellies and others (Karim *et al.*, 2008). Large quantities of starch-rich flour can be extracted from the stem tissue by shredding and sedimentation in water. The amount of starch in the trunk or pith of sago palm has been reported to be 4 times higher than that of paddy rice. Yield between 150 kg to 300 kg of starch can be obtained from one sago palm (Andriana *et al.*, 2010). Bujang (2015) reported that there are about 138 palms/ha available for harvesting each year, potentially producing more than 25 t/ha/year of starch provided the palms are systematically and fully cultivated. Besides starch, small amount of non-starch polysaccharide (NSP), known as lignin, cellulose and hemicelluloses can also be found in sago pith (Awg-Adeni *et al.*, 2010).



Figure 2.1: Sago palm (*Metroxylon* spp)

2.2 Sago Industry in Sarawak

More than 90% of all sago-planting areas are found in the state of Sarawak in Malaysia (Bujang, 2014). Five major sago-planting areas in Sarawak include Mukah, Pusa-Saratok, Oya-Dalat, Igan and Balingan (Andriana *et al.*, 2010). Generally, the sago industries are located along rivers to ease transportation of sago logs. Another reason for this is to directly discharge the generated waste to the rivers as shown in Figure 2.2.



Figure 2.2: Sago mill in Pusa, Sarawak.

Typically, a sago mill consumes about 1000 logs per day. This produces a minimum of 400 tons of sago effluent containing about 5% of solids (20 tons) (Andriana *et al.*, 2010). The sago barks and sago effluent generated from sago debarking and processing are usually discarded to the nearby rivers, leading to water and land pollutions as shown in Figure 2.3. The main problem faced by the large scale sago starch processing industries are the generation of large amount of fibrous by-products containing starch residues. The fibrous by-products have been causing difficulty in its handling as it cannot be easily dried due to its starch content and high moisture (Awg-Adeni *et al.*, 2010).



Figure 2.3: Sago effluent and sago bark waste discarded into water and on land, respectively.

2.3 Sago Starch Extraction Process

A fully mechanical process is used for starch extraction by the modern industries in Sarawak (Awg-Adeni *et al.*, 2010; Bujang, 2015). The sago starch extraction processes include debarking, rasping, sieving, settling, washing and drying. The bark is first removed from the sago logs (Karim *et al.*, 2008). Debarking process is performed manually using a heavy machete or using an automatic debarking machine to produce debarked logs and sago barks (Bujang,

2015). Rasping is a process that is facilitated by the addition of water. About 80 to 100 cm long of logs from each of the debarked sections is fed into the mechanical rasper to rasp the pith into finer pieces, which will release the starch granules (Karim *et al.*, 2008; Bujang, 2015). The finer pieces are then fed into the hammer mill for further pulping of the pith. During pulping, the fine pith will be mixed with water to form white slurry, containing about 20-25% of starch (Bujang, 2015). In order to separate the coarse fibre, the resulting starch slurry is passed through a series of extractors and centrifugal sieves (Karim *et al.*, 2008; Bujang, 2015). The separation in a nozzle separator through sieve bends is carried out for further purification. This is done to obtain highly pure starch (Awg-Adeni *et al.*, 2010). After that, a rotary vacuum drum dryer is used for dewatering of starch, followed by hot air drying (Karim *et al.*, 2008). Figure 2.4 illustrates the schematic flow diagram for sago starch extraction process. The sago starch extraction processes generate three main types of waste namely wastewater, bark of sago trunk and fibrous pith residue or 'hampas'.

2.3.1 Sago Wastewater

Sago mills release large amount of wastewater due to heavy consumption of water in the sago starch extraction process from sago pith. About 94-97% of the bulk of the sago wastewater is liquid, while the remaining is solid waste or better known as 'hampas'. Wastewater is classified as a liquid residue whereas bark and 'hampas' are solid residue. Each sago industry generates about 10-22 tons wastewater per day with high carbon to nitrogen ratio (105:0.12) which usually disposed into the rivers (Awg-Adeni *et al.*, 2010).



Debarking



Rasping



Sieving



Separator



Dewatering and drying



Sago starch

Figure 2.4: Schematic flow diagram for sago starch extraction process.

Sago wastewater is complex and acidic in nature due to high levels of organic matter in dissolved and suspended states. It is highly biodegradable due to its high organic content. Prolonged storage of sago wastewater for several days would result in brownish color, lower pH, obnoxious odours and higher levels of BOD and COD (Anbukumar *et al.*, 2014). Table 2.1 shows the comparison of the characteristics of sago wastewater effluent from Nitsei Sago Mill in Mukah, Sarawak and Malaysia.

Sago wastewater effluent imposes negative impact on soil quality, agriculture production and water quality (Periyasamy & Govindarajalu, 2017). The physical and chemical properties of soil can be altered by sago wastewater effluent. Soils irrigated by sago wastewater effluent have low water holding capacity and has high porosity (Kumar, 2003). Sago wastewater effluent irrigated soils show increased concentrations of essential plant nutrients due to high nutrient status of sago effluent. However, the irrigated soil turned acidic in the long-term application (Kumar, 2003). It has been reported that sago wastewater effluent show no significant effect on plant growth (Kumar, 2003).

Table 2.1: Characteristics of sago effluent.

Parameters	Nitsei Sago Mill* (Sarawak)	Malaysia**
pH	3.82-4.20	3.46-3.58
TSS (mg/L)	3368-15,890	19-20,000
BOD (mg/L)	2528-4647	910-1300
COD (mg/L)	6048-12,594	780-5130

*Personal Communication with industry

**Ibrahim *et al.* (2006) and Rashid *et al.* (2010)

Sago ‘hampas’ or sago pith waste (SPW) is a fibrous starchy lignocellulosic by-product that is generated from the pith of *Metroxylon sagu* (sago palm) during sago starch extraction process (Thangavelu *et al.*, 2014). Typically, the amount of ‘hampas’ generated from the sago processing industries depends on the quality of extraction process (Awg-Adeni *et al.*, 2010). On a dry weight basis, sago ‘hampas’ consists approximately 58% starch, 23% cellulose, 9.2% hemicellulose, and 3.9% lignin (Jenol *et al.*, 2014). Table 2.2 presents the composition of sago ‘hampas’ (Vincent *et al.*, 2015). About 7 tons of sago ‘hampas’ are generated daily from a single sago starch processing mill (Awg-Adeni *et al.*, 2013). The generated sago ‘hampas’ combined with wastewater are either deposited in the sago mill’s compound or discharged into nearby streams.

Another by-product, sago pith residue (SPR) is produced during the hydrolysis of starch material in sago ‘hampas’ into glucose. SPR comprises of 37% cellulose, 20% hemicellulose, and 6% lignin (on a dry weight basis) (Jenol *et al.*, 2014). Lignin and cellulose found in sago ‘hampas’ can be used as a biosorbent such as for the adsorption of copper and lead ions from solution (Awg-Adeni *et al.*, 2010). Activated carbon derived from sago waste has also been reported to be effective and economically attractive as an adsorbent for mercury, Hg (II) (Kardivelu *et al.*, 2004). It was reported that the absorption capacity of Hg (II) was found to be 55.6 mg/g at pH 5.0 with the particle size ranging from 125-250 μm .

Table 2.2: Composition of sago ‘hampas’.

Component	Dry weight basis (%)
Starch	58.00 $\pm$ 1.20
Cellulose	23.50 $\pm$ 1.00
Hemicellulose	8.19 $\pm$ 0.20
Lignin	6.30 $\pm$ 1.00
Ash	1.70 $\pm$ 0.10
Other	2.30 $\pm$ 0.20

Source: Vincent *et al.* (2015)

2.3.2 Sago Bark (SB)

One of the solid residues in the sago production industry is SB. About 17% of the logs processed are occupied by the bark, with the estimate production of 5-15 tons bark per day (Awg-Adeni *et al.*, 2010). In Sarawak, sago mill industries produce more than 20,000 ton/yr of SB as a by-product (Wahi *et al.*, 2014). Due to the corrosion problem caused by SB, which is acidic in nature, only less than 15% of the SB is used as fuel in the sago processing mills. SB degrades slowly due to its woody nature (Wahi *et al.*, 2014). The main component of SB is lignin, which strongly associated with the hemicellulose in the cell walls of sago pith. This lignin contains a large proportion of non-condensed syringyl units, together with fewer non-condensed *p*-hydroxyphenyl units and little amount of non-condensed guaiacyl units (Awg-Adeni *et al.*, 2010). Table 2.3 shows the composition of SB (Ethaiab *et al.*, 2016). The bark can be either used as footpaths of houses or as a platform around the factory, instead of undergoing combustion. Currently, SB is processed *via* biocomposite method to produce various building materials such as particle boards, plywood and wall tiles. Bark and ‘hampas’ are both regarded as pollutants and waste because they comprise of high amounts of lignin and cellulose (Awg-Adeni *et al.*, 2010). A recent study has reported the potential of sago bark for oil removal from

palm oil mill effluent (Wahi *et al.*, 2017). The esterified SB removed 80.23% of oil compared to only 57.77% using unmodified SB.

Table 2.3: Composition of sago bark.

Component	Dry weight basis (% w/w)
Cellulose	40.80
Hemicellulose	22.30
Lignin	25.90
Other	11.00

Source: Ethaib *et al.* (2016)

2.4 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) which utilises powerful oxidizing agents such as hydroxyl or sulphate radicals were first proposed in the 1980s for potable water treatment (Deng & Zhao, 2015). AOPs can be defined as “near ambient temperature and pressure water treatment processes that involves the hydroxyl radicals ($\text{HO}\cdot$) generation in adequate quantity to effectively purify water” (Munter, 2001). The concept of AOPs was later extended to the oxidative processes with sulphate radicals ($\text{SO}_4^{\cdot-}$) (Deng & Zhao, 2015). AOPs rely on the generation of highly reactive chemical species, which are able to degrade even the most recalcitrant organic constituents with high toxicity into biodegradable compounds and mineralise them into CO_2 , H_2O and innocuous inorganic ions (Rioja *et al.*, 2012). AOPs have been employed for the degradation of a variety of organic pollutants, such as ethers, aliphatic and aromatic hydrocarbons, ketones, halocarbons, phenols, etc (Machulek *et al.*, 2012).

In aqueous solution, $\text{HO}\cdot$ radical is one of the most reactive species that surpassed only by the fluorine atoms (Machulek *et al.*, 2012). Although fluorine is regarded as the strongest

oxidant based on the highest oxidation potential ($E^0 = 3.03 \text{ V}$) (Table 2.4), it is rather inappropriate to be applied in wastewater treatment owing to its high toxicity (Yonar *et al.*, 2011). $\text{HO}\cdot$ radicals with a high oxidation potential ($E^0 = 2.80 \text{ V}$) (Table 2.4), able to react with majority of organic compounds in different pathways to achieve complete mineralisation (Mota *et al.*, 2008). Three basic pathways which occur when $\text{HO}\cdot$ radicals attack the organic compounds (R), includes electron transfer (Eq. 2.1), hydrogen abstraction (Eq. 2.2), and radical addition (Eq. 2.3) (Stasinakis, 2008; Antoniou *et al.*, 2016).



Due to a very short lifetime of $\text{HO}\cdot$ radicals, it is only produced *in situ* under different conditions such as in the presence of irradiation or ultrasound, catalysts (Fe^{2+}), and a combination of oxidizing agents (H_2O_2 and O_3) (Huang *et al.*, 1993).

Table 2.4: Oxidation potential for various oxidants.

Oxidants	Oxidation potential (V)
Fluorine (F_2)	3.03
Hydroxyl radical ($\text{HO}\cdot$)	2.80
Atomic oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.70
Hypobromous acid ($\text{H}_{\text{br}}\text{O}$)	1.59
Chlorine dioxide (ClO_2)	1.50
Chlorine (Cl_2)	1.36
Molecular oxygen (O_2)	1.23
Bromine (Br_2)	1.09

Source: Krzeminska *et al.* (2015)

AOPs can be divided into two groups, namely homogeneous and heterogeneous, as shown in Figure 2.5 (Mota *et al.*, 2008). In addition, classification of AOPs can be also based on the involvement or absence of light in the process (Mota *et al.*, 2008). Homogeneous processes are further subdivided into processes that uses energy and without the use of energy (Poyatos *et al.*, 2010). Among numerous AOPs, UV-mediated titanium dioxide (UV/TiO₂), Fenton's reactions, and hydrogen peroxide/UV (H₂O₂/UV) processes are the most popular ones in wastewater treatment (Stasinakis, 2008; Jelonek & Neczaj, 2012; Swaminathan *et al.*, 2013; Day, 2014). Nevertheless, the choice of AOPs varies according to the types of wastewater or pollutants. Furthermore, the efficiency of the chosen AOP treatment significantly relies on the operating conditions and the chemical properties of contaminants (Deng & Zhao, 2015). The advantages of AOPs in wastewater treatment includes (1) reduced toxicity and complete mineralization, (2) fast reaction rates, (3) does not concentrate waste for further treatment, (4) does not create sludge as in physical chemical process or biological processes, and (5) does not produce materials that require further treatment (Sharma *et al.*, 2011). However, most AOPs are capital intensive and the quenching of excess peroxide is required for some applications. In a study performed to compare the efficiency of various AOPs namely ozonation, wet air oxidation, UV/H₂O₂ and Fenton to treat landfill leachate, the latter was found to be the most efficient treatment which resulted between 60 and 86% of COD removal (Jenolek & Neczaj, 2012). TiO₂ photocatalysis is also gaining importance in wastewater treatment due to its high removal efficiency in treating various types of wastewater such as olive mill wastewater (Uğurlu, & Karaoğlu, 2011), molasses fermentation wastewater (Qin *et al.*, 2011), and winery wastewater (Agustina *et al.*, 2008).

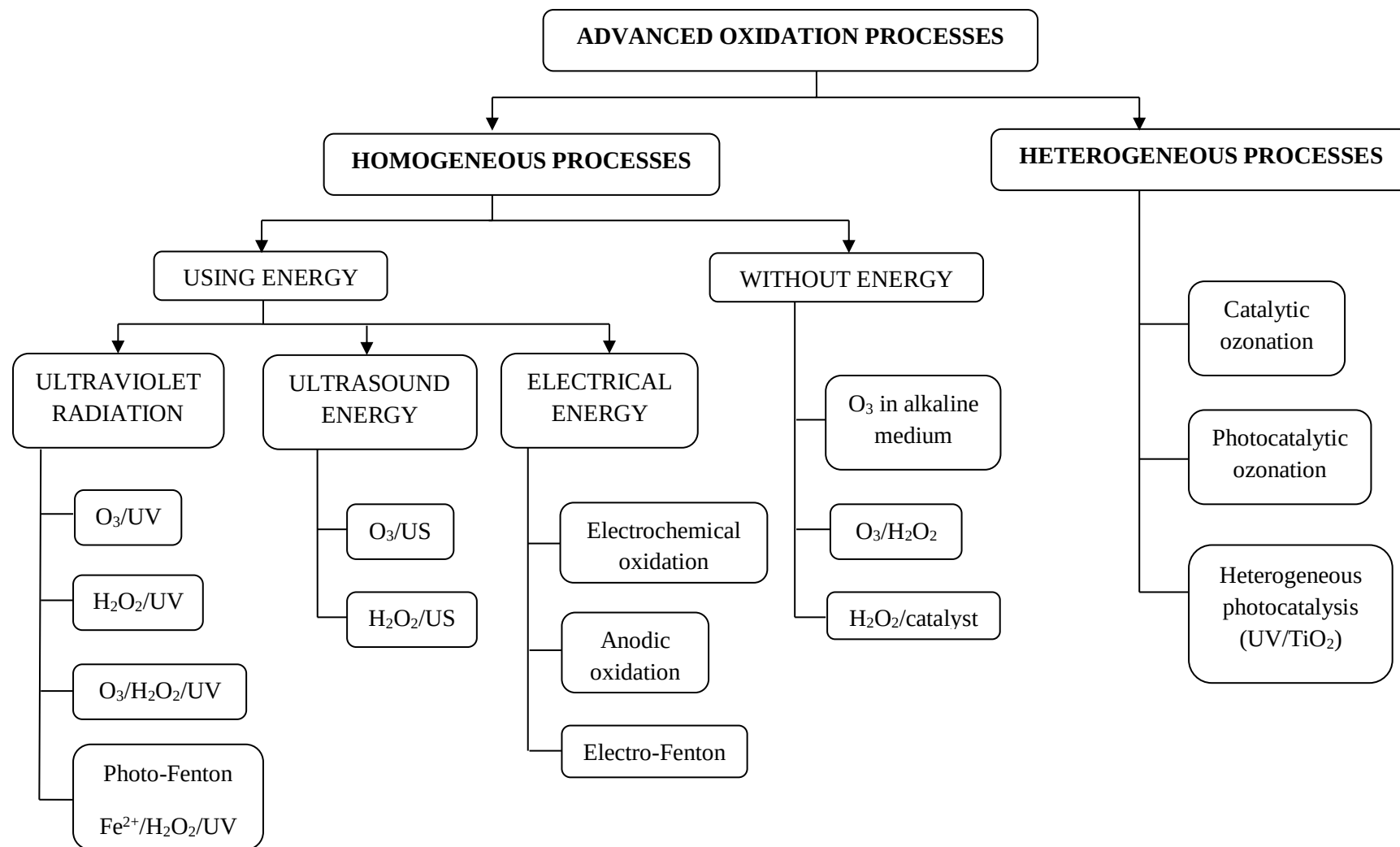


Figure 2.5: Classification of Advanced Oxidation Processes (AOPs) (Source: Poyatos *et al.*, 2010).

2.5 TiO₂ Photocatalysis

The IUPAC defines photocatalysis as “a change in the chemical reactions rate or its initiation under the action of ultraviolet, infra-red, or visible radiation in the presence of a photocatalyst that absorbs light and is involved in the chemical transformation of the reaction partners” (Braslavsky, 2007). Depending on the mechanism of the photoreaction, the catalyst may accelerate the photoreaction by interaction with a substrate in its ground or excited state, and/or with a primary photoproduct (Dalrymple *et al.*, 2007). Figure 2.6 shows the number of publications in the field of TiO₂ photocatalysis from 2000 to 2017.

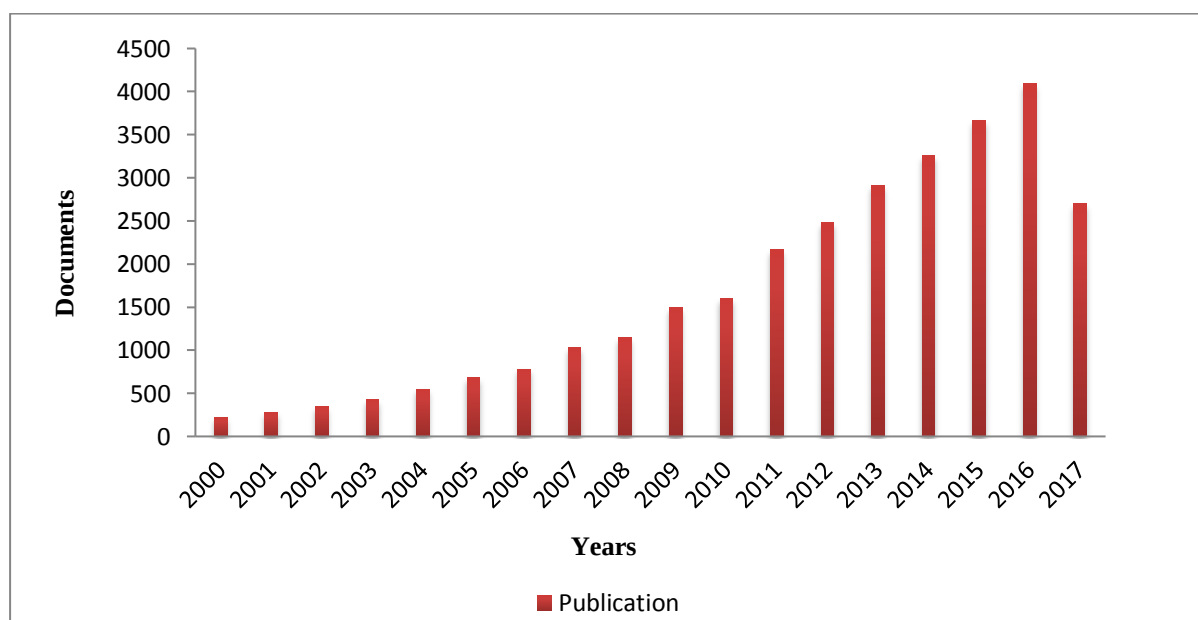


Figure 2.6: Statistics of publications on TiO₂ photocatalysis (Scopus database for search “TiO₂ photocatalysis” AND “water treatment” in all subject areas).

Based on existing publications, much attention has been devoted towards the application of TiO₂ photocatalysis for water purification over the years. Besides TiO₂, various other photocatalysts have also been applied for the above-mentioned purpose such as ZnO, ZnS,

Fe₂O₃, CdS, CeO₂, WO₃, SnO₃, SiO₂ and Nb₂O₃, to name a few (Kanakaraju *et al.*, 2014; Dong *et al.*, 2015). However, among them TiO₂ is clearly a preferred choice of photocatalyst due to its low cost, non-corrosive property, chemical and physical stability, high efficiency and widespread availability (Castellote & Bengtsson, 2011; Byberg & Cobb, 2012; Lazar *et al.*, 2012). Semiconductor TiO₂ has been widely applied in the photocatalytic treatments to induce a series of oxidative and reductive reactions on its surface (Chong *et al.*, 2010).

TiO₂ photocatalysis has emerged as a promising wastewater treatment technology with key advantages including the operation at ambient conditions, lack of mass transfer limitations and the possibility of utilising solar irradiation as a photon source (Pekakis *et al.*, 2006). There are five essential key steps that generally occur on the TiO₂ surface, which include (1) photoexcitation (light absorption and charge carrier generation), (2) diffusion, (3) trapping, (4) recombination, and (5) oxidation (Fox & Dulay, 1993; Gaya & Abdullah, 2008; Dong *et al.*, 2015). The series of chain oxidative-reductive reactions (Eqs. 2.4-2.15) that happen on the photon activated surface has been widely postulated (Chong *et al.*, 2010; Dong *et al.*, 2015). Basically, a photocatalytic reaction is initiated when the absorbed photon energy ($h\nu$) is greater or equal to the band gap energy of the TiO₂ (anatase, ~3.2 eV). Figure 2.7 depicts the mechanism of the formation of electron-hole pair when TiO₂ particle is irradiated with a sufficient photon energy. The wavelength of light for such photon energy usually corresponds to $\lambda \leq 400$ nm (Chong *et al.*, 2010).

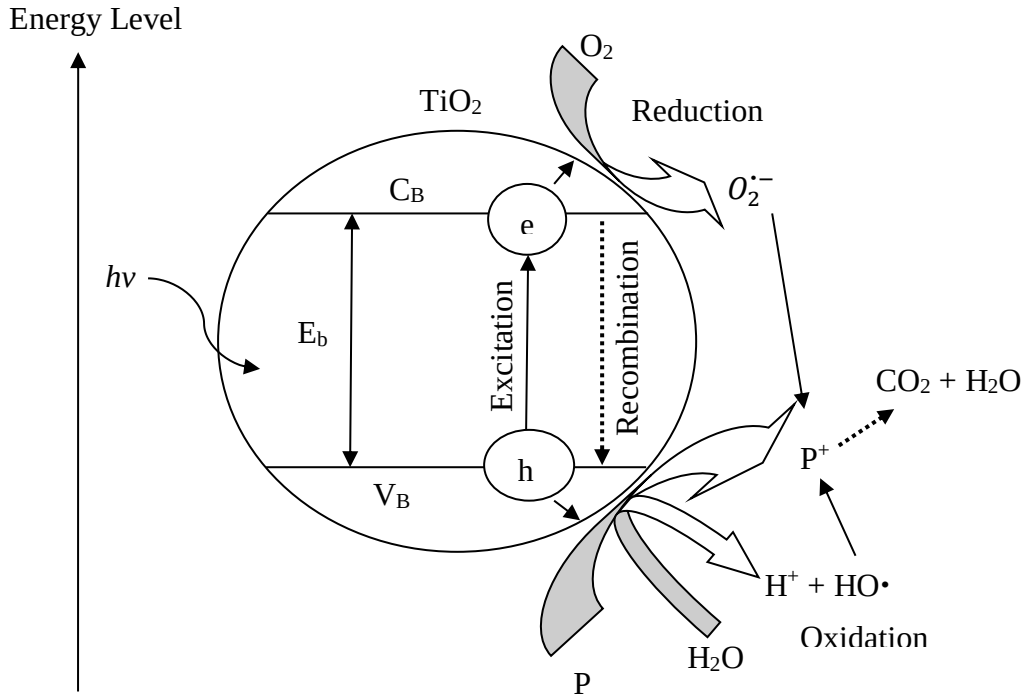
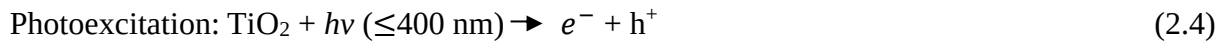


Figure 2.7: TiO₂ photocatalytic processes in the presence of water pollutant (P).

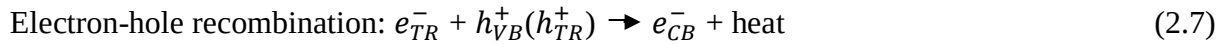
Consequently, this photonic excitation leaves behind a positive hole in the empty unfilled valence band and a negative electron in the conduction band, and therefore, creating an electron-hole pair (e^-h^+), as shown in Eqs. 2.4-2.6 (Fagan *et al.*, 2016).



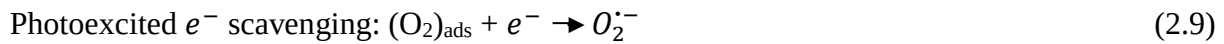
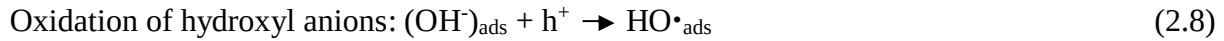
The generated electron-hole pairs migrate to the surface of TiO₂ to either recombine or participate in the redox reactions with the compounds or pollutants adsorbed onto the TiO₂ surface (Dalrymple *et al.*, 2007). The positive hole in the valence band can also oxidise water or OH⁻ anions present at the surface to generate HO• radicals which act as a powerful oxidant

of organic compounds and provide extra pathways for the oxidation of compounds (Dalrymple *et al.*, 2007; Fagan *et al.*, 2016).

The e_{TR}^- and h_{TR}^+ in Eq. 2.7 represents the surface trapped valence band electron and conduction band hole, respectively. These trapped carriers do not recombine immediately after photon excitation and are usually TiO_2 surface bounded (Chong *et al.*, 2010). In the absence of electron scavengers (Eq. 2.7), the photoexcited electron and hole are also able to recombine in nanoseconds with simultaneous heat energy dissipation (Dong *et al.*, 2015). Thus, the presence of electron scavengers plays an important role to prolong the recombination of electron-hole pairs and successful functioning of photocatalysis.

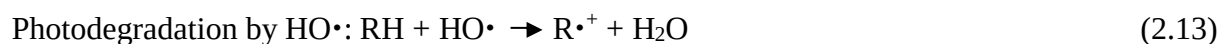


Surface adsorbed hydroxyl radical ($\text{HO}\cdot_{\text{ads}}$) is produced when positive hole reacts with the surface OH^- anions on the TiO_2 particle (Eq. 2.8) (Dong *et al.*, 2015). Recombination of the photogenerated electron-hole pairs can be prevented in the presence of scavengers, such as O_2 , which scavenges the electrons to allow the superoxides radical ($\text{O}_2^{\cdot-}$) formation (Eq. 2.9) (Kumar *et al.*, 2011).

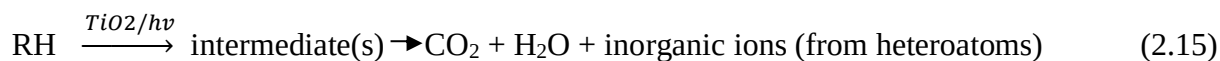


The $\text{O}_2^{\cdot-}$ radical can be further protonated to produce the hydroperoxyl radical ($\text{HOO}\cdot$) and subsequently H_2O_2 , as shown in Eqs. 2.10-2.12 (Dong *et al.*, 2015). The $\text{HOO}\cdot$ radical has scavenging property as O_2 and therefore, the co-existence of this radical species can doubly prolong the recombination time of h_{TR}^+ during the entire photocatalysis reaction (Gaya & Abdullah, 2008; Chong *et al.*, 2010). Eqs. 2.13 and 2.14 shows the formation of reactive oxygen

species (e.g. HO• radical) and the photogenerated holes which can participate in the degradation of organic pollutants, (R) (Dong *et al.*, 2015).



Mechanistic studies of different surrogate organic compounds, such as oxalic acid, phenol and chlorophenol have been investigated using TiO₂ photocatalytic degradation (Chong *et al.*, 2010). The reactive HO• radicals can hydroxylate the aromatic compounds, which leads to the successive oxidation/addition and eventually ring opening (Chong *et al.*, 2010). In addition, intermediates formed during the degradation, particularly carboxylic acid and aldehydes will be further carboxylated to produce innocuous products such as CO₂ and H₂O. As the heterogeneous photocatalysis reaction mostly occurs on the photon activated surface of TiO₂, an understanding of the reaction steps involved in the photodegradation of organic compounds are necessary in the kinetic expressions formulation (Dong *et al.*, 2015). If the irradiation time is increased, the liquid phase organic pollutants (RH) are degraded to their corresponding intermediates and further mineralised into CO₂ and H₂O, as shown in Eq. 2.15 (Chong *et al.*, 2010).



The overall heterogeneous photocatalysis reaction as described by Eq. 2.15 can be divided into five independent steps (Herrmann, 1999):

1. mass transfer of the organic pollutants in the liquid phase to the surface of TiO₂.
2. absorption of the organic pollutants onto the photon activated TiO₂ surface (i.e. surface activation *via* photon energy happens simultaneously in this step).
3. photocatalysis reaction for the adsorbed phase onto the surface of TiO₂.
4. intermediates desorption from the surface of TiO₂.
5. removal of the intermediates from the interface region to the bulk fluid.

2.5.1 Titanium Dioxide (TiO₂) Photocatalyst

According to Lee and Park (2013), a photocatalyst can be defined as “a catalyst that accelerates the solar photo reaction”. In order to be considered as a photocatalyst, the following criteria should be met (1) the photocatalyst should not directly participate in the reaction or be consumed, and (2) the photocatalyst needs to provide additional mechanistic pathways in addition to the existing photo reactions and accelerate the reaction rate. TiO₂ is often used in various photocatalytic applications due to its unique photocatalytic properties and most emerging catalyst are also measured against this benchmark photocatalyst (Dalrymple *et al.*, 2007; Byberg & Cobb, 2012; Dong *et al.*, 2015). TiO₂ is regarded as a multifaceted photocatalyst which can be an electron transport medium in dye-sensitized solar cells, an environmental catalyst (in air and water purification), or an energy catalyst (in water splitting to generate hydrogen fuel) (Lazar *et al.*, 2012). Due to the high degree of dispersion and large surface area of TiO₂ powders in the reaction media, it was reported to be favourable for high photocatalytic performance (Liu *et al.*, 2007). As highlighted by Hashimoto *et al.* (2005), the

chemical stability of TiO_2 holds only in the dark and become photoactivated upon UV irradiation, as shown in Figure 2.8.

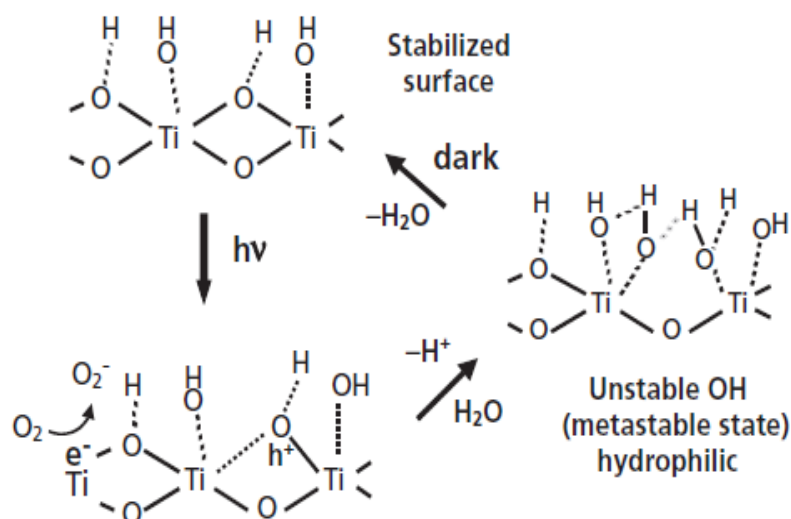


Figure 2.8: Schematic diagram of reversible change in the amount of hydroxyl groups on TiO_2 in the dark condition and under UV irradiation (Source: Hashimoto *et al.*, 2005).

TiO_2 belongs to the family of transition metal oxides. Gianluca *et al.* (2008) stated that TiO_2 exists in four mineral forms, which are brookite, rutile, anatase, and TiO_2 (B). Brookite, rutile and anatase forms of TiO_2 are found to be the most stable phases in different sizes of particles or nanoparticles with 11-35 nm, >35 nm and <11 nm, respectively (Fujishima *et al.*, 2008). TiO_2 (B) which is less known than the three other forms is a monoclinic mineral (Gianluca *et al.*, 2008). The properties of brookite, rutile, and anatase polymorphs are shown in Table 2.5. The most commonly applied forms in water treatment are anatase and rutile, while the least applied one is brookite due to its instability (Ibhadon & Fitzpatrick, 2013). Although rutile is the most abundant and thermodynamically stable, anatase exists as the most photoactive phase due to the higher number of surface hydroxyl group and its enhanced charge-carrier

mobility (Fagan *et al.*, 2016). Furthermore, anatase form of TiO₂ also exhibits higher photocatalytic activity than rutile because of its conduction band position which illustrates stronger reducing power as compared to rutile (Gianluca *et al.*, 2008). Degussa P-25, which is now known as AEROXIDE[®] TiO₂ P25, is a commercially available form of TiO₂ comprising of anatase (80%) and rutile (20%) (Kanakaraju *et al.*, 2013). This commercial TiO₂ has been used in many photocatalytic degradation studies as it is readily available, reproducible, chemically stable and high photocatalytic activity as a catalyst for oxidation process (Ibhadon & Fitzpatrick, 2013). A profound synergistic effect and high photocatalytic activity in different mixture phases of TiO₂ polymorphs were observed against pure or single phase (Luttrell *et al.*, 2014).

Table 2.5: Properties of different forms of TiO₂.

Properties	Brookite	Rutile	Anatase
Crystal structure	Orthorhombic	Tetragonal	Tetragonal
Lattice constant (Å)	a = 9.1840 b = 5.4470 c = 5.1540	a = 4.5936 c = 29587	a = 3.784 c = 9.515
Space group	Pbca	P4 ₂ /mm	I4 ₁ /amd
Molecule (cell)	4	2	2
Volume/molecule (Å ³)	32.1720	31.2160	34.061
Density (g/cm ³)	3.99	4.13	3.79
Ti–O bond length (Å)	1.870-2.040	1.949 (4) 1.980 (2)	1.937 (4) 1.965 (2)
O–Ti–O bond angle	77.0°-105.0°	81.2° 90.0°	77.7° 92.6°

Source: Gupta and Tripathi (2011)

2.5.2 Factors Affecting TiO₂ Photocatalysis

The main factors influencing the TiO₂ photocatalytic process are the amount of catalyst, irradiation time, initial concentration of organic compound, temperature, pH of medium, design of photoreactors, presence of ionic species, and the light intensity (Herrmann, 1999; Gogate & Pandit, 2004; Dalrymple *et al.*, 2007; Gaya & Abdullah, 2008; Stasinakis, 2008; Krzemińska *et al.*, 2015).

2.5.2.1 Effect of TiO₂ Catalyst Concentration

In a true heterogeneous catalytic regime, the overall photocatalysis reaction rate can be affected by the concentration of TiO₂ (Chong *et al.*, 2010). Gaya and Abdullah (2008) stated that the amount of catalyst is directly proportional to the overall photocatalytic reaction rate. It has been reported that the addition of catalyst increased the degradation rate within a concentration range (Dalrymple *et al.*, 2007). This simply means that there will be no marked increase in the degradation efficiency when the concentration of the catalyst reaches an optimum value. This is attributed to the decrease in the photon absorption coefficient and turbid solution as a result of excess amount of TiO₂ (Chong *et al.*, 2010). The excessive loading of TiO₂ also reduces the penetration of light and causes an unfavourable light scattering into the reaction medium (Gaya & Abdullah, 2008). The undesired light scattering effect would somewhat reduce the TiO₂ surface area exposed to the light illumination and eventually diminishing the photocatalytic efficiency (Chong *et al.*, 2010). The TiO₂ loading depends on several factors such as operating conditions of the photoreactor, intensity and wavelength of the light source, and reactor geometry (Pekakis *et al.*, 2006).

2.5.2.2 Effect of pH

pH is one of the most significant operating parameters that affect the size of catalyst aggregates, charge on the catalyst particles, positions of the valence and conduction bands, and the species present in the compounds to be oxidised (or dissociated to form molecular form) (Chong *et al.*, 2010; Yasmina *et al.*, 2014). To study the pH impact on the photocatalytic oxidation performance, the point of zero charge (pzc) of TiO₂ is used. The pzc can be defined as a condition where the TiO₂ surface charge is zero or neutral that lies in the range of pH from 4.5 to 7.0, depending on the catalyst used (Chong *et al.*, 2010). The pzc of Degussa P-25 (80% anatase and 20% rutile) has been reported as 6.9 (Gaya & Abdullah, 2008). The interaction between the TiO₂ particles and water pollutants is minimal at pzc of TiO₂ due to the absence of electrostatic force (Chong *et al.*, 2010). The surface of TiO₂ can be either protonated or deprotonated under acidic or alkaline condition, respectively as shown in Eqs. 2.16 and 2.17 (Gaya & Abdullah, 2008).



As shown in Eqs. 2.16 and 2.17, ‘Titanol’ (TiOH) represents the primary hydrated surface functionality of TiO₂, which is a neutral surface species predominant over a broad range of pH and known to be amphoteric (Dalrymple *et al.*, 2007). The surface of TiO₂ becomes positively charged in an acidic medium (pH < pzc of TiO₂) and negatively charged in an alkaline medium (pH > pzc of TiO₂) (Pekakis *et al.*, 2006). The solution pH has a complex effect on the photocatalytic oxidation rates. At lower pH, the reaction rate increases for weakly acidic pollutants (Andreozzi *et al.*, 2000). However, when the pH increases, the reaction rate also increases for the pollutants which are hydrolysed under alkaline conditions (Choi & Hoffman,

1997). In addition, it has been reported that TiO₂ has higher oxidizing activity at lower pH but excessive amount of H⁺ at a very low pH would reduce the reaction rate (Gaya & Abdullah, 2008). The surface charge density of TiO₂ catalyst and speciation of the substrate varies with pH. Hence, variation of pH will alter the reaction mechanisms and molecular interactions when intermediates are formed (Dalrymple *et al.*, 2007).

2.5.2.3 Effect of Temperature

In general, photocatalytic process is not significantly affected by any minor changes in temperature (Fox & Dulay 1993; Carp *et al.*, 2004). As the photocatalytic reaction is based on photonic activation, the reaction can be performed at room temperature without additional heating. High heat capacity of water makes this treatment to be attractive economically when dealing with water purification as there is no need for heating process (Herrmann, 2005). The dependence of photocatalytic activity on temperature has been reported (Gaya & Abdullah, 2008). Minor effect of temperature was reported for temperature ranging between 20 and 80 °C. At low temperature (<80 °C), adsorption of the reactant is favoured, which is a spontaneous exothermic phenomenon (Chong *et al.*, 2010; Reza *et al.*, 2015). However, reaction rate was found to decline at temperatures higher than 80 °C (Herrmann, 1999). An increase in the temperature (>80 °C) typically enhances the recombination of charge carriers and desorption process of organic compounds onto the TiO₂ surface, thus reducing the overall photocatalytic activity (Gaya & Abdullah, 2008; Chong *et al.*, 2010). Hence, an optimum operating temperature between 20 and 80 °C has been recommended (Herrmann, 1999; Gogate & Pandit, 2004; Chong *et al.*, 2010).

2.5.2.4 Effect of Light Intensity

In general, an increase in the light intensity increases the degradation rate of organic compounds during the photocatalytic degradation (Gaya & Abdullah, 2008). A relatively high light intensity is necessary to provide sufficient photons energy to each active site of TiO_2 surface to accelerate the photocatalytic degradation rate (Chong *et al.*, 2010). The catalyst excitation can be enhanced by increasing the incident light intensity (Saleh *et al.*, 2011). At lower light intensity, free radicals formation will be reduced as a result of the competition between the electron-hole pairs recombination and their separation (Gnanaprakasam *et al.*, 2015). Such phenomenon can be however prevented at higher light intensity. Energy loss as heat and as a result of to light reflection and transmission are unavoidable during photochemical processes (Yang & Liu, 2007).

Liu *et al.* (2006) investigated the effect of three different light intensities viz 1.24 mW/cm^2 , 2.04 mW/cm^2 , and 3.15 mW/cm^2 on the decolorization of Acid Yellow 17 by means of UV/ TiO_2 process. The result revealed that the decolourisation rate increased with the increasing light intensity. Another study by Chanathaworn *et al.* (2012) also reported similar observation for the TiO_2 photocatalytic decolourisation of Rhodamine B.

2.5.3 Limitations and Ways to Improve TiO_2 Photocatalytic Activity

TiO_2 photocatalytic application is rather restricted due to the prevailing limitations of TiO_2 nanoparticles. TiO_2 has a narrow photocatalytic region as a result of narrow band gap, which can only absorb wavelengths below 400 nm and a small fraction (<5%) of incident solar radiation and indoor light (Gulyas, 2014; Dong *et al.*, 2015). Aggregation of the suspended TiO_2 powder in solution especially at high concentrations is another drawback of TiO_2

nanoparticles (Zhang *et al.*, 2005b; Andriantsiferana *et al.*, 2013). This can be explained by the instability of the nanosized TiO₂ particles, which may inhibit the light incidence on the active centers and hence, reducing the photocatalytic activity of TiO₂ (Dong *et al.*, 2015). Also, another well-recognised shortcoming of TiO₂ is the tendency of nanosized TiO₂ to produce slurry during treatment which makes separation and recovery of the nanosized particles tedious (Zhang *et al.*, 2005b; Yao *et al.*, 2010; Andriantsiferana *et al.*, 2013; Dong *et al.*, 2015). As the photocatalytic degradation mainly occurs on the TiO₂ surface, the limitation of mass transfer needs to be minimised to ensure effective TiO₂ application in the wastewater treatment. However, the adsorption of organic pollutants on TiO₂ is relatively low because of its poor affinity towards the organic pollutants, especially for the hydrophobic organic pollutants (Dong *et al.*, 2015). This somehow slows down the degradation rate of photocatalytic treatment. The above-mentioned limitations of TiO₂ nanoparticles in the photocatalytic treatment are summarised in Figure 2.9.

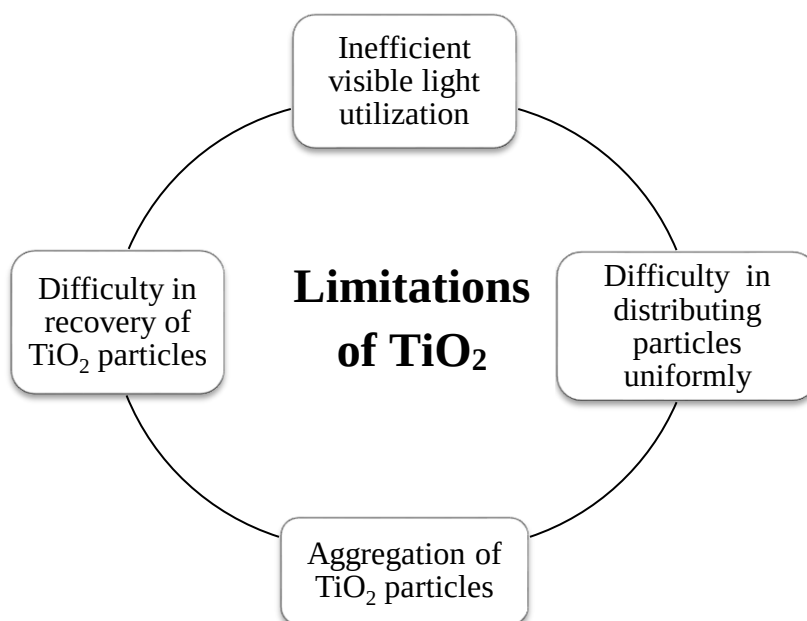


Figure 2.9: Limitations of nano-sized TiO₂.

Existing studies related to the prevailing limitations of TiO₂ photocatalysis have been mainly performed to achieve the following objectives: (1) to extend TiO₂ absorption into the visible light region, (2) to synthesize TiO₂ by various preparation methods to fine tune its properties (e.g. optical and electronic properties, crystallinity, and particle size) for enhanced degradation rate, and (3) to develop second generation TiO₂ photocatalyst with high ability of separation, and improved effectiveness of recovery and regeneration (Dong *et al.*, 2015). Methods such as doping with non-metals and transition metals, noble metals or metal ions incorporation, fabrication of TiO₂ composites or nanocomposites with other materials, surface sensitization, and TiO₂ immobilization on supports have been reported as possible means to improve TiO₂ photocatalytic activity (Fujishima *et al.*, 2008; Chong *et al.*, 2010; Nagmsopasiriskun *et al.*, 2010; Gupta & Tripathi, 2011; Dong *et al.*, 2015; Fagan *et al.*, 2016). Table 2.6 summarises the selected studies on the different approaches that have been applied to improve photocatalytic activity of TiO₂.

2.5.4 Fabrication of Composites, Nanocomposites or Mixtures

Composite can be defined as a multiphase material formed by a combination of materials which differ in form or composition in order to obtain specific properties and characteristics (Mark, 2007). The composites retain an interface between components and act in concert to achieve improved synergistic properties not obtainable by any of the components acting alone (Lee, 1995). Generally, composites can be classified based on the shapes or sizes of the reinforcing material used. There are four common classification of reinforcements which includes (1) particulates which are roughly spherical particles (1-100 µm in diameter), (2) whiskers with lengths <10 mm, (3) short or chopped fibres with length from 10-200 mm, and (4) continuous fibres whose length are very long (Tuttle, 2012).

Table 2.6: Summary of various approaches applied to overcome the limitations of TiO₂.

Type of pollutants	Optimum conditions	Catalyst used	Degradation efficiency	References
Fabrication of TiO₂ composite or nanocomposite				
L-acid	Initial concentration = 1.34×10^{-3} mol/L Dosage = 0.5 g pH = 1.95 Reaction time = 7 h	TiO ₂ /AC	89.88%	Wang <i>et al.</i> (2006)
Acephate, dimethoate and glyphosate	Initial concentration = 0.1 mM Reaction time = 60 min (dimethoate & glyphosate), 105 min (acephate)	TiO ₂ immobilized on silica gel	100.00% for all	Echavia <i>et al.</i> (2009)
Methyl orange (MO) and phenol	Initial concentration = 120 mg/L (MO), 80 mg/L (phenol) pH = 10.00 (MO), 4.00 (phenol) Dosage = 2.5 g/L Reaction time = 2 h (MO), 4 h (phenol)	TiO ₂ with activated carbon (AC) fibre (TiO ₂ /ACF)	MO = 87.00% phenol = 83.58%	Yao <i>et al.</i> (2010)
Methyl orange (MO)	Initial concentration = 10 mg/L Dosage = 0.1 g Reaction time = 5 h	TiO ₂ /ZnO	93.30%	Wang <i>et al.</i> (2013a)
Methylene Blue (MB)	Initial concentration = 10 ppm Dosage = 20 mg Reaction time = 120 min	Fly ash/ TiO ₂ nanofibre	100.00%	Saud <i>et al.</i> (2015)

Table 2.6 continued

Multi-pollutants (Copper (Cu), Bemacid Blau (BB) and Bemacid Rot (BR))	Initial concentration = 0.01 N (Cu), 50 mg/L (BR), 30 mg/L (BB) pH = 6.74 Reaction time = 90 min (Cu), 120 min (BR), 240 min (BB)	Fly ash/TiO ₂ (Degussa P 25)	Cu = 100.00% BR = 90.00% BB = 90.00%	Visa <i>et al.</i> (2015)
Bromocresol green and neutral red	Initial concentration = 10 ppm pH = 3.70 Reaction time = 3 h	Fe ₃ O ₄ @SiO ₂ /TiO ₂	100.00% for both	Ahangar <i>et al.</i> (2016)
Doping with metals				
Paper-making wastewater	Iron content = 0.05% Reaction time = 6 h	Fe/TiO ₂	Colour = 99.00% COD = 90.00%	Chen <i>et al.</i> (2004)
Acid green 16	Initial concentration = 2 x 10 ⁻⁴ mol/L pH = 4.00 reaction time = 60 min	Au/TiO ₂	100.00%	Sakthivel <i>et al.</i> (2004)
Methyl orange	Initial concentration = 20 mg/L pH = 6.20 Reaction time = 30 min Pt in TiO ₂ = 1.5%	Pt-TiO ₂ /zeolites	86.20%	Huang <i>et al.</i> (2008)
Tannery wastewater	H ₂ O ₂ = 0.3% (v/v) pH = 6.70 Reaction time = 40 min (COD), 110 min (Cr ⁶⁺)	Fe ³⁺ /TiO ₂	COD = 85.79% Cr ⁶⁺ = 84.62%	Jia <i>et al.</i> (2009)

Table 2.6 continued

Municipal wastewater	1.2 g/L of 5% Nd ³⁺ /TiO ₂ Reaction time = 3 h	Nd ³⁺ /TiO ₂	COD = 95.00%	Shahmoradi <i>et al.</i> (2010)
Methyl orange (MO)	Cu content = 1.0% Initial concentration = 20.0 mg/L	Cu/TiO ₂	Nil	Yang <i>et al.</i> (2015)
Rhodamine B (RhB)	Initial concentration = 40 µM Dosage = 0.025 g Reaction time = 100 min	Zn-TiO ₂ /C@SiO ₂ (ZTRH)	95.00%	Chen <i>et al.</i> (2016)
Phenol	Initial concentration = 100 mg/L Dosage = 1 g/L Reaction time = 300 min	F-Fe/TiO ₂	100.00%	Liu <i>et al.</i> (2016)
Textile wastewater	pH = 3.00 Dosage = 1.5 g/L H ₂ O ₂ = 9 mM Reaction time = 180 min	Fe/TiO ₂	COD = 97.00%	Ramírez-Franco & Zea-Ramírez (2016)
2,4-dichlorophenol	Ag in TiO ₂ = 1.68 wt% Reaction time = 180 min	Ag/TiO ₂	95.00%	Sarteep <i>et al.</i> (2016)
Doping with non-metals				
Methyl orange (MO)	1.5% S-TiO ₂ Reaction time = 40 min Initial concentration = 20.0 mg/L Dosage = 1.0 g/L	S-TiO ₂	Colour = 96.00%	Tian <i>et al.</i> (2009)
2-Chlorophenol	Initial concentration = 25 mg/L Dosage = 1 g/L Reaction time = 3 h	N-TiO ₂	98.00%	Ananpattarachai <i>et al.</i> (2009)

Table 2.6 continued

Methylene blue (MB)	Initial concentration = 7.5 ppm Dosage = 0.3 g Reaction time = 180 min	N-TiO ₂	TOC = 97.00%	Sacco <i>et al.</i> (2012)
Butyl benzyl phthalate (BPP)	Initial concentration = 20.0 mg/L Reaction time = 240 min	P-TiO ₂	TOC = 97.80%	Mohamed & Aazam (2013)
Olive mill wastewater	Reaction time = 2 h	N-TiO ₂	COD = about 60.00%	Ruzmanova <i>et al.</i> (2013b)
Methylene blue (MB)	Reaction time = 5.5 h Initial concentration = 20.0 mg/L	S-TiO ₂	Colour = 98.60%	Chaudhuri & Paria (2014)
Pharmaceutical wastewater	Reaction time = 90 min Dosage = 3 g/L	N-TiO ₂	TOC = almost 100.00%	Vaiano <i>et al.</i> (2014)
Methyl orange (MO)	Dosage = 0.2 g/L Reaction time = 4 h	C-TiO ₂	Colour = 78.60%	Chalak & Kulkarni (2015)

Nanocomposites are the current trend in novel nanostructured materials, which can be defined as a combination of two or more phases containing different structures and compositions, in which at least one phases show dimensions in the nanometre range ($1\text{ nm} = 10^{-9}\text{ m}$) (Merhari *et al.*, 2002; Camargo *et al.*, 2009). As mentioned by Bogue *et al.* (2011), nanocomposites incorporate materials such as carbon nanotubes (CNTs) or minerals, metal or other nanoparticles, which can significantly improve the properties of a composite. Nanocomposite materials can be classified based on their matrix materials, which divided into three different categories, such as ceramic matrix nanocomposites (CMNC), metal matrix nanocomposites (MMNC) and polymer matrix nanocomposites (PMNC), as shown in Table 2.7 (Camargo *et al.*, 2009).

Table 2.7: Different types of nanocomposites.

Class	Examples
Ceramic	$\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{Al}_2\text{O}_3/\text{CNT}$, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{SiC}$, SiO_2/Ni
Metal	Fe/MgO , $\text{Fe-Cr}/\text{Al}_2\text{O}_3$, Al/CNT , Mg/CNT , $\text{Ni}/\text{Al}_2\text{O}_3$, Co/Cr
Polymer	Polyester/ TiO_2 , polymer/ CNT , polymer/layered silicates, polymer/layered double hydroxides, thermoplastic/thermoset,

Source: Camargo *et al.* (2009)

A mixture can be defined as a physical combination of two or more pure substances in which there is no chemical bonding between the substances and each substance retains its own chemical identity (Daintith, 2014; Stoker, 2015). Mixtures are divided into homogeneous and heterogeneous. A homogeneous mixture is a mixture that contains only one visible phase when the molecules of the substances are mixed, which have uniform properties throughout (Daintith, 2014). For instance, metal alloys such as 14-karat gold (gold and copper mixture) is a homogeneous mixture of solids; gasoline and motor oil are multicomponent homogeneous

mixtures of liquids; and air is a homogeneous mixture of gases (Stoker, 2015). A heterogeneous mixture is a mixture that different visible phases can be distinguished, each of which has different properties (Daintith, 2014). Gunpowder or certain alloys, blueberry muffins and chocolate chip cookies are examples of heterogeneous mixture with non-uniform appearance. Wood, rocks and soils are naturally occurring heterogeneous mixtures (Stoker, 2015).

One of the effective methods to improve the recovery of TiO_2 is *via* immobilization on a support or adsorbent. Immobilization of TiO_2 photocatalyst increases the illuminated specific catalyst area and enhances the adsorption capacity and surface area of the photocatalyst (Ngamsopasiriskun *et al.*, 2010). Various support materials such as glass, zeolite, alumina, clays, glass fibre, quartz, silica, and activated carbon (AC) have been utilised to immobilize TiO_2 (Ngamsopasiriskun *et al.*, 2010; Andriantsiferana *et al.*, 2013; Dong *et al.*, 2015). Choice of a substrate for the immobilization is a crucial step as an ideal support should possess several criteria (1) UV-transparency, (2) offers high specific surface area, (3) strong adherence between catalyst and support, (4) strong adsorption affinity towards the organic pollutants, and (5) non-reduction of the catalyst reactivity from the anchoring process (Gianluca *et al.*, 2008). Choosing a support that addresses all of these criteria without succumbing to any of them is seems to be a difficult task. The efficiency of supported TiO_2 may lead to a decrease in photocatalytic efficiency of the catalyst due to a mass transfer limitation as a result of reduction in the specific surface area (Chong *et al.*, 2010).

Preparations of TiO_2 -based composite catalysts have been reported in various studies. These composites catalysts include TiO_2/ZnO (Habib *et al.*, 2013; Wang *et al.*, 2013a; Aljuboury *et al.*, 2016b), $\text{TiO}_2/\text{zeolite}$ (Guesh *et al.*, 2016), TiO_2/AC (Wang *et al.*, 2006; Ngamsopasiriskun *et al.*, 2010; Aruldoss *et al.*, 2011; Adriantsiferana *et al.*, 2013), $\text{TiO}_2/\text{silica}$ gel (Echavia *et al.*, 2009), $\text{TiO}_2/\text{fly ash}$ (Saud *et al.*, 2015; Visa *et al.*, 2015), and etc. Various

methods have been developed to immobilize TiO₂ catalyst onto a solid surface or to combine it with other materials in the past decade. Sol-gel (Xue *et al.*, 2011; Yao *et al.*, 2012; Wang *et al.*, 2013a), impregnation (Mahadwad *et al.*, 2012), precipitation (Tryba *et al.*, 2003), direct mixing (Rioja *et al.*, 2012), mechanical grinding (Samdani & Thakur, 2014), hydrothermal (Visa *et al.*, 2015), hydrolysis (El-Sheikh *et al.*, 2004), and also metal-organic chemical vapour deposition (MOCVD) (Adriantsiferana *et al.*, 2013) are examples of methods which have been commonly applied.

Preparation of TiO₂-based composite using activated carbon (AC) has been much explored. Table 2.8 summarises examples of TiO₂-based composites which are available in literature. It has been reported that TiO₂ supported on AC successfully degraded phenol (Omri & Benzina, 2014) and reduced 92.00% total organic carbon (TOC) from industrial phosphoric acid solution (Omri *et al.*, 2014) through a series of photocatalytic oxidation processes. Phenol degradation was initiated by HO• radicals attack on the sites of aromatic ring in the compounds leading to ring-opening that produces CO₂, H₂O and other degradation products (Figure 2.10) (Tsai *et al.*, 2009; Xue *et al.*, 2011). During the photocatalytic process, breakdown of the benzene ring and its subsequent mineralisation could be determined by the decrease in TOC level (Lagunas-Allu *et al.*, 2010). Belayachi *et al.* (2015) revealed that TiO₂/grape marc-based AC (GMAC) successfully degraded 98.00% of RB5 azo dye.

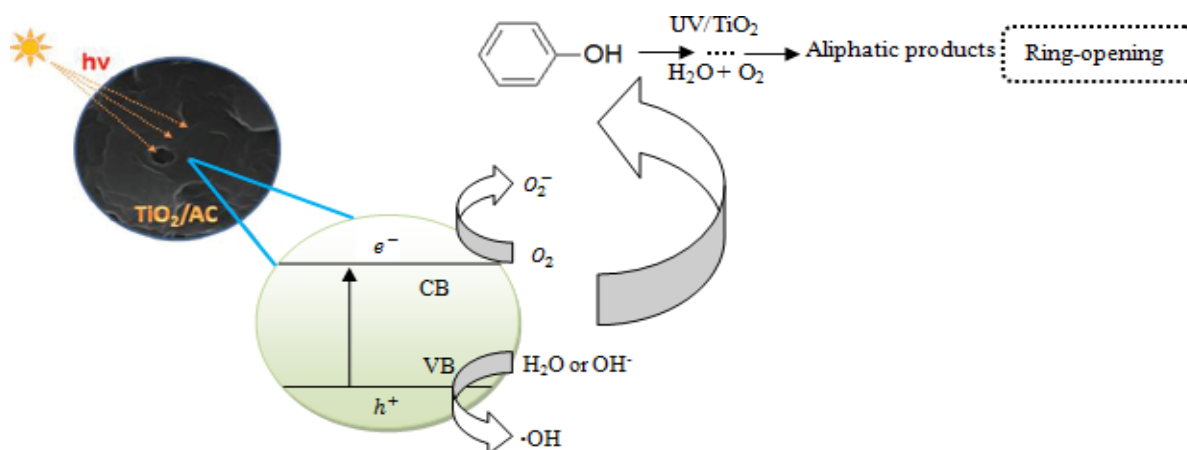


Figure 2.10: Schematic diagram of the photocatalytic degradation of phenol by TiO₂/AC (Source: Colmenares *et al.*, 2016).

The distinctive advantages of AC compared to other supports include its ability to (1) adsorb and release pollutant onto the TiO₂ surface; (2) increase charge transference between TiO₂ and AC *via* acidification of surface hydroxyl groups; and (3) further oxidise the adsorbed intermediates during degradation (Zhang *et al.*, 2005b; Chen *et al.*, 2006). Well-developed pore structure with large surface area and adsorption capacity of AC facilitates adsorption of organic molecules before being transferred to the degradation center of TiO₂ (Colmenares *et al.*, 2016). Synergistic effect between TiO₂ and AC has been reported for TiO₂-supported AC (TiO₂/AC) (Ngamsopasiriskun *et al.*, 2010). In addition, AC also acts as a TiO₂ photosensitizer by injecting electrons into the TiO₂ conduction band that promotes the formation of HO• radicals (Colmenares *et al.*, 2016).

Despite the established importance of TiO₂ photocatalysis in wastewater purification be it natural or synthetic wastewater, there is no reliable evidence whether this technique is capable to degrade sago wastewater effluent. However, local researchers have attempted to investigate the degradation of palm oil mill effluent using commercial TiO₂ and TiO₂-based composite catalyst (Ng *et al.*, 2014; Ng & Cheng, 2015).

Table 2.8: Summary of the performance of TiO₂-based composites on wastewater degradation.

Type of wastewaters	Optimised conditions	Catalyst used	Degradation efficiency	References
Phenol	Initial concentration = 100 ppm Dosage = 0.4 g Reaction time = 4 h	TiO ₂ /AC	68.03%	Ngamsopasiriskun <i>et al.</i> (2010)
Synthetic phenolic syntan (PS) solution	PS concentration = 50.0 mg/L Light intensity = 125 W pH = 2.50 Reaction time = 120 min	TiO ₂ -AC	COD = 87.00%	Aruldoss <i>et al.</i> (2011)
Organic compounds-containing wastewater	Reaction time = 24 h UV = germicidal lamp	TiO ₂ /SiO ₂ beads	TOC = 90.00%	Nakano <i>et al.</i> (2011)
Tannery wastewater	UV = 600 nm Reaction time = 4 h	TiO ₂ supported on glass microspheres	COD = 9.00%	Castiello <i>et al.</i> (2013)
Textile wastewater containing brilliant golden yellow (BGY) and Orange G	ZnO/TiO ₂ molar ratio = 1:3 Dosage = 6 g/L pH = 7.00 Reaction time = 2 h	ZnO/TiO ₂	Decolorization = 80.00%	Habib <i>et al.</i> (2013)
Olive mill wastewater	Dosage = 1.5 g/L Reaction time = 2 h	Fe ₃ O ₄ /SiO ₂ /TiO ₂	COD = 50.00%	Ruzmanova <i>et al.</i> (2013a)
RB-5 azo dye	Initial concentration = 100 µmol/L Reaction time = 60 min Dosage = 2.0 g/L pH = 2.00	TiO ₂ with grape marc-based AC (TiO ₂ /GMAC)	98.00 %	Belayachi <i>et al.</i> (2015)

Table 2.8 continued

Petroleum wastewater	TiO ₂ dosage = 0.5 g/L ZnO dosage = 0.54 g/L Reaction time = 170 min pH = 6.8 Air flow = 4.3 L/min	TiO ₂ /ZnO with aeration processes	COD = 76.00% TOC = 99.30%	Aljuboury <i>et al.</i> (2016b)
Molasses synthetic wastewater	TiO ₂ -ZnO ratio = 3:1 AC = 30% loading Reaction time = 1 h pH = 5.0	TiO ₂ -ZnO-AC	Colour = 96.00% TOC = 9.00%	Benton <i>et al.</i> (2016)
Textile wastewater of Ethopia	Dosage = 10%	TiO ₂ -Zeolite	TOC = 84.00%	Guesh <i>et al.</i> (2016)

2.6 Fenton's Reagent

The Fenton's reagent which was discovered by Fenton in 1894, is a combination of hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) that produces $\text{HO}\cdot$ radicals that are responsible for the oxidation of pollutants (Ebraheim *et al.*, 2013). Fenton's reagent has been applied thus far in wastewater purification with the objectives to (1) induce destruction of organic pollutant, (2) remove BOD or COD, odour and colour, (3) reduce toxicity level, and (4) improve the biodegradability of wastewater. Examples of wastewaters that have been treated using Fenton's reagent include pharmaceutical wastewater (Tekin *et al.*, 2006), coking wastewater (Chu *et al.*, 2012), textile wastewater (Karthikeyan *et al.*, 2011), oil recovery industry wastewater (Dincer *et al.*, 2008), and fish processing wastewater (Cristóvão *et al.*, 2014).

The classical mechanism of Fenton reaction is a simple redox reaction in which the Fe^{2+} ion is oxidised to ferric (Fe^{3+}) ion in an acidic aqueous solution while H_2O_2 is reduced to $\text{HO}\cdot$ radical and hydroxide ion (OH^-), as shown in Eq. 2.18 (Galvao *et al.*, 2006; Machulek *et al.*, 2012):



In the absence of UV light, the generated Fe^{3+} ion (Eq. 18) can be reduced with a second molecule of H_2O_2 to regenerate the Fe^{2+} ion and more radicals (Aljuboury *et al.*, 2014). This reaction which is referred as Fenton's like reaction occurs at a slower rate than the Fenton reaction (Eq. 2.18). Eqs. 2.19 to 2.21 show the series of reactions that take place in the Fenton's like reaction (Habib *et al.*, 2012).





Apart from the regeneration of Fe^{2+} ion, hydroperoxyl ($\text{HO}_2^\bullet$) radicals are also produced in this Fenton's like reaction. Although $\text{HO}_2^\bullet$ radicals are less sensitive than $\text{HO}^\bullet$ radicals, it is also capable to attack the organic compounds (Aljuboury *et al.*, 2014). $\text{HO}_2^\bullet$ radicals are very unstable and can be easily converted into $\text{HO}^\bullet$ radicals as shown in Eq. 2.22 (Habib *et al.*, 2012).



Although the Fenton reaction is chemically very efficient for the removal of organic pollutants, but it slows down appreciably after the initial conversion of Fe^{2+} to Fe^{3+} (Eq. 2.18). Consequently, Fenton reaction may require the addition of relatively large amount of Fe^{2+} ions (Machulek *et al.*, 2012). Another limitation of the Fenton reaction is the formation of recalcitrant intermediates that inhibit the complete mineralisation of pollutants (Machulek *et al.*, 2012). In addition, coagulation by ferric-hydroxides precipitation also takes place in Fenton process, which mostly occurs at a lower $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio (Gogate & Pandit, 2004; Li *et al.*, 2016). As the precipitation of ferric sludge may cause waste disposal problem, an additional step is required to remove the sludge (Kim & Vogelpohl, 1998; Samet *et al.*, 2012). To overcome these limitations, UV irradiation has been introduced to the conventional Fenton process to enhance the production of $\text{HO}^\bullet$ radicals and to reduce the amount of ferric sludge (Li *et al.*, 2016). This process is known as photo-Fenton process.

2.7 Photo-Fenton Process

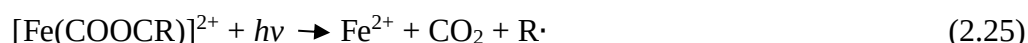
Photo-Fenton typically produces a faster mineralisation of recalcitrant compounds and enhances the degradation kinetics compared to the dark Fenton reaction and it can take

advantage of light in the solar spectral region (Alalm & Tawfik, 2013). Photo-Fenton reaction is the improvement to Fenton's reagent with the addition of UV irradiation (Abdulah *et al.*, 2011). UV irradiation leads not only to the additional formation of HO• radicals but also the recycling of Fe²⁺ ion catalyst from the Fe³⁺ ion reduction (Sharma *et al.*, 2011). According to Wang *et al.* (2014), H₂O₂ can be efficiently decomposed into HO• radicals under UV irradiation to facilitate the oxidation of Fenton's reagent. Photo-Fenton process can be divided into three major steps namely (1) generation of HO• radicals, (2) regeneration of Fe²⁺ ion by action of light, and (3) degradation of organic compounds (RH) by HO• radicals (Silva *et al.*, 2015):

1. Generation of HO• radicals



2. Regeneration of Fe²⁺ ion by action of light



3. Degradation of organic compounds by HO• radicals

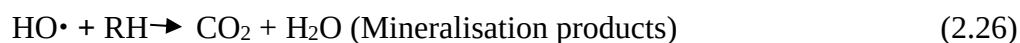
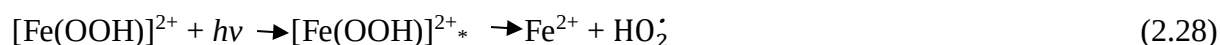


Photo-Fenton reaction begins likewise the classical Fenton's reagent as shown in Eq. 2.23. Fe²⁺ ions are oxidised by H₂O₂ to Fe³⁺ ions and one equivalent HO• radical is produced in the reaction of photo-Fenton process (Alalm & Tawfik, 2013). The presence of UV irradiation enables the photo-reduction of Fe³⁺ ions, represented by the complex [Fe(OH)]²⁺, into Fe²⁺ (Eqs. 2.24 and 2.25) (Galvao *et al.*, 2006; Abdulah *et al.*, 2011). The ferric species can also form complexes with the degradation products and/or initial organic pollutants, resulting to photo-reduction back to Fe²⁺ ions as shown in Eq. 2.25 (Galvao *et al.*, 2006). Photo-reduction of ferric species will not reduce the usage iron catalyst by regeneration of Fe²⁺ ion,

but also produce additional HO• radicals (Eqs. 2.24 and 2.25) (Abdulah *et al.*, 2011). In addition, UV also accelerates the Fe³⁺ ion reduction due to the formation of complex (ferric oxyhydroxides, [Fe(OOH)]²⁺) from the interaction between Fe³⁺ ion and H₂O₂ (Eq. 2.27). Absorption of light by [Fe(OOH)]²⁺ complex results in the formation of an excited state ([Fe(OOH)]^{2+*}), which acts to accelerate the Fe³⁺ reduction, as shown in Eq. 2.28 (Guz *et al.*, 2014).



Moreover, in the presence of UV irradiation (<320 nm), one molecule of H₂O₂ can generate two HO• radicals, as shown in Eq. 2.29 (Mechakra *et al.*, 2016):



When the generated HO• radicals attack the targeted organic pollutants (RH), intermediates or degradation products will be formed during the photo-Fenton treatment (Eq. 2.30). These intermediates will be mineralised into CO₂, H₂O and simpler form of degradants (Tokumura *et al.*, 2013).



There is a growing body of literature that recognises the importance of Fenton and photo-Fenton processes in wastewater treatment. Table 2.9 summarises the selected studies of Fenton and photo-Fenton processes on different types of wastewater.

The main parameters that typically affects the efficiency of the photo-Fenton process include the initial solution pH, H₂O₂, and Fe²⁺ concentrations, structure of organic compounds,

temperature, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, and the reaction time (Gulkaya *et al.*, 2006; Khamaruddin *et al.*, 2011; Segneanu *et al.*, 2013).

2.7.1 Effect of pH

The efficiency of photo-Fenton process is strongly dependent on pH. The optimum pH range for photo-Fenton process has been reported to be between 2.0-4.0 (Khamaruddin *et al.*, 2011; Romero *et al.*, 2016b). Solution pH controls the generation of $\text{HO}\cdot$ radicals and the Fe^{2+} concentration (Aljuboury *et al.*, 2014). The suggested overall reaction for Fenton's oxidation is shown in Eq. 2.31 (Tekin *et al.*, 2006):



A maximum amount of $\text{HO}\cdot$ radicals can be generated when the pH value is in the acidic range. Nevertheless, the pH value should not be too low. At very low pH, $\text{pH} < 2.0$, the degradation rate tends to decline due to the formation of complex iron species, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and oxonium ion $[\text{H}_3\text{O}_2]^+$ (Khamaruddin *et al.*, 2011). A lower amount of $\text{HO}\cdot$ radicals will be produced as a result of a much slower reaction between complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ with H_2O_2 compared to $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+$ (Mota *et al.*, 2008). The stable $[\text{H}_3\text{O}_2]^+$ ion is formed due to the reaction between H_2O_2 and excess H^+ ion, as shown in Eq. 2.32 (Oliveira *et al.*, 2014). The stability of $[\text{H}_3\text{O}_2]^+$ ion impedes it from reacting with Fe^{2+} ions and thus lowering the formation of $\text{HO}\cdot$ radicals (Aljuboury *et al.*, 2014).



Table 2.9: Summary of Fenton and photo-Fenton studies on different types of wastewater.

Types of wastewater	Optimised conditions	Degradation efficiency	References
	Fenton		
Carpet dyeing wastewater	H ₂ O ₂ = 385.0 g/L Fe ²⁺ = 5.5 g/L pH = 3.00 Temperature = 50 °C	COD = 95.00%	Gulkaya <i>et al.</i> (2006)
Pharmaceutical wastewater	H ₂ O ₂ = 0.30 M Fe ²⁺ = 0.002 M pH = 3.50	COD = 45.00-65.00%	Tekin <i>et al.</i> (2006)
Oil recovery industry wastewater	H ₂ O ₂ = 200.52 g/L Fe ²⁺ = 23.16 g/L pH = 3.00 Reaction time = 60 min	COD = 86.00%	Dincer <i>et al.</i> (2008)
Landfill leachate wastewater	H ₂ O ₂ = 1020.0 mg/L Fe ²⁺ = 560.0 mg/L pH = 3.00 Reaction time 120 min	COD = 58.10% Colour = 78.30%	Mohajeri <i>et al.</i> (2010)
Coking wastewater	H ₂ O ₂ = 0.30 M Fe ²⁺ = 3.0 g/L pH = 6.50 Reaction time = 60 min	COD = 44.00-50.00% Phenol = 95.00%	Chu <i>et al.</i> (2012)
Polyaniline wastewater	H ₂ O ₂ = 0.8 mol/L Fe ²⁺ = 0.8 mol/L pH = 1.10 Reaction time = 50 min	COD = 96.00%	Ma <i>et al.</i> (2013)

Table 2.9 continued

Temperature = 19 °C			
Fish-processing wastewater	H ₂ O ₂ = 1558.0 mg/L Fe ²⁺ = 363.0 mg/L pH = 3.20	DOC = 63.00%	Cristóvão <i>et al.</i> (2014)
Photo-Fenton			
Tannery wastewater	H ₂ O ₂ = 15.0 g/L Fe ²⁺ = 1.0 g/L pH = 2.50 Reaction time = 3 h	COD = 87.00%	Dantas <i>et al.</i> (2003)
Synthetic tannin (syntan) solution	H ₂ O ₂ = 300.0 mg/L Fe ²⁺ = 750.0 mg/L pH = 3.00 Reaction time = 5 min	COD = 82.00%	Lofrano <i>et al.</i> (2007)
Biological laboratory wastewater containing formaldehyde	H ₂ O ₂ = 1.0 mol/L Potassium ferrioxalate = 0.5 mmol/L Reaction time = 2 h	DOC = 89.00% Formaldehyde = 100.00%	Fonseca <i>et al.</i> (2010)
Vinasse wastewater	H ₂ O ₂ = 5.0 mL/L Fe ²⁺ = 5.0 g/L pH = 5.50 Reaction time = 80 min	COD = 73.00%	Hadavifar <i>et al.</i> (2010)
Simulated industrial wastewater	H ₂ O ₂ = 30.0 mM Fe ²⁺ = 8.39 mM pH = 1.90	Nil	Dopar <i>et al.</i> (2011)

Table 2.9 continued

Tannery industrial effluent	$\text{H}_2\text{O}_2 = 30.0 \text{ g/L}$ $\text{Fe}^{2+} = 0.5 \text{ g/L}$ $\text{pH} = 3.00$ Reaction time = 120 min	COD = 97.90% TSS = 65.40%	Módeneset <i>et al.</i> (2012)
Pesticide wastewater containing Chloropyrifos	$\text{H}_2\text{O}_2 = 1.0 \text{ g/L}$ $\text{Fe}^{2+} = 3.0 \text{ g/L}$ $\text{pH} = 3.60$ Reaction time = 120 min	COD = 91.00% chloropyrifos = 78.00%	Alalm & Tawfik (2013)
Cosmetic wastewater	$\text{H}_2\text{O}_2 = 1.0 \text{ mL/L}$ $\text{Fe}^{2+} = 0.75 \text{ g/L}$ $\text{pH} = 3.00$ Reaction time = 40 min	COD = 95.50%	Ebraheim <i>et al.</i> (2013)
Car wash wastewater	$\text{H}_2\text{O}_2 = 403.9 \text{ mg/L}$ $\text{Fe}^{2+} = 48.4 \text{ mg/L}$ $\text{pH} = 3.50$	COD = 93.40%	Tony & Bedri (2014)
Petroleum wastewater	$\text{H}_2\text{O}_2 = 850.0 \text{ mg/L}$ $\text{Fe}^{2+} = 60.0 \text{ mg/L}$ $\text{pH} = 3.68$ Reaction time = 127 min	COD = 74.70% TOC = 59.30%	Aljuboury <i>et al.</i> (2016a)

Similarly, at pH >4.0, a diminution in the amount of HO• radicals also take place due to the formation of ferric-hydroxo complexes which would decrease the free iron species in the solution (Khamaruddin *et al.*, 2011). It is known that the oxidation potential of HO• radicals decreases as the pH increases. At basic pH, precipitation of iron hydroxides, (Fe(OH)₂ or Fe(OH)₃), occurs due to the reaction between iron and hydroxide anions (OH⁻) (Mota *et al.*, 2008). As these iron hydroxides do not react with H₂O₂, Fenton reaction will be somewhat retarded. In addition, the stability of H₂O₂ is lowered at high pH values (4.0-5.0) (Aljuboury *et al.*, 2014). In alkaline solution, H₂O₂ suffers the loss of its oxidative capacity as it is readily decomposed into O₂ and H₂O (Wang *et al.*, 2014). Although H₂O₂ is more stable at extreme low pH such condition slows down the decomposition rate of H₂O₂ to generate HO• radicals consequently reducing the degradation efficiency (Wang *et al.*, 2014). Hence, both high and extreme low pHs reduces the efficiency of the photo-Fenton process to degrade organic compounds.

2.7.2 Effect of Hydrogen Peroxide Concentration

Concentration of H₂O₂ plays an important role in determining the overall efficiency of the degradation process (Aljuboury *et al.*, 2014). The optimum concentration of H₂O₂ must be determined experimentally as insufficient amount of H₂O₂ will lead to the deficiency of HO• radicals produced by H₂O₂ decomposition under Fenton processes (Wang *et al.*, 2016). It has been observed that the percentage of pollutant degradation increases with the amount of H₂O₂ (Galvao *et al.*, 2006). Wang *et al.* (2014) reported that high concentration of H₂O₂ (4340 mg/L) dominates the removal efficiency of phenol by Fenton's reagent compared to concentration of Fe²⁺ (1616 mg/L). However, concentration of H₂O₂ should be optimised because it can both produce as well as decompose HO• radicals. An addition of excess H₂O₂ may lead to the

scavenging effect on HO• radicals, subsequently resulting in a decrease of HO• radicals utilisation (Wang *et al.*, 2014). An excessive concentration of H₂O₂ besides increasing the cost of treatment for high volume of organic wastewater, also give rise to an increase in the COD level of the effluent (Wang *et al.*, 2016). Furthermore, excessive H₂O₂ concentration may also negatively impact the degradation kinetics. A possible explanation for this is due to the recombination of HO• radicals and the auto-decomposition of H₂O₂ into O₂ and H₂O as shown in Eqs. 2.33 and 2.34, respectively (Sarria *et al.*, 2003).



2.7.3 Effect of Iron Concentration

Concentration of Fe²⁺ ion also greatly affects the Fenton and photo-Fenton processes (Samet *et al.*, 2012). In general, as the concentration of Fe²⁺ ion increases, the production rate of HO• radicals also increases, correspondingly the degradation rate (Aljuboury *et al.*, 2014). However, an excess of Fe²⁺ ion has been reported to cause several negative effects on Fenton and photo-Fenton degradation processes. Firstly, it can inhibit the degradation process because Fe²⁺ ions may compete with the organic pollutants to react with the HO• radicals, as shown in Eq. 2.35 (Galvao *et al.*, 2006).



In addition, excess amount of Fe²⁺ ions also possess radical scavenger effect, which can scavenge the hydroxyl/hydroperoxyl radicals (Aljuboury *et al.*, 2014; Saber *et al.*, 2014). When Fe²⁺ ions are present in excess, it reduces the penetration of UV radiation into the reaction

system (Galvao *et al.*, 2006). A large quantity of Fe^{3+} sludge could also be generated at the end of wastewater treatment due to the high amount of Fe^{2+} ions (Samet *et al.*, 2012). The permitted maximum level established by Environmental Quality Regulations for the disposal of Fe^{2+} ion is 5.0 mg/L (EQA, 1974). This is because Fe^{2+} and Fe^{3+} ions are classified as aesthetic or secondary pollutants that can affect the flavour and colour of water. For environmental and economic reasons, the concentration of Fe^{2+} should be as low as possible in Fenton or photo-Fenton process (Samet *et al.*, 2012).

2.7.4 Effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ Molar Ratio

It is known that H_2O_2 and Fe^{2+} are the two essential chemicals in both Fenton and photo-Fenton processes that dictates the overall degradation efficiency as well as the operation costs (Aljuboury *et al.*, 2014). It is therefore important to evaluate the optimal operational $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio to obtain maximum results. In Fenton and photo-Fenton oxidation processes, when the concentration of Fe^{2+} ion is higher than the concentration of H_2O_2 , the $\text{HO}\cdot$ radicals will be used up to react with the excess Fe^{2+} ion, thus reducing the availability of $\text{HO}\cdot$ radicals for the oxidation of organic pollutants (Mota *et al.*, 2008). Excessive Fe^{2+} ion concentration also causes the decomposition of H_2O_2 into large amount of $\text{HO}\cdot$ radicals, in which the high concentration of $\text{HO}\cdot$ radicals may lead to the scavenging effect by itself, as shown in Eq. 2.36 (Chan & Chu, 2003; Wang *et al.*, 2014). Chan and Chu (2003) suggested that the oxidation capacity of the Fenton process was found to have a nonlinear correlation to the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ doses due to the several undesired side reactions involved at both high and low $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios.



The optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 1.5 managed to reduce 61.30% of COD in landfill leachate wastewater (Zhang *et al.*, 2005a). Saber *et al.* (2014) reported that over 83.00% of COD level in petroleum refinery wastewater was removed within 90 min of treatment time at pH 3.0 using $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ mass ratio of 2.66. Another study reported a greater ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ (100:1) was required to attain 95.00% of COD removal in kraft pulp wastewater at pH 3.0 (Rabelo *et al.*, 2014). It can be concluded that $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio varies highly with the types of wastewater as well as their pollutant concentration to be oxidised.

2.7.5 Effect of Temperature

The efficiency of wastewater treatment by means of Fenton and photo-Fenton are significantly affected by temperature (Wang *et al.*, 2016). Temperature plays a crucial role in chemical reaction, whereby as the reaction temperature increases, the rate of reaction also increases (Khamaruddin *et al.*, 2011). A possible explanation is that increasing the reaction temperature accelerates the rate of $\text{HO}\cdot$ radicals formation in Fenton and photo-Fenton processes (Xu *et al.*, 2014). In contrast, thermal decomposition of H_2O_2 into O_2 and H_2O at high temperature (40-50 °C) also leads to a decline in the overall removal efficiency (Guedes *et al.*, 2003; Gulkaya *et al.*, 2006; Zazo *et al.*, 2011).

Wang *et al.* (2016) reported that temperature ranging between 25-30 °C was used for Fenton-like processes. Effect of temperature on Fenton and photo-Fenton process has been investigated in numerous studies. The findings however vary significantly between the types of wastewater. Guedes *et al.* (2003) investigated the effect of temperature (20-50 °C) on cork cooking wastewater during Fenton treatment. The result revealed that the TOC removal efficiency decreased at temperature higher than 40-50 °C while maximum TOC removal of

66.40% was achieved at an optimal temperature of 30 °C. As for sawmill wastewater, TOC and COD removal markedly increased from 15% to 50% and 5% to 60%, respectively with an increase in temperature from 50-120 °C (Munoz *et al.*, 2014). No optimal temperature was detected for the TOC removal efficiency in carpet dyeing wastewater when temperature ranging between 25-70 °C was investigated (Gulkaya *et al.*, 2006). Obviously, the effect of temperature shows different removal efficiency on various types of wastewater. However, research findings depict that temperature of wastewater does not affect the efficiency of COD removal in Fenton and photo-Fenton's oxidation (Tekin *et al.*, 2006). In addition, for practical and economic reasons, all experiments were conducted at room temperature and the adequate reaction temperature was reported as 30 °C (Mohajeri *et al.*, 2010).

2.8 Response Surface Methodology (RSM)

RSM was initially advocated and described in 1951 by Box and Wilson in the optimisation of problems related to chemical processing engineering (Amago, 2001; Peasura, 2015). RSM is a collection of mathematical and statistical method being useful for the analysis and modelling of problems (Fasnabi *et al.*, 2016). The variables which influence the response of interest are typically studied. The main objective of RSM is to optimise the industrial processes and/or chemical reactions. Whenever the outputs may be influenced by multiple system variables, RSM can be used to evaluate the relationship between the independent and dependent (response) variables to optimise the relevant processes (Arslan-Alaton *et al.*, 2009). The concept of a response surface involves several independent variables $x_1, x_2, \dots, x_k$ and a dependent variable y , called the response variable (Khidhir *et al.*, 2015).

Usually in a predetermined region of the independent variables, RSM employs a low-order polynomial equation (first-order and second-order), which is later analysed to locate the optimum values of independent variables to achieve the best (highest) response (Ceylan *et al.*, 2008). The first-order model and second-order model are expressed in Eqs. 2.37 and 2.38, respectively (Bezerra *et al.*, 2008; Khidhir *et al.*, 2015).

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (2.37)$$

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \quad (2.38)$$

Generally, $i < j$ is utilised in RSM problems while the β parameters of the polynomials are estimated (Khidhir *et al.*, 2015). The most common first order model designs are Plackett-Burman, 2^k factorial, and simplex designs while the most widely and frequently used second order model designs are 3^k factorial, Box-Behnken, and central composite designs (Khuri & Mukhopadhyay, 2010). As the first order model is generally used at the preliminary stage of a response surface investigation, the optimisation processes are applicable to the second order models (Khuri & Mukhopadhyay, 2010).

The statistical tool of RSM has been suggested to consist of the influence of individual factors and their interactive effects. In order to solve the multivariable equation, RSM is utilised for multiple regression analysis by using quantitative data obtained from properly designed experiments (Subha & Muthukumar, 2012). Process optimisation by means of RSM is more economical and much faster for obtaining experimental research results compared to the full-factorial or time consuming one-factor-at-a-time approach (Alim *et al.*, 2008). Furthermore, the advantage of using RSM is the reduction of the number of experiments needed compared to a full experimental design at the same level (Muthukumar & Muthuchamy, 2014). Central

composite design is considered to be the most popular second order class of RSM and widely used in literature (Arslan-Alaton *et al.*, 2009; Fasnabi *et al.*, 2016).

2.8.1 Full Three-Level (3^k) Factorial Design

3^k factorial design consists of all the combinations of the levels of the k , which have three levels each, where k represents the number of control variables (Khuri & Mukhopadhyay, 2010). These levels can be coded when they are equally spaced, which corresponds to -1, 0, 1. However, the application of 3^k factorial design in RSM is rather limited when the number of factor is higher than 2 (Bezerra *et al.*, 2008). This is due to the number of experimental runs for this design is 3^k , which can be very large for a large k , and hence losing its efficiency in the quadratic functions modelling (Bezerra *et al.*, 2008; Khuri & Mukhopadhyay, 2010). Due to the requirement of more experimental runs for this design, the Box-Behnken, Doehlert, and central composite designs, that present a smaller number of experimental points are more preferred (Bezerra *et al.*, 2008).

2.8.2 Box-Behnken Design (BBD)

Box and Behnken (1960) has developed the BBD, which provides three levels for each factor and contains of a particular subset of the factorial combinations from 3^k factorial design. BBD allows the estimation of the first and second order coefficients of the mathematical model to be efficient (Bezerra *et al.*, 2008). Khuri and Mukhopadhyay (2010) also stated that BBD is popular in industrial research due to economical reason and requires only three levels (-1, 0, 1) for each factor. The number of experiments is expressed according to $N = 2k(k-1) + C_p$, where k represents the number of factors and C_p is the number of the central points (Bezerra *et al.*,

2008). All the experimental points in BBD lie on a sphere of radius $\sqrt{2}$ (Nair *et al.*, 2014). When comparing to the complete factorial design, BBD provides accurate result and minimum effect and also reduces number of runs, as shown in Figure 2.11 (Nair *et al.*, 2014; Sangeetha *et al.*, 2014). Although BBD has been applied to optimise several physical and chemical processes, its application in analytical chemistry is rather restricted compared to the central composite design (Bezerra *et al.*, 2008). Table 2.10 summarises the selected applications of BBD in wastewater treatment. Sangeetha *et al.* (2014) studied the coagulation treatment of sago wastewater using BBD *via* RSM. The result showed that 100 mg/L of alum managed to reduce 67.86% of COD in the initial wastewater concentration (23.5 g/L) at pH 4.50. Another study employed BBD on the electrochemical oxidation process for the treatment of textile wastewater (Sendhil *et al.*, 2015). The optimum conditions were found to be reactor volume = 300 mL, electrolysis time = 6 h, and current density = 4.0 A.dm⁻² for a COD removal of 97.17%.

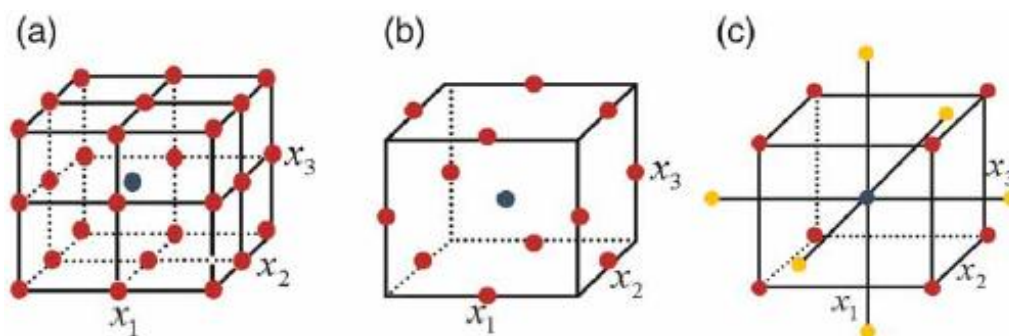


Figure 2.11: Three variables ($k = 3$) of different experimental designs (a) 3^k factorial design ($n = 27$), (b) BBD ($n = 15$) and (c) CCD ($n = 17$). N = number of experiments with $C_p = 1$ for (a) while $C_p = 3$ for (b) and (c) (Nair *et al.*, 2014).

Table 2.10: Applications of BBD in wastewater treatment studies.

Type of wastewater	Independent variables	Response(s)	Results	References
Pulp and paper wastewater	Current density, electrolysis time and pH	COD and colour removal	COD = 55.00% Colour = 87.00%	Solomon <i>et al.</i> (2009)
Landfill leachate wastewater	Initial pH, H ₂ O ₂ dosage and Fe ²⁺ dosage	Overall COD removal, oxidation COD removal, coagulation COD removal, mineralisation, humic substances (HS) removal and sludge volume ratio (SVR)	Overall COD = 71.81% Oxidation COD = 46.22% Coagulation COD = 25.80% Mineralisation = 63.81% HS = 91.53% SVR = 3.50 mL/mM	Wu <i>et al.</i> (2010)
Municipal wastewater	Biopolymer type, biopolymer concentration and initial organic load	COD, turbidity removal, sludge produced and metal content	Nil	Carpinteyro-Urban & Torres (2013)
Rice mill wastewater	Initial pH, current density, electrode distance and flow rate	COD, TSS removal and electrical energy consumption (EEC)	Nil	Karichappan <i>et al.</i> (2013)
Bagasse effluent	Dilution of effluent, initial pH, applied current and electrolyte concentration	COD, TSS removal and electrical energy consumption (EEC)	COD = 98.00% TSS = 93.00% EEC = 2.40 Wh	Thirugnanasambandham <i>et al.</i> (2013)
Synthetic sago wastewater	Alum dosage, pH and wastewater concentration	COD removal	COD = 67.86%	Sangeetha <i>et al.</i> (2014)

Table 2.10 continued

Landfill leachate wastewater	pH, reaction time and coagulant concentration	COD, phosphate, colour and sulphate removal	COD = 71.00% Phosphate = 93.00% Colour = 86.00% Sulphate = 99.60%	Kumar & Bishnoi (2015)
Livestock wastewater	pH, current density, electrolysis time and initial NaCl concentration	Colour and COD removal	Colour = 93.00% COD = 95.30%	Min (2015)
Textile wastewater	Reactor volume, electrolysis time and current density	COD removal	COD = 97.17%	Sendhil <i>et al.</i> (2015)
Meat industry wastewater	Enzyme dose, incubation time, pH and temperature	Colour and COD removal	Colour = 95.35% COD = 85.68%	Thirugnanasambandham & Sivakumar (2015)

2.8.3 Central Composite Design (CCD)

Box and Wilson first introduced CCD in 1951. It consists of three parts, including (1) a full or fractional factorial design, (2) an additional design (often a star design), which experimental points are at a distance α from its center, and (3) a central point (Bezerra *et al.*, 2008; Khuri & Mukhopadhyay, 2010). For full uniformly routable CCD, it requires an experiment number based on $N = k^2 + 2k + C_p$, where k represents the number of factor and C_p is the number of central point replication (Bezerra *et al.*, 2008). Peasura (2015) indicated that the precise value of α depends on the number of factors involved and on the certain properties desired for the design. Furthermore, all the factors studied in CCD are five levels, which are $-\alpha$, -1 , 0 , $+1$, and $+\alpha$ (Bezerra *et al.*, 2008). CCD provides fairly high efficiency to about five or six factors and begins to decrease rapidly thereafter (Nair *et al.*, 2014). CCD is the most popular class of second order designs and is widely applied to estimate the second order response surface (Peasura, 2015). Table 2.11 shows the application of CCD in various types of wastewater treatment. CCD has been used to study the effect of ozonation process for the reduction of excess sludge production in sago effluent by optimising the variables such as ozonation time, pH, and retention time (Subha & Muthukumar, 2012). Under optimum condition, COD reduction of 87.00% was achieved at pH 6.7 with 8 min ozonation time and retention time of 6 days, while volatile suspended solid reduction (81.00%) was achieved at pH 6.9 with 12 min ozonation time and retention time of 10 days. Rastegar *et al.* (2011) also assessed CCD on the upflow anaerobic sludge blanket (UASB) bioreactor for the treatment of petroleum refinery effluent. The result revealed that 76.30% of COD removal was achieved under the optimum influent COD, upflow velocity, and hydraulic retention time of 630 mg/L, 0.27 m/h, and 21.4 h, respectively.

Designs such as Doehlert uniform shell design, D-optimal design and Box-Draper saturated design are less popular than BBD and CCD in water and wastewater purification related studies as the latter designs are rather robust and much simpler to be applied (Nair *et al.*, 2014).

Table 2.11: Application of CCD in wastewater treatment studies.

Type of wastewater	Independent variables	Response(s)	Results	References
Laboratory wastewater	COD:H ₂ O ₂ ratio, H ₂ O ₂ :Fe ²⁺ ratio and pH	COD removal	COD = 92.30%	Benatti <i>et al.</i> (2006)
Paper-recycling wastewater	Coagulant dosage, flocculant dosage and pH	Turbidity and sludge volume index (SVI)	Turbidity = 12.3 NTU SVI = 48.0 mL/g	Wang <i>et al.</i> (2007)
Simulated industrial textile wastewater	Pollution load, applied potential, electrolyte concentration, reaction temperature and reaction time	COD, colour and turbidity removal	COD = 61.60% Colour = 99.60% Turbidity = 66.40%	Körbahti & Tanyolaç (2008)
Bio-digester effluent	Current density, initial pH, inter electrode distance and electrolysis time	COD and colour removal	COD = 50.50% Colour = 95.20%	Kumar <i>et al.</i> (2009)
Landfill leachate wastewater	pH, H ₂ O ₂ /Fe(II) mole ratio and Fe(II) dosage	COD removal efficiency	COD = Nil	Zhang <i>et al.</i> (2009a)
Simulated dairy wastewater	Current density, salt dosage, time of electrolysis and pH	COD removal	COD = 70.00%	Kushwaha <i>et al.</i> (2010)
Petroleum refinery effluent	Influent COD, upflow velocity and hydraulic retention time	COD removal	COD = 76.30%	Rastegar <i>et al.</i> (2011)
Sago effluent	pH, ozonation time and retention time	COD and volatile suspended solid (VSS) removal	COD = 87.00% VSS = 81.00%	Subha & Muthukumar (2012)

Table 2.11 continued

Dye-bath effluent	Initial pH, current density, electrolysis time and inter electrode distance	COD, colour removal and specific energy consumed	COD = 94.00% Colour = 99.70% Specific energy consumed = 0.011 kWh/kg	Mondal <i>et al.</i> (2013)
Papermaking-reconstituted tobacco slice wastewater	Polyaluminium chloride (PAC) dosage, cationic polyacrylamide (CPAM) and pH	COD and colour removal	COD = 67.80% Colour = 77.70%	Wang <i>et al.</i> (2013b)

CHAPTER 3

MATERIALS AND METHODS

3.1 Sampling

Sago wastewater was collected from Herdsen Sago Industry in Pusa, Sarawak. Figure 3.1 shows the outlet point where the wastewater sample collection was performed. As depicted in Figure 3.1, the sago wastewater is directly released through this collection point into a nearby river. Sampling was carried out twice. The effluent samples were filled into polyethylene bottles. The bottles were transported to the laboratory and kept refrigerated at 4°C until further analysis.



Figure 3.1: Sago wastewater collection point.

SB samples were randomly collected from piles of SB which was produced *via* debarking process (Figure 3.2), and stored in sack bags. The sack bags were transported to the laboratory for further use.



Figure 3.2: Sago bark collection point.

3.2 Materials

Ammonium iron (II) sulphate ($\text{Fe}(\text{NH}_2)_2(\text{SO}_4) \cdot 6\text{H}_2\text{O}$) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were purchased from R & M Chemical. Silver sulphate (Ag_2SO_4), mercury (II) sulphate (HgSO_4), iron (II) sulphate-7-hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and hydrogen peroxide (H_2O_2 , 35%) were obtained from Bendosen. Sulphuric acid (H_2SO_4 , 95-97%), titanium dioxide (TiO_2) (Degussa, P25) with particle size of 20-30 nm, and sodium hydroxide (NaOH) were produced from Merck (Germany). Hydrochloric acid (HCl) and ferroin indicator solution were purchased from J. T. Baker and Sigma-Aldrich, respectively.

3.3 Wastewater Characterisations

The raw wastewater samples were characterised for water quality parameters such as pH, BOD, COD, TSS, dissolved oxygen (DO) and turbidity. Characteristics of sago wastewater were analysed based on the Standard Methods for Water and Wastewater Examination (APHA, 1999).

3.3.1 Biological Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) can be defined as the quantity of oxygen used by the non-photosynthetic microorganisms to decompose organic compounds, and therefore, is the indirect quantification of the concentration of organic compound present in wastewater and water bodies (Matos *et al.*, 2014). It is a measure of the organic pollutant in water that can be decomposed biologically. It is usually expressed in milligram O₂ per litre (mg/L) (Jouanneau *et al.*, 2014). The BOD analysis was performed by using Method 5210 B (APHA, 1999).

The procedure of BOD analysis requires the dilution of a known amount of wastewater sample with prepared dilution water in a BOD bottle. The prepared dilution water contained ferric chloride, calcium chloride, magnesium sulphate and phosphate buffer (potassium dihydrogen phosphate, sodium hydroxide, and ammonium sulphate). The mixture of dilution water was aerated with oxygen for 24 h. After that, 1 mL of sago effluent was diluted using 1000 mL of dilution wastewater. Five BOD bottles with capacity of 300 mL were prepared. The first and second BOD bottles were each filled with 300 mL of dilution water (blank dilution water) and raw sago effluent (blank raw sago), respectively. Three other remaining BOD bottles were each filled with 300 mL of diluted sago. Initial DO readings were measured in each BOD bottles by using a DO meter (Milwaukee brand, MW 600 model). All five BOD bottles were then wrapped with aluminium foil and incubated in the dark place for five days before the final DO readings were measured. The BOD₅ value was calculated by using the formula as shown in Eq. 3.1:

$$\text{BOD}_5 \text{ (mg/L)} = \frac{D_1 - D_2}{P} \quad (3.1)$$

where,

D_1 = Initial DO value of water sample (mg/L)

D_2 = Final DO value of water sample after five days incubation (mg/L)

P = Decimal volumetric fraction of the sample used

3.3.2 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is defined as a measure of oxygen needed to oxidise organic compound of a sample by a strong chemical oxidant (Chong *et al.* 2013). In COD analysis, $K_2Cr_2O_7$ has been widely used to completely oxidise a variety of organic compounds. Method 5220 C was applied to determine COD (APHA, 1999). This analysis was carried out by adding 2.5 mL of diluted sago sample into COD tube followed by the addition of 1.5 mL of $K_2Cr_2O_7$ digestion solution and 3.5 mL of concentrated $Ag_2SO_4 \cdot H_2SO_4$ acid solution. The solution mixture was then heated by using a COD digester for 2 h at 150 °C and cooled to room temperature after heating process. The cooled solution was then transferred into a conical flask and titrated with 0.0125N FAS solution. One or two drops of ferroin indicator were added to the solution before titration in order to indicate the colour changes to reddish brown. The volume of titrated FAS solution was recorded and COD was calculated based on the formula stated below (Eq. 3.2):

$$\text{COD value (mg/L)} = \frac{(a-b) \times (N \times 8000)}{V} \quad (3.2)$$

where,

a = Volume of FAS for blank titration (mL)

b = Volume of FAS for sample titration (mL)

N = Normality of FAS solution (N)

V = Volume of sample (mL)

3.3.3 Total Suspended Solid (TSS)

The mass of an empty filter paper (47 mm x 0.22 μm) was weighed and recorded. The filtering apparatus was set up with the pre-weighed filter paper and the vacuum pump was switched on to apply suction to the filter paper. Diluted sago (1:1000) sample in 1000 mL was then slowly poured onto the filtration pump apparatus. The suction was continued until the water sample was pumped through the filter paper. After filtration, the filter paper was removed from the apparatus and placed on an evaporating dish before being dried in an oven at 100 °C for 2 h. The filter paper was left to cool at the room temperature before being weighed. The amount of TSS was calculated by using the following formula:

$$\text{TSS (mg/L)} = \frac{A-B}{C} \quad (3.3)$$

where,

A = weight of filter paper and TSS in mg

B = weight of filter paper in mg

C = volume of sample filtered in L

3.3.4 Turbidity

The turbidity of the sample was measured by means of a turbidity meter (Mi 415 model, Martini Instrument).

3.3.5 pH

The pH value of the sample was measured by using a pH meter (Model H19024 series, HANNA Instrument). The pH meter was calibrated by using the buffer solutions of pH 4, 7, and 8 prior to the measurements.

3.3.6 Dissolved Oxygen (DO)

The DO value was recorded using a DO meter (Milwaukee brand, MW 600 model).

3.4 Synthesis of TiO₂/MSB Mixtures

The sampled SB was washed using distilled water to remove dirt and unwanted materials. The washed SB was dried under sunlight before being cut and ground into powdered form. The powdered form of SB was sieved to remove unwanted fibre and to obtain particles with similar sizes (500 μm). Subsequently, the powdered form of SB was soaked in 1 M HCl for 1 day. The acid modified SB (MSB) was repeatedly washed using distilled water until the pH became neutral. After that, the neutralized MSB was dried in an oven at 100 °C for 2 h. The dried MSB was then mixed with various concentration of TiO₂ to prepare TiO₂/MSB mixtures under mechanical stirring.

Concentration of TiO_2 was varied from 0.2 to 0.8 g/L while the weight percentage of MSB was fixed as either 1 w/w% or 3 w/w%. A total of six TiO_2 /MSB mixtures were prepared (1) 0.2 g/L TiO_2 /1% MSB, (2) 0.2 g/L TiO_2 /3% MSB, (3) 0.4 g/L TiO_2 /1% MSB, (4) 0.4 g/L TiO_2 /3% MSB, (5) 0.8 g/L TiO_2 /1% MSB, and (6) 0.8 g/L TiO_2 /3% MSB. Typically, a fixed concentration of TiO_2 was added to a fixed weight percentage of MSB in a beaker followed by 100 mL of ultrapure water. The mixture was then stirred at 750 rpm for 1-2 h to attain homogeneous suspension. After that, the suspension was filtered and dried in an oven at 100 °C for 2 h. The dried TiO_2 /MSB mixture was pound into powdered form and sieved into similar size (500 μm) for further analysis. Figure 3.3 shows the picture of the prepared TiO_2 /MSB mixture.



Figure 3.3: Prepared TiO_2 /MSB mixture.

3.5 Instrumentation Analysis

The raw SB, MSB and TiO_2 /MSB mixtures were characterised for their surface morphology using Scanning Electron Microscope (SEM) (Model JOEL JSM-6390LA). The

functional groups of TiO₂, MSB and TiO₂/MSB were identified using Fourier Transform Infra-Red spectroscopy (Model Thermo Nicolet iS10). Elemental analysis of TiO₂/MSB was analysed using Energy-Dispersive X-ray spectroscopy (EDX) (Model JOEL JSM-6390LA). The crystalline structures of the composite was observed using X-ray diffraction (XRD, PaNalytical X'pert Pro) method with Cu K α radiation ($\lambda = 0.154$ nm) in the scanning range of 2θ between 10 ° and 80 °, at a rate of 0.04 ° per second. For phase identification, an automatic JCPDS library search and match was used. UV-Vis spectrophotometer (Jasco V-630) was used to record the changes of UV absorbance of sago wastewater samples. TOC was measured using OI Analytical (Aurora 1030 model) TOC analyser.

3.6 Photocatalytic Experiment

For the photocatalytic experiment, the dosage of TiO₂/MSB mixture and contact time was optimised by employing RSM. Different dosages of TiO₂/MSB mixture were added into a beaker containing 200 mL of filtered sago wastewater sample. Sago wastewater sample was filtered prior to treatment to ensure that the roughage or known as 'hampas', being the major portion of the wastewater does not interfere with the final COD reading and block the penetration of UV-C light during the photocatalytic experiment. The solution mixture with an initial COD of 5790.55 ± 3305.42 mg/L was subsequently stirred at 750 rpm in the dark condition for 30 min to establish the equilibrium between TiO₂/MSB mixture and sago effluent. The mixture was then irradiated using a UV-C lamp ($\lambda = 254$ nm, Phillips TUV 8 W) for 2 h under continuous stirring. The distance of the UV-C lamp from the solution beaker was fixed at 9 cm. Temperature and light intensity (measured using a light meter; Sunche HS1010) was recorded during all photocatalytic experiments. Temperatures of the solutions were recorded to

range between 32-34 °C while light intensity of the UV-C lamp ranged from 128 to 135 lux. Samples were withdrawn using syringe prior to irradiation (after 30 min equilibrium) and at fixed time intervals throughout the 2 h irradiation period. The collected samples were centrifuged and the supernatant was subjected to COD analysis. Figure 3.4 summarises the steps involved in the lab-scale TiO₂ photocatalytic experiments performed.

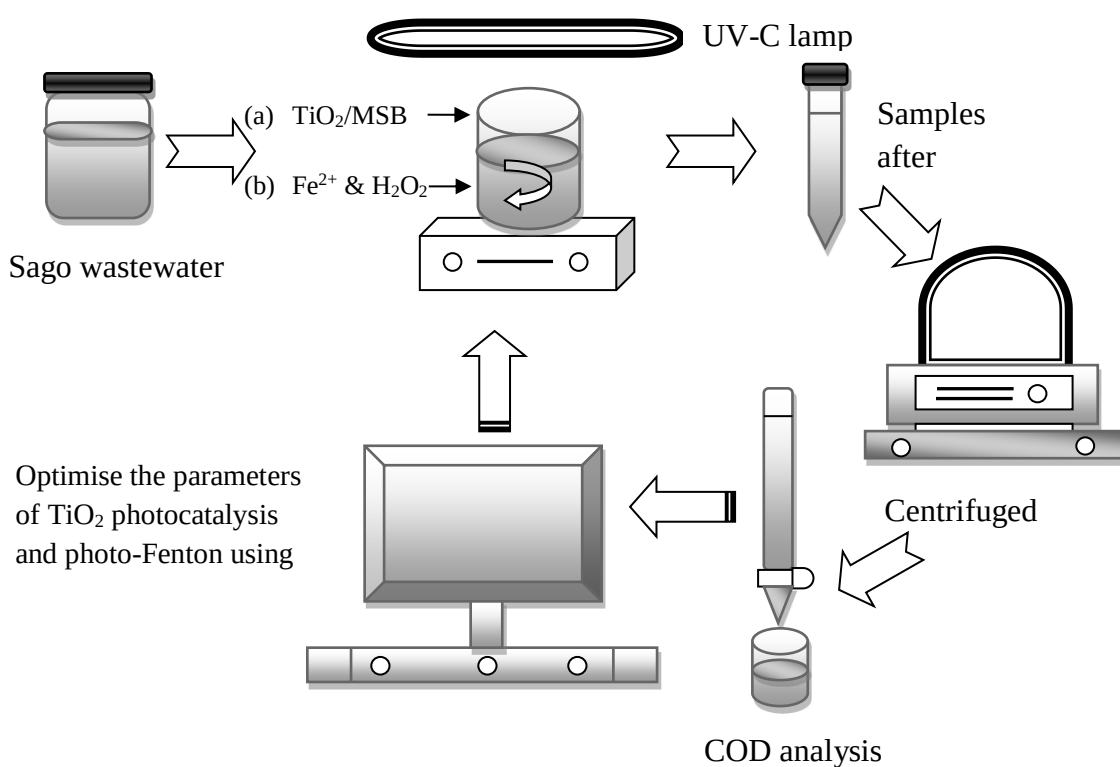


Figure 3.4: Schematic diagram of a lab-scale (a) TiO₂ photocatalytic experiment using TiO₂/MSB mixture and (b) photo-Fenton experiment.

3.6.1 Experimental Design of TiO₂ Photocatalysis

In the present study, central composite design (CCD) was used instead of Box-Behnken design (BBD) as three minimum parameters are required for BBD. CCD consists of 2^k factorial

points augmented with 2^k axial points and a centre point where k represents the number of variables involved (Abdulah *et al.*, 2011). In the present work, the independent variables were TiO_2/MSB mixture dosage and contact time while COD removal was the dependent variable (response). A total of 13 experiments were conducted with 4 factorial points, 4 axial points and 1 centre point. The centre point was repeated five times to obtain an accurate result. Table 3.1 shows the ranges and levels of the independent variables in coded units.

Table 3.1: Range and levels of the independent variables for RSM.

Variables	Coded	Range and levels				
		$-\alpha$	-1	0	1	$+\alpha$
Dosage (g)	X_1	0.06	0.10	0.20	0.30	0.34
Contact time (min)	X_2	11.36	30.00	75.00	120.00	138.64

The initial design includes 13 tests, based on a CCD shown in Eq. 3.4 (Tony & Bedri, 2014):

$$\eta (\%) = \frac{COD_0 - COD_f}{COD_0} \times 100, \quad (3.4)$$

where η represents the percentage of COD removal; COD_0 and COD_f designates the measured COD values before and after the TiO_2 photocatalytic experiment, respectively. Table 3.2 represents the 13 experiments with the ranges and levels in coded units.

Table 3.2: RSM for the two independent variables in corresponding natural values and coded units.

Run	Independent variables		Coded variables	
	Dosage (g)	Contact time (min)	X ₁	X ₂
1	0.20	75.00	0	0
2	0.20	11.36	0	−α
3	0.30	30.00	1	−1
4	0.20	75.00	0	0
5	0.30	120.00	1	1
6	0.34	75.00	+α	0
7	0.10	30.00	−1	−1
8	0.06	75.00	−α	0
9	0.20	75.00	0	0
10	0.20	75.00	0	0
11	0.20	138.64	0	+α
12	0.20	75.00	0	0
13	0.10	120.00	−1	1

A Design-Expert 7.1.6 software was utilised to analyse the experimental data and fitted to a second-order polynomial equation. The interaction between the dependent and independent variables was attained through Eq. 3.5 (Yetilmezsoy *et al.*, 2009):

$$\eta = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} x_i x_j + \varepsilon \quad (3.5)$$

where η represents the predicted response (dependent variable), k is the number of patterns, i and j are the index numbers for pattern, β_0 is the offset or free term called intercept term, $x_1, x_2, \dots, x_k$ are the coded independent variables, β_i is the first-order (linear) main effect, β_{ii} is the quadratic (square) effect, β_{ij} is the interaction effect, and ε designates the random error between experimental and predicted values. Due to the regression and mean square residual error, analysis of variance (ANOVA) was used to test the statistical significance of the ratio of mean square variation (Sangeetha *et al.*, 2014). The value of coefficient of determination (R^2) was used to express the quality of the fit of the polynomial model. The probability values (p-values) with 95% confidence level act as a tool to evaluate the significance of the model terms

(Aljuboury *et al.*, 2016a). Generally, if the significance probability value ($p > F$) is small (< 0.05) and p -value is less than 0.01, the model is considered to be statistically significant and acceptable (Kumar *et al.*, 2007). The main indicators including the probability value ($\text{Prob} > F$), model F -value (Fisher variation ratio), and adequate precision showed the adequacy and significance of the employed model. To find an optimum condition, the response plots such as contour and 3D plot were used. Fischer's F -Test was utilised to determine the statistical significance and optimise the desired target fixed for maximum removal of COD. For process optimisation, the desired target for the response (COD removal) was selected as to "target", while the independent variables (dosage and contact time) were chosen to be "within the range". For maximisation to find the best and optimise local maximum, these individual targets were combined into an overall desirability function by the software (Arslan-Alaton *et al.*, 2009).

3.7 Photo-Fenton Experiment

In a typical photo-Fenton experiment, different concentrations of Fe^{2+} ion (2 to 6 g/L) and hydrogen peroxide (3 to 5 mL/L) were added to a beaker containing 200 mL of filtered sago wastewater sample with an initial COD of 18912.25 ± 9569.27 mg/L. The concentrations of both the Fe^{2+} ion and H_2O_2 were optimised by RSM. The pH value of the solution was adjusted to the desired values with dilute H_2SO_4 or NaOH solution. The pH was measured using a pH meter before being subjected to photo-Fenton oxidation. The solution mixture was subsequently stirred at 750 rpm in the dark condition for 30 min to establish the adsorption and equilibrium by the Fenton's reagent. The solution mixture was irradiated using a UV-C lamp for 2 h. The distance of the UV-C lamp from the solution beaker was fixed at 9 cm. The recorded temperature and UV-C light intensity ranged from 30 to 32 °C and 128 to 135 lux. Samples

were collected prior to irradiation and at fixed time intervals throughout the 2 h irradiation period. To ensure the complete decomposition of H_2O_2 and Fe^{2+} ion in the collected sample prior to COD determination, NaOH pellet was added to the sample to increase the $\text{pH} > 8$. After the samples have stood overnight, they were centrifuged and filtered to remove Fe^{2+} . The supernatant was subjected to COD analysis. Figure 3.4 in Section 3.6 illustrates the typical steps involved in the lab-scale photo-Fenton experiment performed.

3.7.1 Experimental Design of Photo-Fenton

In the present study, the concentration of Fe^{2+} ion and H_2O_2 , and initial pH were considered as the independent variables, while the COD removal efficiency was considered as the dependent variable (response). These independent variables were coded as -1 (low), 0 (centre point) and +1 (high) in the ranges. Table 3.3 summarises the experimental range and levels of independent variables considered in this study. Based on a three-level BBD, a total number of 17 experiments were carried out in a randomized order with five centre points. Table 3.4 shows the 17 experiments with the ranges and levels in coded units. For process optimisation, the desired target for the response (COD removal) was selected as to “maximise”, while the independent variables (concentrations of Fe^{2+} and H_2O_2 , and initial pH) were chosen to be “within the range”.

Table 3.3: Range and levels of the independent variables for RSM.

Variables	Coded	Range and levels		
		-1	0	1
H_2O_2 (mL/L)	X_1	3.00	4.00	5.00
Fe^{2+} (g/L)	X_2	2.00	4.00	6.00
pH	X_3	2.00	2.50	3.00

Table 3.4: RSM for the three independent variables in corresponding natural values and coded units.

Run	Independent variables			Coded variables		
	H ₂ O ₂ (mL/L)	Fe ²⁺ (g/L)	pH	X ₁	X ₂	X ₃
1	4.00	6.00	2.00	0	+1	-1
2	4.00	4.00	2.50	0	0	0
3	3.00	4.00	2.00	-1	0	-1
4	4.00	6.00	3.00	0	+1	+1
5	4.00	2.00	2.00	0	-1	-1
6	3.00	2.00	2.50	-1	-1	0
7	5.00	2.00	2.50	+1	-1	0
8	3.00	6.00	2.50	-1	+1	0
9	4.00	2.00	3.00	0	-1	+1
10	5.00	6.00	2.50	+1	+1	0
11	4.00	4.00	2.50	0	0	0
12	5.00	4.00	2.00	+1	0	-1
13	4.00	4.00	2.50	0	0	0
14	3.00	4.00	3.00	-1	0	+1
15	5.00	4.00	3.00	+1	0	+1
16	4.00	4.00	2.50	0	0	0
17	4.00	4.00	2.50	0	0	0

3.7.2 *Artemia salina* Bioassay

Bioassay study using *Artemia salina* was performed to determine the toxicity of sago wastewater after being treated by photo-Fenton treatment. *A. salina* eggs were added into a clean beaker filled with natural seawater for hatching purpose. The hatching beaker was illuminated by a tungsten filament light and aerated with air at room temperature (25 °C) (Dantas *et al.*, 2003). After 24 h, the hatched *A. salina* was transferred to fresh natural seawater. The hatched *A. salina* was incubated under artificial light with air sparging for further 24 h. For toxicity test, an aliquot of 0.5 mL of treated sago wastewater from each time interval (T₀-T₁₂₀) was poured into each micro-well and added with 5 mL of fresh seawater. Each micro-well was then placed with 10 *A. salina* nauplii and incubated at room temperature with low ambient light (Metcalf *et al.*, 2002). The number of death *A. salina* nauplii was recorded after 24 h.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Sago Wastewater Characterisation

The characteristics of sago wastewater are summarised in Table 4.1. The supernatant of sago effluent is pale brownish in colour with a pungent smell. The sago wastewater demonstrated acidic value. A large amount of TSS (4000-8200 mg/L) would have caused the high BOD and COD of the wastewater, ranging from 800-3300 mg/L and 6192-34048 mg/L, respectively.

Table 4.1: Characteristics of sago wastewater effluent.

Parameters	Range	Average value $\pm$ standard deviation (SD)	Parameters limits of effluent (Standard B)*	Nitsei Sago Mill Sdn Bhd in Mukah**
pH	5.12-6.06	5.58 $\pm$ 0.50	5.50-9.00	3.82-4.20
TSS (mg/L)	4000-8200	6730.00 $\pm$ 1777.80	100.00	3368-15890
BOD (mg/L)	800-3300	1916.67 $\pm$ 1246.46	50.00	2528-4647
COD (mg/L)	6192-34048	19304.00 $\pm$ 9565.11	200.00	6048-12594
Turbidity (NTU)	109-566	328.00 $\pm$ 239.77	Not available	Nil
DO (mg/L)	0.16-1.00	0.53 $\pm$ 0.41	Not available	Nil

*DOE, 2010

**DOE Sarawak (2001)

The BOD, COD and TSS values obtained in this study were compared to the wastewater characteristics from another sago mill, Nitsei Sago Mill Sdn Bhd in Mukah published by the Department of Environmental, Sarawak (2001) (Personal communication with the industry). The BOD and TSS values of sago wastewater from Nitsei Sago Mill were slightly higher than that of recorded in the Herdsen Sago Industry. The TSS, which are mainly roughage or

‘hampas’, suspended in the sago wastewater would have attributed to the high turbidity value. Relatively, the characteristics of sago wastewater from Herdsen Sago Industry were comparable to the Nitsei Sago Mill although the differences in their water qualities are notable for several parameters as mentioned previously. It appears that the traditionally practiced cooling pond system failed to improve the discharge quality of sago wastewater effluent. As the effluent quality did not comply with the regulatory requirement of the (DOE, 2010) (Table 4.1), this thus necessitates the application of a more powerful treatment tool prior to the effluent discharge.

4.2 Characterisation of TiO₂/MSB Mixture

4.2.1 Scanning Electron Microscopy (SEM)

Surface morphologies of raw SB and MSB acquired by SEM are shown in Figure 4.1. SEM micrograph revealed that chemical modification by HCl afforded a rougher surface morphology of MSB (Figure 4.1(b)) compared to the unmodified SB (Figure 4.1(a)). Ngah and Hanifah (2008) reported that the tree barks such as jackfruit, sal and mango were modified using HCl revealed higher adsorption capacity of copper ions than the untreated one. HCl treatment able to extract the soluble organic compounds and reduce the average molecular weight of natural polymers, and therefore, increase the number of chelating sites of treated bark (Reddy *et al.*, 1997). Figure 4.1(a) shows the presence of fibre or starch granules (white arrow) on its surface, which appeared to be lesser or almost disappeared in the SEM micrograph of MSB (Figure 4.1(b)). SB mainly comprises of cellulose, hemicelluloses, and lignin components (Ethaib *et al.*, 2016), which can be dissolved or broken down by pretreatment process (Kristiani *et al.*, 2013). Mosier *et al.* (2005) and Zheng *et al.* (2009) stated that diluted acid pretreatment

process could dissolve almost all hemicelluloses and breakdown the bonding of cellulose and lignin. Due to the release of soluble organic compounds contained in the plant wastes, the application of untreated plant wastes as adsorbents can lead to several problems such as low adsorption capacity, and high BOD, COD and TOC (Ngah & Hanafiah, 2008). The average pore sizes of raw SB and MSB were 0.08 μm and 0.10 μm , respectively. As the difference of the pore sizes between raw SB and MSB was marginal, this could imply that HCl treatment did not alter the pore size of SB.

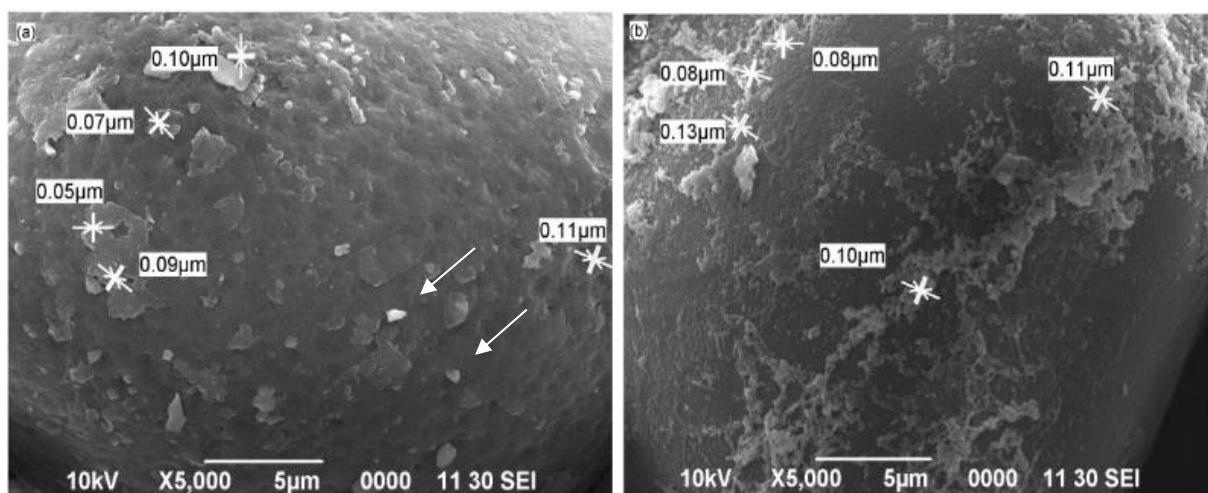


Figure 4.1: SEM micrographs for (a) raw sago bark (SB), and (b) modified sago bark (MSB).

SEM images of 0.2 g/L TiO_2 /1% MSB mixture before and after photocatalytic treatments are shown in Figure 4.2(a) and (b), respectively. SEM micrograph (Figure 4.2(a)) clearly visualised that TiO_2 particles (white circle) have been successfully presented on the surface of MSB (white arrow). The average pore size of TiO_2 /MSB mixture was recorded as 0.16 μm . However, in Figure 4.2(b), the amount TiO_2 particles presented on the MSB surface was observed to reduce after undergoing photocatalytic treatment. This could be due to the fall off of TiO_2 from the MSB during the photo-induced degradation of organic pollutants present

in sago effluent, as TiO_2 /MSB mixture was synthesized *via* mechanical stirring (Zhang & Itoh, 2006). As such, TiO_2 /MSB mixture could not potentially be recycled. Furthermore, there were no pores detected after treatment (Figure 4.2(b)). A possible explanation might be due to adsorption of organic pollutants on the active sites of adsorbent pores (Anisuzzaman *et al.*, 2015).

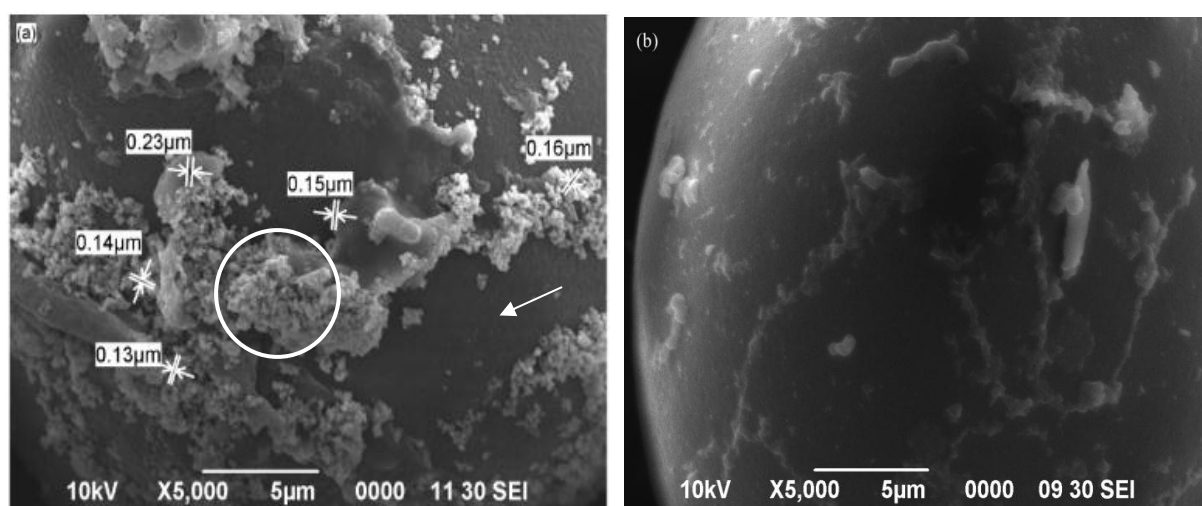


Figure 4.2: SEM micrographs of 0.2 g/L TiO_2 /1% MSB mixture (a) before treatment, and (b) after treatment.

4.2.2 Energy-Dispersive X-ray (EDX) Spectroscopy

The EDX spectrum of optimum TiO_2 /MSB mixture consisting of 0.2 g/L TiO_2 /1% MSB is shown in Figure 4.3. The presence of main elements namely C, Ti, and O in the composite and their mass percentages are summarised in Table 4.2. As shown in Table 4.2, the mass percentages of C, Ti, and O were found to be 14.59%, 26.53%, and 58.88%, respectively. The presence of Ti and O indicates that the TiO_2 /MSB mixture has been successfully prepared in this study.

Table 4.2: Mass percentage of elements in 0.2 g/L TiO₂/1% MSB mixture.

Elements	Mass percentage (%)
C	14.59
O	26.53
Ti	58.88
Total	100.00

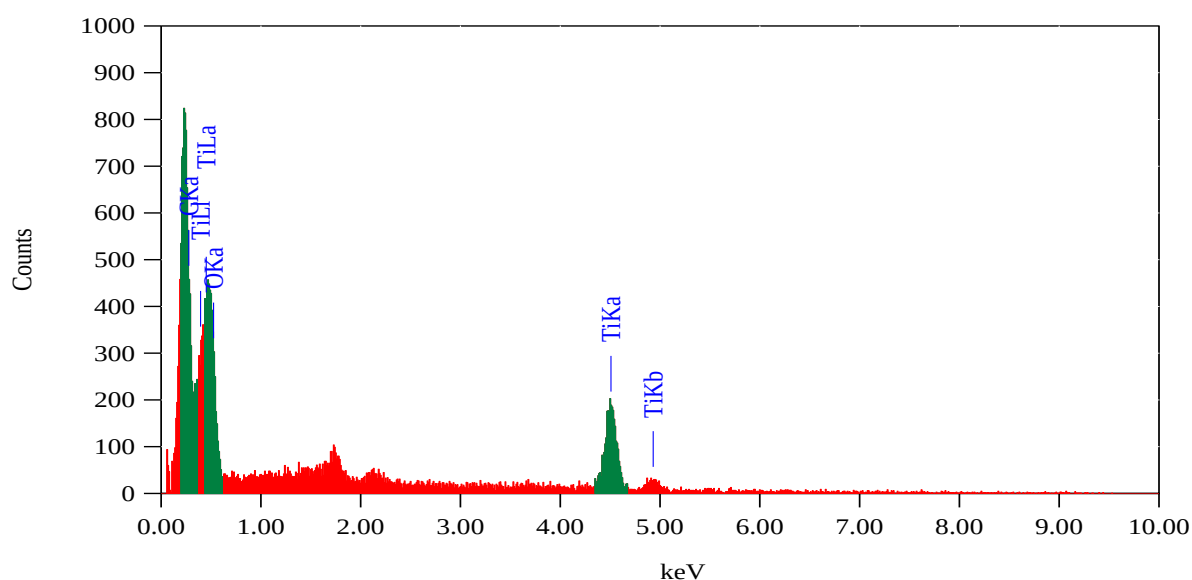


Figure 4.3: EDX data of 0.2 g/L TiO₂/1% MSB mixture.

4.2.3 Fourier Transform Infrared (FTIR) Spectrometry

The FTIR spectra of commercial TiO₂, MSB and 0.2 g/L TiO₂/1% MSB mixture in the range 4000-400 cm⁻¹ wave number are shown in Figure 4.4. The region lying between 400 to 700 cm⁻¹ in Figure 4.4(a) were assigned to Ti-O stretching and Ti-O-Ti bridging stretching modes (Wang *et al.*, 2012). The presence of TiO₂ is confirmed by the peaks at 526.97 cm⁻¹ and 666.97 cm⁻¹ (Figure 4.4(a)). The peaks located at 3352.77 cm⁻¹ and 3326.24 cm⁻¹ in Figures 4.4(b) and (c), respectively corresponded to the stretching vibrations of hydroxyl groups (OH) present in cellulose, hemicelluloses, and lignin of SB (Sathasivam & Haris, 2010). The peak

around 2928 cm^{-1} in both Figure 4.4(b) and (c) corresponded to the C–H stretching vibrations in the methyl, methoxyl and methylene groups present in the saccharide and aromatic structures of the hydrolysed products (Vitolina *et al.*, 2014). The strong stretching vibration peak observed around 1643 cm^{-1} (Figures 4.4(b) and (c)) can be attributed to a carbonyl group (C=O), which provides an evidence of high carbon content in SB (Hegde *et al.*, 2015). As shown in Figure 4.4(c), the peaks at 1425.97 cm^{-1} and 1368.15 cm^{-1} represents the CH_2 and OH bending, respectively (Sathasivam & Haris, 2010). The peaks around 1155 cm^{-1} and 1020 cm^{-1} confirmed the presence of arabinosyl residues and α -glucan of hemicellulose, respectively (Hegde *et al.*, 2015). The peak at 672.29 cm^{-1} indicated the presence of TiO_2 in TiO_2/MSB mixture (Figure 4.4(c)) which was found to be absent in MSB spectrum (Figure 4.4(b)). Furthermore, the appearance of the absorption peaks around 575 cm^{-1} in both Figures 4.4(b) and (c) can be associated to the accumulation of oxide particle in SB (Hegde *et al.*, 2015).

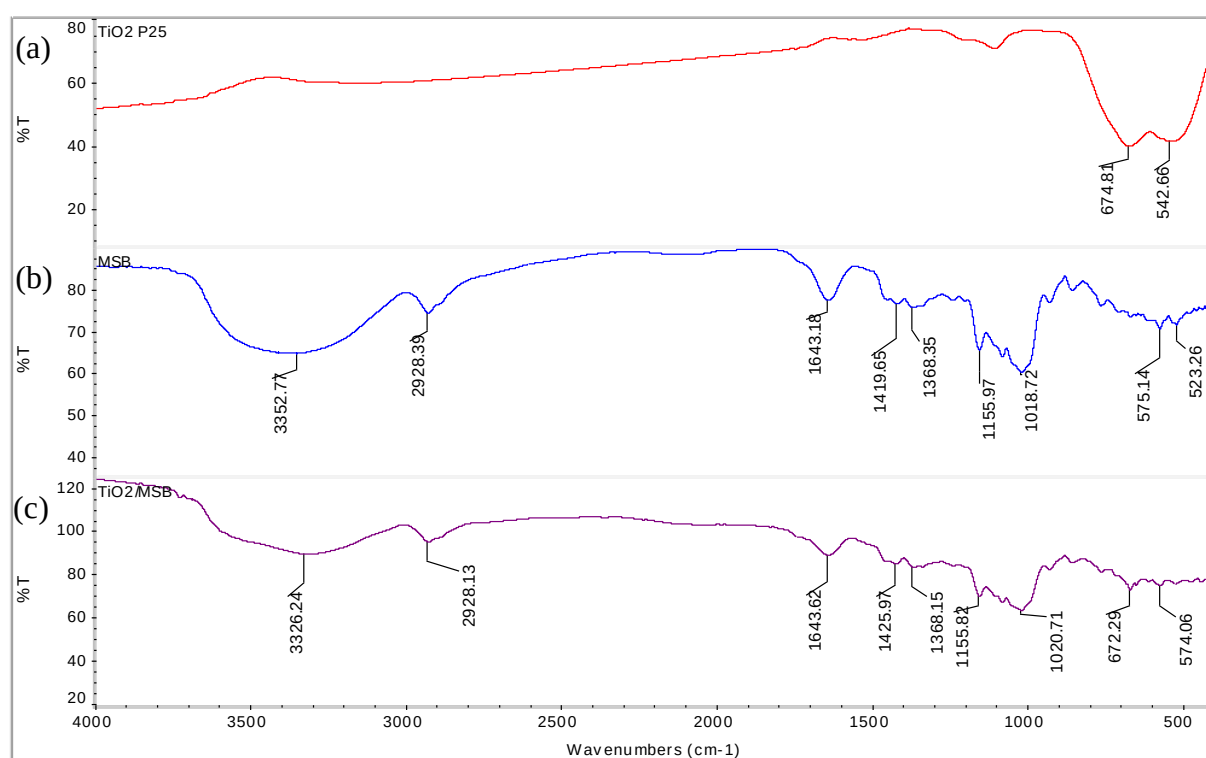


Figure 4.4: FTIR spectra of (a) TiO_2 , (b) MSB, and (c) $0.2\text{ g/L TiO}_2/1\%\text{ MSB}$ mixture.

4.2.4 X-Ray Diffraction (XRD)

Figure 4.5 shows the XRD pattern of the 0.2 g/L TiO₂/1% MSB mixture used in the TiO₂ photocatalytic experiment study. Five of the diffraction peaks centered at $2\theta = 15.03^\circ$ (101), 17.01° (101), 22.82° (002), 25.33° (101) and 47.92° (200) were indexed to 0.2 g/L TiO₂/1% MSB mixture. As shown in Figure 4.5, the diffraction peaks located at 25.33° (101) and 47.92° (200) were corresponded to the anatase TiO₂. Pure anatase TiO₂ possess the strong crystalline peaks at 2θ values of 25.3° , 37.6° , 48.0° , 53.9° and 54.9° , which correspond to the crystal planes of (101), (004), (200), (105), and (211), respectively (Kanakaraju *et al.*, 2017). Meanwhile, the peaks at 15.03° (101), 17.01° (101), 22.82° (002) in Figure 4.5 were corresponded to cellulose. Abou-Sekkina *et al.* (1986) reported the XRD pattern of cellulose for an untreated control fiber with the crystalline peaks at 15.0° (101), 16.5° (101), and 22.8° (002), respectively. XRD pattern suggested that cellulose or hemicelluloses comprised in MSB were not completely removed by HCl pretreatment process.

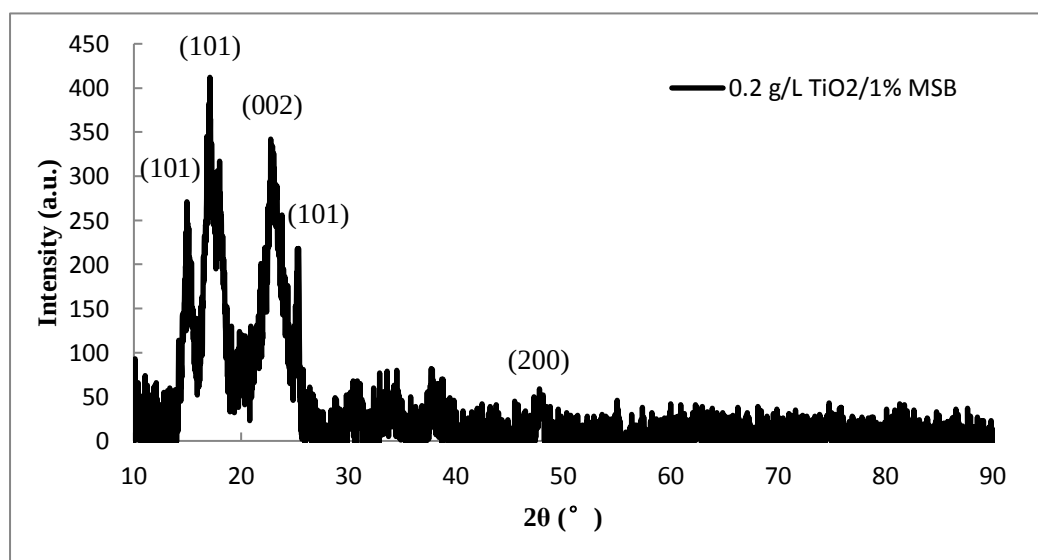


Figure 4.5: XRD pattern of 0.2 g/L TiO₂/1% MSB mixture.

4.3 Photodegradation of Sago Wastewater using TiO₂/MSB Mixture

Several preliminary experiments were conducted under the presence of UV-C irradiation using: (1) sago wastewater only, (2) mixture of SB and sago wastewater, (3) mixture of MSB and sago wastewater, and (4) mixture of sago wastewater and TiO₂. Sago wastewater was treated under UV-C irradiation to investigate the effect of photolysis, while the degradation of sago wastewater in the presence of commercial TiO₂, SB and MSB were performed to assess the individual effects of TiO₂, SB and MSB towards the degradation of organic pollutants. Photolysis of sago wastewater under UV-C irradiation exhibited a poor COD removal with less than 10.00% after 120 min of treatment time (Figure 4.6). This might be possibly due to the poor photolysis effect of UV-C irradiation on the degradation of sago wastewater. In contrast, photocatalytic treatment of sago wastewater treated in the presence of 0.50 g/L TiO₂ yielded a much better COD removal. The highest COD removal, 45.00% was attained after 90 min of UV-C irradiation using 0.50 g/L TiO₂. This value was slightly higher compared to the one obtained in the presence of SB and MSB with 24.24% and 37.90%, respectively after 120 min of treatment. Removal of COD by MSB could be due to the adsorption effect demonstrated by the modified material. TiO₂ photocatalysis has thus ascertained its contribution in removing organic pollutants from sago wastewater despite the slight fluctuation observed during the intervals (Figure 4.6). This could be due to the solution opacity which increases light scattering effect of the TiO₂ nanoparticles used in the treatment (Carp *et al.*, 2004). The solution opacity offered by TiO₂ nanoparticles (Gogate & Pandit, 2004) would have led to a reduction of light penetration in the wastewater solution (Gaya & Abdullah, 2008). Moreover, interaction between pollutants and the intermediates or degradants formed during the course of treatment could have plausibly caused the TiO₂ particles to coagulate leading to reduction of TiO₂ surface area and consequently its photocatalytic efficiency (Gianluca *et al.*, 2008).

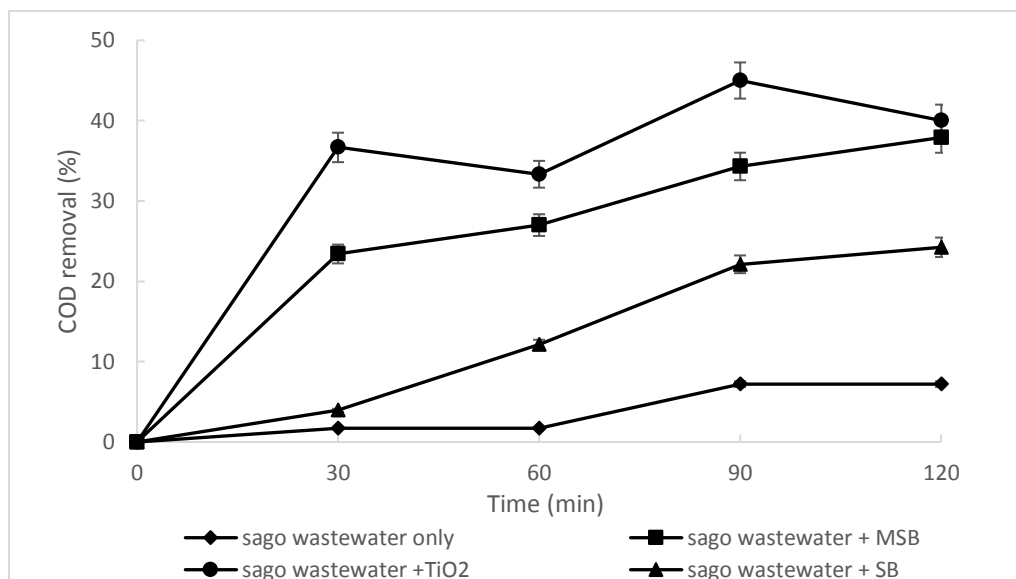


Figure 4.6: Photodegradation of sago wastewater under different conditions (Experimental conditions: 0.5 g/L TiO₂; 0.5 g/L SB; 0.5 g/L MSB).

Six different TiO₂/MSB mixtures which were prepared under different conditions were applied for sago wastewater degradation (Figure 4.7). The concentration of TiO₂ was varied from 0.20 g/L to 0.80 g/L while the amount of MSB was fixed as either 1 w/w% or 3 w/w%. Among them, both 1 w/w% and 3 w/w% of MSB combined with 0.2 g/L TiO₂ yielded relatively higher COD removals with 64.29% and 61.54%, respectively after 120 min of treatment. The obtained COD removal by other four mixtures under similar treatment time varied from 7.69% to 56.52%. The higher COD lowering capacity exhibited by TiO₂/MSB mixtures compared to the results obtained using commercial TiO₂ only and MSB only (Figure 4.6) could be attributed to the synergistic effect between TiO₂ and MSB. The presence of synergistic effect in TiO₂/MSB mixtures probably can be linked to its dual effects, namely, adsorption and degradation. TiO₂ has been reported to be highly favourable in high photocatalytic treatment (Liu *et al.*, 2007). MSB acts as an adsorbent in the fabricated TiO₂/MSB composites to improve the affinity of TiO₂ towards the organic pollutants (Xu *et al.*, 2016). Ngamsopasiriskun *et al.*

(2010) reported that TiO_2 /commercial AC, showed a synergistic effect between TiO_2 and AC in achieving 68.03% of phenol after 4 h of treatment. As 0.2 g/L TiO_2 /1% MSB mixture was considered as optimum based on the obtained COD removal, this mixture was chosen to further investigate sago wastewater degradation by varying two other parameters, namely, dosage and contact time *via* RSM study.

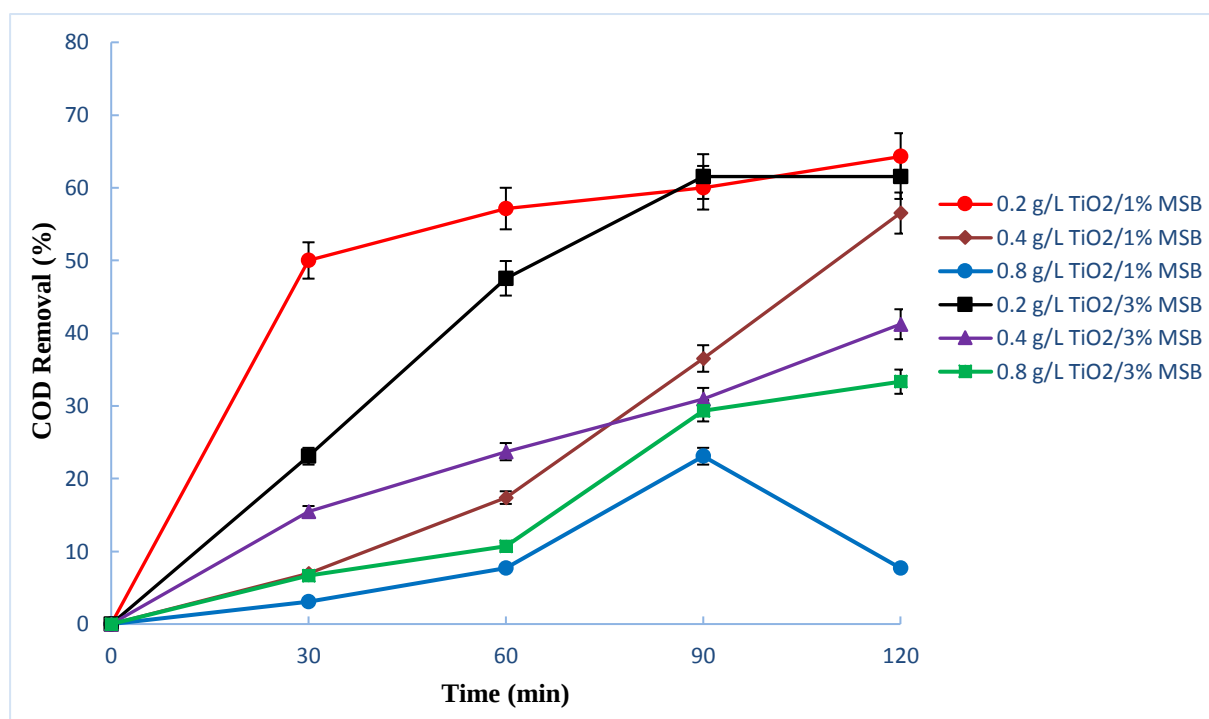


Figure 4.7: Photocatalytic experiments using various TiO_2 /MSB mixtures.

4.4 Photocatalytic Degradation of Sago Wastewater using TiO_2 /MSB Mixture

4.4.1 Model Fitting

Based on the CCD, 13 sets of experiments with operating conditions were conducted to investigate effect of the independent variables (dosage of TiO_2 /MSB mixture and contact time) in the photocatalytic treatment of sago wastewater (Table 3.2). The experimental response (η),

percentage of COD removal was chosen to determine the optimal conditions for the independent variables, which may affect the efficiency of the photocatalytic treatment. The complete 13 sets of the experimental design matrix and response based on the experimental results and predicted values on COD removal proposed by CCD are tabulated in Table 4.3. The resulting second-order fitting polynomial equation was generated and the equation, in terms of coded factors, is shown in Eq. 4.1:

$$\eta(\%) = 20.68 - 13.72X_1 + 5.00X_2 - 3.42 X_1X_2 + 7.84 X_1^2 + 1.68 X_2^2 \quad (4.1)$$

As shown in Table 4.3, the obtained percentage of COD removal efficiencies varied from 15.16% to 55.55% and the model predicted values matched these experimental results satisfactorily (Figure 4.8). Figure 4.8 depicts a regression coefficient (R^2) value of 0.99, which confirmed a reasonably good agreement between the experimental and predicted values. Therefore, the developed model is suitable to predict the COD removal in sago wastewater treatment.

Table 4.3: Experimental results and predicted values of η for percentage of COD removal using RSM.

Run	COD removal, η (%)	
	Experimental results	Predicted values
1	19.49	20.68
2	16.77	16.97
3	15.14	14.90
4	21.43	20.68
5	18.40	18.06
6	16.67	16.96
7	35.71	35.52
8	55.55	55.78
9	21.26	20.68
10	20.41	20.68
11	30.77	31.10
12	20.83	20.68
13	52.63	52.34

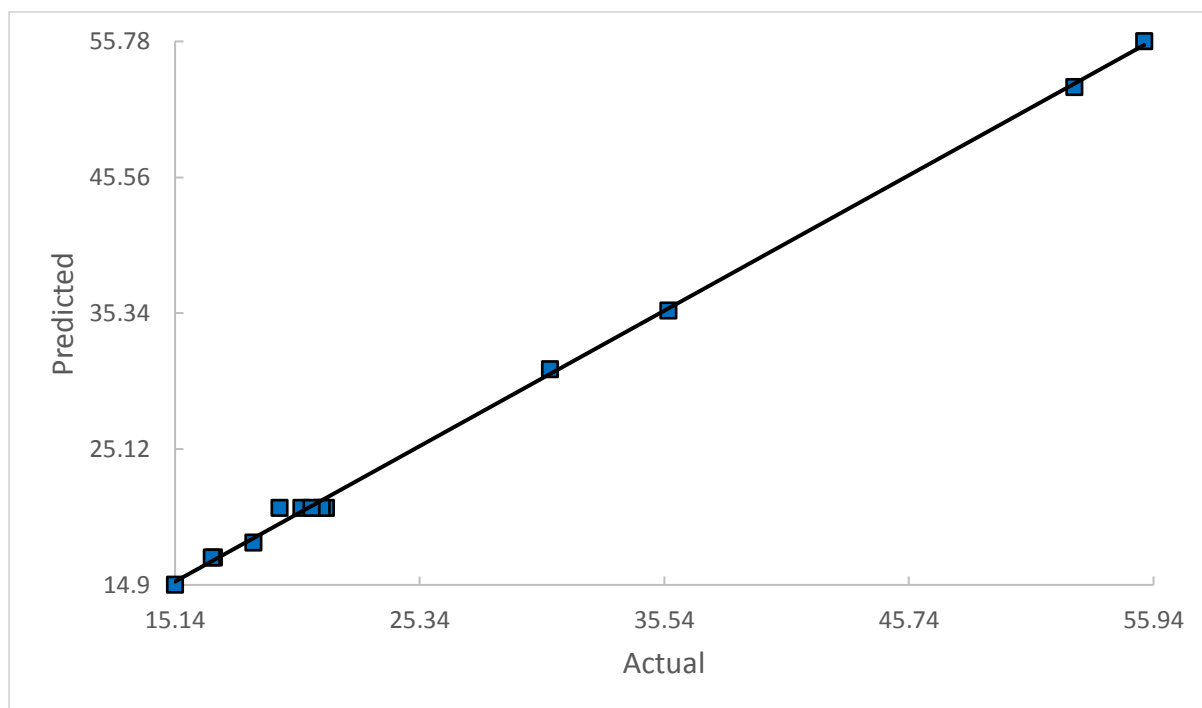


Figure 4.8: The scatter plot of predicted versus experimental values for COD removal (%) ($R^2 = 0.99$).

4.4.2 Statistical Analysis

ANOVA is defined as a statistical technique that subdivides the total variation in a set of data into component parts related with specific variation sources to test the hypotheses on the parameters of the model (Kumar *et al.*, 2009). The statistical significance of the ratio of mean square variation due to the regression and mean square residual error was investigated using ANOVA. Table 4.4 shows the ANOVA results for the second-order equation fitted for COD removal from sago wastewater. As shown in Table 4.4, the F values were high for all regressions. The large F values indicated that most of the variation in the response can be interpreted by the regression equation.

Table 4.4: ANOVA for the percentage of COD removal.

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F value	p-value Prob> F
Model	2184.41	5	436.68	1019.22	< 0.0001
X_1	1506.97	1	1506.97	3515.66	< 0.0001
X_2	199.79	1	199.79	466.10	< 0.0001
$X_1 X_2$	46.65	1	46.65	108.83	< 0.0001
X_1^2	427.98	1	427.98	998.45	< 0.0001
X_2^2	19.54	1	19.54	45.59	0.0003
Residual	3.00	7	0.43		
Lack of Fit	0.59	3	0.20	0.33	0.8076
Pure Error	2.41	4	0.60		
Cor Total	2187.41	12			

$R^2 = 0.9986$, Adj $R^2 = 0.9976$, Pred $R^2 = 0.9964$, Adeq Precision = 91.919, CV = 2.47%

ANOVA results for the COD removal from sago wastewater using TiO_2/MSB mixture produced F-value of 1019.22 for the quadratic model indicating that the model is significant. The “Prob > F” (<0.0001) for the second-order polynomial fitting implies that the model terms are significant at 95% probability level. The adequacy of the model was tested *via* the “Lack-of-fit F-tests” (Hadavifar *et al.*, 2010). The “Lack of fit F-value” of 0.33 implied that the lack of fit was not significant, relative to the pure error. There is an 80.76% of chance for a “Lack of fit F-value” could occur due to noise. The insignificant “Lack of fit” demonstrated that the model is adequate. The ANOVA results for the COD removal (η) showed significant ($P < 0.05$) response surface models with high R^2 value of 0.9986. Adjusted R^2 value of 0.9976 and predicted R^2 value of 0.9964 was found to be maximum, indicating that the quadratic model provided an excellent interpretation for the relationship between the independent variables and the corresponding response. Adequate (adeq) precision measures the signal to noise ratio or, in other words, is a measure of the range in predicted response relative to its associated error. The desired ratio of adequate precision is >4 (Mason *et al.*, 2003). The adequate precision ratio of 91.919 showed an adequate signal (Table 4.4). Hence, based on the ANOVA results, this

quadratic model (Eq. 4.1) could be used to navigate the design space. Low coefficient of variance (CV) value of 2.47% asserted good precision and reliability of the experiments. It is known that the greater the value of CV, the lower or poorer the reliability of the experiment (Sadler, 2013).

4.4.3 Effect of Dosage and Contact Time on the COD Removal

The three-dimensional (3D) response surface and two-dimensional (2D) contour plots of the model-predicted responses were obtained by the Design-Expert software. From the plots, two variables varying within the experimental ranges were plotted and utilised to assess the interactive relationships between the variables and response for TiO_2 photocatalysis of sago wastewater.

Figures 4.9(a) and (b) illustrates the 3D surface and 2D plot of the polynomial model, respectively for COD removal with respect to the dosage of TiO_2 /MSB mixture and contact time during the photocatalytic treatment. The obtained 3D surface plot depicts that the highest COD removal, 52.63%, was achieved at 120 min using 0.10 g of TiO_2 /MSB mixture (Figure 4.9(a)). It is evident that the COD removal increased with the increasing contact time for each TiO_2 /MSB mixture dosage investigated (0.10 g to 0.30 g). Low dosage (0.10 g) demonstrated a significant increase in the COD removal as the contact time increases contrary to the trend observed for high dosage, 0.30 g (Figure 4.9(a)). In the case of photoreaction over high dosage of TiO_2 /MSB mixture, the intermediates or degradation products remained in the suspension could still be structurally similar to the initial organic compounds. Their concentrations and photostability might also differ depending on the applied dosage. The applied contact time might be too short to achieve complete oxidation (Costa & Alves, 2013).

On the other hand, the COD removal declined at tested contact times (30-120 min) when the dosage of TiO₂/MSB mixture was increased from 0.10 g to 0.30 g (Figure 4.9(a)). The lowest COD removal 15.14% was attained at 30 min using the highest dosage of TiO₂/MSB mixture, 0.30 g. COD removal however remained almost constant despite an increase in the contact time from 30 min to 120 min. The reduction of the COD removal at higher dosage of TiO₂/MSB mixture may be explained by several facts. An increased level of suspension turbidity as a result of excessive photocatalyst dosage would have blocked the UV irradiation required for the catalyst activation (Aljuboury *et al.* 2016b). An excessive catalyst loading would also obstruct the available adsorbent pores and active sites on the photocatalyst surface (Zhang *et al.*, 2009b; Aljuboury *et al.*, 2016b). Hence, it is crucial to optimise the dosage of TiO₂/MSB mixture and contact time to maximise the COD removal in sago wastewater.

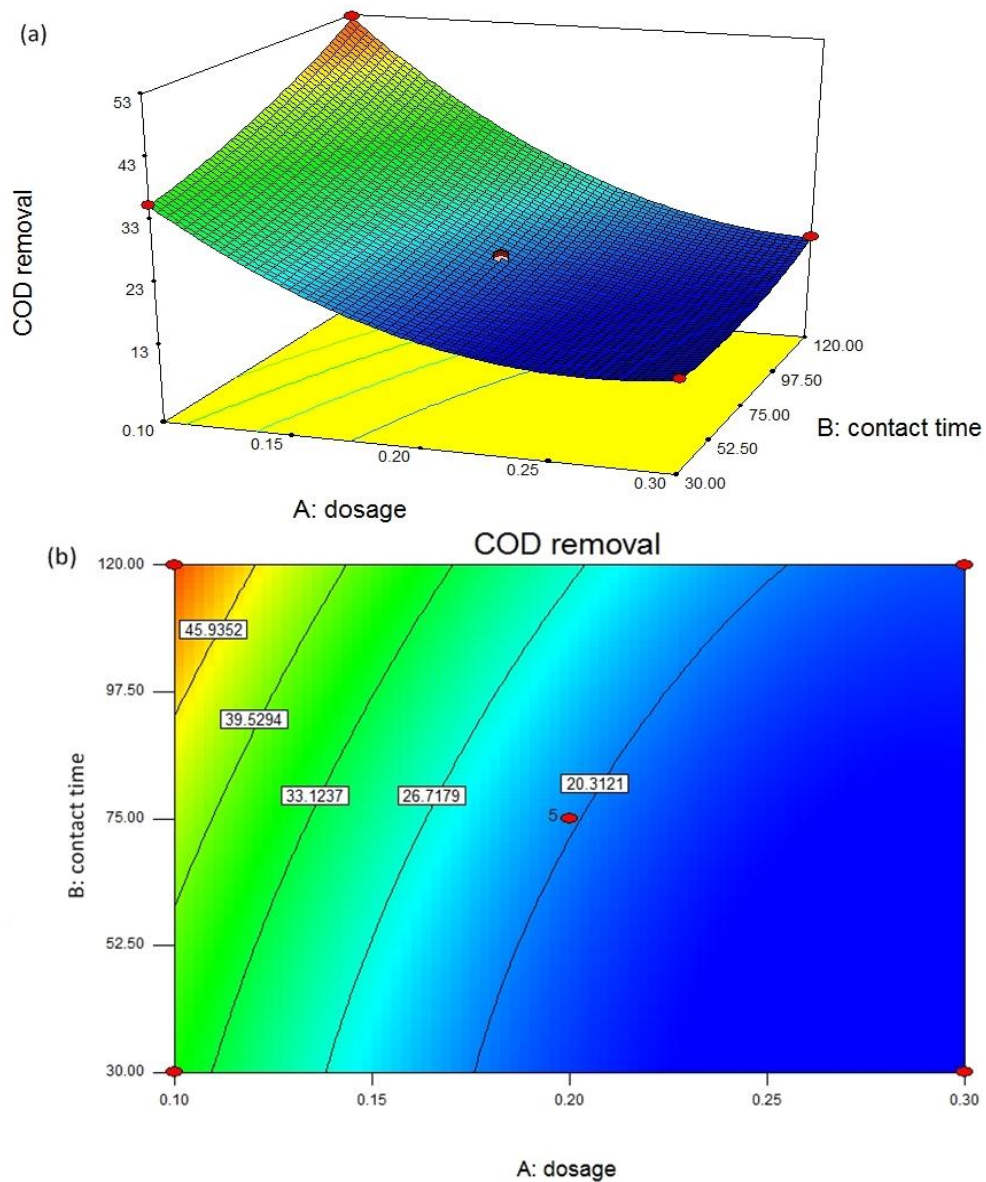


Figure 4.9: Interaction between dosage and contact time on the COD removal (a) 3D surface and (b) contour plot of response surface curve.

4.4.4 Proposed Mechanism of TiO₂/MSB Photocatalytic Degradation

Typically, the photocatalytic degradation process involves three steps (1) adsorption of organic pollutant on the TiO₂ surface, (2) surface photodegradation of organic pollutant, and (3) final products desorption from the TiO₂ surface (Yao *et al.*, 2010; Giraldo & Moreno-Pirajan, 2014). In the TiO₂/MSB photocatalytic oxidation process, the reaction is activated by the

absorption of photon with sufficient energy corresponding to the band gap energy of the photocatalyst, TiO_2 . Upon UV-C irradiation, TiO_2 particles on the MSB surface interact with UV-C light to promote an electron (e^-) from the valence band of TiO_2 to the conduction band, thus generating a positive hole (h^+) in the valence band (Eq. 2.4 in section 2.5). The pertaining reactions at the TiO_2 surface, which govern the degradation of organic pollutants, are expressed in Eqs. 2.8-2.9 and Eqs. 2.13-2.14 in section 2.5. As MSB acts as an adsorbent, it is anticipated that the accumulated pollutants and intermediates on its surface will be oxidised by the photoactivated TiO_2 into simpler products such as CO_2 , H_2O and others (Eqs. 2.13-2.14). Figure 4.10 illustrates the proposed photo-induced mineralisation of organic pollutant over TiO_2/MSB mixture. The synergistic effects, adsorption and photocatalysis exhibited by TiO_2/MSB mixture aided the degradation of organic pollutants in sago effluent.

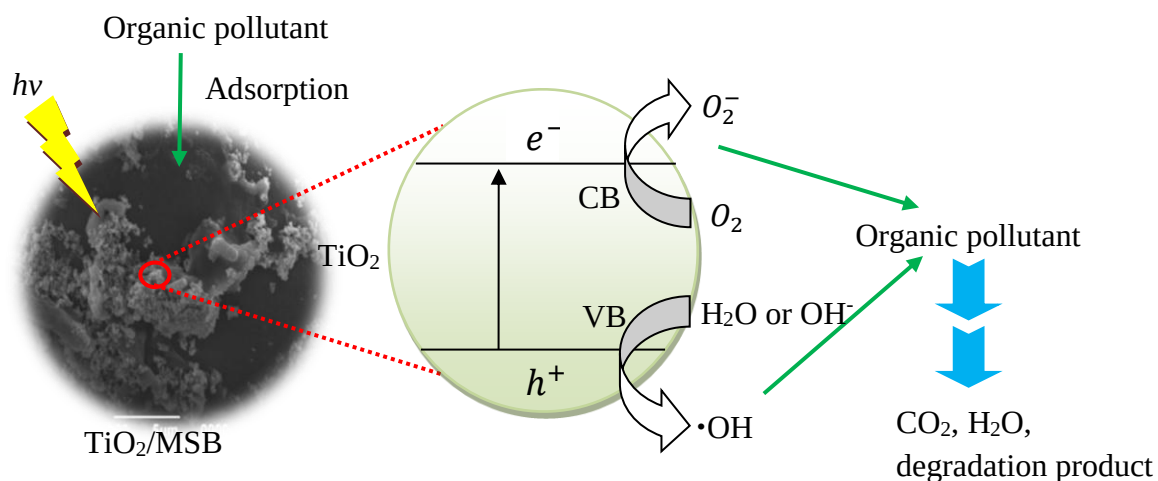


Figure 4.10: Schematic illustration of adsorption and photocatalytic degradation of organic pollutant by TiO_2/MSB mixture.

4.4.5 Kinetic Evaluation

The kinetics of COD degradation for sago wastewater were analysed using the first-order model as expressed in Eq. 4.2 (Omri & Benzina, 2014):

$$\ln \left(\frac{C_0}{C_t} \right) = k_{app} t \quad (4.2)$$

where k_{app} represents the apparent rate constant of the first-order reaction (min^{-1}), C_0 is the equilibrium COD of sago wastewater after adsorption in the dark, and C_t represents the remaining COD of sago wastewater at fixed irradiation time interval. Table 4.5 shows the kinetics of COD degradation for sago wastewater during different treatments performed. The highest rate constants demonstrated by 0.2 g/L TiO_2 /1% MSB mixture confirmed the synergistic effects of adsorption and photocatalysis compared to the individual effects of SB, MSB and TiO_2 .

Table 4.5: Kinetics of COD degradation for sago wastewater during different treatment condition.

Treatments	k_{app} (min^{-1})	R^2 value
Sago wastewater	0.0007	0.86
Sago wastewater + SB	0.0026	0.96
Sago wastewater + MSB	0.0037	0.90
Sago wastewater + TiO_2	0.0039	0.63
Sago wastewater + 0.2 g/L TiO_2 /1% MSB	0.0076	0.78

4.4.6 Optimisation Analysis and Verification of the Results

Optimisation process was performed using RSM with the objective to identify the optimum condition for TiO_2 /MSB photocatalysis in order to minimise the usage of TiO_2 /MSB

and to reduce the contact time. The optimisation process was carried out by verifying the desired target for each of the variables and response. Thus, the process variables such as the dosage of TiO₂/MSB mixture and contact time are chosen to be “in range” while a “target” was declared as the desired target for the COD removal to achieve the highest performance of the treatment. Table 4.6 shows the optimum conditions derived from the statistical software.

Table 4.6: Optimum values of TiO₂/MSB photocatalysis parameters for maximum removal efficiency.

Parameter	Optimum value
COD removal, Y (%)	52.34
Dosage (g)	0.10
Contact time (min)	120

As shown in Table 4.6, it has been predicted that 52.34% of COD can be removed by means of photocatalytic treatment under optimum TiO₂/MSB dosage and contact time of 0.10 g and 120 min, respectively. A series of experiments were conducted to validate the predicted response from optimisation process. An average percentage removal of COD, 52.83% was achieved from the duplicate experiments. Table 4.7 compares the efficiency of the experimental and predicted COD removal under the established optimum conditions. The actual experimental values of COD removal obtained were only marginally different from the predicted values. The validity of the polynomial model developed was thus verified for the COD removal photocatalytically using the fabricated composite material.

Table 4.7: Experimental and predicted values for the COD removal under the optimum conditions.

Type of values	COD removal (%)
Experimental	52.83±0.14
Predicted	52.34

Under the optimum conditions, the COD of treated sago wastewater was reduced from the initial value of 2956.80 mg/L to 1056.00 mg/L after 120 min of treatment time (Figure 4.10). The COD result revealed that the TiO₂/MSB mixture was effective in reducing COD level in sago wastewater. However, TOC level of treated sago wastewater demonstrated an increase from 850.00 mg/L to 1050.00 mg/L at the first 60 min and reduced thereafter to 900.00 mg/L after 120 min (Figure 4.11). The presence of soluble organic compounds such as hemicelluloses and lignin in the MSB which was not fully removed during the acid pretreatment would have contributed to the increase of TOC level (Nghah & Hanafiah, 2008). Besides, the increase of TOC might be due to the presence of stable intermediates or degradants formed during the photocatalytic treatment as a result of the non-selective nature of HO• radicals. HO• radicals can degrade organic pollutants to intermediates, with either stable or unstable natures, and subsequently degrade the intermediates into simple forms including CO₂ and H₂O (Khan *et al.*, 2014). Thus, it can be assumed that the formation of non-degradable intermediates raised the TOC level at first 60 min and which were then mineralised to CO₂ and H₂O thereafter. It was also notable that the initial TOC and final TOC levels showed no significant different despite the changes observed as explained above (Figure 4.11). This thus implies that probably a more stringent oxidizing conditions and longer reaction time might be needed to significantly reduce the TOC level due to the presence of intermediates and degradation products with differing nature (Fasnabi *et al.*, 2016). Generally, the COD value can be considered to be more accurate in the determination of wastewater treatment efficiency compared to the TOC value

(Kanakaraju *et al.*, 2016). COD measures the oxygen required to oxidise the organic compounds in wastewater while TOC measure the amount of carbon in wastewater including dissolved CO₂ and carbon compounds such as amine and aromatic compounds (Aljuboury *et al.*, 2015).

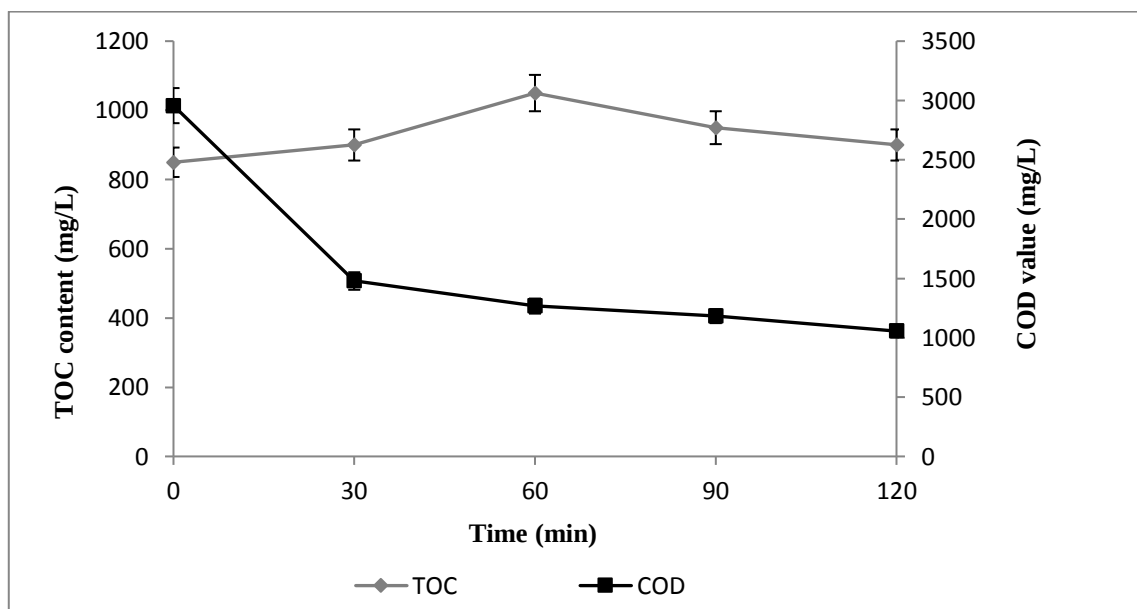


Figure 4.11: Profile of TOC content and COD value of treated sago wastewater under the optimised conditions during TiO₂/MSB photocatalysis (TiO₂/MSB dosage = 0.10 g; contact time = 120 min).

4.4.7 Comparison Efficiency of TiO₂ Photocatalysis under Different Conditions

The presence of O₂ is known to enhance the degradation of wastewater in the TiO₂ photocatalytic treatment as it can inhibit the recombination of electron-hole pairs and produces more HO• radicals during photocatalysis (Yasmina *et al.*, 2014). Experiments were performed to investigate the effect of O₂ on the degradation of sago wastewater using optimised TiO₂/MSB mixture. An air diffuser was used to continuously supply aeration during the photocatalytic treatment. Raw SB (without chemical modification) was also used to prepare TiO₂/SB mixture likewise the optimised 0.2 g/L TiO₂/1% MSB mixture. Figure 4.12 shows the percentage of

COD removal achieved under different conditions. Under aerated condition, COD removal was observed to positively increase to 63.89% compared to 52.83% removal under non-aerated condition using the same TiO₂/MSB mixture. Aljuboury *et al.* (2016b) reported that the presence of air bubbling as a source of oxygen markedly increased the degradation rate of COD in petroleum wastewater by 12%. A maximum 76% of COD removal was achieved by using TiO₂/ZnO/air system.

The role of O₂ in photocatalysis includes being an electron acceptor, getting involved in the formation of other oxidative species (e.g., hydroxyl radical, superoxide radical, hydrogen peroxide), as well as to prevent reduction reactions (Malato *et al.*, 2009). O₂ can also act as electron scavengers to prevent the recombination of photogenerated electron-hole pairs, which could reduce the photocatalytic activity of TiO₂/MSB (Gogate & Pandit, 2004; Kanakaraju *et al.*, 2014). The photo-generated electrons (e_{CB}^-) scavenged by the adsorbed molecular oxygen on the TiO₂/MSB surfaces, resulting in the hydroperoxyl radical ($HO_2^\bullet$), as shown in Eqs. 4.3-4.4 (Pekakis *et al.*, 2006).



The $HO_2^\bullet$ radical can further generate H₂O₂ (Eq. 4.5), and subsequently HO• radicals (Eqs. 4.6-4.8), thus preventing recombination of electron-hole pairs, which known to cause low TiO₂ photocatalytic quantum yield.





When the recombination rate of photogenerated electron-hole pairs is reduced, positive holes can either directly oxidise the organic pollutants or react with OH^- anions to form powerful $\text{HO}\cdot$ radicals. This would aid and promote the reduction of COD because more organic matter in sago effluent can be oxidised to their simpler forms. Hence, COD levels in sago effluent can be reduced by supplying O_2 *via* aeration, which is an economical way for continuously supplying O_2 to enhance the TiO_2 photocatalytic treatment of sago effluent. Additionally, operating costs can be reduced if air is used instead of pure oxygen in pilot scale treatments (Gogate & Pandit, 2004).

TiO_2 mixture prepared using raw SB as an adsorbent yielded only 43.75%. This finding seems to be consistent with those obtained by Acar and Eren (2006) whereby acid treated poplar sawdust (a plant waste) produced appreciably better removal of Cu^{2+} , 92.38%, compared to the untreated one which only removed 47.05%. It was reported that better adsorption efficiency exhibited by acid treated poplar sawdust contributed to the Cu^{2+} removal. Limitations arising from the usage of untreated plant wastes as adsorbents have been reported in literature. For instance, low adsorption capacity and high BOD and COD as well as TOC due to the release of soluble organic compounds from the plant materials (Nghah & Hanafiah, 2008).

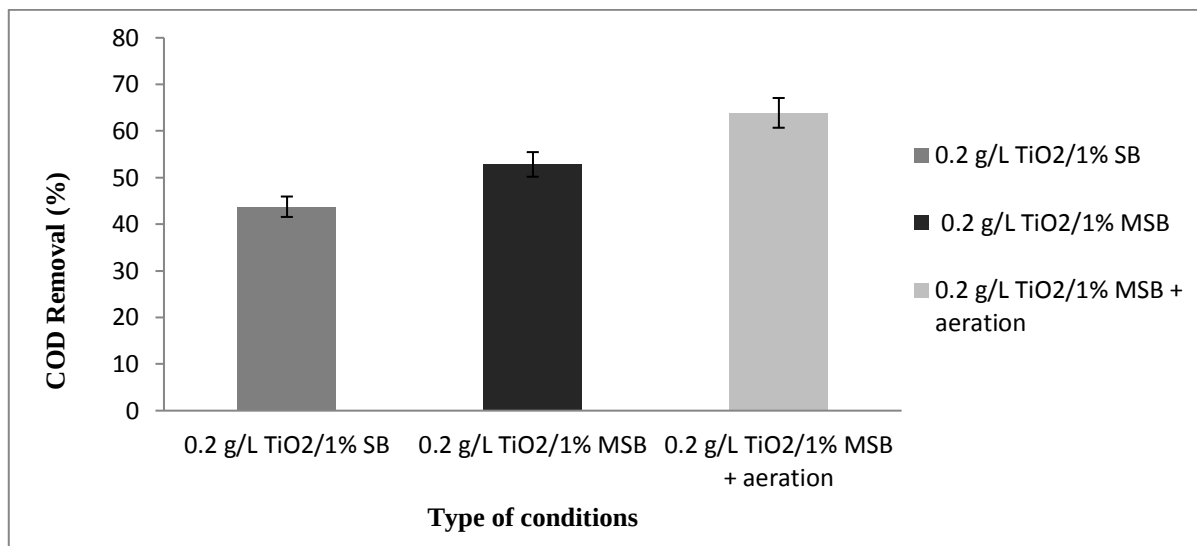


Figure 4.12: Efficiency of TiO₂ photocatalysis in removing COD under different conditions.

4.5 Photo-Fenton Experiment

4.5.1 Model Fitting

According to the experimental design, 17 sets of experiments with operating conditions were conducted in order to investigate the variables (concentration of Fe²⁺ ion and H₂O₂, and initial pH) involved in the photo-Fenton reaction (Table 3.4). The data from the experimental results were fitted to the polynomial equation to quantify the curvature effects. The second-order fitting polynomial equation of coded factors is expressed as shown in Eq. 4.9:

$$\eta (\%) = 85.18 - 4.70X_1 + 21.17X_2 + 5.15X_3 + 11.10X_1X_2 - 2.26X_1X_3 + 7.70X_2X_3 - 20.51X_1^2 - 22.17X_2^2 - 14.46X_3^2 \quad (4.9)$$

The complete 17 sets of the experimental design matrix and response based on experimental results and predicted values on COD removal proposed by BBD are tabulated in Table 4.8. The obtained percentage of COD removal efficiencies varied from 5.66% to 87.02% (Table 4.8) and the model predicted values matched these experimental results satisfactorily

(Figure 4.13). A graph of predicted values and experimental results for COD removal is plotted in Figure 4.13. From Figure 4.13, which depicts a regression coefficient R^2 value of 0.99 confirmed the results between the experimental and predicted data. If the R^2 value is less than 0.80, the model will be rejected (Montgomery, 1991). Accordingly, it is reasonable to declare that the polynomial model (Eq. 3.5) is a reliable tool to delineate the Fenton reaction behaviour in sago wastewater treatment.

Table 4.8: Experimental results and predicted values of η for percentage of COD removal using RSM.

Run	COD removal, η (%)	
	Experimental results	Predicted values
1	57.14	56.87
2	83.33	85.18
3	47.37	47.51
4	82.50	82.56
5	30.00	29.94
6	37.21	37.14
7	5.66	5.53
8	57.14	57.27
9	24.56	24.83
10	70.00	70.07
11	85.00	85.18
12	42.42	42.61
13	84.85	85.18
14	62.50	62.31
15	48.53	48.39
16	87.02	85.18
17	85.71	85.18

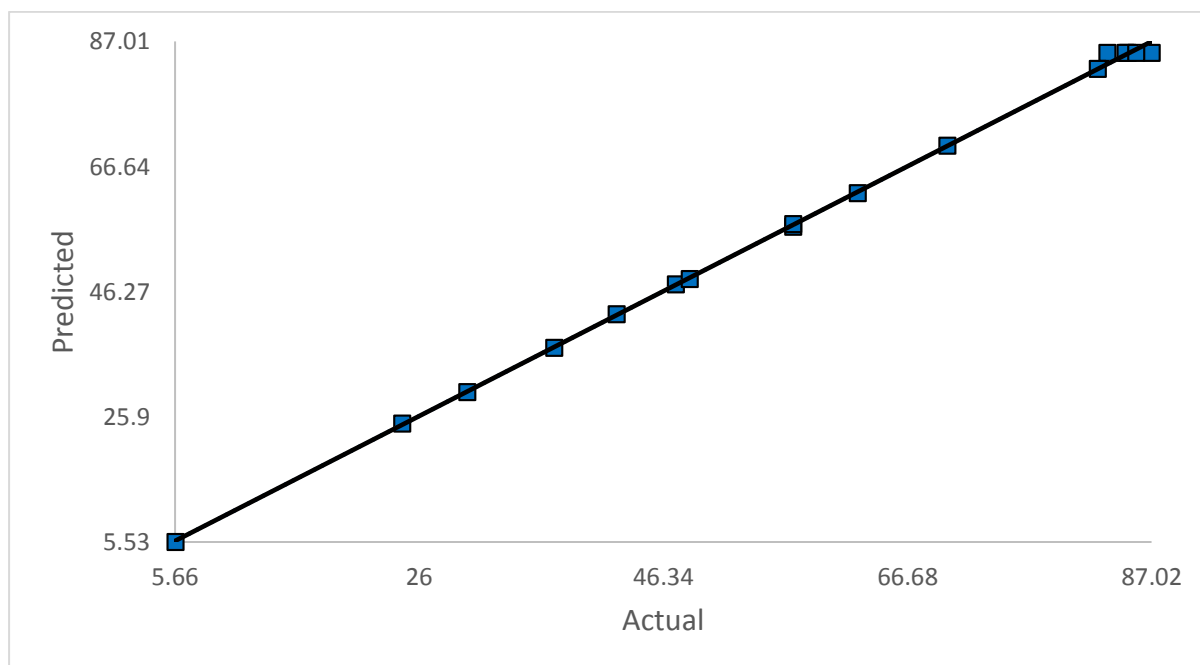


Figure 4.13: Predicted versus experimental values for COD removal (%) ($R^2 = 0.99$).

4.5.2 Statistical Analysis

ANOVA using Design-Expert 7.1.6 software was performed to further assess the polynomial model (Eq. 3.5) taking into account the interaction of independent variables. Fisher's F-test, at which the F-value is the ratio of the mean square of regression to the mean square of the error, was used to determine the statistical significance of the factors towards the response. Table 4.9 shows the ANOVA results for the percentage of COD removal. The F-values were found to be high for all regressions (Table 4.9). The large F-value showed that most of the variation in the response can be interpreted by the regression equation. For all the regressions, the p-values are lower than 0.01, which means that minimum one of the terms in the regression equation has a significant correlation with the response (dependent) variable.

Table 4.9: ANOVA for the percentage of COD removal.

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F value	p-value Prob> F
Model	9977.89	9	1108.65	1029.70	< 0.0001
X_1	176.81	1	176.81	164.22	< 0.0001
X_2	3584.93	1	3584.93	3329.64	< 0.0001
X_3	211.77	1	211.77	196.69	< 0.0001
$X_1 X_2$	493.06	1	493.06	457.95	< 0.0001
$X_1 X_3$	20.34	1	20.34	18.89	0.0034
$X_2 X_3$	237.16	1	237.16	220.27	< 0.0001
X_1^2	1771.59	1	1771.59	1645.43	< 0.0001
X_2^2	2069.00	1	2069.00	1921.66	< 0.0001
X_3^2	880.96	1	880.96	818.23	< 0.0001
Residual	7.54	7	1.08		
Lack of Fit	0.31	3	0.10	0.057	0.9800
Pure Error	7.23	4	1.81		
Cor Total	9985.43	16			

$R^2 = 0.9992$, Adj $R^2 = 0.9983$, Pred $R^2 = 0.9984$, Adeq Precision = 100.087, CV = 1.78%

Based on the ANOVA analysis, the model F-value was 1029.70 which revealed that the model was significant. This indicates that a “model F-value” has < 0.01% probability to occur due to noise. For the response, the square of correlation coefficients was computed as the coefficient of determination (R^2). It depicted high significant regression at 95% confidence level. The “Lack of fit F-value” of 0.06 indicated that the lack of fit was not significant relative to the pure error. This implies that there was 98.00% probability that a “Lack of fit F-value” as large as this would occur due to noise. For further analysis, the quadratic model was chosen as the adjusted R^2 value (0.9983) and predicted R^2 value (0.9984) was found to be the maximum. Adequate precision measures the signal to noise ratio. The desired ratio of adequate precision is 4 or greater. The ratio of 100.087 shows an adequate signal (Table 4.9). Thus, this model can be utilised to navigate the designed space. Low value of CV (1.78%) indicates good precision and reliability of the experiments.

4.5.3 Effect of Fe²⁺ and H₂O₂ Dosage on the COD Removal

From the 3D and 2D plots, two variables varying within the experimental ranges and one factor kept at constant were plotted and utilised to assess the interactive relationships between the variables and response for photo-Fenton treatment of sago wastewater. Figures 4.14(a) and (b) show the 3D surface and 2D plot of the model, respectively for COD removal with respect to the dosage of Fe²⁺ ion and H₂O₂ when the pH was kept constant at 2.50. The percentage of COD removal increased when the Fe²⁺ ion concentration was increased to about 5 g/L (Figure 4.14(a)). However, at higher concentration of Fe²⁺ ion, the COD removal rate was observed to decrease. This simply means that an increase in the concentration of Fe²⁺ ion does not improve the COD removal efficiency of the treated wastewater. Higher H₂O₂ concentration in the presence of Fe²⁺ ion produced more •OH radicals and thus improved the process efficiency. Nevertheless, excessive amounts of H₂O₂ and Fe²⁺ ion particles may inhibit the COD removal efficiency. The undesirable reactions between excessive amounts of H₂O₂ and Fe²⁺ ions and hydroxyl/hydroperoxyl radicals can be explained through Eqs. 4.10-4.13 (Saber *et al.*, 2014):



Although higher Fe²⁺ ion concentration may benefit COD removal in the photo-Fenton process, the scavenging of the hydroxyl/hydroperoxyl radicals may occur due to the high Fe²⁺ ion concentration (Saber *et al.*, 2014). Likewise, the percentage of COD removal increased with

the increasing concentration of H_2O_2 up to 4 mL/L after which the COD removal decreased (Figure 4.14(a)). Lower removal of obtained COD upon reaching the optimum amount of H_2O_2 could be due to the excess amount of H_2O_2 remaining in the solution, which becomes a hindrance in the result of COD of the final effluent (Abdulah *et al.*, 2011). Thus, it can be concluded that optimal dosage of both H_2O_2 and Fe^{2+} ion concentrations are crucial in the photo-Fenton treatment.

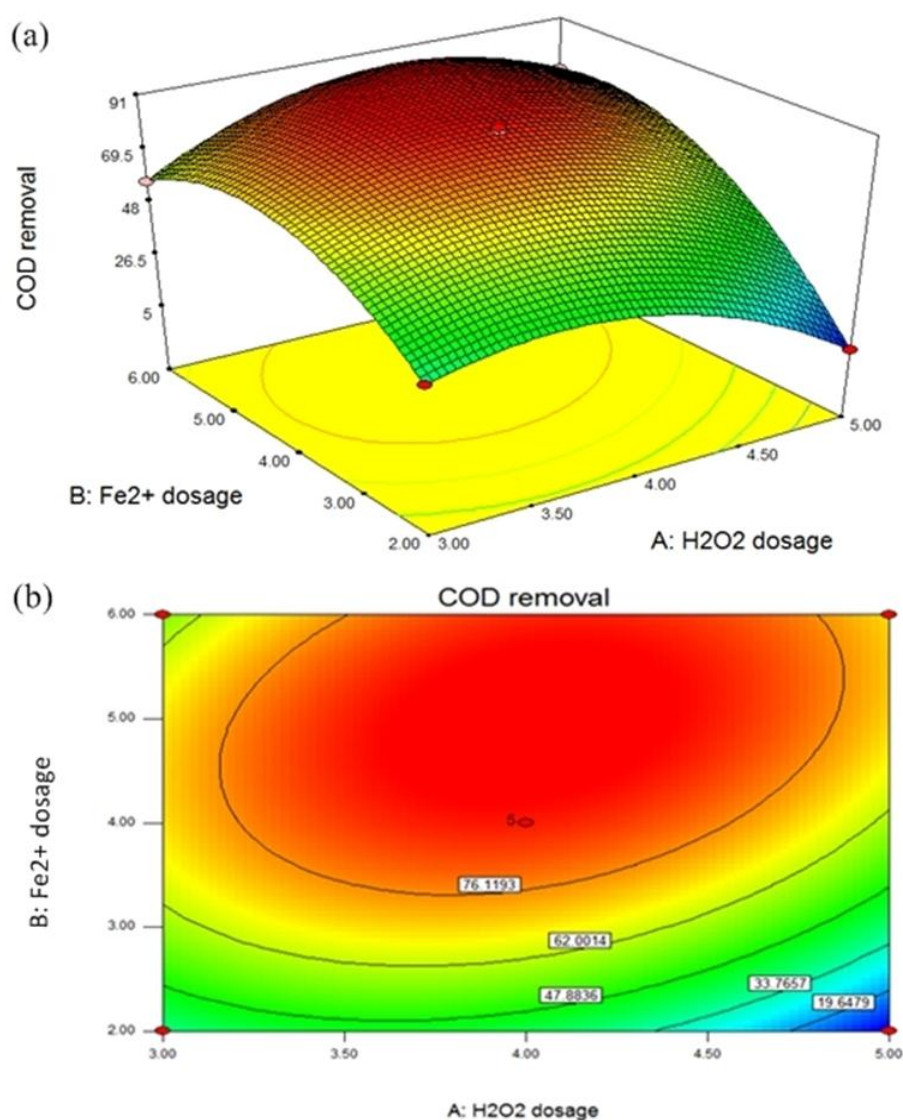


Figure 4.14: (a) 3D surface and (b) contour plot of response surface curve for COD removal showing interaction between Fe^{2+} and H_2O_2 .

4.5.4 Effect of H₂O₂ Dosage and Initial pH on the COD Removal

In the photo-Fenton process, H₂O₂ which acts as a dominant source of •OH radicals play an important role in the organic wastewater treatment (Wang *et al.*, 2016). In the present experiment, the concentration of H₂O₂ is directly associated with the number of •OH radicals generated, and therefore, to the performance achieved. 3D surface and 2D contour plot in Figures 4.15(a) and (b) revealed that the combination of H₂O₂ concentration and initial pH has a significant effect on the COD removal. From Figure 4.15, the percentage of COD removal increased with the increasing concentration of H₂O₂ from 3.00 to 4.00 mL/L at an initial pH of 2.00 to 2.50 when Fe²⁺ ion concentration was kept constant at 4.00 g/L. The highest COD removal (>80.00%) was achieved at pH 2.50 and H₂O₂ concentration of 4.00 mL/L. However, the COD removal percentage was reduced when the H₂O₂ was higher than 4.00 mL/L and when the initial pH was beyond 2.50. The detrimental effect of higher H₂O₂ concentration may be due to the recombination of both •OH radicals and the auto-decomposition of H₂O₂ into O₂ and H₂O (Sarria, *et al.*, 2003). Moreover, the oxidation potential of •OH radicals is known to decrease when the pH increases (Samet *et al.*, 2012).

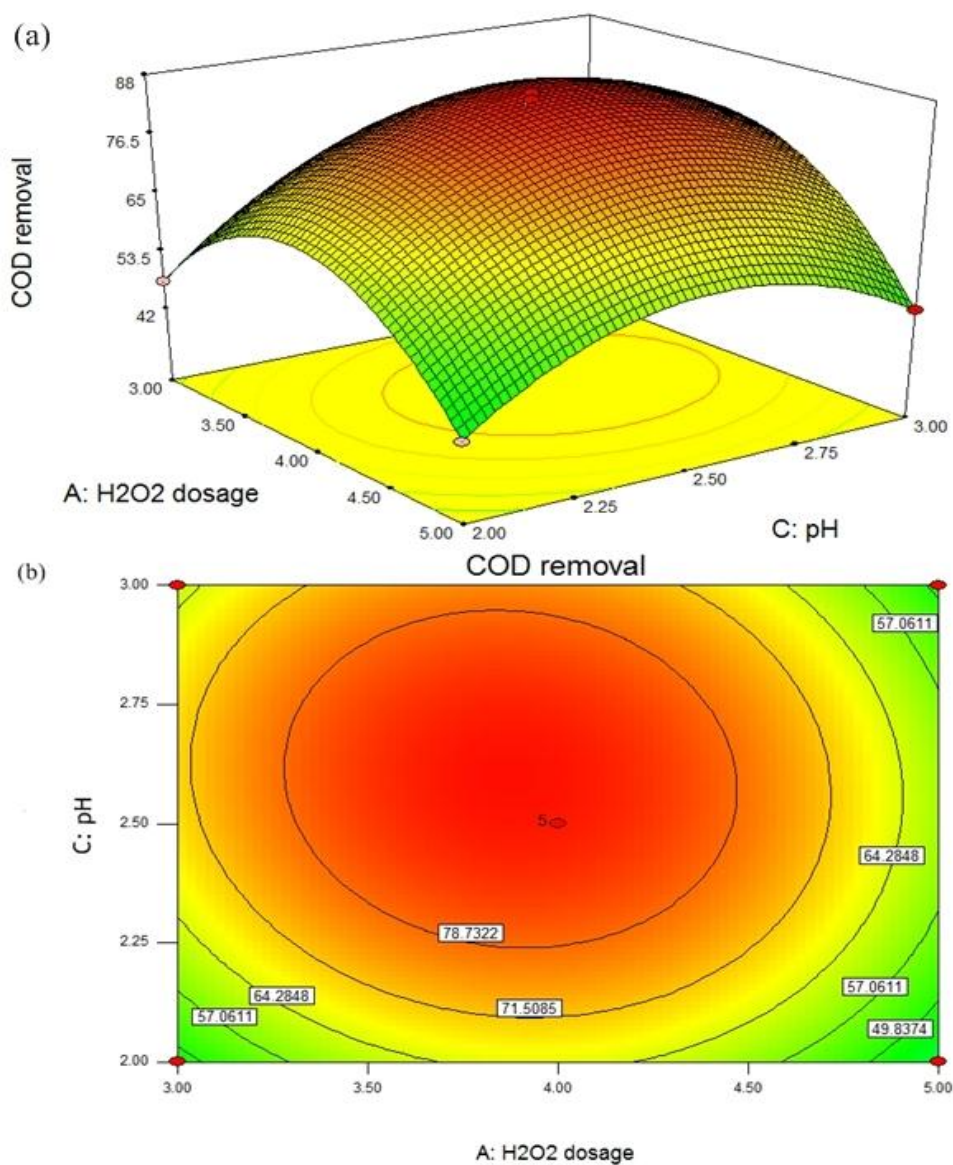


Figure 4.15: (a) 3D surface and (b) contour plot of response surface curve for COD removal showing interaction between H₂O₂ and pH.

4.5.5 Effect of Fe²⁺ Dosage and Initial pH on the COD Removal

One of the main parameters that influence the photo-Fenton process is the amount of Fe²⁺ ion (Samet *et al.*, 2012). Besides that, the photo-Fenton process is strongly pH dependent as the pH value affects the generation of •OH radicals and therefore, the oxidation efficiency. Figures 4.16(a) and (b) demonstrate the 3D surface and 2D plot for the interaction of Fe²⁺ ion

dosage and initial pH in terms of COD removal percentage (%), respectively. Based on Figure 4.16, the efficiency of COD removal can be seen to increase with the increasing concentration of Fe^{2+} ion from 2.00 to 5.00 g/L at all the pHs studied when the H_2O_2 dosage was kept constant at 4.00 mL/L. However, the COD removal percentage slightly decreased at higher concentration of Fe^{2+} (6 g/L). As reported by Samet *et al.* (2012), the amount of Fe^{2+} ions in the Fenton process must be as low as possible for economic and environmental reasons. High amounts of Fe^{2+} ions may lead to the formation of Fe^{3+} sludge in the treated effluent. As a result of this, an additional step would be required for the removal of the iron sludge which would incur in cost and manpower (Samet *et al.*, 2012). As can be seen in Figure 4.16, the initial pH is also a determinant factor. On the pH axis shown in Figure 4.16(a), at two sides of the middle pH (2.50), the efficiency of COD removal decreased as pH changed. At $\text{pH} < 2.50$, the reaction between H_2O_2 and Fe^{2+} ion was significantly affected and thus causing a reduction in the production of $\bullet\text{OH}$ radicals due to the $\bullet\text{OH}$ radical scavenging by H^+ ions (Samet *et al.*, 2012).

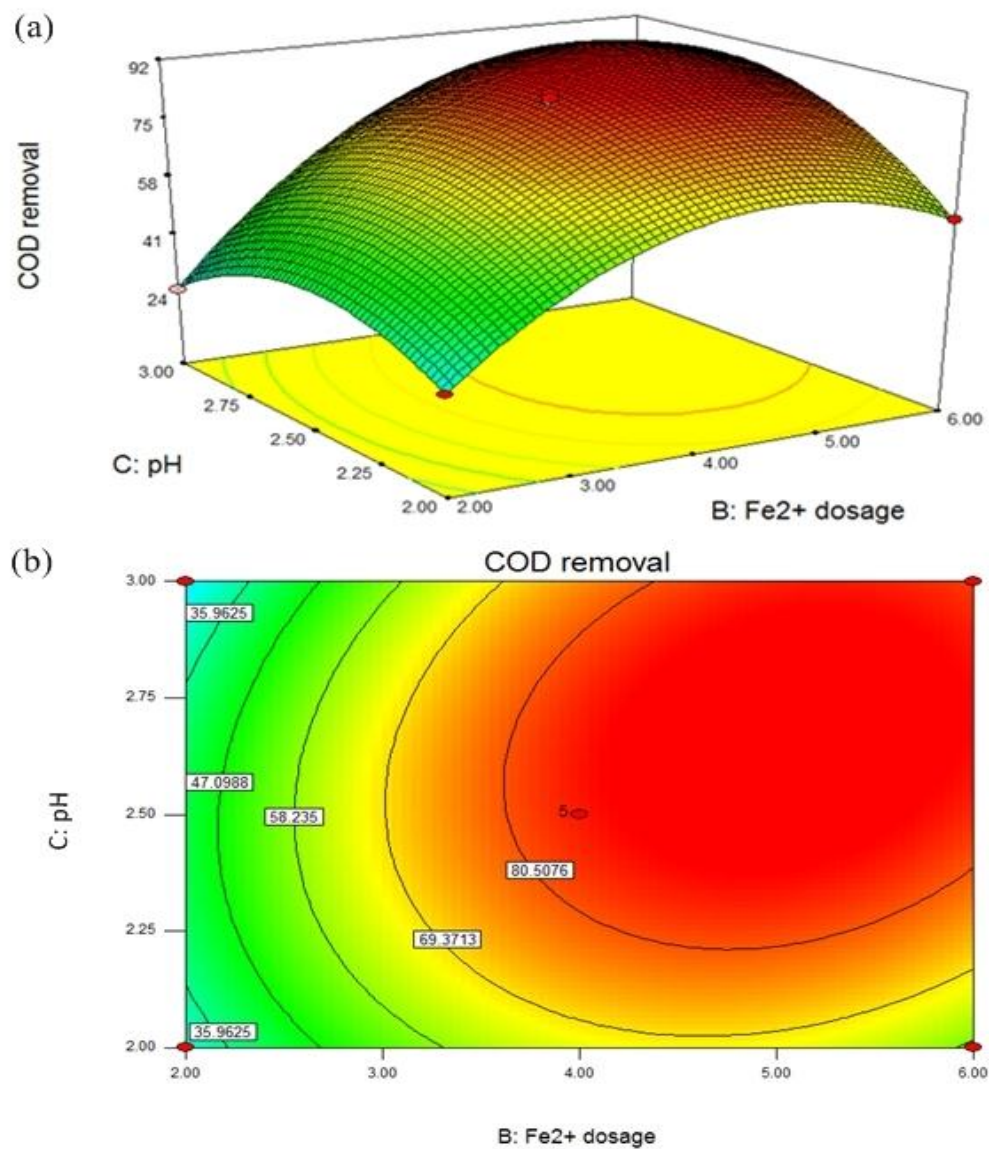


Figure 4.16: (a) 3D surface and (b) contour plot of response surface curve for COD removal showing interaction between Fe²⁺ and pH.

4.5.6 Optimisation Analysis and Verification of the Results

The process variables such as the concentration of H₂O₂ and Fe²⁺ and initial pH are chosen to be “in range”. The optimal conditions derived from the statistical software are shown in Table 4.10.

Table 4.10: Optimum values of photo-Fenton parameters for maximum removal efficiency.

Parameter	Optimum value
COD removal, Y (%)	91.65
H ₂ O ₂ (mL/L)	4.01
Fe ²⁺ (g/L)	5.07
pH	2.66

Three duplicate experiments using the optimum operating conditions were conducted to validate the efficiency of the model. An average percentage of the COD removal of 90.00% was achieved from the duplicate experiments. Table 4.11 shows the efficiency of the predicted COD removal (%) *via* the polynomial model (Eq. 3.5). After the photo-Fenton treatment under the optimum operating conditions, the TSS and BOD of treated sago wastewater were reduced to 4330 mg/L and 427 mg/L, respectively which corresponded to 35.7% and 77.7% removal, respectively. Plotting shown in Figure 4.13 indicated that a good agreement of the data between the experimental and predicted can be obtained with a R² value of 0.99. Thus, it is reasonable to consider that the polynomial model (Eq. 3.5) is a reliable and acceptable model to describe the Fenton reaction behaviour in wastewater treatment.

Table 4.11: Experimental and predicted values for COD removal at optimum conditions.

Type of value	COD removal (%)
Experimental	90.00±6.78
Predicted	91.65

4.5.7 Efficiency of Photo-Fenton Process

To confirm the effectiveness of the photo-Fenton process in treating sago wastewater, dark Fenton experiment was also conducted under optimised condition of photo-Fenton process by addition of 4.01 mL/L H₂O₂ and 5.07 g/L Fe²⁺ at pH 2.66. In the case of Fenton process,

COD removal decreased to 56.52% after 2 h of treatment. The COD removal percentage was relatively lower compared to 90.00% removal obtained from photo-Fenton (Figure 4.17). This can be explained by the lower production of $\bullet\text{OH}$ radicals due to the inhibition of Fe^{2+} ion regeneration in the Fenton process (Badawy *et al.*, 2006; Fasnabi *et al.*, 2016). As shown in Eq. 4.14, one molecule of H_2O_2 and one molecule of Fe^{2+} react to produce one molecule of $\bullet\text{OH}$ radical in the Fenton process.



However, in the photo-Fenton process, the present of UV irradiation enables the conversion of Fe^{3+} complex back to Fe^{2+} and produced $\bullet\text{OH}$ radical, as shown in Eq. 4.15 (Badawy *et al.*, 2006). The regenerated Fe^{2+} can further reoxidised with H_2O_2 to generate additional $\bullet\text{OH}$ radicals, which would accelerate the oxidation of organic pollutants.



Meanwhile, UV irradiation can improve the decomposition of H_2O_2 (Eq. 4.16) to generate $\bullet\text{OH}$ radicals, which would subsequently increase the mineralisation rate of organic pollutants (Wang *et al.*, 2014; Mechakra *et al.*, 2016).



Hence, the photo-Fenton process contributes to a better efficiency in the sago wastewater treatment than the dark Fenton.

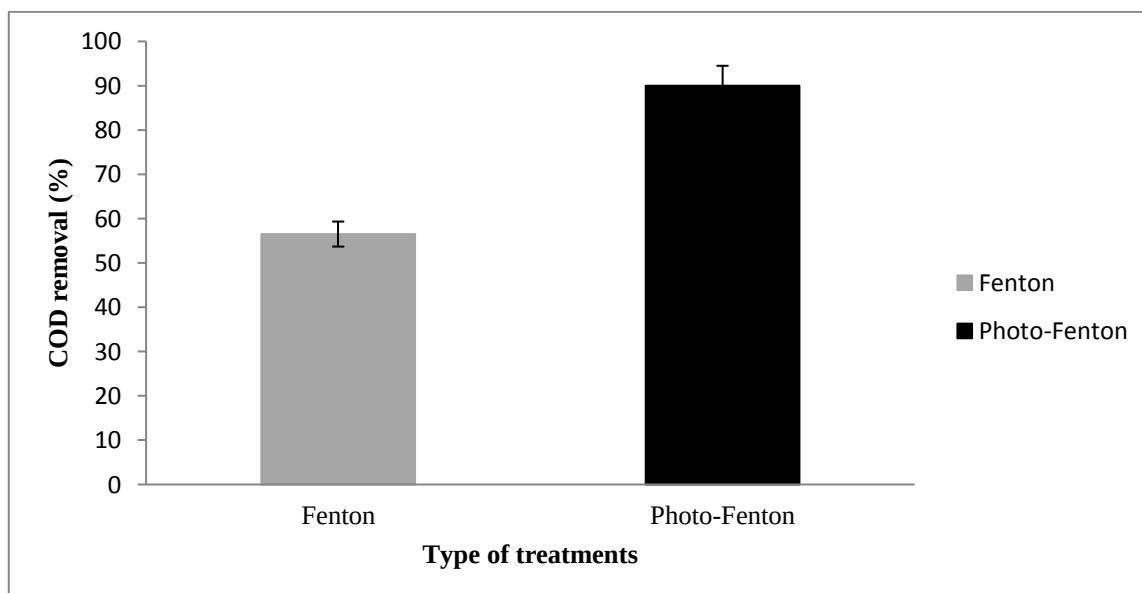


Figure 4.17: Comparison of COD removal between Fenton and photo-Fenton treatments.

4.5.8 Total Organic Carbon Analysis

TOC removal for sago wastewater under optimised photon-Fenton treatment is depicted in Figure 4.18. TOC reduction of 48% was obtained after 2 h of photo-Fenton treatment under the optimised conditions (Figure 4.18) which mean only 48% of organic conversion or decomposition took place. TOC removal was rather low compared to the COD removal (90%) under similarly optimised conditions. A recent study on the solar TiO_2 photocatalytic treatment of petroleum wastewater using RSM reported similar trend to this study whereby the experimental results of COD (45%) removal was relatively higher than the TOC (16.5%) removal (Aljuboury *et al.*, 2015). The COD analysis is used to measure the total quantities of oxygen required to oxidise organic compound present in wastewater into simpler forms such as water and carbon dioxide (Kanakaraju *et al.*, 2016) while TOC measures the amount of the organic carbon in wastewater. COD parameter, however, has been reported to be more accurate when investigating the efficiency of a treatment in wastewater (Aljuboury *et al.*, 2015).

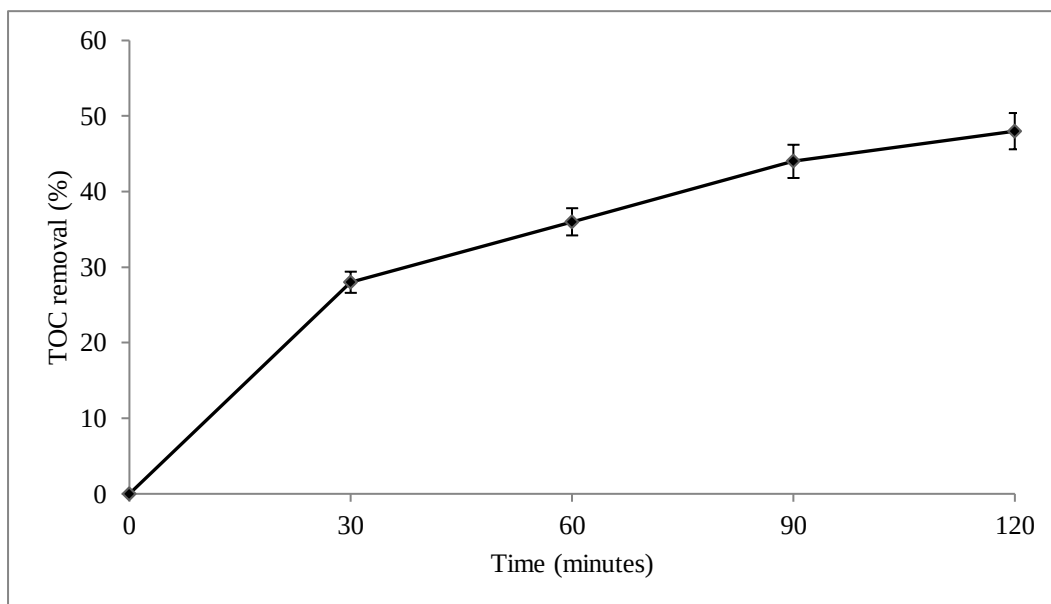


Figure 4.18: TOC removal against time for sago wastewater degradation under optimised photo-Fenton condition ($[\text{Fe}^{2+}] = 5.07 \text{ g/L}$; $[\text{H}_2\text{O}_2] = 4.01 \text{ mL/L}$; $\text{pH} = 2.66$).

The lower TOC conversion obtained could be attributed to the stable intermediates or partially oxidised by-products or organic matter which remained in the solution (Rabelo *et al.*, 2014). UV absorption of sago wastewater samples, 0 min (initial) and 120 min (final) treated under optimised photo-Fenton conditions which were recorded using UV-Vis spectrophotometer (Figure 4.19) supported the above reasoning. The UV profile at 0 min and 120 min indicated that the strong presence of compounds even at the end of the photo-Fenton treatment and bathochromic shift is notable. Judging from the UV profile, the formation or presence of stable intermediates at 120 min of photo-Fenton treatment could have inhibited from the complete mineralisation of organics (Machulek *et al.*, 2012). These stable intermediates could be present at high concentration in the solution, as indicated by the higher absorbance at absorption band at 276 nm (120 min) (Figure 4.19). Therefore, one possible way for achieving conversion of organic compounds present in the sago wastewater effluent is by extending the reaction time.

The mechanism of sago wastewater degradation was proposed. In the photo-Fenton process, the $\bullet\text{OH}$ radicals formed will attack the organics present in the sago wastewater effluent to form the intermediates before decomposing and mineralising them into simpler molecules, CO_2 and H_2O , as shown in Eq. 4.17 (Tokumura *et al.*, 2013).

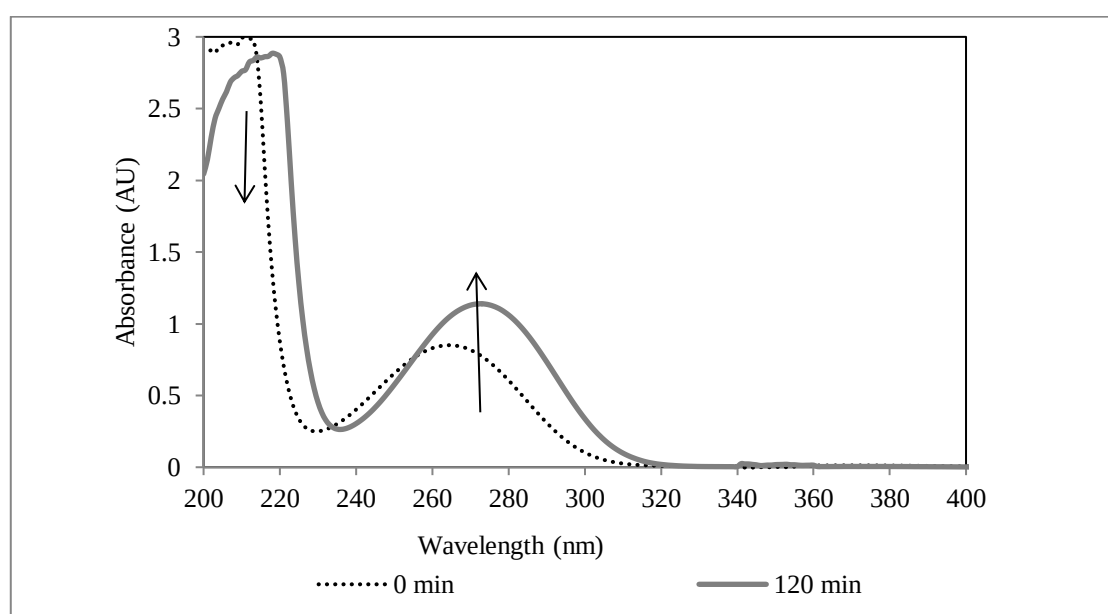


Figure 4.19: UV spectra of untreated sago wastewater and samples (initial and final) of optimised photo Fenton treatment ($[\text{Fe}^{2+}] = 5.07 \text{ g/L}$; $[\text{H}_2\text{O}_2] = 4.01 \text{ mL/L}$ and $\text{pH} = 2.66$).

4.5.9 Toxicity Evaluation

LC_{50} value is the lethal concentration of toxin that can kill 50% of the organisms in the test population (Letourneau & Burrows, 2001). Under the optimised concentration of $\text{Fe}^{2+} = 5.07 \text{ g/L}$ and $\text{H}_2\text{O}_2 = 4.01 \text{ mL/L}$, the mortality of *A. salina* in the treated sago wastewater was less than 50%, as shown in Figure 4.20. This simply means that the effluent produced under the treated under optimised concentration of Fe^{2+} ion and H_2O_2 can be regarded as non-toxic. The

mortality of *A. salina* for the control test was 10% in three replicates. Dojcinovic *et al.* (2016) stated that if the mortality in the control test did not exceed 10%, then the tests can be considered as valid. The mortality of *A. salina* for all the reaction times was found to be less than 50% except for the 60 minutes, as which the mortality was found to be 66.7% (Figure 4.20). This could be explained by the partial oxidation reaction that occurs in the photo-Fenton process. Organic pollutants are converted into stable intermediates such as formic acids, aldehydes and carboxylic acids (Rabelo *et al.*, 2014). Depending on the intermediate products formed, the partial oxidation of organic pollutants is able to lead to less or more toxic components in the wastewater (Dantas *et al.*, 2003). Hence, the highest mortality at 60 min might be due to the presence of stable intermediates in wastewater that could be toxic. Also, it is known that the presence of iron increases toxicity, depending on the iron concentration used in the treatment (Dantas *et al.*, 2003).

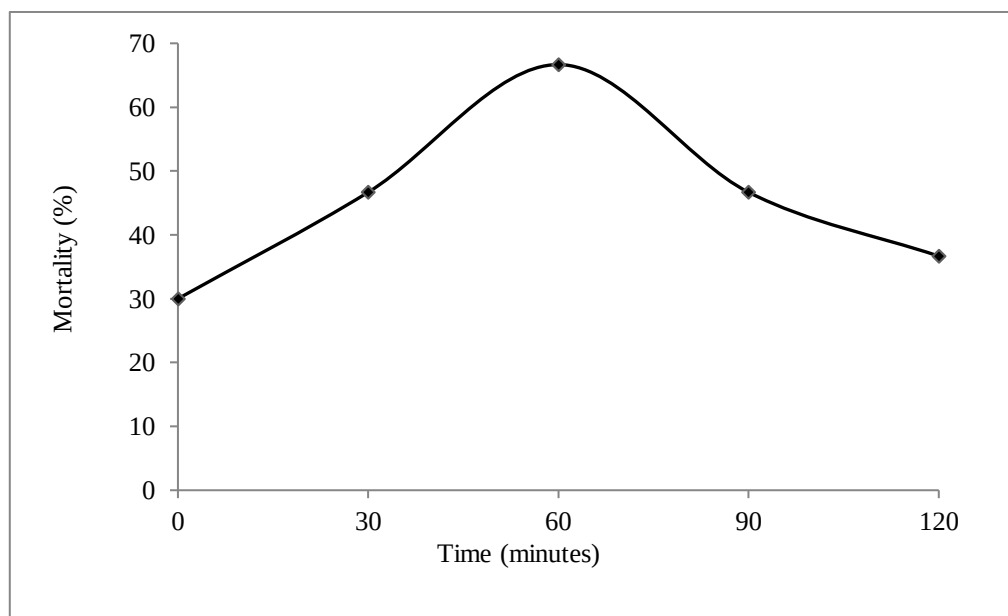


Figure 4.20: Mortality of *A. salina* in treated sago wastewater for different reaction times under optimised photo-Fenton condition ($[\text{Fe}^{2+}] = 5.07 \text{ g/L}$; $[\text{H}_2\text{O}_2] = 4.01 \text{ mL/L}$ and $\text{pH} = 2.66$).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The initial water quality characterisations performed on sago wastewater effluent revealed that appropriate treatment is necessary prior to its discharge into the environment. It has been demonstrated that both TiO_2 -mediated photocatalysis using a self-synthesised composite and photo-Fenton treatment were effective in the degradation of sago wastewater effluent.

Preparation of TiO_2 /MSB mixture was accomplished by attaching TiO_2 to the modified SB pretreated with acid treatment. Six different TiO_2 /MSB mixture samples were prepared to treat sago wastewater by varying TiO_2 and MSB concentrations. Among them, a maximum removal of 64.92% was achieved with an optimum loading of 0.2 g/L TiO_2 /1% MSB after 120 min of irradiation. This composite was chosen for the intensification of sago wastewater degradation by employing CCD based on RSM. The dosage and contact time were fixed as the independent variables while COD percentage removal was chosen as the dependent variable or response. Under optimised RSM condition, 52.83% of COD removal was attained using 0.10 g TiO_2 /MSB mixture and contact time 120 min. The efficiency of the optimised TiO_2 /MSB mixture was found to be appreciably enhanced in the presence of aeration, which increased the COD removal of sago wastewater to 63.89%. Thus, based on the proposed mechanism, the efficiency of the TiO_2 /MSB mixture was attributed to dual functions, namely the adsorption capacity of the MSB and the photocatalytic activity of TiO_2 .

The three main parameters, namely, initial pH, Fe^{2+} , and H_2O_2 concentration governing the performance of photo-Fenton treatment were explored. BBD based on RSM was applied to

optimise these intrinsic parameters. Optimal values of fixed independent variables, Fe^{2+} , and H_2O_2 concentration, and initial pH yielded a maximum percentage of 90.00% COD removal. The optimum conditions obtained with respect to the COD removal were $\text{H}_2\text{O}_2 = 4.01 \text{ mL/L}$, $\text{Fe}^{2+} = 5.07 \text{ g/L}$ and $\text{pH} = 2.66$. The R^2 value of the polynomial model ($R^2 > 0.99$) obtained from both TiO_2 photocatalytic and photo-Fenton treatments depicted the quality of the polynomial model fitting. Dark Fenton study conducted only removed 56.25% of COD from sago wastewater effluent confirming the superiority of photo-Fenton treatment for sago wastewater remediation. Despite the high COD removal, the TOC removal was found to be low, 48.0% under optimised condition. Contributing to the lower TOC removal was the stable intermediates or partially oxidised by-products or organic matter which remained in the solution. Under the optimum concentration of H_2O_2 and Fe^{2+} , the effluent mortality of *A. salina* was less than 50%, in which the toxicity of treated sago wastewater can be considered as non-toxic. Photo-Fenton treatment can be regarded as a suitable treatment for sago wastewater degradation. Although the treated solution demonstrated non-toxic characteristics, the presence of stable intermediates or partially mineralised organics during the treatment process was confirmed from TOC and UV-Vis analyses.

5.2 Recommendations

This study has open doors for possible future research and potential extensions of the TiO_2 photocatalysis and photo-Fenton treatment in treating sago wastewater. This study should be extended to include combined acid-alkali or alkali treatment to activate SB. The performance of TiO_2 /MSB mixture prepared from either acid-alkali or alkali activation can be explored as potential photocatalyst to degrade sago wastewater. The potential of other photocatalysts such

as zinc oxide (ZnO) and silicon dioxide (SiO₂) could be investigated instead of TiO₂ in the preparation of composite. To improve the photocatalytic activity of TiO₂ incorporated on MSB surface, metals doping (e.g. Ag, Pt, Ni, and Au) could be also investigated. Magnetic property can be incorporated in the TiO₂/MSB composite to facilitate better separation efficiency using external magnet after treatment.

Further photo-Fenton treatment needs to be carried out to investigate the contribution of aeration such as oxygen purging to increase the degradation rate and oxidation of organics in sago wastewater. It is also recommended to utilise solar irradiation as photon source to initiate the photo-Fenton process for sago wastewater degradation instead of artificial UV light since Malaysia receives large amounts of solar radiation throughout the year.

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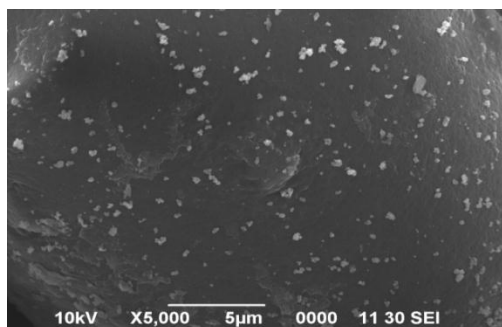
APPENDICES

Appendix 1: Raw data for characterization of sago wastewater.

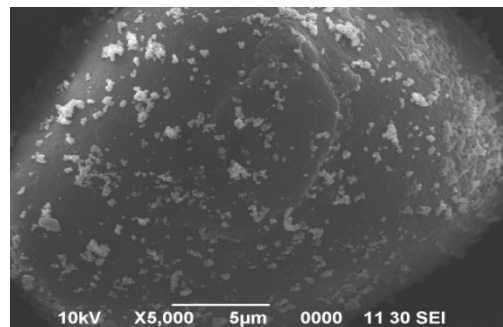
Reading	pH	First Sampling				
		TSS	BOD	COD	Turbidity (NTU)	DO
1 st	5.12	6990	3500	25536	537	0.80
2 nd	5.12	7990	2100	17024	537	0.90
3 rd	5.14	4000	3300	34048	566	1.00
		Second Sampling				
		TSS	BOD	COD	Turbidity (NTU)	DO
1 st	6.01	5100	800	6192	109	0.16
2 nd	6.06	8100	900	14448	110	0.16
3 rd	6.03	8200	900	18576	109	0.16

*All values using mg/L except pH and turbidity

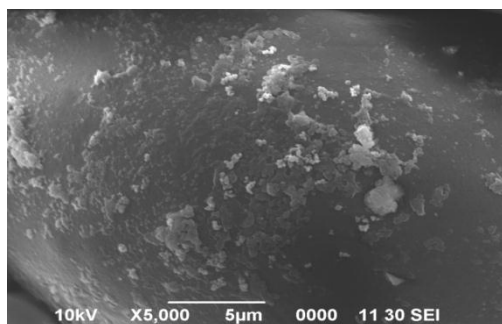
Appendix 2: SEM micrographs for other TiO₂ composites.



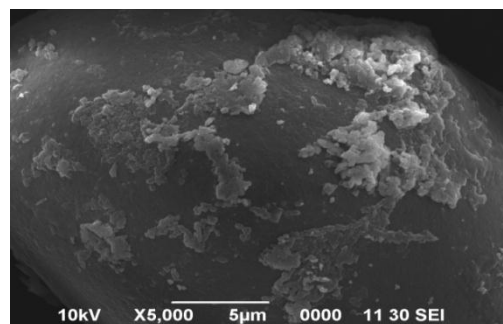
(a) 0.2 g/L TiO₂/3% MSB



(b) 0.4 g/L TiO₂/1% MSB

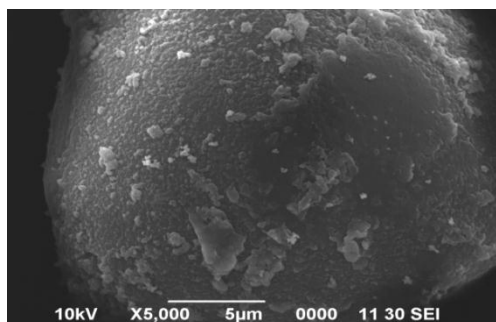


(c) 0.4 g/L TiO₂/3% MSB



(d) 0.8 g/L TiO₂/1% MSB

Appendix 2 continued



(e) 0.8 g/L TiO₂/3% MSB

Appendix 3: Photodegradation of sago wastewater under different conditions (a) sago, (b) MSB and (c) TiO₂ only.

(a) Sago only		
Time (min)	Average COD value$\pm$SD (mg/L)	COD removal (%)
T ₀	73.730 $\pm$ 1.93	0
T ₃₀	72.500 $\pm$ 5.61	1.70
T ₆₀	72.500 $\pm$ 3.14	1.70
T ₉₀	68.400 $\pm$ 7.40	7.20
T ₁₂₀	68.400 $\pm$ 3.01	7.20
(b) MSB only		
Time (min)	Average COD value$\pm$SD (mg/L)	COD removal (%)
T ₀	57.430 $\pm$ 3.53	0
T ₃₀	44.020 $\pm$ 4.55	23.40
T ₆₀	41.920 $\pm$ 6.17	27.00
T ₉₀	37.730 $\pm$ 5.29	34.30
T ₁₂₀	35.630 $\pm$ 7.43	37.90
(c) TiO₂ only		
Time (min)	Average COD value$\pm$SD (mg/L)	COD removal (%)
T ₀	24.960 $\pm$ 6.13	0
T ₃₀	15.808 $\pm$ 14.71	36.67
T ₆₀	16.640 $\pm$ 6.13	33.33
T ₉₀	13.728 $\pm$ 5.88	45.00
T ₁₂₀	14.976 $\pm$ 2.16	40.00

Appendix 4: Photocatalytic experiment using various TiO₂/MSB composites.

(a) 0.2 g/L TiO₂/1% MSB		
Time (min)	Average COD value±SD (mg/L)	COD removal (%)
T ₀	29.568±2.97	0
T ₃₀	14.784±5.97	50.00
T ₆₀	12.672±2.99	57.14
T ₉₀	11.827±6.22	60.00
T ₁₂₀	10.560±5.97	64.29
(b) 0.2 g/L TiO₂/3% MSB		
Time (min)	Average COD value±SD (mg/L)	COD removal (%)
T ₀	60.403±11.26	0
T ₃₀	46.464±4.07	23.08
T ₆₀	31.680±5.47	47.55
T ₉₀	23.232±8.20	61.54
T ₁₂₀	23.232±3.90	61.54
(c) 0.4 g/L TiO₂/1% MSB		
Time (min)	Average COD value±SD (mg/L)	COD removal (%)
T ₀	48.576±6.46	0
T ₃₀	45.197±8.47	15.46
T ₆₀	40.128±7.11	23.71
T ₉₀	30.835±5.98	30.93
T ₁₂₀	21.120±3.51	41.23
(d) 0.4 g/L TiO₂/3% MSB		
Time (min)	Average COD value±SD (mg/L)	COD removal (%)
T ₀	39.110±2.97	0
T ₃₀	33.062±5.90	15.46
T ₆₀	29.837±4.30	23.71
T ₉₀	27.014±4.35	30.93
T ₁₂₀	22.982±5.70	41.23
(e) 0.8 g/L TiO₂/1% MSB		
Time (min)	Average COD value±SD (mg/L)	COD removal (%)
T ₀	26.832±2.92	0
T ₃₀	26.006±10.17	3.08
T ₆₀	24.768±5.84	7.69
T ₉₀	20.640±10.92	23.08
T ₁₂₀	24.768±5.84	7.69
(f) 0.8 g/L TiO₂/3% MSB		
Time (min)	Average COD value±SD (mg/L)	COD removal (%)
T ₀	31.680±8.47	0
T ₃₀	29.568±10.17	6.67
T ₆₀	28.301±5.95	10.67
T ₉₀	22.387±3.64	29.33
T ₁₂₀	21.120±3.24	33.33

Appendix 5: TiO₂/MSB photocatalytic experiment using CCD *via* RSM.

Run	Time	Average COD value $\pm$ SD (mg/L)	COD removal (%)
1	T ₀	49.466 $\pm$ 6.36	0
	T ₁₂₀	39.824 $\pm$ 7.13	19.49
2	T ₀	58.688 $\pm$ 6.05	0
	T ₁₂₀	48.846 $\pm$ 6.14	16.77
3	T ₀	146.720 $\pm$ 19.21	0
	T ₁₂₀	124.502 $\pm$ 2.18	15.14
4	T ₀	57.344 $\pm$ 7.75	0
	T ₁₂₀	45.056 $\pm$ 2.45	21.43
5	T ₀	68.330 $\pm$ 7.26	0
	T ₁₂₀	55.754 $\pm$ 7.26	18.40
6	T ₀	88.032 $\pm$ 4.54	0
	T ₁₂₀	73.360 $\pm$ 7.36	16.67
7	T ₀	56.448 $\pm$ 4.26	0
	T ₁₂₀	36.288 $\pm$ 8.39	35.71
8	T ₀	7.546 $\pm$ 6.18	0
	T ₁₂₀	3.354 $\pm$ 2.18	55.55
9	T ₀	53.238 $\pm$ 9.44	0
	T ₁₂₀	41.920 $\pm$ 0.00	21.26
10	T ₀	39.514 $\pm$ 0.02	0
	T ₁₂₀	31.450 $\pm$ 2.85	20.41
11	T ₀	53.248 $\pm$ 4.03	0
	T ₁₂₀	36.864 $\pm$ 6.12	30.77
12	T ₀	50.304 $\pm$ 8.38	0
	T ₁₂₀	39.824 $\pm$ 8.89	20.83
13	T ₀	23.894 $\pm$ 0.00	0
	T ₁₂₀	11.318 $\pm$ 7.26	52.63

Appendix 6: ANOVA analysis for linear model of TiO₂/MSB photocatalysis.

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F value	p-value Prob> F
Model	1706.76	2	853.38	17.75	0.0005
X ₁	1506.97	1	1506.97	31.35	0.0002
X ₂	199.79	1	199.79	4.16	0.0688
Residual	480.65	10	48.06		
Lack of Fit	478.24	6	79.71	132.28	0.0001
Pure Error	2.41	4	0.60		
Cor Total	2187.41	12			

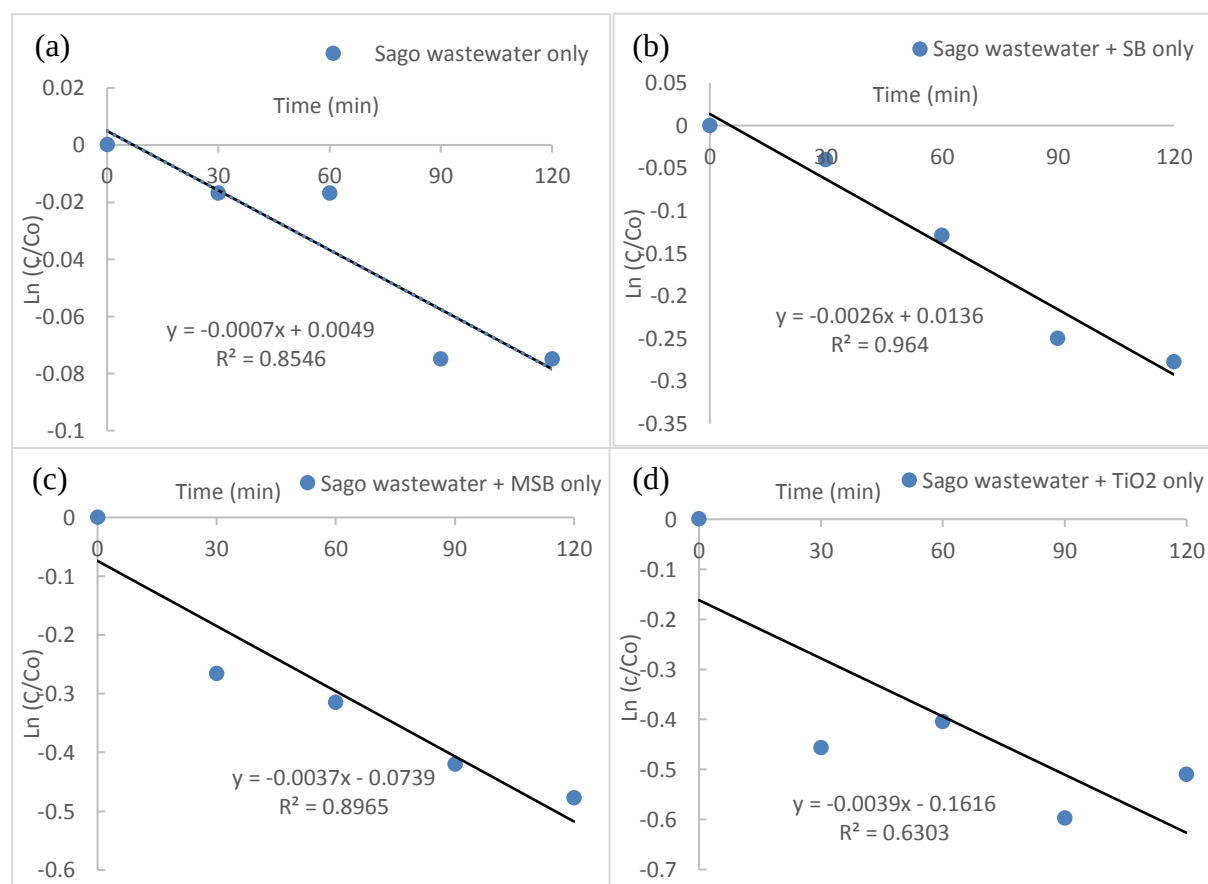
R² = 0.7803, Adj R² = 0.7363, Pred R² = 0.5972, Adeq Precision = 11.656, CV = 26.12%

Appendix 7: ANOVA analysis for 2F1 model of TiO₂/MSB photocatalysis.

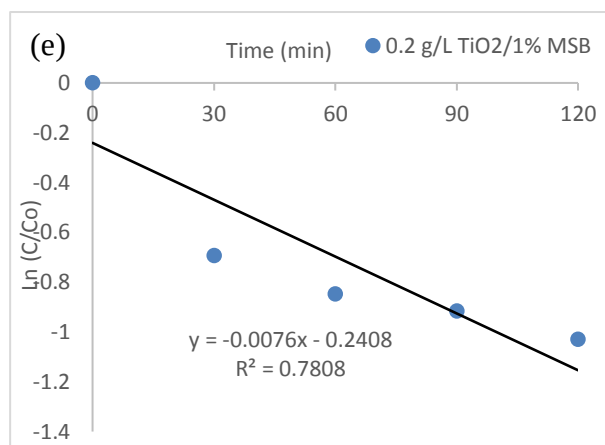
Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F value	p-value Prob> F
Model	1753.41	3	584.47	12.12	0.0016
X_1	1506.97	1	1506.97	31.25	0.0003
X_2	199.79	1	199.79	4.14	0.0723
X_1X_2	46.65	1	46.65	0.97	0.3510
Residual	434.00	9	48.22		
Lack of Fit	431.59	5	86.32	143.25	0.0001
Pure Error	2.41	4	0.60		
Cor Total	2187.41	12			

$R^2 = 0.8016$, Adj $R^2 = 0.7355$, Pred $R^2 = 0.5489$, Adeq Precision = 10.786, CV = 26.16%

Appendix 8: Kinetic graph for (a) sago wastewater; (b) sago wastewater + SB; (c) sago wastewater + MSB; (d) sago wastewater + TiO₂; and (e) sago wastewater + TiO₂/MSB mixture.



Appendix 8 continued



Appendix 9: COD and TOC value of treated sago wastewater under optimum condition.

COD value	
Time (min)	Average value $\pm$ SD (mg/L)
T ₀	2956.80 $\pm$ 298.68
T ₃₀	1478.40 $\pm$ 597.36
T ₆₀	1267.20 $\pm$ 298.68
T ₉₀	1182.70 $\pm$ 622.20
T ₁₂₀	1056.00 $\pm$ 597.36
TOC value	
Time (min)	Average value (mg/L)
T ₀	850.00
T ₃₀	900.00
T ₆₀	1050.00
T ₉₀	950.00
T ₁₂₀	900.00

Appendix 10: Comparison of TiO₂ photocatalysis under different conditions.

(a) 0.2 g/L TiO ₂ /1% SB		
Time	Average COD value $\pm$ SD (mg/L)	COD removal (%)
T ₀	13.107 $\pm$ 6.03	0
T ₁₂₀	7.373 $\pm$ 6.03	43.75
(b) 0.2 g/L TiO ₂ /1% MSB		
Time	Average COD value $\pm$ SD (mg/L)	COD removal (%)
T ₀	21.200 $\pm$ 5.89	0
T ₁₂₀	10.000 $\pm$ 8.49	52.83

Appendix 10 continued

(c) 0.2 g/L TiO₂/1% MSB + aeration		
Time	Average COD value±SD (mg/L)	COD removal (%)
T ₀	14.400±4.50	0
T ₁₂₀	5.200±5.67	63.89

Appendix 11: Photo-Fenton experiment using BBD *via* RSM.

Run	Time	Average COD value±SD (mg/L)	COD removal (%)
1	T ₀	14.000±5.66	0
	T ₁₂₀	6.000±0.00	57.14
2	T ₀	37.440±29.12	0
	T ₁₂₀	6.240±2.94	83.33
3	T ₀	23.712±9.37	0
	T ₁₂₀	12.480±0.00	47.37
4	T ₀	16.640±18.13	0
	T ₁₂₀	2.912±2.16	82.50
5	T ₀	37.440±11.00	0
	T ₁₂₀	26.208±4.69	30.00
6	T ₀	17.613±2.13	0
	T ₁₂₀	11.059±2.13	37.21
7	T ₀	21.200±8.17	0
	T ₁₂₀	20.000±6.93	5.66
8	T ₀	14.336±5.47	0
	T ₁₂₀	6.144±2.38	57.14
9	T ₀	24.259±2.21	0
	T ₁₂₀	18.301±2.21	24.56
10	T ₀	20.000±5.66	0
	T ₁₂₀	6.000±2.83	70.00
11	T ₀	8.064±4.03	0
	T ₁₂₀	1.210±2.33	85.00
12	T ₀	134.112±7.04	0
	T ₁₂₀	77.216±25.38	42.42
13	T ₀	13.517±2.13	0
	T ₁₂₀	2.048±2.90	84.85
14	T ₀	3.200±2.83	0
	T ₁₂₀	1.200±0.00	62.50
15	T ₀	27.418±5.94	0
	T ₁₂₀	14.112±6.98	48.53
16	T ₀	9.421±8.36	0
	T ₁₂₀	1.223±2.36	87.02
17	T ₀	14.336±7.09	0
	T ₁₂₀	2.048±0.00	85.71

Appendix 12: ANOVA analysis for linear model of photo-Fenton process.

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F value	p-value Prob> F
Model	3973.51	3	1324.50	2.86	0.0775
X_1	176.81	1	176.81	0.38	0.5470
X_2	3584.93	1	3584.93	7.75	0.0155
X_3	211.77	1	211.77	0.46	0.5105
Residual	6011.92	13	462.46		
Lack of Fit	6004.69	9	667.19	369.11	<0.0001
Pure Error	7.23	4	1.81		
Cor Total	9985.43	16			

$R^2 = 0.3979$, Adj $R^2 = 0.2590$, Pred $R^2 = 0.0896$, Adeq Precision = 5.045, CV = 36.89%

Appendix 13: ANOVA analysis for 2F1 model of photo-Fenton process.

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F value	p-value Prob> F
Model	4724.07	6	787.35	1.50	0.2730
X_1	176.81	1	176.81	0.34	0.5749
X_2	3584.93	1	3584.93	6.81	0.0260
X_3	211.77	1	211.77	0.40	0.5400
$X_1 X_2$	493.06	1	493.06	0.94	0.3558
$X_1 X_3$	20.34	1	20.34	0.039	0.8481
$X_2 X_3$	237.16	1	237.16	0.45	0.5172
Residual	5261.35	10	526.14		
Lack of Fit	5254.12	6	875.69	484.46	<0.0001
Pure Error	7.23	4	1.81		
Cor Total	9985.43	16			

$R^2 = 0.4731$, Adj $R^2 = 0.1570$, Pred $R^2 = -0.2526$, Adeq Precision = 4.823, CV = 39.35%

Appendix 14: Efficiency of photo-Fenton process.

(a) Fenton (Optimum condition)		
Time	Average COD value $\pm$ SD (mg/L)	COD removal (%)
T_0	9.421 $\pm$ 2.11	0
T_{120}	4.096 $\pm$ 0.00	56.52
(b) Photo-Fenton (Optimum condition)		
Time	Average COD value $\pm$ SD (mg/L)	COD removal (%)
T_0	12.192 $\pm$ 0.00	0
T_{120}	1.219 $\pm$ 0.81	90.00

Appendix 15: TOC removal under optimum photo-Fenton condition.

Time (min)	Average TOC value (mg/L)	TOC removal (%)
T ₀	2.5	0
T ₃₀	1.8	28.00
T ₆₀	1.6	36.00
T ₉₀	1.4	44.00
T ₁₂₀	1.3	48.00

Appendix 16: Toxicity test of treated sago wastewater under optimum photo-Fenton condition.

Time (min)	Average death of <i>A. salina</i> ±SD	Percentage of death (%)
T ₀	9±1.73	30.00
T ₃₀	14±3.21	46.67
T ₆₀	20±1.15	66.67
T ₉₀	14±1.53	46.67
T ₁₂₀	11±0.58	36.67

*Total *A. salina* for each interval in triplicate = 30