

**TREATMENT OF SIMULATED REFINERY BASED SULFIDIC SPENT
CAUSTIC USING PHOTO-FENTON OXIDATION**

SHARIFAH HANIS YASMIN BINTI SAYID ABDULLAH

UNIVERSITI TEKNOLOGI MALAYSIA

TREATMENT OF SIMULATED REFINERY BASED SULFIDIC SPENT CAUSTIC
USING PHOTO-FENTON OXIDATION

SHARIFAH HANIS YASMIN BINTI SAYID ABDULLAH

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For my beloved family that strengthen
me comes in every ways.

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ABSTRACT

Sulfidic spent caustic is the spent solution produced as a result of scrubbing process in a refinery operation. The hazardous and toxicity nature of sulfidic spent caustic indicated that this waste must be thoroughly treated before being dumped into the water sources. Since photo-Fenton oxidation has been widely applied for treatment of various types of wastewater, this study was performed to investigate the applicability of photo-Fenton oxidation for treating sulfidic spent caustic produced by refinery operation. The photo-Fenton oxidation of sulfidic spent caustic was carried out in a lab scale photo-reactor with working volume of 250 mL for 40 minutes reaction time. By using Response Surface Methodology (RSM), the optimal conditions for photo-Fenton oxidation process were found to be at Fe/H₂O₂ and H₂O₂/COD dosage ratio of 0.07 and 1.84 respectively. It was also found that photo-Fenton process exhibited higher degradation efficiency up to 96% chemical oxygen demand (COD) removal as compared to 83% in conventional Fenton. Higher reaction rate constant was obtained in photo-Fenton process (0.251 min⁻¹) as compared to Fenton process (0.169 min⁻¹). Furthermore, the degradation route of sulfidic spent caustic oxidation was established in this study where nearly all the sulfide compounds in the solution were degraded into sulfate end-products. The catalyst recycling study confirmed that the formed ferric sludge can be recycled back into the system as a catalyst up to six treatment cycles. In conclusion, photo-Fenton oxidation process was found to be an effective treatment option for the remediation of sulfidic spent caustic wastewater.

ABSTRAK

Air sisa kaustik merupakan air sisa yang terhasil daripada proses penyentalan yang dijalankan dalam operasi penapisan. Sifat air sisa ini yang sangat berbahaya dan juga toksik menyebabkan air sisa ini perlu dirawat dengan teliti sebelum dilepaskan ke dalam sumber air. Disebabkan aplikasi Fenton-cahaya yang meluas dalam merawat pelbagai jenis air sisa, kajian ini dijalankan untuk menyiasat keupayaan kaedah pengoksidaan Fenton-cahaya dalam merawat air sisa alkali yang dihasilkan daripada operasi penapisan. Proses pengoksidaan Fenton-cahaya telah dijalankan di dalam reaktor-cahaya dengan isipadu kerja sebanyak 250 mL selama 40 minit masa tindakbalas. Keadaan optimum telah ditemui pada nisbah dos $\text{Fe}/\text{H}_2\text{O}_2=0.07$ dan $\text{H}_2\text{O}_2/\text{COD}=1.84$ dengan menggunakan "Response Surface Methodology" (RSM). Didapati bahawa proses pengoksidaan Fenton-cahaya mempunyai keupayaan penguraian yang lebih tinggi yang mana sehingga 96% pengurangan permintaan oksigen kimia (COD) berjaya diperolehi apabila dibandingkan dengan hanya 83% dalam proses Fenton lazim. Nilai pemalar kadar tindakbalas yang lebih besar diperolehi dalam proses pengoksidaan Fenton-cahaya (0.251 min^{-1}) berbanding di dalam proses Fenton lazim (0.169 min^{-1}). Tambahan pula, laluan penguraian air sisa alkali turut dikaji di mana hampir semua bahan sulfida telah diuraikan kepada produk akhir sulfat. Kajian penggunaan semula pemangkin mendapati bahawa enapcemar yang terhasil dapat dikitar semula ke dalam sistem sebagai sumber pemangkin sehingga enam kali kitaran proses. Kesimpulannya, proses pengoksidaan Fenton-cahaya telah dikenalpasti sebagai satu rawatan berkesan dalam merawat air sisa alkali.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
AOPs	-	Advanced oxidation processes
AP	-	Adequate precision
BOD	-	Biochemical oxygen demand
CCD	-	Central composite design
COD	-	Chemical oxygen demand
CO ₂	-	Carbon dioxide
CV	-	Coefficient of variance
DMDS	-	Dimethyl disulfide
USEPA	-	United State environmental protection act
ET	-	Ethanethiol
FCC	-	Fluid catalytic cracking
FeSO ₄ .7H ₂ O	-	Ferrous sulfate
Fe ²⁺	-	Ferrous ion
Fe ³⁺	-	Ferric ion
FeOH ₃	-	Ferric hydroxide
[Fe(H ₂ O)] ²⁺	-	Ferric hydroxide complex
Fe/H ₂ O ₂	-	Ratio of ferrous ion with respect to hydrogen peroxide
H ⁺	-	Hydrogen cation
HCl	-	Hydrogen chloride
HPLC	-	High performance liquid chromatograph
H ₂ S	-	Hydrogen sulfide
H ₂ SO ₄	-	Sulphuric acid

H_2O_2	-	Hydrogen peroxide
$\text{HO}_2\bullet$	-	Hydroperoxy radical
HNO_3	-	Nitric acid
$\text{H}_2\text{O}_2/\text{COD}$	-	Ratio of hydrogen peroxide with respect to COD
LPG	-	Liquefied petroleum gas
LSR	-	Low straight run gasoline
MT	-	Methanethiol
MSDS	-	Material safety data sheet
NaOH	-	Sodium hydroxide
NaCl	-	Sodium chloride
NO_x	-	Nitrogen oxide
$\text{OH}\bullet$	-	Hydroxyl radical
O&G	-	Oil and grease
RCRA	-	Resource conservation and recovery act
RSM	-	Response surface methodology
R^2	-	Coefficient of determination
SD	-	Standard deviation
S^{2-}	-	Sulfide
S_2^{2-}	-	Disulfide
S_x^{2-}	-	Polysulfide
$\text{S}_2\text{O}_3^{2-}$	-	Thiosulfate
$\text{S}_x\text{O}_3^{2-}$	-	Polythiosulfate
$\text{S}_x\text{O}_6^{2-}$	-	Polythionate
SO_3^{2-}	-	Sulfite
SO_4^{2-}	-	Sulfate
SO_2	-	Sulfur dioxide
UV	-	Ultraviolet
UV/Vis	-	Ultraviolet/Visible light

WAO - Wet air oxidation

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Since ages ago, water is one of the most important parts in human's life. It is utilized to fulfil human needs of domestic use; foods, drinks, baths as well as agricultural activities, transportation, manufacturing and industrial activities. As the population grows, the demand for freshwater has boosted up concurrently with the industrialization and urbanization needs. Thus, a significant amount of wastewater was generated as a result of human activity in both domestic and industrial activities to increase their quality of life. However, those highly polluted water-carried waste is being vaguely treated and later tossed down into the environment. Consequently, the water pollution has resulted in other environmental crisis such as health problems, air pollution, odor problems and adversely affect aquatic life.

The main point sources of water pollution are domestic and industrial wastes. There are many types of industrial activities being held in Malaysia such as chemical,

petroleum, petrochemical, pulp and paper and dye and paint industries. Each type of industry differs in their basis of operation thus producing various types of waste. Due to the variety of waste produced, a great concern about the disposal of these wastes is growing in order to preserve and protect the environment. Thus, more stringent control of industrial effluent is being performed in order to promote greener and cleaner environment. Concomitant to that, development and implementation of new treatment technologies are encouraged to overcome the problems.

Petroleum refinery operation is a manufacturing process that converts crude oil and liquid gases into more useful products. Generally, in a refinery operation and hydrocarbon processing industries, sodium hydroxide or well-known as caustic solution is widely used in scrubbing process. Since it has been proven safe and economical, it is used as a medium to remove any contaminant mainly hydrogen sulfide and organic sulfur that are present in the hydrocarbon streams. Once the impurities are absorbed into the caustic solution, the solution is known as spent caustic.

Sulfidic spent caustic mainly have a large amount of residual alkalinity resulted from the absorption of caustic soda and high content of sulfide. It may create high odour problem (sulfurous) as it contains various toxic constituents which consist of hydrogen sulfide, thiols, phenols, amines, mercaptans and other organic compounds depending on the source. Sulfidic spent caustic is considered as highly reactive materials and incompatible with oxidizing agents, reducing agents, organic materials, acids and water (Rajganesh *et al.*, 1995a; Rajganesh *et al.*, 1995b; Sipma *et al.*, 2003, Park *et al.*, 2009). Typically, this spent caustic inhibited high toxicity in nature since it contains a high concentration of organic toxic compounds and inorganic ions. With these characteristics, spent caustic would be a hazardous polluting agent when it is liberally released to the environment.

Consequently, sulfidic spent caustic has been classified as scheduled waste (SW402) in Malaysia (www.doe.gov.my) and hazardous waste under the US Resource and Recovery Act (ecfr.gpoaccess.gov) due to its characteristic. Thus, a stringent practice should be conducted in order to manage the removal of this waste so that it will not pollute the environment in any way.

Previously, sulfidic spent caustic is typically being disposed by traditional methods such as deep well injection or either being sent-off to any commercial operations such as pulp and paper industry for recovery and reuse (Luck, 1999). However, with the growing concern among public, these traditional practices seem to be environmentally unacceptable. Additionally, reuse application is also a limited option since in the actual practice the transportation and handling costs are usually higher than the product value (Sipma *et al.*, 2004). Thus, new technologies and treatment methods are being explored with the intention of finding a better solution for sulfidic spent caustic disposal in line with the sustainable development endorsed by the government.

A number of options are available for the treatment of sulfidic spent caustic including both biological treatment as well as the chemical treatment processes. However, the extent of the performance is purely dependent on the nature and strength of the sulfidic spent caustic waste itself. Biological treatment is the most popular and widely used method all over the world in treating variety of waste. It is a cost effective approach for the removal of organics, sulfur and nitrogen compound in wastewater. The implementation of biological treatment is also being performed in removal of organic and sulfur compound in spent caustic waste (Rajganesh *et al.*, 1995a; Rajganesh *et al.*, 1995b; Sipma *et al.*, 2004). Several studies also show that chemical treatment is widely used in treating spent caustic. The practice includes extraction, acidification, combustion, oxidation or incineration process.

Recently, applications of advanced oxidation processes (AOPs) show a great potential in treating highly toxic organic contaminants (Luck, 1999). Numerous types of AOPs are frequently used including wet air oxidation, Fenton's reagent, treatment with ozone and photo-catalytic oxidation. Wet air oxidation (WAO) is an oxidation process of organic and inorganic materials in aqueous form by oxygen or air at elevated temperature and pressure (Luck, 1999; Sanchez-Oneto *et al.*, 2006; Bhargava *et al.*, 2006). Under this condition, the toxic organic compound will be decomposed into carbon dioxide, water and simpler organic compound which are readily biodegradable. WAO has been successfully applied in treating various type of wastewater.

Another AOPs is Fenton's reagent which was also being studied as the potential treatment method in spent caustic treatment (Shih and Hung, 2001). Fenton's oxidation process is an oxidation process that utilizes the use of hydrogen peroxide and iron salt. Reaction of both reagents resulted in generation of strong oxidizing agent which is hydroxyl radical. Application of Fenton's reagent in treating spent caustic shows great potential, since it is a simple process, effective, environmentally benign and taking place at low temperature and pressure compared to the WAO.

1.2 Problem Statement

Growing concern on the disposal method for sulfidic spent caustic has been increasing. Due to the toxic and hazardous nature of the wastewater, the release of this waste into the water bodies may bring potential hazards to the human health as well as the environment. Thus, sulfidic spent caustic must be properly and fairly treated before being dumped or disposed.

Currently, spent caustic waste is mostly being treated using on-site biological oxidation facility. Although the treatment is considered an inexpensive disposal option, the high toxicity and reactive nature of spent caustic often retard this practice. The capability of various chemical treatment processes in treating sulfidic spent caustic is proven by the reduction of sulfide compound in the treated effluent. However, high operational costs of these processes seem to prohibit further application in industry. For example, high operating condition in WAO causes it to be an economically ineffective option while Fenton's oxidation on the other hand, produces sludge at the end of the treatment which may create disposal problems.

Photo-Fenton oxidation is an improvement to the Fenton's reagent. In photo-Fenton oxidation process, an additional source of ultraviolet (UV) irradiation is included in the system. With the presence of UV irradiation, higher rate of reaction could be achieved, thus resulting in higher degradation efficiency (Bauer and Fallman, 1997; Huang *et al.*, 2007; Malato *et al.*, 2001; Nunez *et al.*, 2007; Tamimi *et al.*, 2008; Mosteo *et al.*, 2008). Its ability of oxidizing and mineralizing almost any organic and inorganic compound was proven in previous works. In addition, the ambient operational condition in photo-Fenton becomes an additional benefit when compared to other AOPs. Lower sludge production could be obtained in photo-Fenton via photo-reduction of ferric ion with the aid of UV illumination. However, apparently, not much study has been conducted on the treatment of sulfidic spent caustic using photo-Fenton oxidation. For this reason, photo-Fenton treatment is chosen as the proposed treatment method for the treatment of sulfidic spent caustic.

1.3 Objective of Study

The objectives of this study are:

- To determine the impact of various operating conditions such as hydrogen peroxide dosage, ferrous ion dosage and UV light intensity on photo-Fenton's performance.
- To determine the applicability of recycling ferric sludge into the process.
- To determine the hydroxyl radical oxidation pathway of sulfidic spent caustic.

1.4 Scope of Study

Several scopes have been drawn in order to achieve the study objectives as stated before which include:

- The photo-Fenton oxidation is carried out in a lab-scale operation which utilized the use of synthetic wastewater as the influent.
- Study the effect of different operating conditions such as dosage of ferrous ion and hydrogen peroxide, UV exposure and UV irradiation time towards the performance of photo-Fenton oxidation.
- The variables are being investigated in the range of Fe/H₂O₂ (0.01 – 0.20), H₂O₂/COD (1.00 – 4.00), UV exposure (0 – 100%) and UV irradiation time (0-40 min).
- The performance of photo-Fenton process is indicated by the percentage removal of COD and sulfide concentration.

- Optimization of the reagent dosing using response surface methodology (RSM).
- Catalyst recycling is being investigated by recycling of the precipitated ferric back into the system.
- Chemical pathway and kinetics of the reaction are determined by using high performance liquid chromatography.
- Comparison study on the performance of Fenton and photo-Fenton processes in terms of chemical degradability and degradation kinetics.

1.5 Significance of Research

The significance of this research are highlighted as follows:

- Development of photo-Fenton oxidation as a treatment option for treating sulfidic spent caustic wastewater.
- Development of the empirical models describing the relationship between reacting conditions and performance of photo-Fenton in terms of both COD and sulfide removal.
- Understanding on the reaction pathway for sulfide oxidation by using photo-Fenton oxidation.

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