INDUSTRIAL WASTEWATER TREATMENT
VIA PHOTO FENTON

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ABSTRACT

Fenton reagent has been in existence for more than 100 years, but interest in investigating the feasibility of Fenton reagent in degrading different organics is quite recent (about 20 years). The purpose of this study is to conduct experimental tests employing the Fenton oxidation process in treating the industrial detergent wastewater with the presence of UV-light. In order to achieve the objective of the research study, several scopes have been identified: to characterize and analyze the industrial detergent wastewater before and after Fenton process, to study the effect of ultraviolet exposure on Fenton process in treating industrial detergent wastewater, and to investigate the optimal process parameters (H_2O_2 dosage, Fe^{2+} concentrations, optimal Fe^{2+}/H_2O_2 molar ratios), and mineralization rates as well as the overall process efficiency. From the result obtained, the optimum operating condition of photo-Fenton oxidation process were involve 1500mg/L $FeSO_4.7H_2O$ & 0.1M H_2O_2, (comply with Standard B) which COD achieve 23mg/L (98.7%) and turbidity reduction exceed 99%, optimum molar ratio more than 1 (COD removal > 94 %), X25 dilution factor (WW concentration to distilled water) and pH under 3. 1500 mg/L H_2O_2 was chosen as the best result of all the experiment. Total COD reduction of COD was up until 94%, while the turbidity reduce was 99.6%, and the color become totally clear. As conclusion, the treated wastewater is up to standard of Department of Environment Malaysia (DOE) 1974, which is comply the discharge permit of Standard B, means it is safe to be discharge to the river/downstream because it will not harm the environment, or else to undergo the next mineralization process, such as membrane filtration.

ABSTRAK

Bahan uji Fenton telah wujud lebih daripada 100 tahun, tetapi kepentingan dalam penyiasatan kemungkinan bahan uji Fenton tidak meluas berbanding organik pada hari ini (sekitar 20 tahun). Tujuan kajian ini ialah untuk menjalankan eksperimen tentang proses pengoksidaan Fenton dalam merawat air buangan bahan pencuci dari industri dengan kehadiran cahaya UV. Dalam mencapai objektif kajian, beberapa ruang lingkup telah dikenalpasti: untuk menganalisa air buangan bahan pencuci dari industri sebelum dan selepas proses Fenton, untuk mengkaji kesan pendedahan ultralembayung pada proses Fenton dalam merawat air buangan bahan pencuci dari industry dan bagi menyiasat proses parameter yang optimum (Jumlah H_2O_2 dan Fe^{2+}, nisbah Fe^{2+}/H_2O_2 yang optimum), dan tahap penulenan serta kecekapan keseluruhan proses. Daripada keputusan diperolehi, kadar optimum foto Fenton dalam proses pengoksidaan melibatkan 1500mg / L $FeSO_4.7H_2O$ & 0.1M H_2O_2, (memenuhi Standard B) yang COD mencapai 23mg / L (98.7%) dan pengurangan kekeruhan melebihi 99%, nisbah molar optimum lebih daripada 1 (Penyingkiran COD > 94 %), faktor pencairan X25 (Nisbah air buangan: air suling) dan pH di bawah 3. 1500 mg / L H_2O_2 telah dipilih sebagai keputusan terbaik semua eksperimen. Pengurangan COD berjumlah COD sehingga 94%, manakala mengurangkan kekeruhan sehingga 99.6%, dan warna menjadi jelas. Sebagai kesimpulan, diperlakukan air buangan bergantung kepada standard Bahagian Kualiti Alam Malaysia 1974, yang mematuhi permit buangan Standard B, adalah selamat untuk dilepaskan ke sungai kerana ia tidak akan merosakkan persekitaran atau untuk meneruskan proses penulenan yang seterusnya seperti membran penurasan.

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% Removal	-	Percentage of removal
$[H_3O_2]^+$	-	Peroxone ion
AOPs	-	Advanced oxidation process
COD	-	Chemical oxygen demand
COD_0	-	Initial COD
COD_t	-	COD at t time
Fe^{2+}	-	Ion ferum (+2)
Fe^{3+}	-	Ion ferum (+3)
$FeSO_4.7H_2O$	-	Ferrous sulphate
H^+	-	Hydogen ion
H_2O_2	-	Hydrogen peroxide
HCl	-	Hydrochloric Acid
HO•	-	Hydroxyl radical
hr	-	Hour
LAS	-	Linear Alkylbenzene Sulfonate
NaOH	-	Sodium hydroxide
NTU	-	Nephelometric *Turbidity* Units
ppm	-	part per million
t	-	Time

T_0	-	Initial turbidity
TSS	-	Total suspended solid
TSS_0	-	Initial total suspended solid
TSSt	-	Total suspended solid at time, t
Tt	-	Turbidity at time, t
UV	-	Ultraviolet

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CHAPTER 1

INTRODUCTION

1.1 Background of the study

The water and wastewater pollution control is one of today's main fields of scientific activity. More and more the ecosystem is loaded with large quantities of surfactants, which are the main component of widely used household detergents. Surfactants have also been widely used in textile, fiber, food, paints, polymers, plant protection, cosmetics, pharmaceuticals as well as mining, pulp and paper industries. Among wide range of surfactant types, linear alkylbenzene sulfonate (LAS), the most common synthetic anionic surfactant used in domestic and industrial detergents, has a global production of about $2.4x10^6$ tonnes per year (Papic *et al.,* 2008). LAS are produced by sulfonation of linear alkylbenzene with sulfur trioxide. LAS is a mixture of closely related isomers and homologues, each containing an aromatic ring sulfonated at the *para* position and attached to a linear alkyl chain with the length which varies between C_{10} and C_{14} (Papic et al., 2008). Detergents usually contain 5 - 25 % of LAS.

From the environmental point of view, it is the major anthropogenic source of organic compounds in primary sludge of the municipal wastewater treatment plants. It can be adsorbed onto suspended solids ranging from 30 to 70 % and, hence, escaping aerobic treatment. It has also been identified in surface water supplies in the concentrations lower than 1 μg dm^{-3}, and in the drinking water with the concentrations of 0.001 - 0.008 mg dm^{-3} (Tabrizi *et al.,* 2006). It has been reported that LAS at higher concentrations, between 20 and 50 mg dm^{-3}, such as in detergent manufacturing wastewaters, is not biodegradable. It is implied that some of chemical processes need to be used to degrade aqueous LAS. Among these processes advanced oxidation processes (AOPs) are attractive alternatives for the treatment of wastewater containing bioresistant compounds. AOPs are processes that produce highly reactive intermediates, mainly hydroxyl radicals (·OH), which are able to oxidize almost all organic pollutants to CO_2 and H_2O. An alternative advanced oxidation method which achieves high efficiency with a low treatment cost would be highly desirable.

The methods meeting these requirements are Fenton and photo-Fenton processes. These AOPs have been successfully applied for the treatment of the surfactant wastewater. Fenton and photo-Fenton reactions are AOPs where oxidant species are generated from hydrogen peroxide and Fe^{2+}/Fe^{3+} as a catalyst (Nunez et al., 2006). In Fenton reaction ferrous salts react with hydrogen peroxide and generate the hydroxyl radicals as follows (reaction 1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + HO^- \quad (1)$$

Then, Fe^{3+} can be reduced by reaction with exceeding H_2O_2 to form ferrous ion again and additional amount of hydroxyl radicals. This second process is called "Fenton like process". It is slower than Fenton reaction and allows Fe^{2+} regeneration giving the place to a catalytic mechanism (reactions 2 -4):

$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^+ \quad (2)$$

$$FeOOH^{2+} \rightarrow HO\cdot_2 + Fe^{2+} \quad (3)$$

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

The rate of contaminant's degradation can be considerably increased via photochemical reaction in the photo-Fenton process. In this case, the regeneration of Fe^{2+}, with additional production of HO· radicals, is followed by photo reduction process (reactions 5 and 6):

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \quad (5)$$

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO\cdot \quad \lambda < 410 \text{ nm} \tag{6}$$

The UV irradiation radiation (UV-C 254 nm), was used to enhance degradation (mineralization) of surfactant present in synthetic wastewater.

1.2 Problem statement

The domestic use and industrial activity, of especially impact among the developed countries, generate high amounts of residual wastewater, whose direct disposal to natural channels causes a considerable effect in the environment. This fact, together with the need to restore this water for new uses, makes practically essential the purification of wastewater to achieve the desired degree of quality.

Addressing these problems calls out for a tremendous amount of research to be conducted to identify robust new methods of purifying water at lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on the environment. The many problems worldwide associated with the lack of clean, fresh water are well known: 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, and millions of people die annually – 3900 children a day – from diseases transmitted through unsafe water or human excreta.

Conventional methods of water disinfection and decontamination can address many of these problems. However, these treatment methods are often chemically, energetically and operationally intensive, focused on large systems, and thus require considerable infusion of capital, engineering expertise and infrastructure, all of which precludes their use in much of the world. Furthermore, intensive chemical treatments (such as those involving ammonia, chlorine compounds, hydrochloric acid, sodium hydroxide, ozone, permanganate, alum and ferric salts, coagulation and filtration aids, anti-scalants, corrosion control chemicals, and ion exchange resins and regenerates) and residuals resulting from treatment (sludge, brines, toxic waste) can add to the problems of contamination and salting of freshwater sources.

Municipal wastewaters are commonly treated by activated sludge systems that use suspended microbes to remove organics and nutrients, and large sedimentation tanks to separate the solid and liquid fractions. This level of treatment produces wastewater effluent suitable for discharge to surface waters or for restricted irrigation and some industrial applications. Current wastewater reuse systems use a conventional activated sludge process, followed by a microfiltration pretreatment of the secondary effluent, which has high quantities of suspended and dissolved solids. The effluent water still partially contains dissolved species and colloidal substances that act to foul the membranes of the subsequent Reverse Osmosis (RO) system used as a final barrier to contaminants in the product water.

The past study for the treatment of surfactant wastewater by the advanced oxidation processes (AOPs), are well known for their capacity for oxidizing and mineralizing almost any organic contaminant. Nevertheless, technical applications are still scarce. As the process costs may be considered the main obstacle to their commercial application, several promising cost-cutting approaches have been proposed, such as integration of AOPs as part of a treatment train. In the typical basic process design approach an AOP pretreats non-biodegradable or toxic wastewater, and once biodegradability has been achieved, the effluent is transferred to a cheaper biological treatment. The key is to minimize residence time and reagent consumption in the more expensive AOP stage by applying an optimized coupling strategy.

Other proposed cost-cutting measures are the use of renewable energy sources, i.e., sunlight and UV-lamp as the irradiation source for running the AOP. So, for this present study, an alternative advanced oxidation method will be proposed. The methods meeting these requirements are Fenton and photo-Fenton processes. Fenton and photo-Fenton reactions are AOPs where oxidant species are generated from hydrogen peroxide and Fe^{2+} as a catalyst. This process will achieve high efficiency with a low treatment cost, which will be highly desirable.

1.3 Objectives

The purpose of this study is to conduct experimental tests employing the Fenton oxidation process in treating the industrial detergent wastewater with the presence of UV-light.

1.4 Scope of study

In order to achieve the objective of the research study, several scopes have been identified:

i. To characterize and analyze the industrial detergent wastewater before and after Fenton process.
ii. To study the effect of ultraviolet exposure on Fenton process in treating industrial detergent wastewater.
iii. To investigate the optimal process parameters (H_2O_2 dosage, Fe^{2+} concentrations, optimal Fe^{2+}/H_2O_2 molar ratios), and mineralization rates as well as the overall process efficiency.

While the experimental schedule to test all this parameter are Chemical, Oxygen Demand (COD), turbidity of the surfactant, and total suspended solid with the effect of color and odor.

CHAPTER 2

LITERATURE REVIEW

2.1 Industrial wastewater

This chapter will covers sources of industrial wastewater, detergent, the treatments including basic principles in advanced oxidation processes (AOPs), physical and biological treatment, Chemical Oxygen Demand (COD), flocculation, turbidity, total suspended solid, Fenton's reagent process description including solar photo-Fenton and UV photo Fenton, the reactor lamp configuration and overview of previous study.

2.1.1 Introduction

Industrial wastes are those wastes arising from industrial activities and typically include rubbish, ashes, construction wastes, special waste and hazardous wastes. A treatment of the wastewater is compulsory to any factories before disposing process into the waterways, such that the treated wastewater discharge standard. In minimizing the operational and maintenance cost of the conventional wastewater treatment utilities, an alternatives such as photo degradation and Fenton's reagent has been addressed as for its simplicity operational and cost effectiveness.

2.1.2 Sources of industrial wastewater

There are a few of sources of the industrial wastewater that may be existence nowadays. In this subtopic will be discuses a little bit about the sources of wastewater in related industries, for instance iron and steel, mines and quarries, food industries and complex organic chemicals industries.

2.1.2.1 Iron and steel industry

The production of iron from its ores involves powerful reduction reactions in blast furnaces. Cooling waters are inevitably contaminated with products especially ammonia and cyanide. Production of coke from coal in coking plants also requires water cooling and the use of water in by-products separation. Contamination of waste streams includes gasification products such as benzene, naphthalene, anthracite, cyanide, ammonia, phenols, cresols together with a range of more complex organic compounds known collectively as polycyclic aromatic hydrocarbons (PAH).

The conversion of iron or steel into sheet, wire or rods requires hot and cold mechanical transformation stages frequently employing water as a lubricant and coolant. Contaminants include hydraulic oils, tallow and particulate solids. Final treatment of iron and steel products before onward sale into manufacturing includes pickling in strong mineral acid to remove rust and prepare the surface for tin or chromium plating or for other surface treatments such as galvanization or painting. The two acids commonly used are hydrochloric acid and sulfuric acid. Wastewaters include acidic rinse waters together with waste acid. Although many plants operate acid recovery plants, (particularly those using Hydrochloric acid), where the mineral acid is boiled away from the iron salts, there remains a large volume of highly acid ferrous sulfate or ferrous chloride to be disposed of. Many steel industry wastewaters are contaminated by hydraulic oil also known as soluble oil.

2.1.2.2 Mines and quarries

The principal waste-waters associated with mines and quarries are slurries of rock particles in water. These arise from rainfall washing exposed surfaces and haul roads and also from rock washing and grading processes. Volumes of water can be very high; especially rainfall related arising on large sites. Some specialized separation operations, such as coal washing to separate coal from native rock using density gradients, can produce wastewater contaminated by fine particulate hematite and surfactants. Oils and hydraulic oils are also common contaminants. Wastewater from metal mines and ore recovery plants are inevitably contaminated by the minerals present in the native rock formations. Following crushing and extraction of the desirable materials, undesirable materials may become contaminated in the wastewater.

For metal mines, this can include unwanted metals such as zinc and other materials such as arsenic. Extraction of high value metals such as gold and silver may generate slimes containing very fine particles in where physical removal of contaminants becomes particularly difficult.

2.1.2.3 Food industry

Wastewater generated from agricultural and food operations has distinctive characteristics that set it apart from common municipal wastewater managed by public or private wastewater treatment plants throughout the world: it is biodegradable and nontoxic, but that has high concentrations of biochemical oxygen demand (BOD) and suspended solids (SS). The constituents of food and agriculture wastewater are often complex to predict due to the differences in BOD and pH in effluents from vegetable, fruit, and meat products and due to the seasonal nature of food processing and post harvesting.

Processing of food from raw materials requires large volumes of high grade water. Vegetable washing generates waters with high loads of particulate matter and some dissolved organics. It may also contain surfactants.

2.1.2.4 Complex organic chemicals industry

A range of industries manufacture or use complex organic chemicals. These include pesticides, pharmaceuticals, paints and dyes, petro-chemicals, detergents, plastics, paper pollution, etc. Wastewaters can be contaminated by feed-stock materials, by-products, product material in soluble or particulate form, washing and cleaning agents, solvents and added value products such as plasticizers.

2.1.3 Detergent

A detergent is a material intended to assist cleaning. The term is sometimes used to differentiate between soap and other surfactants used for cleaning. Sometimes the word detergent is used to distinguish a cleaning agent from soap. During the early development of non-soap surfactants as commercial cleaning products, the term syndet, short for synthetic detergent was promoted to indicate the distinction. The term never became popular and is incorrect, because most soap is itself synthesized (from glycerides). The term soapless soap also saw a brief vogue.

2.1.3.1 Terminology

The term detergent by itself is sometimes used to refer specifically to clothing detergent, as opposed to hand soap or other types of cleaning agents. Plain water, if used for cleaning, is a detergent. Probably the most widely-used detergents other than water are soaps or mixtures composed chiefly of soaps. However, not all soaps have significant detergency and, although the words "detergent" and "soap" are sometimes used interchangeably, not every detergent is soap. The term detergent is sometimes used to refer to any surfactant, even when it is not used for cleaning. This terminology should be avoided as long as the term surfactant itself is available.

2.1.3.2 Components

Detergents, especially those made for use with water, often include different components such as surfactants to 'cut' (Emulsify) grease and to wet surfaces, abrasive to scour, substances to modify pH or to affect performance or stability of other ingredients, acids for descaling or caustics to break down organic compounds, water softeners to counteract the effect of "hardness" ions on other ingredients, oxidants (oxidizers) for bleaching, disinfection, and breaking down organic compounds, non-surfactant materials that keep dirt in suspension, enzymes to digest proteins, fats, or carbohydrates in stains or to modify fabric feel, ingredients that modify the foaming properties of the cleaning surfactants, to either stabilize or counteract foam, ingredients to increase or decrease the viscosity of the solution, or to keep other ingredients in solution, in a detergent supplied as a water solution or gel, ingredients such as corrosion inhibitors to counteract damage to equipment with which the detergent is used, ingredients to reduce harm or produce benefits to skin, when the detergent is used by bare hand on inanimate objects or used to clean skin and preservatives to prevent spoilage of other ingredients.

2.1.4 Linear alkylbenzene sulfonate (LAS)

Hydro treated kerosene is the feedstock for high purity linear paraffins which are subsequently dehydrogenated to linear olefins. The resulting linear mono-olefins are reacted with benzene in the presence of a catalyst to produce linear alkylbenzene. Linear alkylbenzene is sulfonated to produce linear alkylbenzene sulfonate (LAS), a biodegradable surfactant detergent. LAS replaced dodecylbenzene sulfonates which have slower biodegradation rates. There are currently challenges to the dominance of LAS from detergent alcohol derivatives.

Hydrogen fluoride (HF) and aluminum chloride ($AlCl_3$) are the two major catalysts for benzene alkylation with linear mono-olefins (C_{10}-C_{16}). The HF-based process became commercially dominant; however, the risk of releasing HF (a poisonous substance) into the environment became a concern particularly after the Clean Air Act Amendment. In 1995, a solid catalyst system (the DETAL process) became available. The process eliminates catalyst neutralization and HF disposal. Consequently, most LAB plants built since then have utilized this process.

2.2 Treatment for industrial wastewater

The different types of contamination of wastewater require a variety of strategies to remove the contamination. Below will be discussed about the some of the treatment in industries, such as physical and chemical treatment, primary treatment and secondary treatment, like oil and grease removal and solid removal.

2.2.1 Oils and grease removal

Many oils can be recoverd from open water surface by skimming devices. Considered a dependable and cheap way to remove oil, grease and other hydrocarbons from water, oil skimmer can sometimes achieve the desired level of water purity. At the other times, skimming is also a cost-efficient method to remove most of the oil before using membrane filters and chemical processes. Skimmers will prevent filters from blinding prematurely and keep chemical cost down because there is less oil to process.

The wastewater from large-scale industries such as oil refineries, petrochemical plants, chemical plants, and natural gas processing plants commonly contain gross amounts of oil and suspended solids. Those industries use a device known as API oil-water separator which is designed to separate the oil and suspended solids from their wastewater effluents. The name is derived from the fact that such separators are designed according to standards published by the American Petroleum Institute (API).

The API separator is a gravity separation device designed by using Stokes Law to define the rise velocity of oil droplets based on their density and size. The design is based on the specific gravity difference between oil and the wastewater because that difference is much smaller than the specific gravity difference between the suspended solids and water. The suspended solids settles to the bottom of the separator as a sediment layer, the oil rises to top of the separator and the cleansed wastewater is the middle layer between the oil layer and the solids.

2.3 Physical treatment

In this physical, it is contains solid removal, total suspended solid, flocculation and turbidity. This subsection below will explain detail about the treatment occur during the experiments.

2.3.1 Solids removal

Most solids can be removed using simple sedimentation techniques with the solids recovered as slurry or sludge. Very fine solids and solids with densities close to the density of water pose special problems. In such case filtration or ultrafiltration may be required. Alternatively, flocculation may be used, using alum salts or the addition of polyelectrolyte.

2.3.2 Total Suspended Solid (TSS)

Most turbidity is related to the smaller inorganic components of the suspended solids burden, primarily the clay particles. Suspended material is objectionable because it provides adsorption sites for biological and chemical agents. So, suspended solids in water may be degraded biologically resulting in objectionable byproducts. The removal of these solids is of great concern in the production of clean, safe drinking water and wastewater effluent.

2.3.3 Turbidity

Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended material in water. Most turbidity is related to the smaller inorganic components of the suspended solids burden, primarily the clay particles. The colloidal material associated with turbidity provides absorption sites for microorganisms and chemicals that may be harmful or cause undesirable tastes and odors. Turbidity is useful in measuring drinking-water quality. Detergents, soaps, and various emulsifying agents contribute to turbidity

2.4 Biological and chemical treatment

For biological and chemical treatments, there are several treatment that possible to be apply to the wastewater, for examples removal of biodegradable organics, activated sludge, as well as Chemical Oxygen Demand (COD).