TREATMENT OF INDUSTRIAL WASTEWATER BY FENTON PROCESS
COMBINE WITH COAGULATION

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the requirement of the award of the degree of
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Attempts were made in this study to examine the efficiency of Fenton process combined with coagulation for treatment of water-based printing ink wastewater. Parameters affecting the Fenton process, such as pH, dosages of Fenton reagents and the contact time, were determined by using jar test experiments 98% of turbidity and 54% of chemical oxygen demand (COD) and 14% of biological oxygen demand (BOD) could be removed at pH 4, 0.8 ml/L H2O2, 25 mg/l FeSO4 and 40 minutes contact time. The coagulation using fenugreek and ferrous sulfate (FeSO4) was beneficial to improve the Fenton process treated effluent in reducing the flocs settling time, enhancing turbidity, COD and BOD removal. The overall turbidity, COD and BOD removal reached 99%, 63% and 39.5% under selected conditions, respectively. Thus this study might offer an effective way for wastewater treatment of water-based ink manufacturer and printing corporation.
ABSTRAK

Percubaan telah dibuat dalam kajian ini bagi meneliti kecekapan Fenton proses bergabung dengan penggumpalan untuk rawatan air buangan dakwat cetak berasaskan air. Parameter mempengaruhi proses Fenton, seperti pH, sukat reagen Fenton dan masa yang diperlukan untuk rawatan telah ditentukan dengan menggunakan ujian balang bereksperimen. Keputusannya, 98 % kekeruhan dan 54% keperluan oksigen kimia (COD) dan 14% keperluan oksigen biologi (BOD) boleh dirawat di pH 4, 0.8 ml / L H2O2, 25 mg / l FeSO4 dan 40 minit masa rawatan. Penggumpalan menggunakan halba dan ferus sulfat (FeSO4) bermanfaat bagi meningkatkan proses Fenton diperlakukan efluen dalam mengurangkan flocs masa penetapan, mempertingkatkan kekeruhan, COD dan penyingkiran BOD. Kekeruhan menyeluruh, COD dan penyingkiran BOD dicapai 99%, 63% dan 39.5% di bawah keadaan-keadaan terpilih, masing-masing. Maka kajian ini mungkin menawarkan satu cara berkesan untuk rawatan air buangan pengeluar dakwat berasaskan air dan perbadanan percetakan.
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CHAPTER 1

INTRODUCTION

1.1 Background.

In industrial scale, wastewater treatment is always highly concerned in the sake of environmental protection. A considerable effort has been made into exploring and implementing new methods of wastewater treatment. The principle way to remove the pollutants from wastewater is by combining different treatment methods in one wastewater treatment system. In some treatments, the combination of physical, chemical and biological methods are required to achieve high removal efficiency of pollutants. As an example of these combinations, chemical oxidation and coagulation flocculation process was recently used to remove the nonbiodegradable pollutants from wastewater.

1.2 Treatment of wastewater.

The wastewater whether it’s from industrial or domestic waste cause deep concerned to the government. The threats from these issues can’t be neglected and further stringent actions must be taken. Treatments of any wastewater are compulsory before it’s discharged into the ecosystem. There are three general types of wastewater treatment, chemical methods, biological methods and also physical methods. In chemical methods, the examples are reaction to produce insoluble solids, reaction to produce insoluble gas and oxidation-reduction process. Meanwhile for biological methods, there are only anaerobic and aerobic methods and last but not least is the physical method of gravity separation, reverse osmosis and ion exchange.
The implementations of these methods are all depend on the type of wastewater treated and the efficiency of the treatments in economical way.

1.2.1 Chemical oxidation methods.

In this method, there are several main oxidation methods such as the oxidation of ferrous ions to ferric ions by oxygen, the oxidative destruction of organics by free radicals, oxidation by hydrogen peroxide, oxidation with ozone, oxidation with UV-lights and oxidation with hydrogen peroxide. Here, the oxidation with hydrogen peroxide is chosen. Chemical oxidation methods are being applied to treat my water based printing ink wastewater. The chemical oxidation method here is the Fenton process oxidation by hydrogen peroxide (H2O2) and also ferrous sulfate (FeSO4). The oxidation of hydrogen peroxide may or may not involved free radicals but it is catalyze by transition metal salts, ozone and also UV-lights. The oxidation-reduction process of Fenton reaction cannot occur without being catalyzed by either three of the factors. Free radicals are powerful oxidizers that can convert organics all the way to carbon dioxide, water and fully oxidized states of other atoms that were part of the original organic pollutants including sulfates and nitrates. Free radicals can be generated by adding hydrogen peroxide, adding hydrogen peroxide to a solution that contains ferrous ions, either present in the wastewater or added along with the hydrogen peroxide (Fenton’s reagent), adding ozone and hydrogen peroxide and adding ozone and irradiating with ultraviolet light.

1.2.2 Coagulation.

In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. Although the terms coagulation and flocculation are often used interchangeably, or the single term flocculation is used to describe both; they are, in fact, two distinct processes. Coagulation is the destabilization of colloids by neutralizing the forces that keep
them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. Coagulation process is necessary in wastewater treatment as it can help to sediment the flocs formed during chemical treatment of the wastewater.

**Figure 1.1** Charge Neutralization and Colloid Destabilization Mechanisms.

### 1.3 Problem Statement.

Water-based ink is nonflammable, produces less objectionable vapors in the workplace, and does not contaminate packaged products. Therefore, it has been widely used in printing the packaging of food, drug, toy, wine product and so on. However, wastewater obtained after cleaning/washing of the laboratory and industrial equipment is highly colored by the pigments and is highly contaminated with organic materials. This wastewater may also be an aesthetic concern and cannot
be discharged to a water system without treatment. Acrylics often used in water-based ink formulations and pigments are very difficult to break down biologically.

Moreover, more stringent requirements of wastewater discharge standards have promoted recent research efforts to identify other more efficient and economic chemical treatment methods in an attempt to meet these demands.

In this work, a combination of oxidation process using Fenton reagents and coagulation-flocculation process are implemented to reduce the concentration of nonbiodegradable pollutants in wastewater to increase the removal efficiency of turbidity, COD and BOD.

1.4 Objectives

The aim of this research is to study the efficiency of wastewater treatment using Fenton Process combine with Coagulation and determine the optimum pH, dosages and contact time of FeSO4, H2O2 and fenugreek for the treatment.

1.5 Scopes of study.

By conducting the Jar Test in treating this water based printing ink, we will:

a) Investigate the pH range selected which is pH 2 to pH 9.

b) Investigate the dosages of FeSO4 from 25 mg/L to 500 mg/L.

c) Investigate the dosages of H2O2 from 1 ml/L to 2 ml/L.

d) Study the dosages of fenugreek from 0.5 ml/L to 2 ml/L.
CHAPTER 2

LITERATURE REVIEW.

2.1 Introduction.

Wastewater treatment is very general and being applied throughout the world. But the most efficient methods are still being discussed and many researchers are continuing their study to better amplify the research outcomes. In this chapter, I will discuss of my selected wastewater, the general treatment methods and the process involved in my experiments. Fenton process combine with coagulation is the selected chemical oxidation methods that I will apply in my research.

2.2 Wastewater from printing industry.

Waterbased ink uses water as carrier to substitute a majority of organic solvent, thus its development and application have led to the reduction of volatile organic compounds (VOC) emissions, as one of the main driving forces of product innovation Water-based ink is nonflammable, produces less objectionable vapors in the workplace, and does not contaminate packaged products. Therefore, it has been widely used in printing the packaging of food, drug, toy, wine product and so on. However, wastewater obtained after cleaning/washing of the laboratory and industrial equipment is highly colored by the pigments and is highly contaminated with organic materials. This wastewater may also be an aesthetic concern and cannot
be discharged to a wastewater system without treatment. Acrylics often used in water-based ink formulations and pigments are very difficult to break down biologically. Moreover, more stringent requirements of wastewater discharge standards have promoted recent research efforts to identify other more efficient and economic chemical treatment methods in an attempt to meet these demands.

2.3 Treatment methods.

Treatment methods vary with the wastewater characteristics. In economic point of view, the most economical and efficient methods are preferable compare to the other. Chemical methods, biological methods and physical methods are the general treatment that are being used and further investigations by researchers proves that chemical methods are the most efficient and economical compare to the other two methods. Chemical oxidation by Fenton process combine with coagulation can remove up to 98% of turbidity, 87% COD and also 83.2% of the BOD [Xiang-Juan Ma, et al, 2009].

2.4 Theory of Fenton Process.

Fenton process requires the usage of hydrogen peroxide (H2O2) as the oxidation agents. However, hydrogen peroxide alone is still not enough to conclude the reaction because of high concentration of certain refractory contaminants and the low rate of reactions at reasonable H2O2 concentration. Further research improves this Fenton process by using transition metal salts, ozone and also UV-light. Oxidation process that use H2O2 and metal salts are classically known as Fenton process. In previous reaction scheme of the reaction between H2O2 and iron salts (Chapter 1), it will results in the formation of hydroxyl radicals, HO•. This advances
oxidation techniques [E. Neyens et. al., 2002] with the presence of HO•, will non-specifically oxidize target compounds at high reaction rates.

2.4.1 Hydrogen Peroxide.

Hydrogen peroxide (H2O2), is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. The molecules of H2O2 consist of two hydrogen molecules and two oxygen molecules. By the dissociation into oxygen and water, H2O2, can also supply oxygen for microorganism in biological treatment facilities and in bioremediation of contaminated sites. It can be used as a disinfecting agent in the control of undesirable bio-film growth. H2O2 can be decomposed into water and oxygen by enzymatic and non enzymatic routes.

![Figure 2.1 Hydrogen Peroxide Molecule.](image)

2.4.2 Hydrogen peroxide in Fenton Process.

Still H2O2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at reasonable H2O2 concentrations. Improvements can be achieved by using transition metal salts (e.g. iron salts) or ozone and UV-light can activate H2O2 to form hydroxyl radicals, which are strong oxidants. Oxidation processes utilizing activation of H2O2 by iron salts, classically
referred to as Fenton’s reagent is known to be very effective in the destruction of many hazardous organic pollutants in water.

2.5 Oxidation by Fenton process

Oxidation is defined as the interaction between oxygen molecules and all the different substances they may contact, from metal to living tissues. Technically, however, with the discovery of electrons, oxidation came to be more precisely defined as the loss of at least one electron when two or more substances interact. Those substances may or may not include oxygen. Incidentally, the opposite of oxidation is reduction — the addition of at least one electron when substances come into contact with each other [M. Pollick et al., 2009]. In wastewater treatment, oxidation is done for example, by using hydrogen peroxide (H2O2) as the oxidation agent, called as the Fenton process. The agent used for Fenton process is mainly hydrogen peroxide (H2O2). Hydrogen peroxide (H2O2) is a strong oxidant (standard potential 1.80 and 0.87V at pH 0 and 14, respectively) [Degussa et al., 2001] and its application in the treatment of various inorganic and organic pollutants is well established.

Numerous applications of H2O2 in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, cyanides, and chlorine, are known [Venkatadri, Peeters et al., 1993]. H2O2 is also useful in the treatment of the gaseous sulphur oxides and nitrogen oxides being converted to the corresponding acids. H2O2 has applications in the surface treatment industry involving cleaning, decorating, protecting and etching of metals (L’air Liquide). Oxidation by H2O2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low rates of reaction at reasonable H2O2 concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H2O2 to form hydroxyl radicals which are strong oxidants.
Transition metal salts (e.g. iron salts) are used in this experiment later. In aqueous solution, hydrogen peroxide can oxidize or reduce a variety of inorganic ions. When it acts as a reducing agent, oxygen gas is also produced. In acidic solutions Fe\(^{2+}\) is oxidized to Fe\(^{3+}\), hydroxyl radicals will also be produced in the oxidation by hydrogen peroxide,

\[
\text{Fe}^{2+}(aq) + \text{H}_2\text{O}_2 + 2 \text{H}^+(aq) \rightarrow 2 \text{Fe}^{3+}(aq) + 2\text{H}_2\text{O}(l)
\]

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^* 
\]

In this study, Fenton process combined with coagulation are used to treat the water based printing ink wastewater. It has been proven feasible industrially for removing contaminants [Xiang-Juan Ma, Hui-Long Xia et al., 2009]. Fenton’s reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s (Huang et al.). Now Fenton’s reagent are widely used to treat wastewater to get a complete destruction of contaminants to harmless compound, e.g. CO2, water and inorganic salts. [Xiang et. al., 2009]. There are three methods in treating wastewater nowadays, chemical methods, physical methods and biological methods. It all depends on the pollutants and how feasible it is to be done. For example, to treat dissolved charged substance, we can apply membrane separation (electrodialysis) and also chemical oxidation by \(\text{H}_2\text{O}_2\). Other method such as coagulation/flocculation to treat dissolved inorganic substance, filtration of undissolved colloidal substance and also sedimentation/flocculation of undissolved settleable substance. But improvements are always there as many researchers are trying to get the most efficient and economical ways to treat wastewater.

The effectiveness of Fenton’s oxidation (FO) process and ozone (O3) oxidation compared with a coagulation–flocculation (CF) process to remove effluent toxicity as well as colour and COD from a textile industry wastewater are studied [Sureyya et. al., 2004] to focus on the color and chemical oxygen demands (COD) removal. Fenton’s oxidation proved to be one of the most efficient methods. Other previous studies were conducted by comparing the coagulation/flocculation method and the
Fenton-coagulation/flocculation in the wastewater treatment from the cork industry [Jose et. al., 2003]. When Fenton process is added in this experiment, the rate of COD, total polyphenols and aromatic compounds are reduced significantly. Last but not least is the treatment of water-based printing ink wastewater [Xiang Juan Ma et. al., 2009]. Fenton process combined with coagulation are used and the results are the reduced of flocs settling time, enhanced color removal and also the reduced amount of chemical oxygen demands (COD).

2.5.1 Oxidation by hydrogen peroxide (H2O2)

Hydrogen peroxide produced hydroxyl radicals, OH• when used as the oxidation reagents. It oxidized the Fe2+ ions into Fe3+. The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants.

2.5.2 Kinetic schemes.

Fenton’s reagent is a mixture of H2O2 and ferrous iron, which generates hydroxyl radicals according to the reaction (Kitis et al. Yoon et al. ; Lu et al.)

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^• + \text{OH}^– \quad (1)
\]

The ferrous iron (Fe2+) initiates and catalyses the decomposition of H2O2, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction sequence in an aqueous solution

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^• + \text{OH}^– \\
\text{OH}^• + \text{Fe}^{2+} & \rightarrow \text{OH}^– + \text{Fe}^{3+}
\end{align*}
\]

(1) (chain initiation) (2) (chain termination)

Moreover, the newly formed ferric ions may catalyse hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and radicals are also formed in the reactions. The reactions are as shown in Equations (3) – (7).
Fe$_3^+$ + H$_2$O$_2$ ↔ Fe−OOH$_2$ + H$^+$ \hspace{1cm} (3) \\
Fe−OOH$_2$ → HO$_2$ • + Fe$^{2+}$ \hspace{1cm} (4)

The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction

Fe$^{2+}$ + HO$_2$ • → Fe$^{3+}$ + HO$^-$ \hspace{1cm} (5) \\
Fe$^{3+}$ + HO$_2$ • → Fe$^{2+}$ + O$_2$ + H$^+$ \hspace{1cm} (6) \\
OH• + H$_2$O$_2$ → H$_2$O + HO$_2$ • \hspace{1cm} (7)

As seen in reaction (7), H$_2$O$_2$ can act as an OH• scavenger as well as an initiator [reaction (1)].

Hydroxyl radicals can oxidise organics (RH) by abstraction of protons producing organic radicals (R•), which are highly reactive and can be further oxidised (Walling Kato et. al.,)

RH + OH• → H$_2$O + R• → further oxidation \hspace{1cm} (8)

If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO$_2$, water and in the case of substituted organics, inorganic salts if the treatment is continued.

2Fe$^{2+}$ + H$_2$O$_2$ + 2H$^+$ → 2Fe$^{3+}$ + 2H$_2$O \hspace{1cm} (9)

This equation suggests that the presence of H$^+$ is required in the decomposition of H$_2$O$_2$, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. Previous Fenton studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidations [Hickey et al.]. In the presence of organic substrates (RH), excess ferrous ion, and at low pH, hydroxyl radicals can add to the aromatic or heterocyclic rings (as well as to the unsaturated bonds of alkenes or alkynes). They can also abstract a hydrogen atom, initiating a radical chain oxidation

RH + OH• → H$_2$O + R• (chain propagation) \hspace{1cm} (10) \\
R• + H$_2$O$_2$ → ROH + OH• \hspace{1cm} (11) \\
R• + O$_2$ → ROO• \hspace{1cm} (12)

The organic free radicals produced in reaction (10) may then be oxidised by Fe$^{3+}$, reduced by Fe$^{2+}$, or dimerised according to the following reactions

R• + Fe$^{3+}$-oxidation → R+ + Fe$^{2+}$ \hspace{1cm} (13)
$\text{R}^\bullet + \text{Fe}^{2+}-\text{reduction} \rightarrow \text{R}^- + \text{Fe}^{3+}$ \quad (14)

$2\text{R}^\bullet-\text{dimerization} \rightarrow \text{R}^-\text{R}$ \quad (15)

The sequence of reactions (1), (2), (10) and (13) constitute the present accepted scheme for the Fenton’s reagent chain. The ferrous ions generated in the above redox reactions (8) and (9) react with hydroxide ions to form ferric hydroxo complexes.

$[\text{Fe(H}_2\text{O)}6]^{3+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe(H}_2\text{O)}5\text{OH}]^{2+} + \text{H}_3\text{O}^+$ \quad (16)

$[\text{Fe(H}_2\text{O)}5\text{OH}]^{2+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe(H}_2\text{O)}4(\text{OH})2] + \text{H}_3\text{O}^+$ \quad (17)

Within pH 3 and 7, the above complexes become

$2[\text{Fe(H}_2\text{O)}5\text{OH}]^{2+} \leftrightarrow [\text{Fe(H}_2\text{O)}8(\text{OH})2]^{4+} + 2\text{H}_2\text{O}$ \quad (18)

$[\text{Fe(H}_2\text{O)}8(\text{OH})2]^{4+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe}_2(\text{H}_2\text{O})7(\text{OH})3]^{3+} + \text{H}_3\text{O}^+$ \quad (19)

$[\text{Fe}_2(\text{H}_2\text{O})7(\text{OH})3]^{3+} + [\text{Fe(H}_2\text{O)}5\text{OH}]^{2+} \leftrightarrow [\text{Fe}_2(\text{H}_2\text{O})7(\text{OH})4]^{5+} + 2\text{H}_2\text{O}$ \quad (20)

This accounts for the coagulation capability of Fenton’s reagent. Dissolved suspended solids are captured and precipitated. It should be noted that large amounts of small flocs are consistently observed in the Fenton oxidation step. Those flocs take a very long time to settle but can be precipitated after that.

This Fenton oxidation reaction depends on the stoichiometric relationship. The key features of the Fenton system are believed to be its reagent conditions, i.e. $[\text{Fe}^{2+}]$, $[\text{Fe}^{3+}]$, $[\text{H}_2\text{O}_2]$ and the reaction characteristics (pH, temperature and the quantity of organic and inorganic constituents). Because these parameters determine the overall reaction efficiency, it is important to understand the mutual relationships between these parameters in terms of hydroxyl radical production and consumption. [Yoon et. al]. High ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]0$ ($\geq 2$), medium ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]0$ (=1), and low ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]0$ ($<1$) are the three conditions that we must take into account for.
2.6 Theory of Coagulation Process.

In water treatment plant, chemical coagulation is usually accomplished by the addition of trivalent metallic salts such as aluminum sulfate, $\text{AL}_2\text{(SO}_4\text{)}$ or ferric chloride, $(\text{FeCL}_3)$. Although the exact method cannot be determined, there are four mechanisms that are thought to occur which are ionic layer compression, adsorption and charge neutralization, sweep coagulation and inter-particle bridging [Howard S. Peavy, 1985]. Coagulation is not yet an exact science, although recent studies have been made in understanding the mechanics of the process. Selections of optimum dosages of coagulants are done by using JAR Test instead of quantitatively by formula. The JAR Test must be performed on each water that is to be coagulated and must be repeated with each significant change in the quality of a given water.

2.6.1 Ionic layer compression.

The quantity of ions in the water surrounding a colloid has an effect on the decay function of electrostatic potential. If this layer is sufficiently compressed, then the van der Waals force will be predominant across the entire area of influence so the net force will be attractive and no energy barriers will exist. Ion content of water increases drastically and coagulation and settling will occur. Eventually, deposits (deltas) are formed from material which was originally so small that it could have settled without coagulation.

2.6.2 Adsorption and charge neutralization.

The nature rather than the quantity of ions is of prime importance in the theory of adsorption and charge neutralization.
2.6.3 Sweep coagulation.

The ferric ions form in amorphous, gelatinous flocs that are heavier than water and will settle by gravity forces. Colloids may become entrapped in flocs as it is formed or they may become enmeshed by its ‘sticky’ surface as the flocs settle. The process by which colloids are swept from suspension into this manner is known as sweep coagulation.

2.6.4 Inter-particle bridging.

Large molecules can be formed when ferric salts dissociate in water. Synthetic polymers also used instead of metallic salts. These polymers may be linear or branched and are highly surface reactive. Thus, several colloids may become attached to one another and become enmeshed resulting to a settleable mass.

2.7 Combine Fenton – Coagulation Process.

Previous research to treat wastewater applies the usage of Fenton process and/or coagulation. For example, the treatment of cork processing wastewater [Jose A. et. al., 2003]. In the present work, two methods are tested. For the first method, coagulation/flocculation technique using FeCl₃ as flocculation agent and Ca(OH)₂ as base precipitant. Different speed of cycle (rpm), then tested and the results are analyze. In the second method, the integrated Fenton-coagulation/process is tested using the addition of H₂O₂. JAR test are conducted with different dosage of H₂O₂ tested. Considerable improvements had been achieved with more COD reduced; polyphenol and aromatic compounds can be removed.

Other researches such as the acute toxicity removal in textile finishing wastewater using Fenton oxidation/ozonation, and coagulation/flocculation process
[Sureyya et al., 2004] have also been conducted. For Fenton/ozoneation process, H2O2 are used as the oxidation agents and FeSO4 as the iron salts. 1.4 g/L-h of O3 are added into the wastewater from the bottom of the reactor. Then the coagulation/flocculation method is tested. A series of JAR test experiments are applied on the raw wastewater using an anionic polyelectrolyte at different mixing speed (rpm) and pH. Results are analyzed and Fenton/ozoneation process has better efficiency then coagulation/flocculation process in economic terms (heat needed).

Another research is the Fenton peroxidation and coagulation processes of combined domestic and industrial wastewater treatment [M.I Badawy et al., 2006]. In the coagulation process, anionic and cationic polymers, powdered activated carbon and bentonite are added as the coagulant aids. JAR testing are done in different rpm speed. The samples are then retrieved to continue with the Fenton process with various dosage of FeSO4. Here, without Fenton process, the removals of suspended and insoluble matter are very low. With a higher cost, Fenton process has the advantage in avoiding the formation of sludge disposal and lower consumption in disinfecting agents.

In this water-based printing ink wastewater treatment, Fenton process combined with coagulation is the most efficient method [Xiang et al., 2009]. Up to date, several researches are conducted to get the most feasible method. In Fenton process, H2O2 are added with FeSO4 as the iron salts. For the coagulation process, polyaluminium chloride and FeSO4 are chosen to be the coagulant and coagulant aid. JAR test are run at different pH, dosage, and mixing speed (rpm). Once the treatment is finished, removal of COD, BOD and also the color of wastewater are considerably acceptable. In this experiment, polyaluminium chloride is used as the coagulant, less type of chemicals are also used (as FeSO4 are used in the Fenton process, and also for the coagulation process). It proves that FeSO4 are also efficient as the coagulant aid.
CHAPTER 3.

METHODOLOGY.

3.1 Introduction.

The purpose of this study is to evaluate the effect of oxidation by Fenton process and improving the wastewater treatment by coagulation. The main parameters that will be focus on is the biological oxygen demand (BOD), chemical oxygen demand (COD) and turbidity removal. The wastewater which is water-based printing ink are collected from a printing company in Kuantan and analyze initially to determine the initial turbidity, pH, COD and also BOD content. It is important to analyze the initial conditions of the wastewater to manipulate the experiments and achieving the objectives of the experiments. The main materials used in this experiment later are ferrous sulfate (FeSO4), hydrogen peroxide (H2O2), and fenugreek. For Fenton Process, ferrous sulfate and hydrogen peroxide are used meanwhile for Coagulation process; fenugreek is the coagulant and ferrous sulfate will be the coagulant aide. Ferrous sulfate and hydrogen peroxide are purchased by the Chemical Engineering Lab and fenugreek will be prepared in the lab. Experimental methods are all done using the Jar test.
3.2 Materials and chemicals

3.2.1 Wastewater.

The wastewater used is the water based printing ink wastewater from a printing company in Kuantan, Pahang. I obtained 50 L of the raw wastewater for my research and the objective here is to remove the turbidity, COD and BOD of the water based printing ink wastewater.

Table 3.1 Water based printing ink properties

<table>
<thead>
<tr>
<th>Wastewater Properties</th>
<th>Initial Conditions Before Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Yellow</td>
</tr>
<tr>
<td>Biological oxygen demands</td>
<td>2976 mg/L</td>
</tr>
<tr>
<td>Chemical oxygen demands</td>
<td>4600 mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
<td>287 NTU</td>
</tr>
<tr>
<td>Characteristics</td>
<td>Nonflammable, produce less objectionable vapors and does not contaminate packaged products</td>
</tr>
</tbody>
</table>

3.2.2 Materials

The main chemical used for Fenton process is hydrogen peroxide (H2O2). Hydrogen peroxide (H2O2) is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. Still H2O2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at reasonable H2O2 concentrations. Improvements can be achieved by using transition metal salts (e.g. iron salts) or ozone and UV-light can activate H2O2 to form hydroxyl radicals, which are strong oxidants. Oxidation processes
utilizing activation of H2O2 by iron salts, classically referred to as Fenton’s reagent is known to be very effective in the destruction of many hazardous organic pollutants in water. Hydrogen peroxide used in this experiment is in liquid form of 6% purity.

Secondly is ferrous sulfate (FeSO4). Ferrous sulfate appears in a green crystals figure with a molecular weight of 151.908 g/mol. It is also known as reducing agents and in this research, ferrous sulfate is used as an iron salts to catalyze Fenton process and aid as the coagulant for coagulation process.

Fenugreek will be use to conduct chemical coagulation once Fenton Process is done. To prepare the fenugreek solution, 100 g of fenugreek is weigh up and mix with 1 L of distilled water inside a 1 L beaker. Then, the solution was mixed gently before leaving it 24 hours inside the heated mixer. After 24 hours, the fenugreek will be withdrawn and centrifuge in the refrigerated centrifuge to get the final solution of fenugreek. The fenugreek is yellow in color and is very viscous.

3.3 Fenton Process Experiment.

3.3.1 Effect of pH

The effect of pH on Fenton Process in the water based printing wastewater treatment was conducted by testing the variables pH: 2, 3, 4, 6, 8 and 9. The dosages of ferrous sulfate (FeSO4) and hydrogen peroxide (H2O2) will be set according to previous journal of the same study and remain unchanged during the experiment. 6 beakers of 1 L were set up in the JAR Test with the same amount of water based printing ink wastewater. Acid and alkali solutions were used to set up the desired pH of pH 2, 3, 4, 6, 8 and 9. The dosages of ferrous sulfate (FeSO4) and hydrogen peroxide (H2O2) were set at 25 mg FeSO4 and 0.0008 L H2O2 each. Firstly, in rapid mixing, FeSO4 and H2O2 were added and mixed in the JAR Test for 120rpm of