SPENT CAUSTIC TREATMENT USING ADVANCED

OXIDATION PROCESSES

by

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Acknowledgments

Abstract

Mixed refinery spent caustic is an industrial wastewater that is generated from oil refineries. Spent caustic undergo two treatment steps, chemical oxidation followed by biological post treatment step. The goal of chemical oxidation is to drop the contamination concentration to a level that biological treatment can take place. The maximum contaminants concentration, which can be measured by chemical oxygen demand, that biological treatment can be applied, is 1,000 ppm. Advanced oxidation processes, in specific, fenton's reaction is tested to check if the method can be applied to spent caustic treatment. The research is divided into two parts, bench scale study followed by pilot plant study. The goal of bench scale study is to treat spent caustic to achieve a final chemical oxygen demand of 1,000 ppm with minimum hydrogen peroxide to chemical oxygen demand ratio possible by manipulating other factors affecting chemical oxygen demand removal. It was found out that the highest chemical oxygen demand removal achieved is 97% at optimum hydrogen peroxide to ferrous sulfate to chemical oxygen demand mass ratio of 3.8/2.1/1. Moving on to the pilot plant study, the objective of the pilot plant study is to check if fenton's process can be applied in large scale. The best result obtained is a final chemical oxygen demand of 525 ppm while operating at hydrogen peroxide to ferrous sulfate to chemical oxygen demand mass ratio of 3.5/1.6/1.

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List of Abbreviations:

AOP's	-	Advanced Oxidation Processes
COD	-	Chemical Oxygen Demand
CDM	-	Clean Development Mechanism
$FeSO_4$	-	Ferrous Sulfate
Fe^{+2}	-	Ferrous Ion
Fe^{+3}	-	Ferric Ion
$OH^{.}$	-	Hydroxyl Radical
H_2O_2	-	Hydrogen Peroxide Peroxide
H_2S	-	Hydrogen Sulfide
OHP	-	Oxidation with Hydrogen Peroxide
O_3	-	Ozone
Ppm	-	Part Per Million
PFD	-	Process Flow Diagram
TDS	-	Total Dissolved Solids
TSS	-	Total Suspended Solids
US	-	Ultrasound
UV	-	Ultraviolet
WAO	-	Wet Air Oxidation

CHAPTER 1:
Introduction

1.1 Background

Over the last century, the rapid increase in the industrial activity has adversely impacted the environment especially water resources [1]. Discharging poorly treated industrial wastewater to the environment by either dumping the waste in land fill or discharging to water recourses can result in severe contamination [4]. This will not affect the environment only as it may affect the health of people in this area as well. An accident occurred in Ivory Coast where untreated industrial wastewater was dumped near village which resulted in contamination of ground water, dozens of people died, 10,000 were injured and more than 35,000 were infected [3]. In order to preserve water resources as well as human's health, more strictly environmental regulations were issued [4]. These regulations are not favorable by industries as it will increase both operational and capital cost for additional treatment [1]. However, to encourage industries to follow these regulations, some awards were issued like Clean Development Mechanism (CDM) under Kyoto Protocol [2]. These awards can compensate with the extra cost required to properly treat industrial wastewater before discharging [2].

Petroleum refineries are one of the industries that produce industrial waste that must be treated properly. Petroleum refineries convert crude oils into more refined products such as gasoline, kerosene, jet fuel etc [5]. These products usually contains impurities that must be extracted prior usage such as naphthenic acids, phenols, sulfur compounds like hydrogen sulfide, mercaptans, and thiophene [6]. The process used to remove these impurities is called

sweetening [6]. One of the most famous methods of sweetening is the Merox Process in which caustic soda (NaOH) is used as an extraction liquid to remove impurities from hydrocarbon streams[7]. Once the caustic is used in this process, a waste stream is generated and it is called spent caustic or refinery spent caustic [7]. Spent caustic is a hazardous waste that must be treated and handled properly. It is highly toxic to both environment and human as well. Spent caustic is highly corrosive mixer due to the high pH. Average pH value of spent caustic is around 12. Spent caustic is highly odorous waste due to mercaptans, sulfide and some volatile organic that exists in it. Also, it has high affinity to foam due to naphthenic acids. Spent caustic has high chemical oxygen demand which inhibits biological treatment [6, 8, 9]. Other characteristics of spent caustic depend on the source. Typical refinery spent caustic consists residual sodium hydroxide concentration of 6-13 wt% [6]. Spent caustic may also consist of, sulfide, phenols, amines, paraffins, hydrocarbon and emulsified naphthenates.[6, 9].

There are three main types of refinery spent caustic, sulfidic, cresylic, and naphthenic caustics [10]. The composition and strength of refinery spent caustic is variable depending on the source [6]. Usually refineries don't separate each type of spent caustic rather it is mixed and the mixed waste is called mixed refinery spent caustic [10]. This type what is usually produced by refineries and it is considered as a fourth type. Mixed refinery spent caustic can be considered as a forth type. Table 1.1 shown sample spent caustic characteristic:

Table 1.1: Characteristics of Refinery Spent Caustic [9]

	Sulfidic Spent caustic	Naphthenic Spent caustic	Cresylic Spent caustic
Chemical oxygen demand COD(ppm)	5,000-90,000	50,000-100,000	150,000-240,000
Total organic carbon(TOC)(ppm)	20-3,000	10,000-24,000	24,000-60,000
Sulfides(ppm)	2,000-52,000	< 1	0-63,000
Sulfite(ppm)	1.5-500	4-8	800-1,500
Mercaptans(ppm)	0-30,000	< 30	0-5,400
Thiosulfate(ppm)	0-4,000	70-1,200	10,000-13,000
Total phenol(ppm)	2-30	1,900-1,000	14,000-19,000

Type of spent caustic is generated according to the fuel that fresh caustic wash. Sulfidic spent caustic is generated when fresh caustic is used to extract impurities from fuel gas and liquefied petroleum gas. This type has high sulfides concentration and it is highly odorous [10]. The second type is napthetic spent caustic. It is generated when spent caustic is used to wash of diesel and jet fuels. This type has low sulfides concentration [9]. The last type is cresylic spent caustic which is generated from treating gasoline. This type has aromatics, acid oils, cresols and other organic acids as water soluble cresylates[10]. Spent caustic is considered waste stream that needs excessive treatment prior discharge [6, 10].

Spent caustic treatment undergoes two steps, chemical oxidation followed by biological treatment. Biological treatment cannot be used directly to treat spent caustic because of the following reasons. Spent caustic has phenols which inhibit biological treatment. 400 ppm phenols can inhibit phosphorous, ammonia and COD removal in biological treatment. Also, feed with high phenol can kill bacteria responsible for biological oxidation resulting in complete inhibition. Spent caustic consists of some compounds that have low biodegradability such as naphthenic acids. Existence of naphthenic acids can result in operational problems in aerated biological due to foaming. Finally, high chemical oxygen of spent caustic makes biological treatment not feasible [11].

Chemical oxidation used in spent caustic goal is to pre-treat spent caustic so biological oxidation is feasible [6, 11]. Among chemical oxidation, two famous processes that are used in spent caustic treatment are wet air oxidation (WAO) and Advanced Oxidation Processes (AOP's) [10].

1.2   Literature Review

1.2.1   Wet air oxidation

Wet air oxidation (WAO) is the liquid phase oxidation of soluble and suspended compounds using oxygen, or air, as an oxidant [12]. The oxidation is carried out at elevated temperature and pressure depending on both feed strength and desired effluent criteria. Elevated temperature and pressure accelerate oxygen transfer as well as rate of containment's destruction, thus, efficient operation [13]. Operational conditions can be divided into three ranges, low, medium and high temperature systems [14]. Oxidation is carried out at 200 °C and 27.5 barg in low temperature systems. This system partially oxidizes sulfides to sulfates and thiosulfates. [13]. In Medium temperature system, oxidation is carried out at range of 200 °C and 27.5 barg to 260 °C and 86 barg. Typical feed to this system is naphthenic refinery spent caustic. Sulfides are oxidized to sulfates and mercaptans are destroyed as well. [12]. High temperature systems oxidize cresylic refinery spent caustic at a range of 240 °C and 55 barg to 260 °C and 85 barg. Complete oxidation of sulfides, mercaptans and some organic contaminant like cresylic acids can be achieved [10, 14].

Typical WAO industrial system can receive a flow rate of 1-50 m^3/h and a COD range of 10000 to 100000 ppm. However, for COD levels above 50000 ppm dilution with fresh water and/or fresh caustic is required [12, 15]. Fresh caustic dilution can be used to serve more than one goal. It is used to keep dissolved salts concentration below solubility limits to avoid scaling. The other reason is to insure the alkalinity isn't consumed by oxidation where acidic effluent can damage the material of construction of the system [10]. Also, addition of caustic can help oxidation of contaminants which can be shown in the following reaction [9], [16]:

- Sulfide
  - $NaSH + 2O_2 + NaOH \longrightarrow Na_2SO_4 + H_2O$ \hfill (1.1)
  - $NaSH + O_2 \longrightarrow 1/2Na_2S_2O_3 + \frac{1}{2} H_2O$ \hfill (1.2)

- Thiosulfate
  - $Na_2S_2O_3 + 2O_2 + 2NaOH \longrightarrow 2Na_2SO_4 + H_2O$ (1.3)
- Mercaptan
  - $NaSR + 3/2\ O_2 \longrightarrow RSO_3\text{-}Na$ (1.4)
- Cresylic Acids
  - $C_6H_5O\text{-}Na + 7\ O_2 + 11\ NaOH \longrightarrow 6\ Na_2CO_3 + 8\ H_2O$ (1.5)
  - $C_6H_5O\text{-}Na + 5\ O_2 + 8\ NaOH \longrightarrow 4\ Na_2CO_3 + CH_3COO\text{-}Na + 5\ H_2O$ (1.6)
- Naphthenic Acids
  - $Na\text{-}C_{12}H_{22}O_2 + 67/7\ O_2 + 23\ NaOH \longrightarrow 12\ Na_2CO_3 + 45/2\ H_2O$ (1.7)
  - $Na\text{-}C_{12}H_{22}O_2 + 59/4\ O_2 + 20\ NaOH \longrightarrow 10\ Na_2CO_3 + CH_3COO\text{-}Na + 39/2\ H_2O$ (1.8)
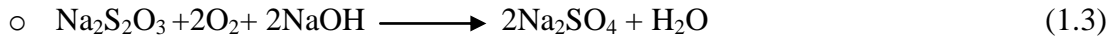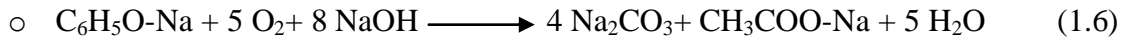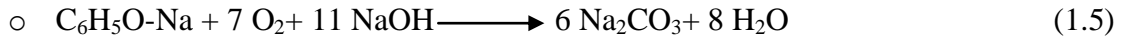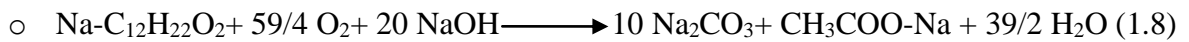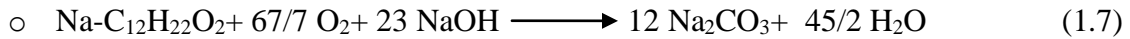
WAO is commonly used to pre-treat spent caustic prior biological treatment since it has the ability to reduce the COD of the effluent [9]. Also, WAO can be applied to any waste stream with suspended or dissolved oxidizable compounds [16]. It has the ability to treat streams containing cyanide, various heterocyclic compounds, industrial sludge, and spent carbon from adsorption processes [17]. Also, WAO is applied in many industries like, municipal sewage sludge, paper manufacturing waste, industrial sludge and textile sludge [16].
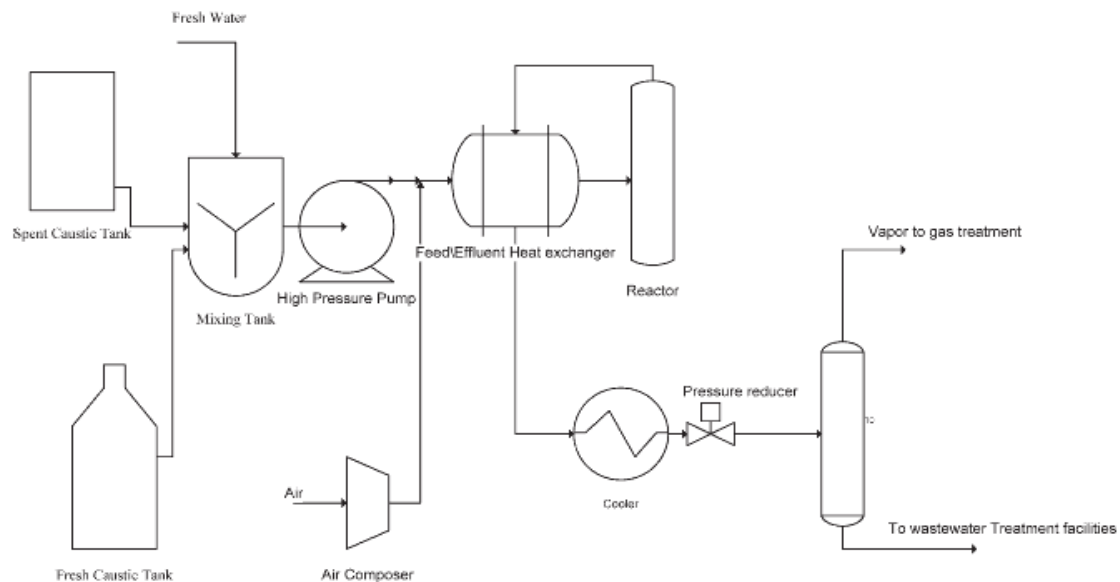
Figure 1.1: Typical Wet Air Oxidation PFD [10]

The basic scheme of wet air oxidation system is shown in figure 1.1. Spent caustic is diluted with fresh caustic and/or water. The dilution ratio depends on the strength of spent caustic [10]. Diluted spent caustic is pumped to 27.5-85 barg via high pressure pump. Air is compressed and mixed with the pressurized diluted spent caustic to supply oxygen required for the reaction [15]. The mixture is preheated to 200-260 °C by feed/effluent heat exchanger. Sufficient residence time is important to allow oxidation to achieve the desired reduction in COD. Reactor effluent has higher temperature than the inlet stream due to exothermic reaction. Effluent stream can be utilized to preheat reactor influent in the feed/effluent heat exchanger and thus enhances heat recovery [18]. The reactor's effluent is then cooled, depressurized and sent to a separator. The treated effluent is separated from the gas by the separator. The treated liquid is send to biological plant for further treatment. The effluent gas has 5-21 wt% oxygen and some volatile organic compounds [15]. Table 1.2 shows a sample of WAO operational conditions from Refinaria de Petroleos de Manguinhos, S. A. (Manguinhos) in Rio de Janeiro.

Table 1.2: WAO Operational Conditions [18]

	Feed	Effluent (after dilution)
Residence time (hr)	-	1.5
Oxidation Temperature(K)	-	533
COD, g/L	114	≈ 23
Sulfides sulfur, g/L	≈ 24	<0.001
Total phenols,g/L	≈ 0.54	<0.002

Figure 1.2: Two Refinery Spent Caustic Samples (left and center) and Treated Effluent (right) [18]

To ensure successful and efficient operations, specific process factors must be evaluated. These factors are oxidation temperature and pressure and residence time [10, 18-20]. For WAO system, the average oxidation temperature to achieve full treatment is 260 °C [10]. At this temperature, average COD reduction varies between 70-80% [18]. The COD reduction of WAO is not high; however, some compounds like sulfides can have a reduction over 99%. In addition, most of the remaining COD in the treated effluent is mainly from low molecular weight aliphatic acids that can be biologically oxidized [20]. The oxidation pressure is directly related to oxidation temperature. Oxidation pressure is responsible to keep the reaction in the liquid phase. So, as the reaction temperature increases, the oxidation pressure increases to keep the reaction in the liquid phase [19]. For WAO process, typical residence time varies between 45-120 min [10]. Residence time affect the degree of oxidation that occurs in the reactor. As the residence time increases, more oxidation occur and thus increasing degree of oxidation. Each WAO plant uses different residence time to achieve the required degree of COD reduction specified by the plant. Selection of material of construction is very important in WAO operation. As shown previously, WAO operates at high temperature and pressure [10]. As a result, the material of construction should be able to stand these conditions. A recommended material used in WAO plants is nickel 200 [10].

WAO is an excellent way to pre-treat spent caustic, however, it has some drawbacks. The main drawback of this process is the cost. The cost of WAO mainly depends on the operation conditions which are related to feed strength [10]. As the feed's strength increases,

more severe operational conditions are required which increases the operational cost of the plant [18]. An estimated capital cost of WAO to treat mixed refinery spent caustic with a COD ranges between 60,000 ppm to 100,000 ppm and a feed capacity of 10 gal/min is $10 million [10].

1.2.2 Advanced oxidation processes

Advanced oxidation processes (AOP's) are defined as processes which involve generation of hydroxyl radicals to oxidize both organic and inorganic contaminants in water or wastewater [21, 22]. Hydroxyl radical is the second most powerful oxidant after fluorine [25].Unlike physical processes such as adsorption, filtration and air stripping, AOP's has the ability to destroys the contaminants rather than transfer them from one media to another [23]. AOP's can be used to treat wastewater steams with high chemical oxygen demand and low biodegradability [24]. AOP's can achieve complete oxidation of the waste by converting the contaminants into water, carbon dioxide and harmless inorganic products [23]. Nevertheless, it is expensive and impractical to use AOP's for complete mineralization because of the intermediate products that are resistance to chemical oxidation. A practical solution is to AOP's as a pre-treatment step followed by biological treatments. Partial mineralization by AOP's produces intermediates with higher biodegradability and less toxicity which makes biological oxidation feasible [25]. It is very important to determine feed's quality before selection of any AOP's system as it can affect process efficiency [24]. High alkalinity waste contains excess carbonate and bicarbonate compounds that can interfere with oxidation reaction of hydroxyl radicals. Hydroxyl radical will react with these compounds forming a much weaker radical which result in lower efficiency [27]. This problem can be solved by reducing the alkalinity to ensure there is no excess carbonate and bicarbonate in the waste. Alkalinity can be simply reduced by reducing the pH [24]. Nitrates and nitrites can also affect the efficiency of AOP's system that utilizes ultraviolet light (UV) to generate hydroxyl radicals [28]. Nitrates and nitrites can absorb UV light which lowers hydroxyl radical generation rate. Thus, degree of oxidation will be reduced [24]. Turbidity has the same effect on AOP's effectiveness as nitrates and nitrites. Turbidity will lower the hydroxyl radical generated by acting as a barrier preventing the UV light to penetrate through the waste that is desired to treat [28].

AOP's reaction systems consists a catalyst and an oxidant. The job of the catalyst is the generation of hydroxyl radicals from oxidants. There are several ways to generate the hydroxyl radical which are photochemical, photo-catalysis, ultrasound and chemical oxidation [24]. Photochemical processes include UV, ozone system (UV/O_3) and (UV/H_2O_2) system. Photo-catalysis includes photo fenton. Chemical oxidation includes, O_3/H_2O_2 and H_2O_2/Fe^{+3} [22].

1.2.3 Ozone and ultraviolet radiation (O_3/UV)

Advanced oxidation processes with ozone and ultraviolet radiation is initiated by photolysis of ozone according to the following reaction [22]

$$O_3 + H_2O \xrightarrow{\quad h\nu \quad} H_2O_2 + O_2 \qquad\qquad (1.9)$$

Hydrogen peroxide is formed, then, ozone will react with hydrogen peroxide to produce hydroxyl radical [22]

$$2\,O_3 + H_2O_2 \xrightarrow{\quad\quad} 2\,OH \bullet + 3\,O_2 \qquad\qquad (1.10)$$
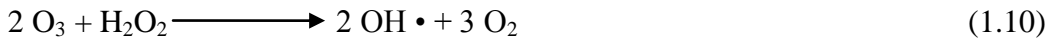
The photolysis of ozone occurs when ultraviolet radiation is applied to ozone saturated water with a wavelength of 254 nm [29]. Hydroxyl radical produced in reaction 1.10 has an oxidation potential higher than ozone or hydrogen peroxide [26]. From reaction 1.10, to produce one mole of hydroxyl radical, one mole of ozone and one half mole of hydrogen peroxide are consumed. In this system, degradation of pollutants can occur due to chemical oxidation of hydroxyl radical, direct ozone oxidation as well as photolysis by UV light [29]. There are two important parameters in O_3/UV system that must be evaluated which are UV dose and ozone concentration [21, 22]. UV dose is defined as the energy transmitted by UV radiation per volume of treated wastewater. The UV dose per ozone required is responsible for the generation of hydroxyl radical and it depends on the feed's strength [21]. Other important parameters that should be evaluated to assure efficient operations are the pH and the radiation lamp cleaning system [29, 30]. The pH can affect the generation of hydrogen peroxide. As shown in reaction 1.10, one mole of ozone is photolysis to 1 mole of hydrogen peroxide for pH < 1.8. As pH increases, the ratio will decrease [29]. UV Lamp cleaning system is very important to avoid UV fouling. Frequency of cleaning depends on the feed fouling concentration compounds which are iron, calcium and magnesium [30]. The main

advantages of O_3/UV system are higher pollutant removal than ozone or UV light and it produces more hydroxyl radicals than other AOP's. The main drawbacks of this system are ozone gas must diffuse through the liquid which may result in mass transfer limitation. Turbidity can inhibit UV light penetration resulting in lower process efficiency. Absorbing UV light compounds can absorb UV light lowering process efficiency. Low stability of ozone on water can result in more energy demand which increases both capital and operational cost of the system [22, 24, 30].

1.2.4 Hydrogen peroxide and ultraviolet radiation (H_2O_2/UV)

Another type AOP's is hydrogen peroxide and ultraviolet radiation (H_2O_2/UV) system. Hydroxyl radicals are generated this system via two mechanisms, photolysis of hydrogen peroxide and decomposition of hydrogen peroxide [21],[22], [24],[29] [30], [31] . Hydroxyl radical generation by photolysis of hydrogen peroxide is shown in the following reaction [29]:

$$H_2O_2 \xrightarrow{h\nu} 2\ HO\bullet \qquad (1.11)$$

Each Mole of hydrogen peroxide produces one half moles of hydroxyl radical. The required wave length for this reaction to occur is below 250 nm [29]. This Reaction depends on pH. As the pH increases the amount of hydroxyl increases more hydroxyl radical is produced [24]. The propagation reactions of hydrogen peroxide are the following [31]:

$$H_2O_2 + HO^\bullet \longrightarrow HO_2\bullet + H_2O \qquad (1.12)$$

$$H_2O_2 + HO_2^\bullet \longrightarrow HO\bullet + O_2 + H_2O \quad (1.13)$$

$$2\ HO_2\bullet \longrightarrow H_2O_2 + O_2 \qquad (1.14)$$
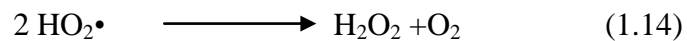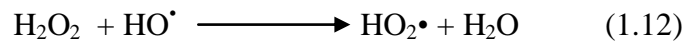
Finally the chain reaction is terminated [31]:

$$2\ HO\bullet \longrightarrow H_2O_2 \qquad (1.15)$$
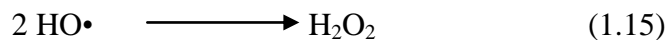
Hydrogen peroxide fallows two paths, either the radiation or decomposition path. However, radiation path is more efficient as more hydroxyl radicals are formed for less hydrogen peroxide consumed. It is important to keep the amount of hydrogen peroxide consumed in this system as low as possible since it is an expensive material and can affect the cost [22]. Some of the important parameters of this system are UV lamp intensity, reactor contact time,

operational temperature and pressure and hydrogen peroxide dose [21]. UV lamp intensity is necessary to generate hydroxyl radicals and it is mainly a function of feed's strength [30]. It is important to keep hydrogen peroxide concentration low so hydroxyl radical generation would follow the radiation path [22]. The main advantage of H_2O_2/UV system is higher pollutants removal compared to UV or H_2O_2 system alone. Where is, the main disadvantages of H_2O_2/UV system are turbidity can inhibit UV light penetration resulting in lower process efficiency. Absorbing UV light compounds can absorb UV light lowering process efficiency. High residual hydrogen peroxide can promote microbial growth which is not desirable when treating drinkable water. The amount of hydroxyl radicals produced is less not O_3/UV [21, 22, 24, 29-31].

1.2.5 Ozone with hydrogen peroxide system

Ozone is unstable compound is water. It dissociates in alkaline water and forms hydroxyl radicals according to the following mechanism [32]:

$$O_3 + OH^- \longrightarrow O_3^{\bullet -} + OH^{\bullet} \qquad (1.16)$$

$$O_3^{\bullet -} \longrightarrow O_2 + O^{\bullet -} \qquad (1.17)$$

$$O^{\bullet -} + H^+ \longrightarrow OH^{\bullet} \qquad (1.18)$$
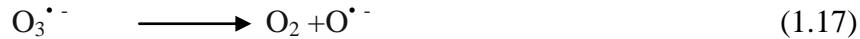
Increasing pH promotes hydroxyl radicals formation [24]. The main disadvantage of ozone water system is the small amount of hydroxyl radicals generated. One way to improve this problem is usage of ozone with hydrogen peroxide system [32]. Hydrogen peroxide is added to the system to enhance hydroxyl radical production rate. As shown previously, hydrogen peroxide reacts with ozone to produce hydroxyl radicals through series of reactions. The overall reaction is [22]

$$2\,O_3 + H_2O_2 \longrightarrow 2\,OH \bullet + 3\,O_2 \qquad (1.10)$$
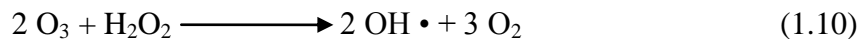
The system is similar to UV hydrogen peroxide system. However, Ozone hydrogen peroxide system is less affected by feed's quality characteristic like turbidity [33].

1.2.6 Ozone, Hydrogen Peroxide, and Ultraviolet Radiation (O_3/H_2O_2/UV)

One way to improve contaminants' removal is the usage of ozone, hydrogen peroxide, and ultraviolet radiation system (O_3/H_2O_2/UV). This system utilizes two oxidants, hydrogen peroxide and ozone to increase hydroxyl radical generation. Although the contaminants'

removal increases, the cost of treatment will increase rapidly because of the usage of the two oxidants [22]. The following table compares the operational treatment cost for 90 % COD removal using $O_3/H_2O_2/UV$, O_3 /UV and H_2O_2/UV.

Table 1.3: Operational Cost of Different AOP's Systems [33]

System	Operational cost($\$/m^3$)
H_2O_2/UV	4.5
O_3/UV	8.6
$O_3/H_2O_2/UV$	11.3

As shown in the table, the treatment cost of $O_3/H_2O_2/UV$ system is much higher compared to other AOP's. This system is best utilized to wastewater when pollutant weakly absorb UV radiation light [33].

1.2.7 Ultrasound systems

In these systems, ultrasound is used to generate hydroxyl radicals [21, 22, 34, 35]. Ultrasound waves are transmitted and introduce to the wastewater as alternating compression and expansion cycles. Micro-bubbles occur when the expansion's cycle amplitude is large enough to stretch the molecular a distance larger than its distance to stay in the liquid phase. The following compression cycle will collapse the micro-bubbles producing extremely high temperature and pressure. These conditions are capable of breaking water molecular producing hydroxyl radicals [35]. There are factors affecting ultrasound systems like ultrasound frequency, temperature and pressure of the dissolved gas [34]. Ultrasound intensity is related to the rate of hydroxyl radicals' generation. Higher ultrasound frequency will provide shorter time for the microbubble to collapse resulting in lower possibility of hydroxyl radicals to recombine which result in higher generation rate of hydroxyl radicals [21]. Usually ozone or hydrogen peroxide is used along ultrasound to promote hydroxyl radical's generation which enhances pollutants' removal [21, 22, 35].

1.2.8 Ozonation and ultrasound

The reaction between ozone and ultrasound to generate hydroxyl radicals are shown in following reactions [21]:

$$H_2O \xrightarrow{\text{US}} H^{\bullet} + OH^{\bullet} \tag{1.19}$$

$$O_3 \xrightarrow{\text{US}} O_2(g) + O(^3P) \tag{1.20}$$

$$O(^3P)(g) + H_2O \longrightarrow 2OH^{\bullet} \tag{1.21}$$

$$O_3 + OH\bullet \longrightarrow O_2 + HO_2^{\bullet} \tag{1.22}$$

$$O_2 + H^{\bullet} \longrightarrow HO_2^{\bullet} \tag{1.23}$$

$$O_3 + HO_2^{\bullet} \longrightarrow 2O_2 + OH^{\bullet} \tag{1.24}$$

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \tag{1.25}$$

$$HO_2^{\bullet} + OH^{\bullet} \longrightarrow H_2O + O_2 \tag{1.26}$$
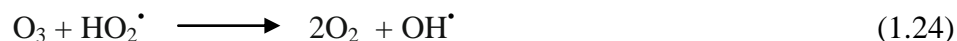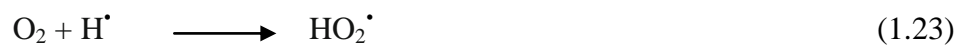
Where US is ultrasound

In this system, ozone is added to increase hydroxyl radicals. Also, ozone can enhance purification percentage [21].

1.2.9 Hydrogen peroxide and ultrasound systems

Hydrogen peroxide is added to provide sufficient hydroxyl radical to achieve the desired pollutant removal. The reaction mechanism of hydrogen peroxide ultrasound is as follows [22, 35]:

$$H_2O_2 \longrightarrow 2OH^{\bullet} \tag{1.27}$$

$$H_2O_2 + O_2 \longrightarrow 2HO_2^{\bullet} \tag{1.28}$$

$$H_2O_2 + OH^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O \tag{1.29}$$

The main advantages of ultrasound systems are the energy required to generate hydroxyl radical is lower than other AOP's especially the ones that uses UV radiation light and the operational costs is much lower than UV radiation systems. The main disadvantages are no commercial plant using this system has been built yet and the amount of oxidant either ozone or hydrogen peroxide required to increase hydroxyl radical is large which increases the cost of operations [21, 22, 34, 35].

1.2.10   Fenton's reagent

Another example of AOP's is Fenton's reaction. The system consists of hydrogen peroxide as an oxidant and ferrous ion as a catalyst [36]. The reaction of hydrogen peroxide and ferrous ion is called fenton's chemistry. Usually, Fenton's reagent or fenton's reaction are

other names used to describe this system [37]. The system was found by fenton over 100 years ago. Although this system has been found for over 100 years ago, its application was not applied until the late 1960's [38]. Currently, fenton's reagent has been used in various applications such as textile wastewater, laboratory wastewater, industrial wastewater, dye wastewater, pulp mill effluent, petroleum refinery sour water [39]. The main advantages of fenton's are its high efficiency and its ability to treat various contaminants [36]. Usually, fenton's reaction is used as a pre-treatment before sending the feed into biological treatment. This is often the case since some low molecular weight organics resists fenton's oxidation such as paraffin's, chlorinated alkanes and some short chin carboxylic acids[39].

The oxidation ability of fenton's reaction arise from generation of hydroxyl radical which is the second most powerful oxidant after fluorine[25] and [26]. Hydroxyl radical is generated according to the following reaction [39]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \tag{1.30}$$

Ferrous will react with hydrogen peroxide forming ferric ion, hydroxyl radical and hydroxyl anion. This reaction is the chain initiation of Fenton's reaction [37]. The generation of hydroxyl radicals follow complex chain reaction. Once the ferric ion is formed, it can reacts with hydrogen peroxide according to the following reactions [39]:

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe{-}OOH^{2+} + H^+ \tag{1.31}$$

$Fe{-}OOH^{2+}$ is an intermediate that will decompose to form HO_2 radical as shown in the following reaction [37]:

$$Fe{-}OOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \tag{1.32}$$

Reaction 1.31 is called fenton's like reaction [39]. HO_2 radical can oxidize pollutants, however, its oxidation power is much lower than hydroxyl radical [25, 26]. Other chain reactions occur in fenton's reaction are the following [38]:

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO^{-2} \tag{1.33}$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \tag{1.34}$$

$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet \tag{1.35}$$
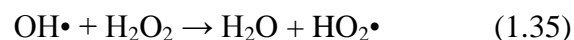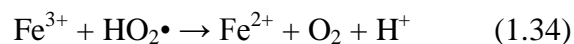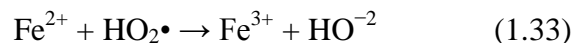
As seen in reaction 1.35, hydrogen peroxide can scavenge hydroxyl radicals to form water and $HO_2\bullet$ [36]. Finally the termination step is shown in the following reaction [39]:

$$OH\bullet + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad (1.36)$$
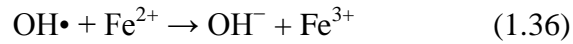
In reaction 1.36, hydroxyl radical reacts with ferrous ions forming hydroxyl anion and ferric ions. An overall reaction for this mechanism can be given by the following reaction [38]:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \qquad (1.37)$$
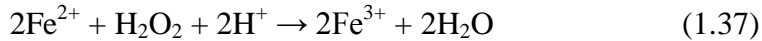
According to reaction 1.37, forming hydroxyl radicals requires H^+. This means that fenton's require acidic media so the reaction occurs [36]. Once hydroxyl radicals are formed, it will oxidize organic contaminants. If complete oxidation occurs, contaminants can decompose into water, carbon dioxide and some harmless inorganic salts [40]. Hydroxyl radicals can oxidize organics (RH) by removal of protons from organics forming organic radical[39]:

$$RH + OH\bullet \rightarrow H_2O + R\bullet \qquad (1.38)$$

Where R refers to any organic contaminant

This reaction is chain propagation. Once organic hydroxyl is formed, further oxidation will occur [41]:

$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \qquad (1.39)$$
$$R\bullet + O_2 \rightarrow ROO\bullet \qquad (1.40)$$
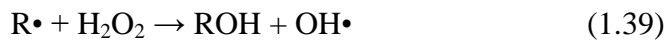
Another pathway can occur for organic radicals. They can be oxidize by ferric ions, reduced by ferrous ions or two radicals can dimerised as shown in the following reaction [38]:

Oxidation: $\qquad R\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \qquad (1.41)$

Reduction: $\qquad R\bullet + Fe^{2+} \rightarrow R^- + Fe^{3+} \qquad (1.42)$

Dimerizarion: $\qquad 2R\bullet \rightarrow R\text{–}R \qquad (1.43)$
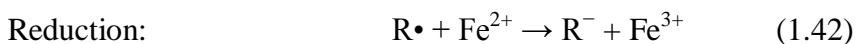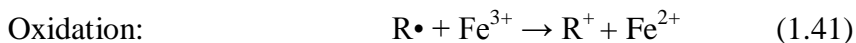
Beside chemical oxidation of contaminants by fenton's reagent, this method can show coagulation effect. Adjusting the pH to a range of 5-7 will result in precipitation of dissolved ferric particle. Precipitated ferric particle solids will combine to form flocs that will help

remove the dissolved solids. As a result, fenton's method can achieve both chemical oxidation as well as coagulation treatment [43]. The ratio of hydrogen peroxide to ferrous salt can determine the degree of oxidation to coagulation. Chemical oxidation is dominant in fenton's reaction when the ratio of hydrogen peroxide to ferrous salt is above 2. On the other hand, the coagulation effect of fenton's reaction is dominant when the ratio of hydrogen peroxide to ferrous salt is below 1/5 [38]. It is important to select the right ratio to ensure destruction of contaminant since the goal of this method is destruction of contaminants and not to physically separate the contaminants [23]. Other important parameters in fenton's reaction that must be evaluated are pH, temperature, ferrous salt concentration and reaction time [43-45]. The pH is important in fenton's reaction and can affect the system's efficiency. From the overall reaction of fentin's chemistry, acidic media is necessary for the reaction to occur. Typical optimal pH value falls in the range of 3 to 5 [44]. The second parameter is the reaction temperature. Fenton's reaction is an exothermic reaction. As temperature increases, exothermic reaction rate increases and vise versa. However, reaction temperature can affect decomposition of hydrogen which affects the efficiency of the process. Thus, it is important to study the effect of temperature on hydrogen peroxide decomposition [43]. Moving to ferrous sulfate concentration, it is used as the catalyst in fenton's reaction [38]. Ferrous sulfate can contribute in fenton's reaction in two main ways. Ferrous sulfate is responsible for the generation of hydroxyl radicals. Generation of hydroxyl will convert ferrous ions to ferric particles. Ferric particle is known as a coagulation agent. As ferrous concentration increases, more coagulation treatment occurs [45]. The final parameter is the reaction time. It is important to ensure sufficient residence time to allow oxidation to occur to the desirable extend [44]. Also, it is important to ensure that there is hydrogen peroxide residual as it will interfere with many wastewater quality tests especially COD tests [45]. Once fenton's reaction proceeds to completion, high strength contaminants are oxidized into low molecular weight organic acids and some organics that are easily treated by conventional biological treatment [23]. Usually ferric particles in the in the treated effluent enable coagulation treatment easily by neutralizing pH in which ferric ion converts into insoluble solid that precipitate. The precipitated solid can be easily removed by sedimentation basin [38]. Also, the treated effluent can be sent to biological treatment for post treatment to achieve the desirable degree of treatment [23].

The application of fenton's method in the field of spent caustic is done by a company called 'FMC Foret". They utilized modified fenton's reaction to treat spent caustic. The company calls the process oxidation with hydrogen peroxide (OHP) [46]. There are two main differences between this method and classical fenton's reaction. The first difference is the catalyst used. In FMC Foret, the catalyst used is ferrous salt without specifying the type of salt. The second difference is the operational conditions. Classical fenton's reaction operates at ambient temperature and pressure while FMC Foret operates at mild conditions [43], [45] , [46]. The process flow diagram of OHP is shown in the figure below.
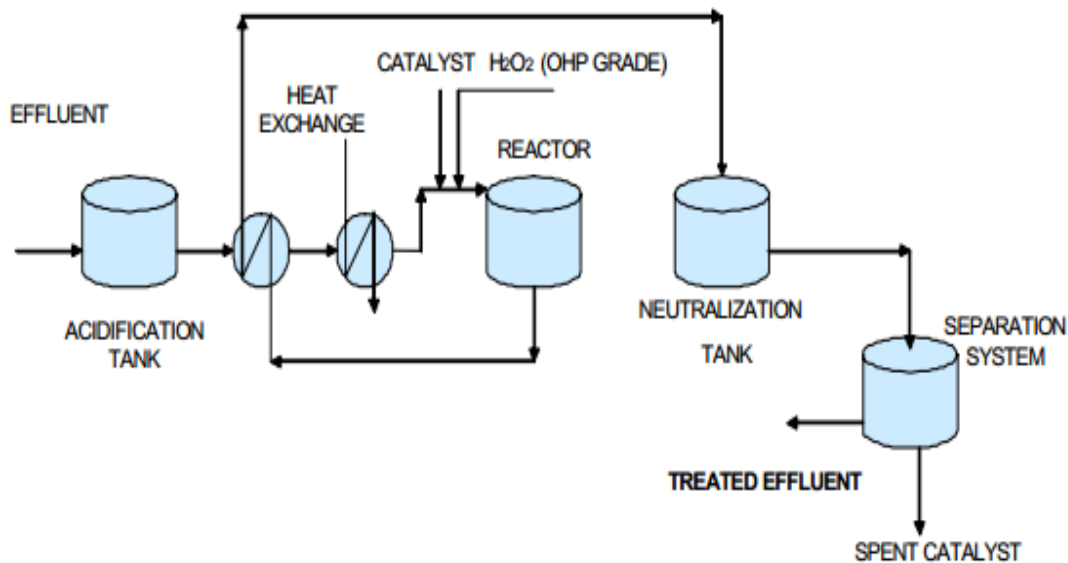
Figure 1.3: OHP Process Flow Diagram [46]

Spent caustic is first pumped to acidification tank. In the acidification tank the pH is adjusted to value of 3-5 so fenton's reaction can occur [44]. Strong acid is used in this step like sulfuric acid. Acidification can also play a role in treatment as well as preparing the feed. Contribution of acidification in treatment comes from releasing acidic compounds that are captured by alkaline compounds like H_2S [47]. After the acidification step, the feed is pumped to the reaction pressure which is 2-2.5 bar. The pressurized spent caustic is then fed into two heat exchanger to raise the temperature to 110-120 °C [46]. The heated feed is mixed with the ferrous salt catalyst and hydrogen peroxide. The residence time is adjusted in the reactor to achieve the desired degree of oxidation. After the reaction proceeds to

completion, the reactor effluent is sent to a heat exchanger to cool the product. The cooled effluent is then sent to neutralization tank. In the neutralization tank, base is added to adjust the pH to value around 7. Adjusting the pH will precipitate ferric ion generated in the reaction [38]. The final step is a decanter where the precipitated solids are separated from the treated effluent. The treated effluent is then sent to biological treatment for post treatment [23]. Spent catalyst can be reused after reactivation of the spent catalyst [46].

The main advantage of this process is the ability of treating influents with different organic content and flow rates. Another advantage is high COD removal. COD removal can reach up to 95 % which is higher than other processes[46, 47]. Also, the system is able to destroy some inorganic contaminants such as sulfides and mercaptans as well as the process is easy to install and has low capital cost [46].

1.3   Research Methods and Material: Bench Scale

The Spent Caustic used was obtained from Enoc oil refinery; two different samples were obtained. Two samples were used in order to determine whether the Fenton reaction could be used as a pretreatment for mixed refinery spent caustic prior to biological treatment, without significant change in the chemistry of the reaction. The main characteristics of the two spent caustic samples are represented in the table below; common to both samples is a severe foul odor.

Table 1.4: Spent Caustic Characteristics

Constituent	Sample 1	Sample 2
pH	13	7.5
Specific Gravity	1.12	1.1
Chemical Oxygen Demand (mg/L)	65,000	41,000

1.3.1 Materials

In order to produce the Fenton reagent 30 wt% lab grade hydrogen peroxide (panreac) was implemented in the study, along with lab grade ferrous sulfate heptahydrate (panreac) which was used as a saturated solution. 5.0 M sodium hydroxide solution was prepared by dissolving in de-ionized water. 25wt% Sulfuric acid (panreac) was used by diluting samples of the reagent from an original concentration of 99.8wt%. Lab grade potassium hydrogen phthalate (KHP) (Hach) was used to check the accuracy of the COD spectroscopic measurements by using standard samples of KHP with known COD. Standard samples of 1,000 ppm COD were supplied by Hach. If the COD measurement is exceeding the 1,000 $\pm$ 100 ppm, then the machine is recalibrated.

1.3.2 Experiential setup and procedure
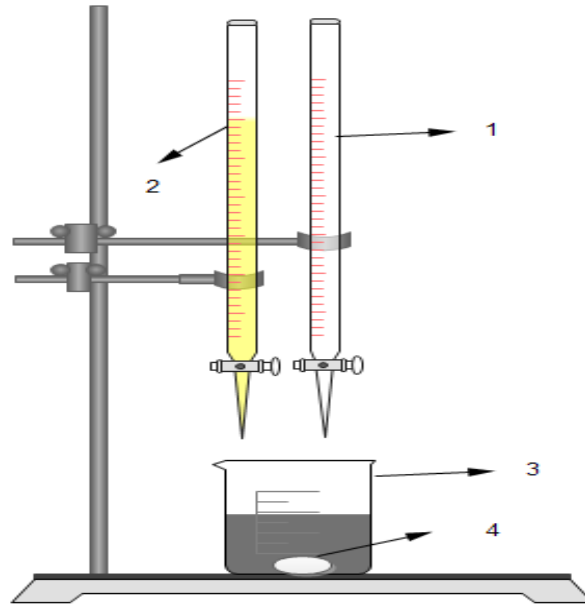
Figure 1.4: Bench Scale Experiential Setup

All the experiments were conducted in a 200 mL batch reactor filled with 50 mL of the spent caustic sample at a time, no dilution was performed so as to evaluate the feasibility of the process for high COD mixed refinery spent caustic as well as other industrial wastewaters. The reactor was made of pyrex glass beaker (3) equipped with a magnetic stirrer (4) to ensure a homogeneous condition within the reactor, the degree of stirring was kept mild as any excessive stirring lead to excessive foaming. The reactor is equipped with two 50 mL burettes (1,2), one for ferrous sulfate solution and the other is for hydrogen peroxide. A mercury thermometer, when needed, was also placed within the reactor to monitor the temperature increase throughout the reaction.

The pH of the sample is then adjusted to a value of 3 using 25wt% sulfuric acid; the value was decided based on previous work by other investigators [42]. As the pH of the spent caustic sample is lowered, a drastic color change occurs. The hydrogen peroxide and ferrous sulfate solution are then dosed into the reactor from their respective burettes at specific time intervals; it is critical to dose the Fenton reagents slowly so as to avoid excessive foaming and poor COD removal. The Fenton reagents are added isolated from one another because it is desirable for the reaction to occur within the wastewater [48]. Upon the addition of the first

drop of hydrogen peroxide, the color of the sample darkens with respect to the color of the acidified spent caustic which indicates the occurrence of the reaction. Once the dosing is completed, the sample is left to react until the end of the remaining defined batch time which was fixed at 50 minutes. The batch time was selected given that almost 90% of the COD removal occurs within the first ten minutes of the reaction [42]. Once the batch time was completed, the sample is immediately neutralized to a pH of 7 using 5.0M sodium hydroxide. The addition of the NaOH immediately quenches the Fenton reaction, as well as precipitates the ferrous added as ferric hydroxide. The neutralized sample is then withdrawn and centrifuged to separate the iron floc from the treated liquid, the liquid is then decanted and its COD tested. The iron floc is tested to determine the components present in it, so as to ensure that the contaminants are in fact destroyed and not coagulated along the floc.

1.3.3 Analytical methods.

The of samples was tested using COD digestion vials (Hach), where 0.2mL of the sample is placed within digestion vials which in turn are heated at 150^oC for 2 hours. Digestion vials were then allowed to cool naturally to ambient temperature before having the COD measured. The vials are then placed in the Hach DR5000 spectrophotometer, which is tested against a COD digestion vial blank prepared using COD free water. The accuracy of the testing method was temporarily checked by preparing samples of known COD by using KHP (Panreac)

1.3.4 Parameters investigated and objectives.

The objective of the bench scale experiments is to treat undiluted mixed refinery spent caustic to achieve a final COD around 1000 ppm with minimum hydrogen peroxide to initial COD mass ratio by manipulating other variable that affects Fenton's reaction. The parameters investigated are:

1. The effect of hydrogen peroxide concentration on COD removal

2. The effect of ferrous sulfate concentration on COD removal

3. The amount of Fenton reagents added to the sample based on the initial COD, hence defining optimal mass ratio with respect to the COD of the sample

4. The rate at which the Fenton reagents were added investigated

5. The addition of an initial dose of the Ferrous Sulfate solution

6. The use of more than one reactor in series

1.4   Research Methods and Material: Pilot Plant

The Spent Caustic used was obtained from oil refineries in the region; five different samples were obtained. Two samples were used in order to determine whether the Fenton reaction could be used as a pretreatment for mixed refinery spent caustic prior to biological treatment, without significant change in the chemistry of the reaction. The main characteristics of the two spent caustic samples are represented in the table below.

Table 1.5: Spent Caustic Characteristics Used in the Pilot Plant

Parameters	Sample 1	Sample 2
COD(mg/L)	13100	98800
TOC (mg/L)	156	2360
pH	12.2	12.1
Oil and Grease (mg/L)	28.7	1506.9
Sulfide(mg/L)	2160	3600
Phenols(mg/L)	1.6	2.0
TSS(mg/L)	294	126
Turbidity (NTU)	166	16
Odor	High odor	Very high
Ammonia(mg/L)	21.7	26.5
Na_2S (wt%)	0.526%	0.409%
Sulfates(SO_4) (mg/L)	468	5820
Na_2CO_3 (wt%)	2.02%	2.92%
NaOH (wt%)	2.92%	1.99%
TDS (mg/L)	158000	146000
H_2S (mg/L)	6.5	22.5

1.4.1 Materials

In order to produce the fenton reagent, 35 wt% commercial grade hydrogen peroxide was implemented in the study, along with commercial grade ferrous sulfate heptahydrate which was used as a saturated solution. 5 M sodium hydroxide solution was prepared by dissolving

in de-ionized water. 25wt% sulfuric acid (panreac) was used by diluting samples of the reagent from an original concentration of 99.8wt%. Lab grade potassium hydrogen phthalate (Hach) was used to check the accuracy of the COD spectroscopic measurements.

1.4.2 Experimental Procedure

Once the optimal conditions were determined at the bench scale level, they were implemented on a pilot plant scale. Seen in the figure 1.5 is the process flow diagram of the pilot plant. A reactor constructed of 316 stainless steel (SS) is charged with the spent caustic waste in a batch manner from a feed tank using diaphragm pumps, part of the flow is recycled to the feed tank to ensure good mixing. The reactor is equipped with a mechanical mixer, which is fitted with two 3 blade marine type propellers. The first lower impeller is placed for mixing purposes, while the other and higher placed propeller acts as a foam breaker. Hydrogen peroxide and the ferrous sulfate solutions are fed to the reactor using diaphragm dosing pumps from their respective PVC dosing tanks; the reagents are fed into the reactor through submerged 316 SS pipes which lead to the bottom of the reactor. The Fenton reagents are fed in such a manner to avoid foaming within the reactor. Liquid is withdrawn from the bottom of the reactor; part of it is recycled while the remainder is sent to the next unit for neutralization. The liquid leaving the reactor is fed to a conical shaped tank where it is neutralized; the sodium hydroxide is fed by gravity to the tank. A recirculation pump is used to ensure good mixing, along the recirculation line a sampling port is placed to ensure that the pH is at the required level.

The outlet from the neutralization tank is fed to a sedimentation tank, where the feed enters through a submerged pipe which leads to the bottom layer to avoid disturbing the liquid layer. The sedimented iron floc is withdrawn from a drain at the bottom of the sedimentation tank, while the liquid is withdrawn from a higher level and then sent on to filtration. The liquid from the sedimentation undergoes a two filtration process, in order to capture any unsedimented fine particles. In the first stage of filtration, fiber cartridge filtration with porosity of 5 microns is implemented with two in series. The fiber cartridge can easily and inexpensively be replaced when exhausted. The permeate is then fed to the second stage of filtration which implements ceramic filtration with a porosity of 0.9 microns, which is backwashed periodically. The permeate from the second stage of filtration is then fed to a

final polishing step, mainly to remove remaining odor and color. The polishing step consists of a column packed with ion exchange resin and activated carbon, two of the columns were used to allow backwash without interruption in flow.
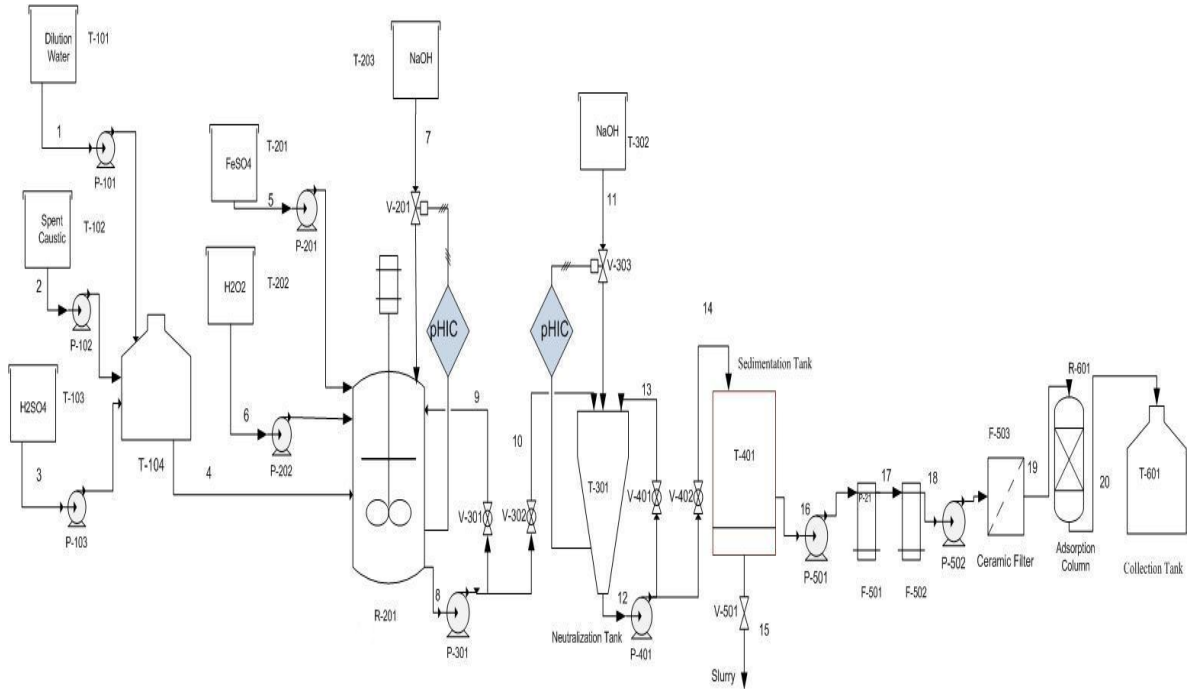
Figure 1.5: Pilot Plant PFD

1.4.3 Objectives

The objectives of the pilot plant experiment are the following:

- Verify the ability of fenton's reaction to treat large quantity of spent caustic and achieve the required degree of treatment
- Verify the ability of fenton's reagent process to compete economically with other alternatives by estimating cost of chemicals

1.5 Thesis Outline

- Chapter 1: Covers the introduction of the thesis, background information of the topic, literature review and material and methods used in the research
- Chapter 2: Covers the bench scale experiment. This chapter shows the study of different parameters affect fenton's reaction and how optimum condition were obtained

- Chapter 3: This chapter covers the pilot plant experiments. The results obtained from the pilot plant are displayed in this chapter and costing of chemicals is included too.
- Chapter 4: this chapter is the conclusion chapter. It summarizes the important result obtained in the research and recommendation that can improve the study is also included.

CHAPTER 2:
Bench Scale Experiments

2.1 Effect of hydrogen peroxide & ferrous sulfate concentrations on COD removal

2.1.1 Procedure

The effect of ferrous sulfate concentration and hydrogen peroxide concentration on COD removal were studied. The procedure, in this set, is different where both reagents hydrogen peroxide and ferrous sulfate are added to the system at once without dosing. Spent caustic is diluted with de-ionized water with a ratio of 1 to 4. pH is adjusted to a value of 3 using 25wt% sulfuric acid. Ferrous sulfate catalyst is added to spent caustic as solid and enough mixing is applied to dissolve the catalyst. 30 wt% hydrogen peroxide is added to spent caustic and 50 minutes reaction time was fixed. Treated sample is neutralized to a pH of 7 by 5.0M sodium hydroxide. The neutralized sample is then withdrawn and centrifuged to separate the Iron floc from the treated liquid, the liquid is then decanted and its COD tested.

2.1.2 Results and discussion

The first parameter studied is the effect of hydrogen peroxide concentration on COD removal. The following table shows the effect of hydrogen peroxide on COD removal.

Table 2.1: Effect of Hydrogen Peroxide Concentration on COD Removal when Hydrogen Peroxide and Ferrous Sulfate are added at Once

Sample number	Spent Caustic Volume (mL)	Ferrous Sulfate(g)	H_2O_2 (mL)	Ferrous Sulfate (mol/L)	H_2O_2 (mol/L)	Initial COD(ppm)	Final COD(ppm)	COD Removal %
1	50	14	4	1.84	2.61	8200	4670	43%
2	50	14	6	1.84	3.92	8200	2690	67%
3	50	14	7	1.84	4.57	8200	2560	69%
4	50	14	8	1.84	5.22	8200	2980	64%
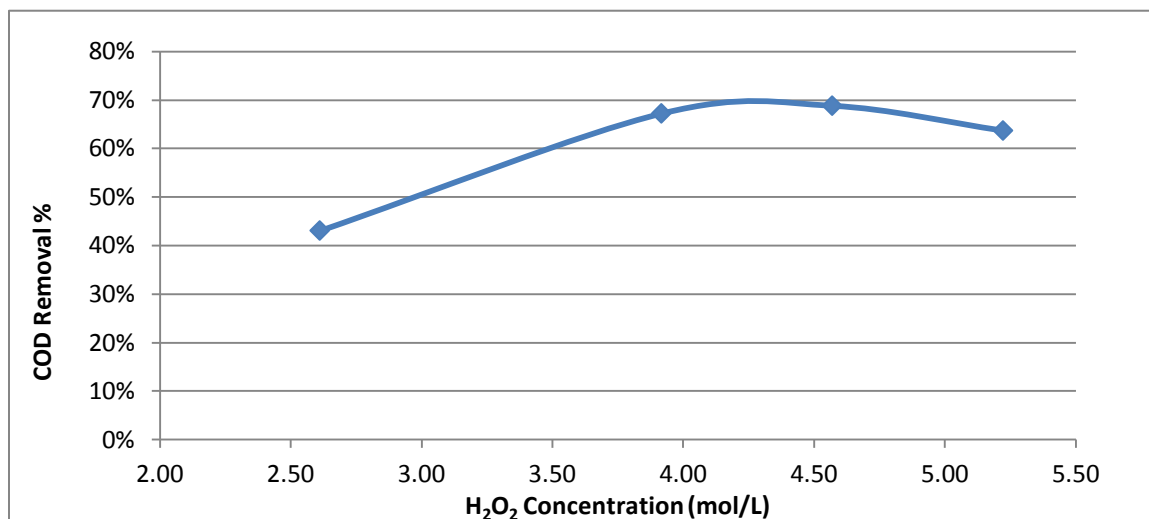
Figure 2.1: Effect of Hydrogen Peroxide Concentration on COD Removal when Hydrogen Peroxide and Ferrous Sulfate are added at Once

The figure above shows the effect of hydrogen peroxide concentration on COD removal. For all samples, 1.84 mol/L of ferrous sulfate is fixed and hydrogen peroxide concentration is varied. As shown in the figure, COD removal increases as the concentration of hydrogen peroxide increases due to the generation of hydroxyl radicals. COD removal keeps on increasing until it reaches a maximum value and then it starts to decrease. The maximum COD removal is around 70 % at hydrogen peroxide concentration of 4.57 mol/L. Above this concentration, COD removal decreases as the concentration of hydrogen peroxide increases. COD decreases at high concentration of hydrogen peroxide because of the scavenging effect

of hydrogen peroxide [42]. Hydrogen peroxide is the oxidant of fenton's reaction. The desired reaction pathway of hydrogen peroxide is to react with ferrous sulfate to produce hydroxyl radical as it was shown in reaction 1.30. However, at high concentration of hydrogen peroxide, hydrogen peroxide tend to react with hydroxyl radical to produce a weaker radicals $HO_2\bullet$ as as it was shown in reaction 1.35. Reactions 1.30 and 1.35 will compete and at high concentration of hydrogen peroxide, scavenging of hydroxyl radical is dominant. As a result, hydrogen peroxide is not fully utilized to generate hydroxyl radicals. This will decrease the efficiency of the process as more hydrogen peroxide is needed to achieve the desired COD removal. This reaction can also implies that for the same volume of hydrogen peroxide, higher COD removal can be achieved if the concentration of hydrogen peroxide is kept low [49].

The second parameter is the effect of ferrous sulfate concentration on COD removal. Ferrous iron concentration is important to activate fenton's reaction. The main goal of ferrous sulfate catalyst is release hydroxyl radicals from hydrogen peroxide. [50]. That is why it is important to estimate the optimum ferrous sulfate concentration that will generate the maximum amount of hydroxyl radicals. The following table and figure shows the effect ferrous sulfate concentration on COD removal.

Table 2.2: Effect of Ferrous Sulfate Concentration on COD Removal when Hydrogen Peroxide and Ferrous Sulfate are added at Once

| Sample Number	Spent Caustic Volume (mL)	Ferrous Sulfate(g)	H_2O_2 (mL)	Ferrous Sulfate (mol/L)	H_2O_2 (mol/L)	Initial COD(ppm)	Final COD(ppm)	COD Remeval
1	50	8	5	1.05	3.26	8200	3190	61%
2	50	10	5	1.32	3.26	8200	3160	61%
3	50	12	5	1.58	3.26	8200	3260	60%
4	50	16	5	2.11	3.26	8200	3480	58%
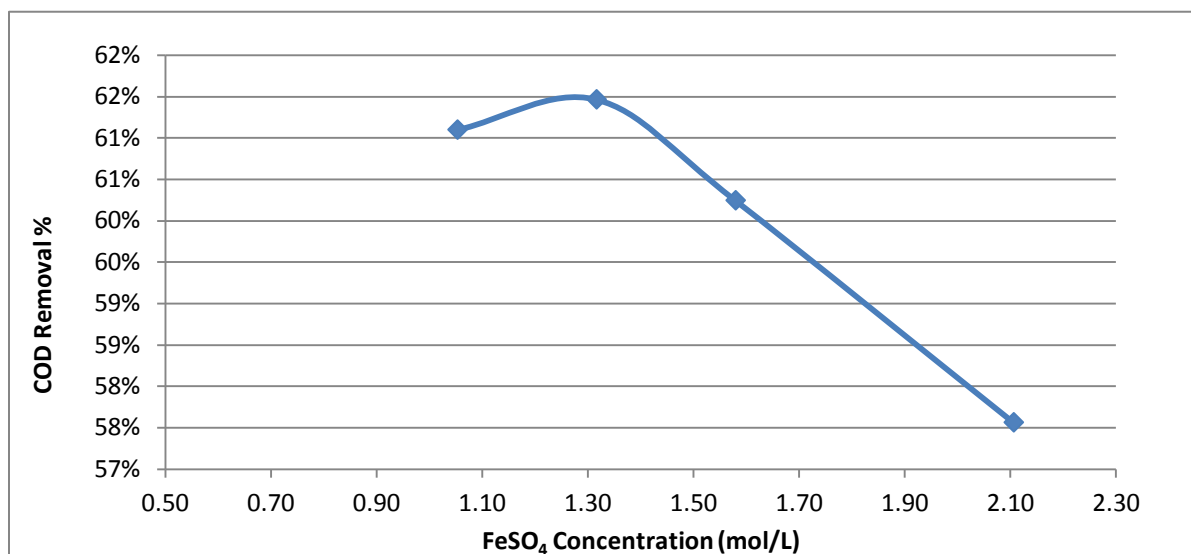
Figure 2.2: Effect of Ferrous Sulfate Concentration on COD Removal when Hydrogen Peroxide and Ferrous Sulfate are added at Once

The figure above shows the effect of ferrous sulfate concentration on COD removal. For the all samples, 3.26 mol/L of hydrogen peroxide is fixed and ferrous sulfate added to spent caustic is varied. As shown in the figure, COD removal increases as the concentration of ferrous sulfate increases since ferrous ions will activate hydroxyl radicals. The maximum COD removal is around 62 % at ferrous sulfate concentration of 1.32 mol/L. Above this concentration, a drop in COD removal occurs. This decreases in COD removal happens due to the scavenging effect of ferrous ion which was shown in equation 1.34. This reaction is more likely to occur when the concentration of ferrous ions is high. In this reaction, ferrous ions consume hydroxyl radicals to form hydroxyl radicals resulting in lower COD removal [50].

Addition of hydrogen peroxide and ferrous sulfate at once to spent caustic shows low COD reduction. As mentioned earlier, high concentration of hydrogen peroxide and ferrous sulfate decreases COD removal, so dosing both reagents must be studied. Beside low COD reduction, other operational problems were noticed during the experiments. Addition of hydrogen peroxide to spent caustic without dosing cause both excessive foaming and excessive temperature increase. Spent caustic has foaming tendency because of the presence of naphthenic acids. Naphthenic acids can generate foam upon mixing or oxidation [51].

When hydrogen peroxide is added to the system at once without dosing, excessive oxidation occurs and massive foaming occurs. Foaming can cause safety problems as foam can spill outside the reactor as shown in the figures below. One way to control foaming is to control oxidation reaction. Oxidation can be controlled by dosing hydrogen peroxide. When hydrogen peroxide is dosed, the rate of oxidation can be controlled to eliminate foaming. Another way to eliminate foaming is the addition of anti-foaming agents. However, addition of anti-foaming agents increases operational cost of the system which is undesirable [52].

Figure 2.3: Foaming in Fenton's Reaction after Few Seconds
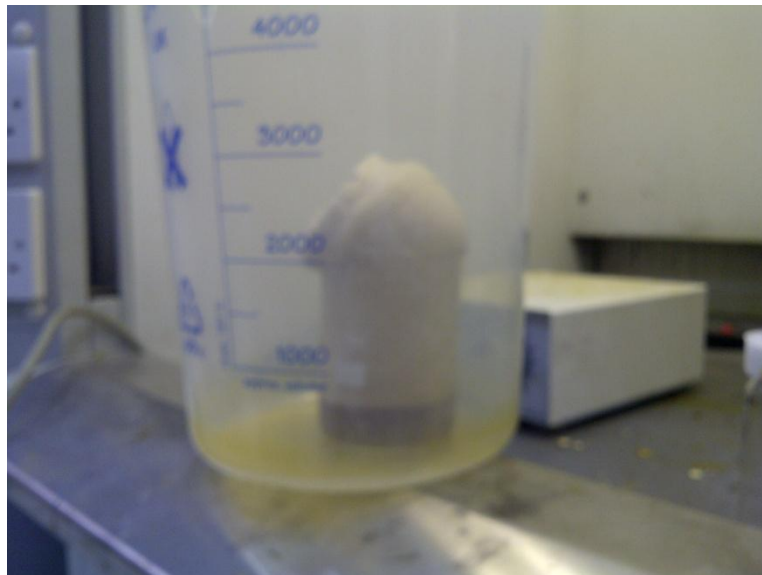
Figure 2.4: Foaming in Fenton's Reaction after Few Minutes

In this set of experiments, temperature increase in the system was observed. When hydrogen peroxide is added at once, rapid oxidation occurs and temperature increase was observed. Reaction temperature was recorded and the maximum temperature reached was 80 °C. At this temperature, utilization of hydrogen peroxide can be affected. For exothermic reactions, as temperature increases, reaction rate increases. At temperatures above 60 °C, reaction rate becomes too rapid that hydrogen peroxide decomposes more quickly to oxygen and water[48]. As a result, it is important to keep the temperature in this range to ensure full utilization of hydrogen peroxide. To control reaction temperature, hydrogen peroxide can be dosed instead of being added at once. .

2.2   Effect of hydrogen peroxide to ferrous sulfate ratio on COD removal

In this stage, the main objective is to eliminate foaming, temperature increase and improve COD removal. It is believed that dosing hydrogen peroxide can eliminate excessive foaming and excessive temperature increase. The effect of dosing hydrogen peroxide on these two operational problems will be studied. Also, different hydrogen peroxide to ferrous sulfate ratios on COD removal are studied to find optimum ratio for COD removal. The optimum ratio can be defined by the ratio of hydrogen peroxide to ferrous sulfate that will generate maximum amount of hydroxyl radicals. Since amount of hydroxyl radicals can't be measured, COD measurement is used. Hydroxyl radicals oxidize contaminants in spent caustic which result in lower COD. As COD reduction increases, it means that more hydroxyl radicals are being generated and vise versa.

2.2.1 Procedure

In this section, the procedure used is similar to the procedure used in the previous section except 30 wt% hydrogen peroxide was dosed over 10 minute period and 41,000 ppm undiluted spent caustic.

2.2.2 Results and Discussion

Hydrogen peroxide to ferrous sulfate ratios ranging from 1.65(wt%) to 0.18(wt%) were studied. This ratio is very important to achieve the desirable COD removal efficiently. As hydrogen peroxide volume added to spent caustic, with proper dosing, increases, COD removal will increase since more hydroxyl radicals are available to oxidize pollutants. However, to achieve efficient operations, it is important to find the best hydrogen peroxide to

ferrous sulfate ratio that will achieve the maximum COD removal. Hydrogen peroxide to ferrous ions ratio can be categorized into three classes [38]. The first category is high hydrogen peroxide to ferrous ions ratio. In this class, hydrogen peroxide added to the system is much higher than ferrous ions. At mentioned earlier, fenton's reaction can achieve both oxidation as well as coagulation treatment. When hydrogen peroxide added is much higher than ferrous ions, oxidation treatment is dominant [38]. This class is desirable since the goal of fenton's reaction is the oxidation of contaminants rather than physical separation. The problem with this ratio is competition of hydrogen peroxide and contaminants to react with hydroxyl radicals. At this ratio, hydroxyl radicals tend to react with hydrogen peroxide rather than reacting with contaminants producing $HO_2\bullet$ as shown in reaction 1.35. In addition, $HO_2\bullet$ reacts with ferrous or ferric ions as shown in reactions 1.33 and 1.34. As a result, COD removal will be lowered and a loss in efficiency will occur. The second type is very low hydrogen peroxide to ferrous ions ratio. In this ratio, coagulation treatment is dominant rather than oxidation [42]. This is undesirable since the goal of fenton's reaction is oxidation treatment. Also, at this ratio, ferrous ions concentration is too high compared to hydrogen peroxide. Ferrous ions will compete with contaminants to react with hydroxyl radicals [49]. Ferrous ions will terminate hydroxyl radicals as shown in reaction 1.36. This reaction can transform ferrous ions from a catalyst to a reactant. This can result in lower hydroxyl radicals' utilization in the desirable path which is oxidation of contaminants. The third ratio is medium ratio of hydrogen peroxide to ferrous ions which falls in between the previous two extremes. At this range, hydrogen peroxide is best utilized. As mentioned earlier, hydroxyl radicals can undesirably react with either hydrogen peroxide or ferrous ions. However, at this range, hydroxyl radicals tend to react with contaminants (RH) instead hydrogen peroxide or ferrous as shown in reaction 1.38. At this range, ferrous ions react with hydrogen peroxide rather than reacting with hydroxyl radicals and maximum amount of hydroxyl radicals are generated. As a result, at this range, hydroxyl radicals tend to react with the desirable path and optimum hydrogen peroxide to ferrous sulfate ratio can be obtained [38]. The following table shows the data collected from the lab:

Table 2.3: Effect of Hydrogen Peroxide to Ferrous Sulfate Ratio on COD Removal when Hydrogen Peroxide is dosed

Sample Number	Ferrous Sulfate(g)	H_2O_2 (ml)	Initial COD (ppm)	Final COD(ppm)	COD Removal	$H_2O_2/FeSO_4$ (g/g)
1	2	3	41000	18000	56%	1.65
2	9	3	41000	13120	68%	0.37
3	10	3	41000	8000	80%	0.33
4	12	3	41000	9400	77%	0.28
5	14	3	41000	11400	72%	0.24
6	16	3	41000	10800	74%	0.21
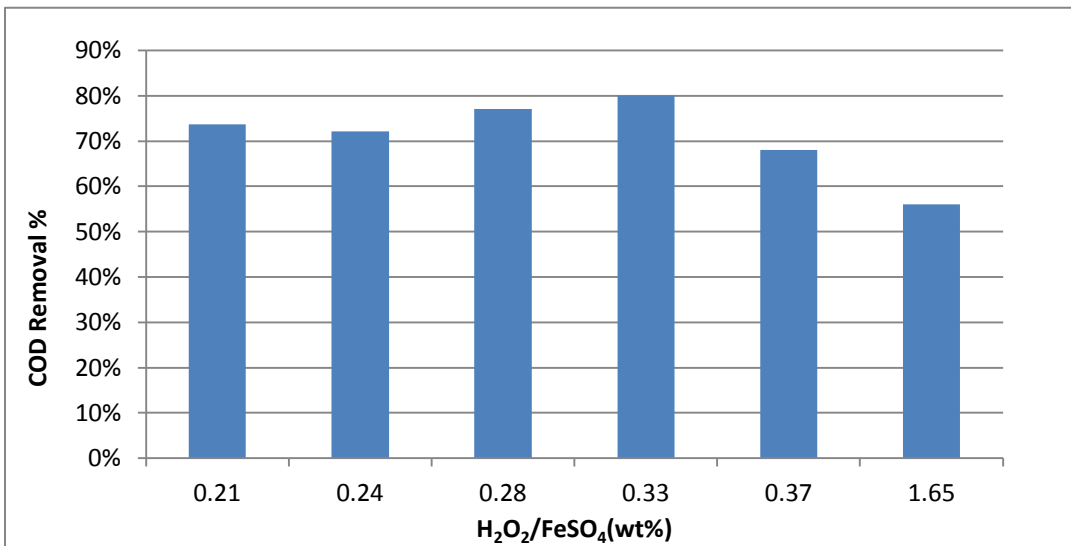
Figure 2.5: Effect of Hydrogen Peroxide to Ferrous Sulfate Ratio on COD Removal when Hydrogen Peroxide is dosed

The figure above shows the COD removal for different hydrogen peroxide to ferrous sulfate ratios. Amount of hydrogen peroxide added to spent caustic is fixed at 3 ml for all the

samples. The maximum COD removal of 80 % is achieved at hydrogen peroxide to ferrous sulfate ratio of 0.33 wt% while the minimum COD removal is 56% at a ratio of 1.65 wt%. It can be noticed that the COD removal has been improved compared to the previous section. Sample number 4 in table 2.2 shows a COD removal of 58% at hydrogen peroxide to ferrous sulfate ratio of 0.31 wt%. An increase of 32% in COD removal is achieved in this section compared to previous section although almost the same ratio was used in both runs. The only difference between the two sections is the dosage of hydrogen peroxide. Dosing hydrogen peroxide eliminates the foaming, temperature increase and reduces scavenging of hydroxyl radicals by hydrogen peroxide. As a result, the increase in COD removal is due to the reduction in the inhibition done by foaming, temperature and scavenging of hydroxyl radicals

Samples analyzed in this section can go through more than one of hydrogen peroxide to ferrous ions category explained earlier. At the beginning of the run, concentration of ferrous ions in spent is high since it is all added at once while concentration of hydrogen peroxide is low since it is dosed to the system. As a result, ferrous ions consume hydroxyl radicals as explained earlier. As the reaction proceeds, ferrous ions concentration drops as more ferrous ions react with hydrogen peroxide and hydrogen peroxide to ferrous ions ratio approaches optimum ratio. This phase can occur through the reaction if enough hydrogen peroxide is added. The third probably didn't occur during the runs done since it requires high amount of hydrogen peroxide. To avoid this change in reaction pathway, it is important to dose ferrous sulfate along with hydrogen peroxide to keep concentration of hydrogen peroxide and ferrous ions constant. Due to shift in reaction pathway, optimum hydrogen peroxide to ferrous sulfate ratio can't be found without dosing both hydrogen peroxide and ferrous sulfate

2.3   Effect of dosing rate of hydrogen peroxide and ferrous sulfate on COD removal

2.3.1 Procedure

The procedure in this section is similar to the previous section except ferrous sulfate catalyst was dosed to the system as ferrous sulfate solution.

2.3.2 Results and Discussion

The goal of this set of experiments is to evaluate the optimum dosing rate of hydrogen peroxide to ferrous sulfate ratio. Dosing rate includes optimum hydrogen peroxide to ferrous sulfate ratio. Also, it includes the time interval in which hydrogen peroxide and ferrous sulfate solution should be dosed. The time interval is necessary to allow hydrogen peroxide dose to react with ferrous ions completely before the later dose is added to spent caustic to keep the ratio constant. This can also eliminate reaction pathway shifting which was explained in the previous section. COD measurement is used to find the best dosing rate. The following table shows the different dosing rates that were studied.

Table 2.4: Effect of Dosing Time of Hydrogen Peroxide and Ferrous Sulfate on COD Removal

Ferrous Sulfate(g)	H_2O_2(ml)	Dosing Rate	Initial COD(ppm)	Final COD(ppm)	COD Removal(%)	$H_2O_2/FeSO_2$ (wt%)
10.2	4	1ml $FeSO_4$, 0.1 ml H_2O_2/25s	41000	6600	84%	0.43
10.2	4	1ml $FeSO_4$, 0.1 ml H_2O_2/20s	41000	5000	88%	0.43

The table above shows two testing points for the effect of dosing time on COD removal. Hydrogen peroxide to ferrous sulfate mass ratio was fixed at 0.43 wt%. It can be shown from the table that dosing both reagent every 20 s yield better COD removal. According to the results, It is believed that 20s is enough for 0.1 ml of 30 wt% hydrogen peroxide to react completely and so keeping the concentration of hydrogen peroxide as low as possible. Another run was conducted in which both reagents were dosed every 15s. However, this dosing rate resulted in foaming. As a result, this dosing time was not considered as a good choice for the process.

Table 2.5: Effect of Hydrogen Peroxide to Ferrous Sulfate Ratio of Each Dose on COD Removal

H_2O_2(mL)	Dosing Rate	Initial COD(ppm)	Final COD(ppm)	COD Removal(%)	H_2O_2/$FeSO_2$ (wt%)
4	1ml $FeSO_4$, 0.1ml H_2O_2/20s	41000	5000	88%	0.43
4	0.5ml $FeSO_4$, 0.1 ml H_2O_2/20s	41000	6200	85%	0.86
4	0.3ml $FeSO_4$, 0.1 ml H_2O_2/20s	41000	6400	84%	1.42
4	0.7ml $FeSO_4$, 0.1 ml H_2O_2/20s	41000	5500	87%	0.61
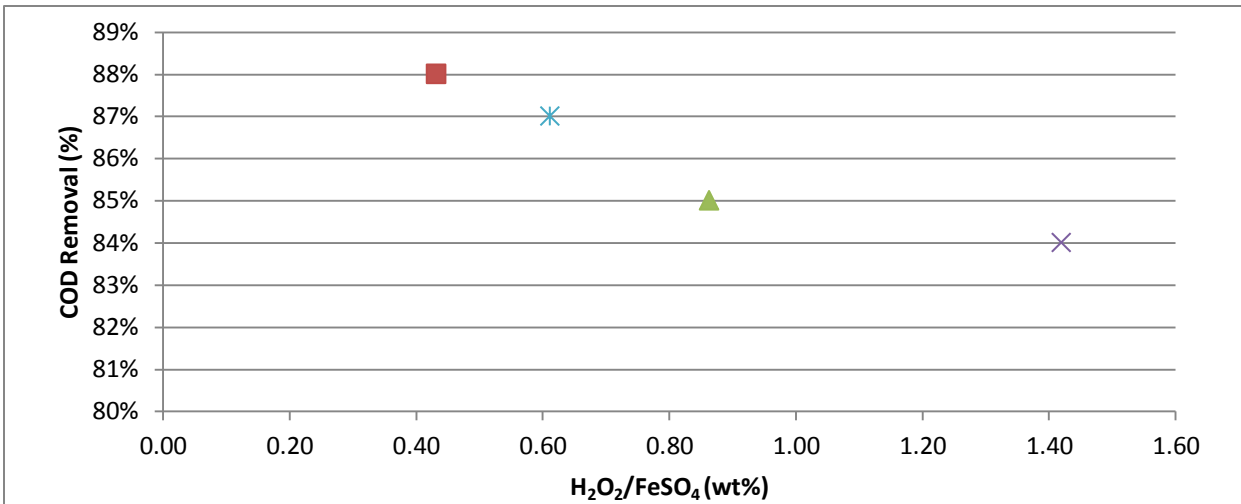
Figure 2.6: Effect of Hydrogen Peroxide to Ferrous Sulfate Ratio of Each Dose on COD Removal

The second parameter studied is fenton's reagent ratio. Four different ratios were tested, 0.43, 0.86, 1.4 and 0.61 wt%. For each ratio, 0.1 ml of hydrogen peroxide was dosed with different amount of ferrous sulfate solution every 20s. It can be seen from the figure, as hydrogen peroxide to ferrous sulfate ratio increases, lower COD removal is achieved. This can be explained as ferrous sulfate dose decreases, less ferrous ions are available to activate hydroxyl radicals. The maximum COD removal achieved is 88 % with a ratio of 0.43 wt%. The ratio 0.43 wt% means that 0.1 ml of 30 wt% hydrogen peroxide is dosed with 0.256 g of ferrous sulfate every 20s. Lower ratios than 0.43 wt% were not tested to avoid occurrence of coagulation treatment beside oxidation. The result from this set will be used in all other runs.

An important observation was noticed at the beginning of the reaction that at the first few drops, the reaction didn't occur. This can be explained as there is not enough ferrous ions catalyst to activate hydroxyl radicals. It is very important to fully utilize each drop of hydrogen peroxide as it controls the running cost of the process. To test this explanation, set of experiments has been done in which initial dose of ferrous sulfate solution is mixed with spent caustic before start dosing to insure that there are sufficient ferrous ions to activate hydroxyl radicals. Different ferrous sulfate initial dose was added to the system and the COD was tested. If COD removal is higher with initial catalyst dose, the explanation mentioned is true.

Four samples were tested. Fenton's reagent ratio was fixed and different ferrous sulfate catalyst initial dose effect on COD removal was tested. The following table shows the data collected:

Table 2.6: Effect of Initial Dose of Hydrogen Peroxide on COD Removal

Ferrous Sulfate solution (mL)	H_2O_2(mL)	Dosing Rate	Initial COD(ppm)	Final COD(ppm)	COD Removal (%)	$H_2O_2/FeSO_2$ (wt%)
43(3 initial)	4	1ml $FeSO_4$, 0.1 H_2O_2/20s	41000	4500	89%	0.4
45(5 initial)	4	1ml $FeSO_4$, 0.1 H_2O_2/20s	41000	4580	89%	0.39
47(7 initial)	4	1ml $FeSO_4$, 0.1 H_2O_2/20s	41000	4590	89%	0.37
49(9 initial)	4	1ml $FeSO_4$, 0.1 H_2O_2/20s	41000	4250	90%	0.35
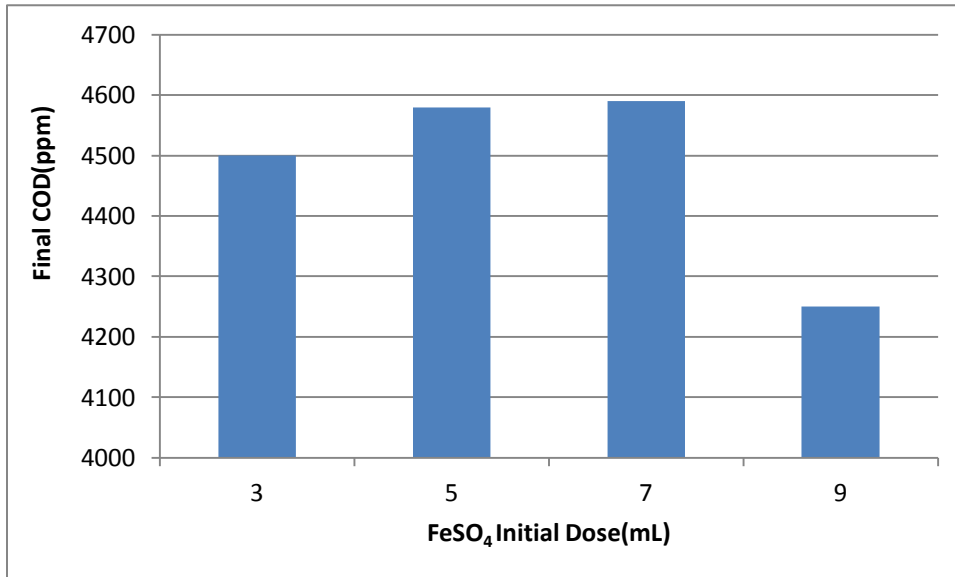
Figure 2.7: Effect of Initial Dose of Hydrogen Peroxide on COD Removal

Four samples were studied. Dosing rate was held constant and different initial dosage of ferrous sulfate is tested. According to the figure, 9 mL initial dose of ferrous sulfate solution gives the lowest final COD of 4250 ppm. The highest final COD is 4590 ppm which obtained at initial dose of 7 mL of saturated ferrous solution. There is only 340 ppm difference in the final COD of the treated effluent between adding 3 ml initial catalyst solution and 9 ml initial catalyst solution. So, 3 mL of catalyst solution is used for all proceeding samples. Previously, a sample was conducted with the same fenton's reagent ratio and the same dosing rate without usage of initial catalyst dose. The final COD of this sample is 5000ppm while when initial dose is used, the final COD is 4500ppm. As a result, initial catalyst dose increases COD removal and verify the observation mentioned earlier. For all proceeding runs, only 3 ml initial dose of ferrous sulfate will be used. This section concludes that hydrogen peroxide to ferrous sulfate ratio. For every 1 g of hydrogen peroxide, 2.5 g of ferrous sulfate is used with 0.07 mass fraction of ferrous sulfate to be added as initial dose.

2.4 Effect of Hydrogen peroxide to COD ratio
on COD Removal

After finding optimum ratio of hydrogen peroxide to ferrous sulfate ratio, hydrogen peroxide to spent caustic initial COD is to be found. This ratio is crucial in fenton's reaction since it determine the amount of hydrogen peroxide should be used to treat spent caustic. Fenton's treatment process operational cost mainly depends on the cost of chemicals. Chemicals used in fenton's reaction are hydrogen peroxide, ferrous sulfate, sulfuric acid and sodium hydroxide. The cost of hydrogen peroxide is much more expensive than all other chemicals, so the running cost mainly depends on hydrogen peroxide to COD ratio. The objective is to treat spent caustic prior post biological treatment. As a result, COD should be brought down to around 1,000 ppm. Since spent caustic used in all the runs is undiluted, final COD of 1,500 ppm is acceptable. With proper dosing, as hydrogen peroxide to COD ratio increases, COD removal increases because more hydroxyl radicals can be generated to oxidize contaminants. Different hydrogen peroxide to COD ratios are tested to find out the required ratio to achieve the desirable treatment degree.

2.4.1 Procedure

The same procedure is used as shown in page 23.

2.4.2 Results and Discussion

In this section, the effect of hydrogen peroxide on COD removal is studied and table 2.7 shows data collected.

Table 2.7: Effect of Hydrogen Peroxide to COD ratio on COD Removal at Fixed Hydrogen Peroxide to Ferrous Sulfate Ratio

Sample	H_2O_2(mL)	Initial COD(ppm)	Final COD(ppm)	COD Reduction (%)	g H_2O_2/ g COD	H_2O_2/FeSO$_4$ (wt%)
1	1.5	41000	8740	79%	0.8	0.4
2	2	41000	6000	85%	1.1	0.4
3	3	41000	6200	85%	1.6	0.4
4	3.5	41000	5250	87%	1.9	0.4
5	4	41000	4580	89%	2.1	0.4
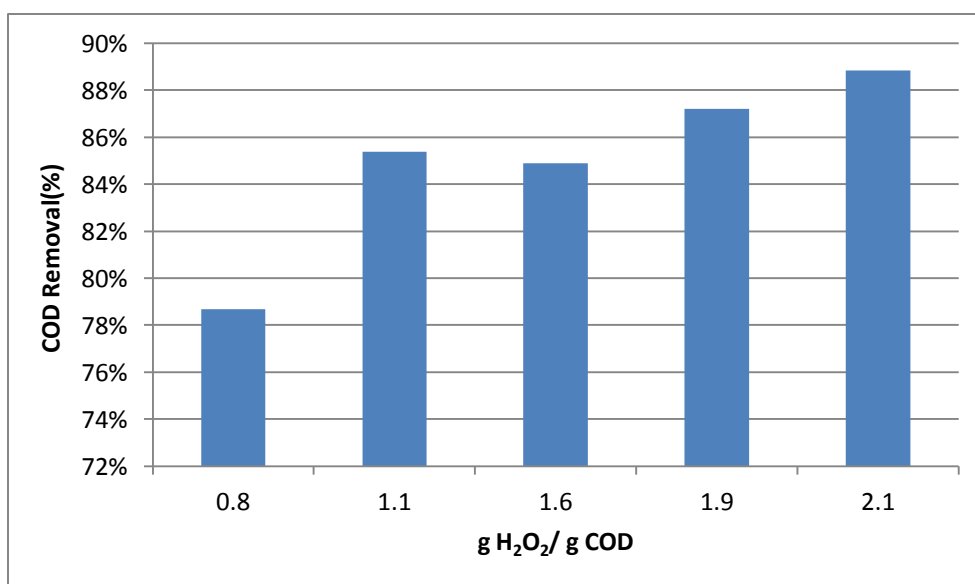
Figure 2.8: Effect of Hydrogen Peroxide to COD ratio on COD Removal at Fixed Hydrogen Peroxide to Ferrous Sulfate Ratio

From figure above, as the hydrogen peroxide to COD ratio increases, COD removal increases because increasing hydrogen peroxide to COD ratio will increase the amount of hydroxyl radical available to oxidize contaminants. The maximum COD removal achieved is 89% with a ratio of $2.1\frac{g\ H2O2}{g\ COD}$ and the lowest COD removal of 79% is at a ratio of $0.8\frac{g\ H2O2}{g\ COD}$. COD removal at a ratio of $1.6\frac{g\ H2O2}{g\ COD}$ is lower than that of $1.1\frac{g\ H2O2}{g\ COD}$. This is probably due to some experiential errors like accuracy of dosing. Maximum COD removal obtained is still lower than the desirable removal. At this removal, final COD is 4,580 ppm. This COD is much higher than the desirable COD. COD removal can be improved by increasing the ratio; however, it is undesirable to keep the running cost as low as possible. As a result, $2.1\frac{g\ H2O2}{g\ COD}$ will kept the same and other factors will be changed to improve COD removal.

2.5 Effect of Two Rectors in Series On COD Removal:

The impact of two reactors in series on COD is tested. It is required to achieve a final COD in the range of 1,000 ppm by keeping hydrogen peroxide to influent COD at $2.1\frac{g\ H2O2}{g\ COD}$ or lower.

2.5.1 Procedure

The same procedure is used as shown in page 23.

2.5.2 Results and Discussion

The effect of two reactors on COD removal is studied and the table below shows data collected.

Table 2.8: Effect of Two Rectors in Series on COD Removal:

Sample	Reactor	H2O2(mL)	Initial COD(ppm)	final COD(ppm)	COD Removal %	Overall COD Removal %	g COD Inlet	Single gH_2O_2/ g COD	Overall gH_2O_2/ g COD
	1	3	41000	6200	85%		2.1	1.6	
1	2	1	6200	1300	79%	97%	0.3	3.5	2.1
	1	3.5	41000	5250	87%		2.1	1.9	
2	2	0.5	5250	1590	70%	96%	0.3	2.1	2.1
	1	1.7	41000	7500	82%		2.1	0.9	
3	2	1.8	7500	1500	80%	96%	0.3	6.6	1.9
	1	1.5	41000	8740	79%		2.1	0.8	
4	2	1.5	8740	2340	73%	94%	0.4	3.8	1.6
	2	2	41000	6250	85%		2.1	1.1	
5	2	2	6560	1350	79%	97%	0.3	6.7	2.1
	2	1.7	41000	7850	81%		2.1	0.9	
6	2	2.3	6560	1100	83%	97%	0.3	7.7	2.1
	2	1.5	41000	8560	79%		2.1	0.8	
7	2	2.5	6560	1400	79%	97%	0.3	8.4	2.1

Figure 2.9: COD Removal at Different g H2O2/g COD in Each Reactor

The first figure compares the COD removal at different ratios of hydrogen peroxide to COD ratio in both reactors. For all the runs, hydrogen peroxide to ferrous sulfate was fixed at 0.4 wt% and the initial dose was fixed at 0.07 mass fraction of the total ferrous sulfate dosed. It can be noticed from the graph that COD removal is higher in the first reactor even though lower hydrogen peroxide to COD ratio used. This observation can be explained by the initial COD fed to each reactor. Oxidation of containments by hydroxyl radical depends on the structure of contaminants. Hydroxyl radicals react with organics by either removing hydrogen from carbon-carbon bond, carbon-nitrogen. Another way of oxidation is adding OH to carbon-carbon double bond [54]:

$$OH\bullet + C=C \longrightarrow OH\text{-}CH\bullet$$
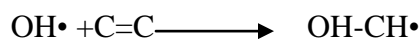
Also, it is very reactive with aromatics. Feed to the first reactor consists of aromatic and long chains of alkynes, alkenes and alkanes that can be easily oxidized. Hydroxyl radicals will react with these contaminants producing low molecular weight acids that are more resistance to oxidation. As a result, more hydrogen peroxide is needed in the second reactor to further reduce COD because of existence of oxidation resistance compounds. It is important to stop chemical treatment when biological treatment is feasible as it will oxidize these compounds that resist chemical oxidation with much cheaper cost [53]. Three different ratios of hydrogen peroxide to COD were tested. The figure below shows the results:
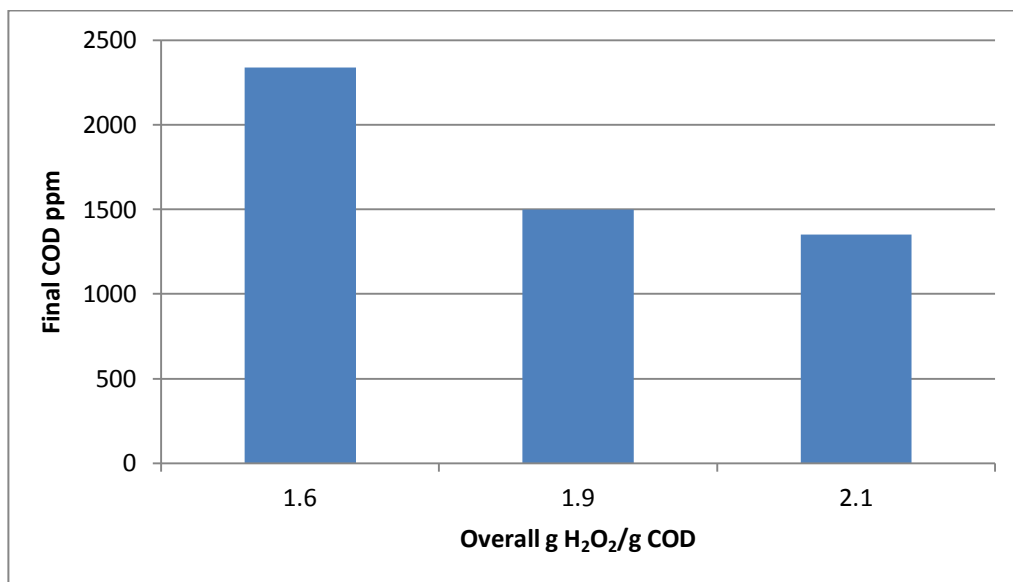
Figure 2.10: Final COD at Different Overall g H_2O_2/g COD After the Second Reactor

The figure shows the final COD of spent caustic for various hydrogen peroxide to COD ratios. The fraction of total hydrogen peroxide volume fed to the first reactor is fixed at 0.5. At a ratio of 1.9, the fraction is fixed at 0.49 because to get a ratio of 0.5, 1.75 mL of hydrogen peroxide should be dosed to each reactor. Since the minimum amount of hydrogen peroxide can be dosed by a burette is 0.1 mL, a ratio of 0.49 is used instead. The lowest final COD achieved is 1350 ppm with overall hydrogen peroxide to COD of 2.1 (g/g). This ratio will be further analyzed to try finding a way to get better COD removals.

Hydrogen peroxide to COD ratio is fixed at 2.1 (g/g) and different fractions of total hydrogen peroxide used are fed to the first reactor. The final COD after the second reactor are recorded in the following table.

Table 2.9: Effect of Different Fractions of Total H_2O_2 Added to the First Reactor on Final COD

Fraction of Total H_2O_2 Added to the First Reactor	final COD
3/8	1400
3/7	1100
1/2	1350
3/4	1300
7/8	1590
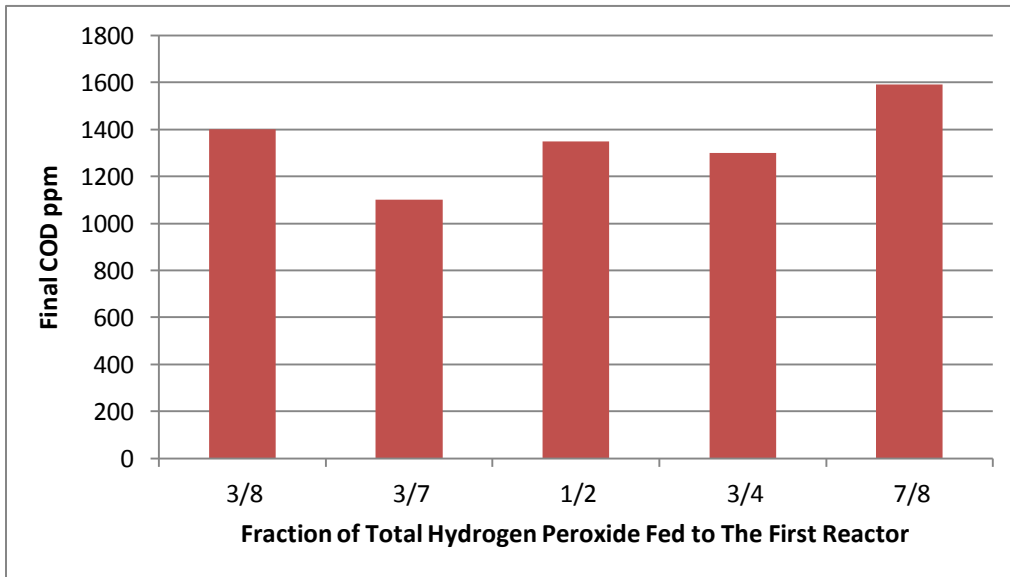
Figure 2.11: Effect of Different Fractions of Total H_2O_2 Added to the First Reactor on Final COD

Several fractions were tested from 3/8 up to 7/8. The lowest COD is achieved at fraction of hydrogen peroxide of 3/8 to be fed to the first reactor where the highest COD is achieved when 7/8 is fed to the first reactor. The lowest final COD achieved is 1100 ppm which is an excellent result. It can be observed from the figure, that fractions around 1/2 achieve lower final COD. There are two reasons that can explain this observation. The first explanation is due to the effect of pH on fenton's reaction. The optimum operating pH for fenton's reaction falls in the range of 2-5 [54]. Outside this range, a drop in COD removal will occur. When pH falls below 2, production rate of hydroxyl radicals will decrease resulting in lower COD removal. Throughout fenton's reaction, the pH will decrease because of two main reasons which are the acidic nature of the catalyst and degradation of pollutants into low molecular weight carboxylic acids. Ferrous sulfate, has residual sulfuric acid which will lower the pH. As hydrogen peroxide is added to the system, contaminants will be oxidized and some low molecular weight organic carboxylic acids will be produced dropping the pH down [53]. When fraction is either high or low, majority of hydrogen peroxide will be dosed in one reactor resulting in high drop of pH. The second explanation is concentration of ferric ions in the system. Properly dosing ferrous sulfate and hydrogen peroxide to spent caustic can keep the concentration of both species low as hydrogen peroxide is converted to hydroxyl radicals and ferrous ions is converted to ferric ions. Ferric ions react with hydrogen peroxide to produce $HO_2\bullet$. This radical can react with ferric ion as shown in reaction 1.34. This reaction will further decrease COD removal. Reactions 1.34 can be have major effect on COD removal when the concentration of ferric ions is high [38]. As a result, adding too much hydrogen peroxide to one reactor result in lower COD removal. The usage of two reactors allows the removal ferric ions from spent by precipitation and so eliminating inhibition resulting from high concentration of ferric ions. Another point to mention, the best fraction is lower than 1/2 because the structure of the feed is easier to oxidize as explained previously.

It can be clearly seen that the usage of two reactors has improved COD removal. The maximum COD removal achieved in two reactors is 97% with hydrogen peroxide to COD ratio of 2.1 $\frac{g\ H2O2}{g\ COD}$. Comparing the COD removal achieved using only one reactor with the same ratio. The maximum COD removal achieved is around 90 % with the same ratio. An increase of 7% in COD removal is good since no increase in hydrogen peroxide volume. At

this stage, both hydrogen peroxide to ferrous sulfate ratio and hydrogen peroxide to COD ratios are found. Mass ratio of hydrogen peroxide to ferrous sulfate to initial COD is 2.1/5.9/1. The initial dose to each reactor is equivalent to 0.07 mass fraction of the total ferrous sulfate used.

To test if fenton's reaction works properly, different sample of spent caustic is used to test if the same COD reduction can be achieved using different spent caustic feed. The second type of spent caustic has a COD of 65,000 ppm and the other characteristics are shown in the methodology section. The same procedure is used. The optimum mass ratio of hydrogen peroxide to ferrous sulfate to initial COD of 2.1/5.9/1 is used. The result obtained from this run is excellent. The final COD obtained is 1,200 ppm. The overall COD removal is 98%. The figure below shows the different between untreated spent caustic and treated effluent

Figure 2.12: Refinery Spent Caustic (left) and Two Treated Samples (middle and right)

To ensure that contaminants are being oxidized rather than being removed by coagulation, a sample from the solid sludge was analyzed using ICP test. The result showed that the solid contains Na^+, Ca^{2+} and some iron with huge amount of Na^+ compared to the other two components. This result verifies that pollutants are being oxidized and the solid sludge produce is not hazardous. Also, treated spent caustic was also analyzed to ensure that it doesn't contain compounds that can be toxic to microorganism for post biological treatment.

The results showed that spent caustic liquid can be having no toxic compound to microorganism.

Although COD removals obtained in this section are excellent, the amount of solid sludge produced is very high. Although the sludge produced is not hazardous, the amount produced is really high. The amount of solids produce depends on the dissolved solids in the sample as well as the amount of catalyst used. According to the sample we treated, for 50 ml of 41,000 ppm COD sample, the amount of sludge generated is around 100 g while the second sample produced solids of around 30 g for every 50 ml sample. Although solid sludge can be sent to landfill, the amount produced is huge so solid sludge generated must be lowered. One way to reduce solid generated is lowering the amount of catalyst used. This might require increasing the amount of hydrogen peroxide to achieve the same COD removal.

2.6   Solid reduction

As mentioned in the previous section, solid sludge generated by fenton's reaction is very high. As a result, amount of solid generated must be lowered. It is believed that amount of catalyst used in the process increases sludge generation. Ferrous sulfate catalyst will be lowered and the amount of sludge generated will be measured. Decreasing ferrous sulfate catalyst will result in lower COD reduction. The volume of hydrogen peroxide added to the system should increase to compensate with the loss in COD reduction. Minimum dosing rate of ferrous sulfate will be use. The minimum dose of ferrous sulfate solution is 0.1 mL. To be consistence with the procedure used along the research, both reagents are added at every 20 s. The dosing rate used in this section is 0.1 mL of 30 wt% hydrogen peroxide along with 0.1 mL saturated ferrous sulfate every 20s. The initial dose of ferrous sulfate solution added to spent caustic is 5 mL. Hydrogen peroxide to ferrous sulfate to COD ratio is increased and the amount of COD reduction is tested and the amount of solid sludge generated is measured.

2.6.1 Procedure

The same procedure is used as shown in page 23.

2.6.2 Results and Discussion

Various hydrogen peroxide to ferrous sulfate to COD ratios were tested and data collected is shown in the table below

Table 2.10: Overall COD Removal in Two Reactors in Series

Sample	Reactor	Ferrous Sulfate(g)	H_2O_2(mL)	Initial COD(ppm)	Final COD(ppm)	Overall COD Removal	$H_2O_2/FeSO_4/COD$ (g/g/g)	Solid Generated(g)
1	1	6.7(5 initial)	1.7	41000	-	95%	2.1/1.7/1	6
	2	7.3(5 initial)	2.3	-	2200			16
2	1	7.1(5 initial)	2.1	41000	-	95%	2.7/1.9/1	4
	2	7.9(5 initial)	2.9	-	2000			17
3	1	7.6(5 initial)	2.6	41000	-	96%	3.2/2.0/1	6
	2	8.4(5 initial)	3.4	-	1800			13
4	1	8(5 initial)	3	41000	-	97%	3.8/2.1/1	5
	2	9(5 initial)	4	-	1350			15
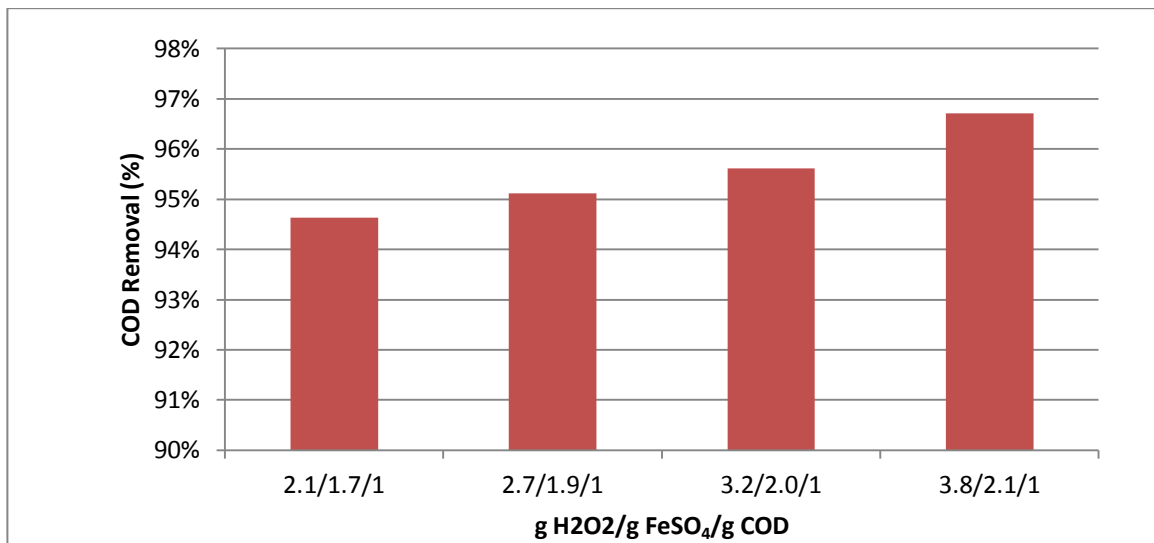
Figure 2.13: Overall COD Removal in Two Reactors in Series

The figure shows expected results. When hydrogen peroxide to COD ratio increases COD removal and vice versa. The maximum COD removal achieved is 97% with a ratio of 3.8/2.1/1 and the lowest COD removal achieved is 95% at a ratio of 2.1/1.7/1 The result obtained agrees with the expectation. In the previous section, the ratio $2.1\frac{g\ H2O2}{g\ COD}$ gave a final COD of 1100 ppm while the ratio of $3.8\frac{g\ H2O2}{g\ COD}$ used in this section gave a final COD of 1350 ppm. However, the amount of sludge generated is around 20g which is five times less than before. It is not advisable to further decrease ferrous sulfate catalyst to avoid increasing hydrogen peroxide volume. Sludge generation in the process consists of calcium, sodium and some iron which can be disposed to landfill [54]. To conclude this test, COD removal of 97% can be achieved at a mass ratio of hydrogen peroxide to ferrous sulfate to COD of 3.8/2.1/1 mass ratio where 0.29 mass fraction of ferrous sulfate to be added as initial dose to each reactor.

2.7　Optimization using one reactor:

In this section, it required to find the hydrogen peroxide to ferrous sulfate to COD ratio for one reactor by controlling pH. It was seen previously that the usage of two reactor exhibits high COD removals compared to removals achieved in one reactor. pH is one of the reasons that contributed in better COD removals. A study of the COD removal that can be achieved in one reactor by controlling the pH throughout the reaction to a value of 3 was conducted. The base that was used to adjust pH is 5.0M KOH. 5.0M KOH was dosed to spent caustic to keep pH in the range of 2.5-3.One adjustment is done to the procedure in which the reaction time is 2 hrs instead of 50 minutes. The reason is to keep the same conditions used in two reactors. Also, dosing rate is lowered in which 1 ml of 30 wt% hydrogen peroxide is dosed with 0.256 g of ferrous sulfate every 30s. Initial dose of ferrous sulfate is fixed at 1.28 g. The following table shows the results obtained:

Table 2.11: COD Removal in One Reactor at Various Overall Hydrogen Peroxide to Ferrous Sulfate to COD Ratio

Sample	Ferrous Sulfate(mL)	H_2O_2(ml)	Initial COD(ppm)	Final COD(ppm)	COD Removal (%)	g COD	H_2O_2/$FeSO_4$/ COD (g/g/g)
1	12(5 initial)	7	41000	4000	90%	2.1	3.7/1.5/1
2	13(5 initial)	8	41000	2500	94%	2.1	4.2/1.6/1
3	13.5(5 initial)	8.5	41000	2300	94%	2.1	4.5/1.6/1
4	14(5 initial)	9	41000	2400	94%	2.1	4.7/1.7/1
5	14.5(5 initial)	9.5	41000	1800	96%	2.1	5/1.8/1
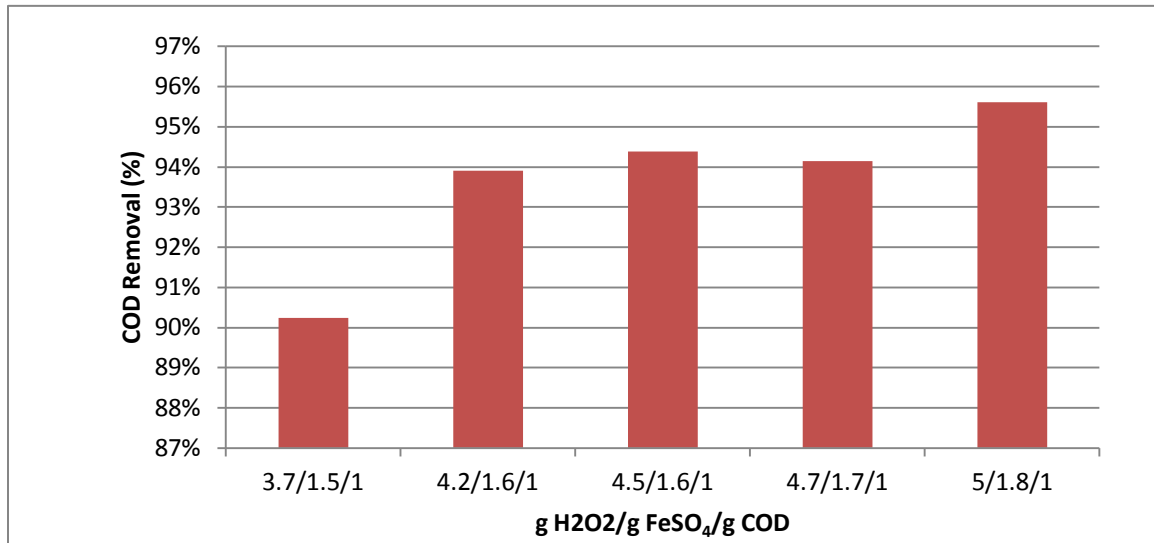
Figure 2.14: COD Removal in One Reactor at Various Overall Hydrogen Peroxide to Ferrous Sulfate to COD Ratio

The figure above shows the results. It can be shown that COD removal increases as hydrogen peroxide to ferrous sulfate to COD ratio increases. Controlling pH has reduced inhibition occurrence due to drop of pH in the acidic side. However, controlling pH should be carefully done. If the pH is increased above 5, ferric ions are transferred from soluble condition into insoluble ferric hydroxide. When controlling pH, weak base should be used like bicarbonate instead of hydroxide. Strong base can adjust pH and keep below pH of 5, however local mixing point's pH can increase more than 5 resulting in lowering COD removal [54]. This section solved the inhibition that occurs due to the drop of pH below 2. However, it can't solve the problem concerning the inhibition that occurs from high concentration of ferric ions. As a result, higher overall ratio is needed to achieve the same COD removal compared to the usage of two reactors. The maximum COD removal achieved is 96% with a mass ratio hydrogen peroxide to ferrous to COD ratio of 5/1.8/1 mass ratio with a mass fraction of ferrous sulfate of 0.34 to be dosed as initial dose.

CHAPTER 3:
Scale Up & Pilot Plant

3.1 Scale Up

After finding the optimum conditions in the bench scale, the process will be scaled up. In the bench scale, 50 mL samples of spent caustic were tested. Two steps scale up will be conducted, 1 L sample run and then scale up and use the pilot plant. Operational conditions found in the bench scale experiment will be implemented. Commercial hydrogen peroxide and ferrous sulfate catalyst will be used instead of lab grade.
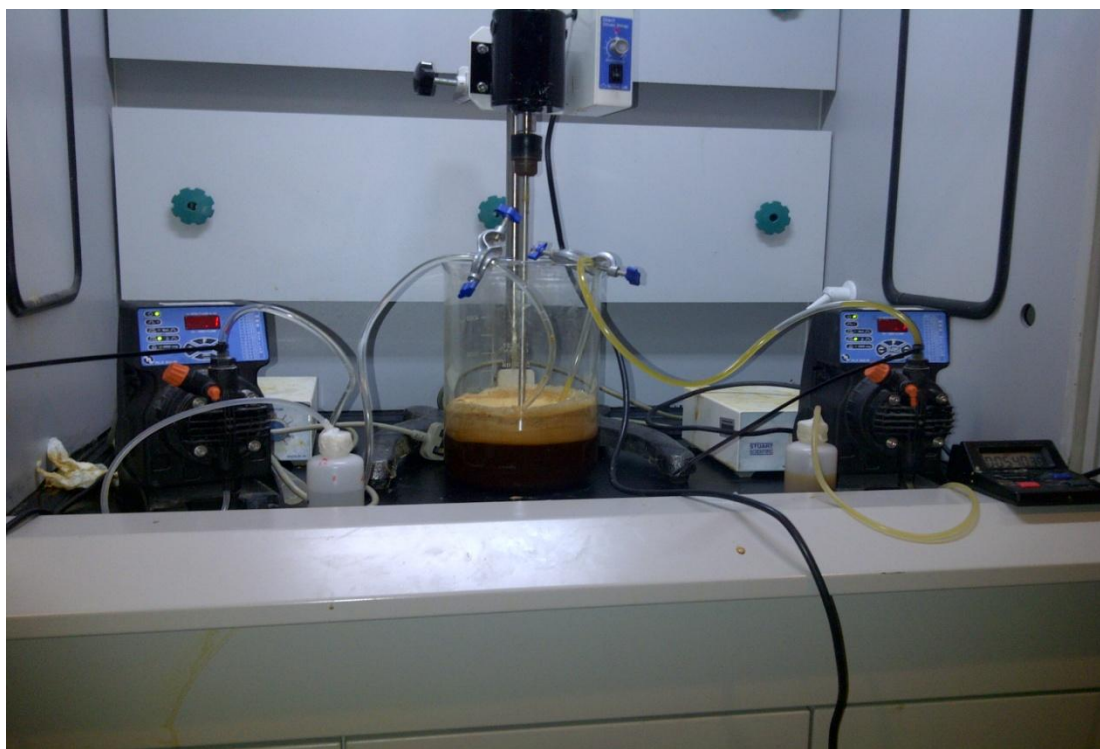
Figure 3.1: Scale Up Equipment

3.1.1 Procedure

One liter solution is spent caustic is prepared by diluting 100 mL of 41,000 spent caustic with 900 mL water. Sulfuric acid is added to spent caustic solution to adjust pH to a value of 3. Mass ratio of hydrogen peroxide/ ferrous sulfate/COD used is 3.8/2.1/1. Initial dose of saturated ferrous sulfate solution of 10 mL is added to spent caustic solution in each reactor. Two dosing pumps are used to adjust flow rate of hydrogen peroxide and ferrous sulfate solution to the system. Flow rate of hydrogen peroxide is adjusted at 0.6 mL/min and the same flow rate is used for saturated ferrous sulfate solution. 3/7 of total hydrogen peroxide is added the first reactor and the remainder is added to the second reactor. Once the reaction is completed, treated spent caustic is neutralized to pH of 7 using 5M KOH and precipitated solids are removed from the treated liquid. The same procedure is repeated for the second reactor and COD of treated sample is measured.

3.1.2 Results and Discussion

Two runs were conducted for the 1L sample. In the first run, two burettes were used to dose hydrogen peroxide and ferrous sulfate solution. There were several problems appeared in this run which made it unsuccessful. Dealing with large volume of spent caustic requires carful dosing since foaming can be a big problem in fenton's reaction. Hydrogen peroxide dosing was not controlled properly and it resulted in foaming as shown in the figure 3.2. It was also observed that it is important for the reagents to be connected to pipes submerged in the liquid because foam layer will not block hydrogen peroxide and ferrous sulfate solution from reaching spent caustic. The reaction will occur on the foam causing foam to grow even larger. Since the reagents are reaching spent caustic liquid, a drop in COD removal will occur. Due to the foaming problem, dosing pumps with submerged feeding were used to minimize foaming and to insure that fenton's reagents are reaching liquid layer of spent caustic.

Figure 3.2: Foaming During Scale Up

The second run, dosing pumps with submerged dosing were used. In the first reactor 6 ml of 35 wt% hydrogen peroxide was fed along with 4.4 g (18 mL) of ferrous sulfate solution. In the second reactor, 8 ml of 35 wt% hydrogen peroxide was fed along with 4.9 g(19 mL) of ferrous sulfate solution. The initial COD of spent caustic was 4,100 ppm and the final COD of treated spent caustic is 250 ppm which means a COD removal of 94%. Reduction in COD conversion is expected in scale up plus usage of commercial grades since there purity is lower. In this run, small layer of foam was observed but it did not affect the reaction and the desirable result is obtained.

3.2   Pilot plant

The second step in scale up is the pilot plant. The results obtained from the bench scale experiments are used in the pilot plant. The main objective of testing the pilot plant is to check if the process can be done in large scale. Also, it is desired to achieve the desirable degree of treatment (final COD of 1000 ppm) and compare the cost of chemicals of this process with different alternative. It is assumed that the cost of chemical is almost the running cost of the plant since the energy requirement and other running are small compared to cost of chemicals. In the reagent, an alternative that normally done is sending spent caustic to the United Stats of America(USA) where spent caustic is treated at a price of 1.23 $/gal [10]. This price will be compared with the cost of operations in fenton's process.

3.2.1 Procedure

The procedure used in the pilot plant is the same as the one mentioned in the method and material section. In summary, 100 liters of spent caustic is loaded into the acidification tank where it was acidified with sulfuric acid to bring down the pH in the range of 3 to 5. The acidified spent caustic is pumped to the reactor. Required quantities of $FeSO_4$ and H_2O_2 are calculated using an overall ratio of 5/1.8/1 added. The residence time of the reactor is fixed at 1.5 to 2 hours. Treated spent caustic is transferred to a conical tank where it is neutralized with 5M NaOH to adjust the pH in the range of 7 to 8. Then, the neutralized effluent is transferred to the settling tank. The supernatant from the settling tank is then passed through a series of filters and finally through resin/activated carbon bed and the treated effluent is collected in containers. The raw spent caustic samples and the treated samples were collected for each tests and analyzed.

3.2.2 Material

Two different feeds are used in the pilot plant and four runs were conducted to verify the results. The following table shows the characteristics of the first feed and the results obtained from the three tests done.

Table 3.1: Spent Caustic Characteristic Used in the Pilot Plant

Parameters	Sample 1	Sample 2	Diluted sample 2
COD(mg/L)	13100	98800	19760
TOC (mg/L)	156	2360	472
pH	12.2	12.1	
Oil and Grease (mg/L)	28.7	1506.9	301.4
Sulfide(mg/L)	2160	3600	720
Phenols(mg/L)	1.6	2.0	0.4
TSS(mg/L)	294	126	25.2
Turbidity (NTU)	166	16	
Odor	High odor	Very high	High
Ammonia(mg/L)	21.7	26.5	5.3
Na_2S (wt%)	0.526%	0.409%	0.08%
Sulfates(SO_4) (mg/L)	468	5820	1164
Na_2CO_3 (wt%)	2.02%	2.92%	0.584%
NaOH (wt%)	2.92%	1.99%	0.398%
TDS (mg/L)	158000	146000	29200
H_2S (mg/L)	6.5	22.5	

3.2.3 Results and Discussion

The following table shows the amount of chemicals used in all four runs

Table 3.2: Chemicals Used in the pilot For Each Test

	Run 1	Run 2	Run 3	Run 4
Quantity of spent caustic treated	100 liters	60 liters	20 liters diluted to 100 liters	20 liters diluted to 100 liters
Chemical Consumption				
H_2SO_4	4 liters	0.4 liters	0.7 liters	0.7 liters
$FeSO_4$	3.7 kg	5 liters (1.25 kg)	10 liters (2.5 kg)	10 liters (2.5 kg)
H_2O_2	10 liters (11 kg)	2.5 liters (2.75 kg)	6 liters(6.6 kg)	7 liters (7.7 kg)
NaOH	10 liters (2 kg)	2.5 liters (0.5 kg)	1.8 liters (0.36 kg)	1.8 lit (0.36 kg)
Water	-	-	80 liters	80 liters

The feed used in runs 1 and 2 is the same and tests 3 and 4 are the second feed. Spent caustic used in tests 1 and 2 wasn't diluted where tests 3 and 4 was diluted with a ratio of 1:4. Spent caustic is diluted because COD is very high and all other processes dilute spent caustic before treatment [10]. Fenton's reagent ratio is used according to the results obtained for optimization for one reactor. From table of chemicals, the amount of hydrogen peroxide used is higher in the first run and lower in all other runs. Hydrogen peroxide to ferrous sulfate to COD mass ratio was found in the bench scale experiment for one reactor to be 5/1.8/1. Table below show the required amount of hydrogen peroxide and ferrous sulfate should be used and the difference in the amount actually used in the runs

Table 3.3: Comparison between Actual Chemical Used and Estimated Chemicals

	Initial COD (kg)	Estimated H_2O_2 (kg)	Estimated $FeSO_4$ (kg)	Difference in H_2O_2 (kg)(Actual − Estimated)	Difference in $FeSO_4$ (kg)(Actual − Estimated)
run 1	1.31	6.55	2.36	4.45	1.34
run 2	0.79	3.93	1.41	-1.18	-0.16
run 3	1.98	9.88	3.56	-3.28	-1.06
run 4	1.98	9.88	3.56	-2.18	-1.06

In Run 1, the amounts of fenton's reagents are much higher than the estimated values in the bench scale. All remaining runs used lower fenton's reagent than estimated. If the degree of treatment is achieved, then these amounts used in runs 2,3 and 4 are better than the estimated ones. For the first run, cost of chemicals will be high since too much hydrogen peroxide is used. The plant operates manually, so it is expected to have differences in the chemicals used for each run.

Moving on to the results, the table below shows the results for all 4 tests:

Table 3.4: Results of the Pilot Plant Tests

Parameters	Limits	Run 1	Run 2	Run 3	Run 4
COD(mg/L)	<1000	120.5	525	699	820
pH	6-8.4	7.4	11	12.5	12.1
Oil and Grease (mg/L)	<8	<2	0.4	0.4	5.4
Sulfide(mg/L)	<0.1	6	12	74	22
Phenols(mg/L)	<0.1	<0.1	<0.1	<0.1	<0.01
TSS(mg/L)	<15	17.2	13.8	15.2	16.6
Turbidity (NTU)	5 NTU	26	5	12	3
Odor	Un-objectionable	Very slight smell	Very Slight smell	Objectionable	Slight smell
Ammonia(mg/L)		0.45	34.5	23.9	21.6
Na_2S (wt%)		0.00125%	0.0029%	0.0180%	0.0054%
Sulfates(SO_4) (mg/L)		160.5	17100	9250	16000
Na_2CO_3 (wt%)		<0.002%	0.0281%	0.0224%	0.0337%
NaOH (wt%)		<0.0002%	0.0106%	0.0868%	0.0212%
TDS (mg/L)		316	22400	23700	22800
H_2S (mg/L)		<0.01	<0.01	<0.01	<0.01

The final COD of all tests are below 1000 ppm which is the desirable degree of treatment required. All treated effluents, except run 1, have very high pH. The way pH was adjusted is by taking sample from the bottom of the conical tank to measure pH. NaOH was added to neutralize pH. At first, pH value requires high volume of base to change; however, it reaches a point where small volume of base can shift pH to 10 or even 12. That is why adjusting pH manually is a bit difficult. Addition of acid can solve the problem of pH adjustment but it wasn't used in the runs.

 Total suspended solids (TSS) in the treated effluent are a bit higher than the limit. The pilot plant was designed with four treatment steps to remove TSS. It starts with the sedimentation tank which removed majority of TSS followed by two fiber cartridge filters with porosity of 5 microns followed by 3 ceramic filters in series with a porosity of 0.9 microns and finally followed by adsorption step. Adsorption bed can act as an additional filter media. As a result,

TSS should be low for all the samples. High TSS in the effluent stream means that the sedimentation wasn't given enough time to properly sediment the solid. Even in the second run, which yields a value of TSS below the limit, not enough time was given for sedimentation. Longer time for sedimentation is required for better results. Turbidity and odor mainly depends on the polishing step. The main propose of the adsorption column is to remove both smell and turbidity from treated spent caustic. However, adsorption packing should be regenerated periodically and after that the bed should be changed. The result shows the odor is below the limit except for run 3. As for the turbidity, the second run of each feed yield turbidity lower than the limit because the adsorption column was washed well with water. Another factor affecting turbidity is TSS. Lower TSS values normally yield in better turbidity. An important note to mention, both turbidity and odor won't affect the post biological treatment. The limits specified are just to get better effluent quality.

All the tests shows elevated amount of sulfides in the treated samples. Most of the sulfides in spent caustic are in the form of hydrogen sulfide. In the acidification step, most of the hydrogen sulfide escapes from spent caustic as pH decreases because it is solubility decreases with pH [47]. Acidified samples are shown in the table below.

Table 3.5: Acidified Spent Caustic Samples

Parameters	Run 1	Run 2	Run 3	Run 4
pH		6.2	4.4	6.4
Sulfide(mg/L)		42	24	60
Na_2S (wt%)		0.0029%	0.0058%	0.0146%
Sulfates(SO_4) (mg/L)		25900	17400	18400
H_2S (mg/L)		<0.01	<0.01	<0.01

It is clearly seen that as the pH decreases, sulfides concentration decrease as well as sodium sulfide. Acidified gasses can't be vented to atmosphere since it has hydrogen sulfide. One way to solve this problem is the addition of scrubber to clean the vented gas. Along with the scrubber, the acidification tank can be connected with the reactor. The gasses can be injected to the reactor to force hydrogen sulfide to react. This can result in better mixing in the reactor. However, pressure gauge should be connected to monitor the pressure. When the

pressure increases in the reactor, the gas can be then sent to the scrubber. This way, the amount of hydrogen sulfide sent to the scrubber can be lowered.

Also, high concentration of sulfides, total dissolved solids (TDS) and sulfates exists in the effluent. All of them are affected by the effluent pH. The pH in the treated effluent was not adjusted to around 7. Addition of excess NaOH will dissolve back a lot of the TSS coagulated using Ferric hydroxide, not to mention that NaOH itself will contribute significantly to the TDS. When pH is adjusted to around 7, big portion of the sulfates are removed in the sedimentation tank by the coagulation effect of ferric hydroxide. At high pH, it is believed that sulfate will form sodium sulfate and it remains in the treated spent caustic. Moving on to the sulfide concentration, excessive NaOH increases the sulfide concentration in the treated effluent. When the pH is above of 7, bisulfide (HS−) is fevered by equilibrium. At pH much higher than 7, bisulfide react with $OH-$ forming sulfide($S-2$) ions which increases the concentration of sulfides. It can be shown in the results that as the pH increases, higher concentration of Na_2S exists. Although the pH in run 1 was adjusted to pH of 7, still sulfides concentration is high. However, pH should be adjusted and more runs are required to evaluate sulfides concentration to check if adjusting pH can solve the problem. Another suggestion, if the cost of chemicals are low, high amount of hydrogen peroxide can be added which will reduce sulfide concentration for sure. Another reason for high concentration of sulfate is due to the usage of sulfuric acid and ferrous sulfate catalyst which increases sulfate concentration. Also, sulfides are oxidized to produce sulfate.

3.2.4 Cost of Chemicals

After that, the cost of chemicals to treat spent caustic using the same feed and same condition that each test used is calculated. The amount of chemicals used are summarized in the table below along with the bulk price of each chemical [55].

Table 3.6: Chemicals Used For Each Test

	Run 1	Run 2	Run 3	Run 4	Price of chemical
H_2SO_4 (kg)	4.72	0.472	0.826	0.826	0.25$/kg
$FeSO_4$ (kg)	3.7	1.25	2.5	2.5	0.07 $/kg
H_2O_2 (kg)	11	2.75	6.6	7.7	0.3 $/kg
NaOH (kg)	2	0.5	0.36	0.36	0.1 $/kg
Water (L)	0	0	80	80	0.0027 $/kg

The table below shows the cost of treatment for each run:

Table 3.7: Cost of Chemicals For Each Test

	Cost of Treatment for 100L of run 1	Cost of Treatment for 60L of run 2	Cost of Treatment for 100L of run 3	Cost of Treatment for 100L of run 4
	4.94$	1.08$	2.61$	2.94$
cost to treat /L	0.05$	0.02$	0.03$	0.03$
cost to treat/gal	0.19$	0.07$	0.10$	0.11$

Since runs 2 and 3 were diluted 5 times, then the cost to treat 1 gal of undiluted spent caustic of the same kind is 5 times the cost written in the table. Then, the cost of runs 3 and 4 are 0.49$ and 0.56$ respectively. This cost is the major running cost of the plant. Comparing this cost with the 1.23 $/gal, the running cost of fenton's process is much lower than the cost of sending the feed to USA to be treated there. The running cost of the plant includes other costs like labor cost and utility costs (excluding cost of water), they are much lower than the cost of chemicals. Also the capital cost of the plant is low. The cost the pilot plant is 100,000 DHS that has a minimum capacity of 600 L/d of spent caustic. To conclude, the average treatment cost of feed 1 is 0.13 $/gal and 0.53 $/gal for the second feed.

CHAPTER 4:
Conclusion

Mixed refinery spent caustic is an industrial wastewater that is generated from oil refineries. Spent caustic undergo two treatment steps, chemical oxidation followed by biological post treatment step. The goal of chemical oxidation is to drop the contamination concentration to a level that biological treatment can take place. The maximum contaminants concentration, which can be measured by chemical oxygen demand, that biological treatment can be applied, is 1,000 ppm. Advanced oxidation processes, in specific, fenton's reaction is tested to check if the method can be applied to spent caustic treatment.

The research is divided into two parts, bench scale study followed by pilot plant study. The goal of bench scale study is to treat spent caustic to achieve a final chemical oxygen demand of 1,000 ppm with minimum hydrogen peroxide to chemical oxygen demand ratio possible by manipulating other factors affecting chemical oxygen demand removal. It was found out that the highest chemical oxygen demand removal achieved is 97% at optimum hydrogen peroxide to ferrous sulfate to chemical oxygen demand mass ratio of 3.8/2.1/1.

Moving on to the pilot plant study, the objective of the pilot plant study is to check if fenton's process can be applied in large scale. The best result obtained is a final chemical oxygen demand of 525 ppm while operating at hydrogen peroxide to ferrous sulfate to chemical oxygen demand mass ratio of 3.5/1.6/1. Finally, the cost of chemicals to treat 1 gal of refinery spent caustic was estimated. The cost of chemicals to treat 1 gal of 100,000 ppm COD refinery spent caustic is 0.56$/gal.

4.1   Future work

Further analysis can be done to fenton's process. A kinetics study can be done in the bench scale. For the pilot plant, some modification can be done. Both the reactor and neutralization tank can be equipped with pH controllers. The amount of hydrogen peroxide can be increased to check if sulfide concentration can be lowered. Adsorption bed can be changed to get better results.

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APPENDIX A

Reagent Preparation

Ferrous Sulfate Solution:

The solution to be used will be a saturated one, the solubility of ferrous sulfate heptahydrate in water is 0.256 g/ml . So for each liter of water add 0.256 Kg of ferrous sulfate heptahydrate, mix thoroughly and store in the appropriate dosing tank.

Hydrogen Peroxide:

The hydrogen peroxide is to remain undiluted and should be used as received from the supplier

Sodium Hydroxide:

A 5 molar solution of sodium hydroxide will be used, so for every liter of water add 200 g of sodium hydroxide. When preparing the solution, it is vital to add the sodium hydroxide slowly and mix it well as adding it too quickly will lead to an excessive increase in temperature. The excessive increase in temperature could lead to harmful fumes being given off.

Spent Caustic:

The Spent Caustic should be acidified to a pH in the range of 3.5-4 unless otherwise recommended, use sulfuric acid. Constantly add the acid while mixing and monitoring the pH of the solution.

Sulfuric acid:

For safety reasons, it is preferable to use 25wt% sulfuric acid when acidifying the spent caustic. Depending on the concentration of the source of sulfuric acid, dilute accordingly.

Pilot Plant Operating Procedure

1. Ensure that all vessels are empty by opening respective drains located at the bottom of each vessel

2. Open control panel and turn on the main power switch (Orange Switch)

3. Ensure that the dosing tank valves are all closed (located immediately at the outlet of each one)

4. Fill the blue dosing tanks to the top of the sight glass from the top as follows:
    I.   Sodium Hydroxide
    II. Ferrous Sulfate Soln.
    III. Sodium Hydroxide
    IV. Hydrogen Peroxide

5. Fill the white feed tank at the bottom with the acidified spent caustic

6. Using the attached Excel sheet, determine the required dosing rates of the reagents

7. Turn on the Spent caustic feed tank pump (p on the control panel) adjusting the inline valve after the outlet of the pump to achieve the desired flow rate

8. Ensure that the valves at the reactor outlet are in position so that complete recycle will occur (the valve closest to the outlet will be in the fully open position while the other in fully closed position)

9. Switch on the reactor outlet pumps labeled pump 1 on the control panel

10. Enter the required dosing rates into the two dosing pumps, they are switched on by switches T-4 and T-2

11. Slightly open the valve(approximately a 20% opening) at the beginning of the ferrous dosing tank (2) and fully open the smaller inline valve leading to the reactor

12. Start the ferrous dosing pump

13. Repeat steps 10-11 for the hydrogen peroxide (tank4, switch t-4)

14. Turn the switch labeled mix-1 on the control panel to start the reactor mixer

15. Adjust the reactor speed from the lower dial on the side of the control panel (50-75V)

16. Dose the ferrous and hydrogen peroxide over a 30 min period and another 30 min for reaction

17. Wait for one hour (at all times monitor the sight glass levels in the dosing tanks to ensure there is enough reagents left, if not add immediately)

18. After the passing of one hour adjust the opening of the second valve from the reactor outlet to achieve the desire outlet flow

19. Ensure that the outlet valves from the conical separator are adjusted such that complete recycle will be achieved (the blue plastic valve at the outlet must be closed for complete recycle)

20. Monitor the level in the sight glass of the conical separator, once it is half filled switch on the recirculation pump labeled cp-101 on the control panel

21. Close the inline valve leading from the reactor outlet to the conical separator

22. Begin feeding sodium hydroxide from tank 1 by manually adjusting the tanks valve and opening the inline valves leading to the conical separator (there are two inline valves)

23. Monitor the pH level in the tank by using the sampling port

24. Once the desired pH is achieved, adjust the valve arrangement such that the circulation pump (cp-101) begins to feed the sedimentation tank

25. Once the contents of the conical separator are emptied adjust the valve arrangement to return to complete recycle

26. Repeat steps 17-24 until the sight glass in the sedimentation tank is full

27. Perform steps 17-24 one more time

28. Allow 60 minutes for complete sedimentation to occur

29. Open the top valve out of the sedimentation tank

30. Ensure that all the valves leading from the sedimentation to pump-2 are open

31. Ensure that all the valves leading from pump-2 to the cartridge filter are open

32. Ensure that all the valves leading from the cartridge filter to the ceramic filter are open

33. On the ceramic filtration unit, the valves for each individual filter must remain full open during operation.

     I.   Black steel valves are the inlet to each filter

    II.   Orange valves are the outlet for each filter

    III.   Blue valves are the main inlet and outlet to the entire unit, where the inlet is the lower valve

34. Ensure that all the valves leading from the ceramic filter to the polishing column are open

35. Arrange the valve openings in the polishing column so that the flow will go down either column

36. Start the filtration pump by turning the switch labeled pump-2 on the control panel

37. At all times monitor the pressure gauge of the ceramic filtration ensuring it does not exceed 5 bar

38. Collect the product from the bottom of the polishing column

39. Continue to neutralize, sediment and filter until the run is complete

40. The dosing pumps should be switched off 40 minutes after the last of the spent caustic is fed to the reactor

Safety

To ensure the safe operation of the mixed refinery spent caustic treatment pilot plant, the following must be observed:

1- The operation must be performed either in an outdoor or very well ventilated area, the untreated spent caustic posses a foul odor

2- The pilot plant is skid mounted so before operation it must be ensured that the wheels are all locked

3- All operators must wear protective clothing including: overalls, hard cover boots, heavy-duty gloves and perforated masks.

4- If any of the materials come in direct contact with any part of the body, rinse immediately with plenty of water. Skin contact with hydrogen peroxide will leave a white mark for the duration of a day.

5- Avoid touching the reactor vessel as it will be extremely hot during operation

6- In case of an emergencies with the reactor, feed large quantities of sodium hydroxide as it will quench the reaction.

VITA

Mohammed Wajih Al Jabari was born on April 23,1987,in Abu Dhabi. He was educated in public schools in Abu Dhabi. He graduated from high school with an overall of 96% in 2005. He received his degree with magna cam laude in Chemical Engineering from the American university of Sharjah in Spring 2010. He was awarded full scholarship from the American University in 2010 to continue his studies in Chemical Engineering.