DEVELOPMENT OF NATURAL PRODUCT BASED FLOCCULANT AGENT TO TREAT PETROLEUM REFINERY INDUSTRY WASTEWATER

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ABSTRACT

Spent caustic or used caustic soda generated from the scrubbing process in the petroleum refinery industry. Treatment is needed for spent caustic because it typically has high chemical demand (COD), oil-grease (OG) and Biochemical oxygen demand (BOD_5) concentration, pH and temperature that exceeded the limit of Department of Environment (DOE) regulations. In this study, the spent caustic was treated by using adsorption method by using natural product such as charcoal and coconut husk based flocculants agent in batch mode. The benefits of natural product usage is a green technology approaches and cheaper. The treated spent caustic was tested for its COD, OG and BOD_5 concentration, pH also the temperature to determine respectively the percentage of reduction measured using Spectrophotometer, Standard 5520B liquid-liquid partition-gravimetric method, Dissolved Oxygen meter (DO meter), and pH meter. Results show COD concentration for untreated spent caustic is at a range of 4910 - 13980 mg/L, OG concentration is 32 - 6285 mg/L, BOD_5 concentration at range of 41 - 78 mg/L, pH at a range of 11.9 – 13.0, and temperature at range 20 ^{0} C - 29 ^{0} C. The highest percentages reduction by using charcoal and coconut husk was able to reduce 50.38 % (6885 mg/L) and 45.19 % (7605 mg/L) COD, 46.88 % (17 mg/L) and 21.88 % (25 mg/L) OG, 55.13 % (35 mg/L) and 45.51 % (42 mg/L) BOD_5, 60.05 % (5.15) and 48.02 % (6.70) pH, 20.88 % (23 °C) and 4.0 % (28 °C) temperature respectively. The optimum amount in large scale by using charcoal and coconut husk is 600 g and 800 g based flocculants agent soda ash, alum, and ferum sulphate that have a ratio of 0.05:0.42:0.53 with activated carbon and clay as additional adsorbents that have a ratio of 0.74:0.26, which able to reduced 91.78 % (1140 mg/L) and 81.19 % (2610 mg/L) COD concentration by recycle in eight times respectively. Flocculants agent was used in pre-treatment in order to increase adsorption method efficiency of natural product. Hence, natural product by using charcoal is more efficient than coconut husk. The information obtained from this study is useful for scale up purpose in the petroleum refining industry that choose adsorption method by using natural products based flocculants agent to treat spent caustic wastewater.

ABSTRAK

Sisa kaustik atau kaustik soda yang telah digunakan, dihasilkan daripada proses menyental dalam industry penapisan petroleum. Rawatan diperlukan untuk sisa kaustik kerana ia biasanya mempunyai nilai keperluan oksigen kimia (COD), minyak dan gris (OG), oksigen biokimia (BOD_5), pH dan suhu yang melebihi had yang ditetapkan oleh Jabatan Alam Sekitar (JAS). Dalam kajian ini, sisa kaustik akan dirawat mengunakan kaedah penjerapan dengan mengunakan bahan semulajadi sebagai contoh arang dan sabut kelapa berasaskan ejen gumpalan secara kumpulan. Faedah penggunaan bahan semulajadi adalah sebagai pendekatan teknologi hijau dan murah. Sisa kaustik yang telah dirawat, diuji untuk nilai COD, OG, BOD_5, pH juga suhu untuk menentukan peratusan pengurangan masing-masing dengan mengunakan spektrofotometer, Standard 5520B kaedah cair-cecair pembahagian-gravimetrik, meter oksigen terlarut (DO meter), dan meter pH. Kajian menunjukkan nilai COD untuk sisa kaustik yang belum dirawat antara 4910-13980 mg/L, nilai OG adalah 32 - 6285 mg/L, nilai BOD_5 antara 41 - 78 mg/L, nilai pH antara 11.9 - 13.0 dan nilai suhu antara 20 ^{0} C - 29 ^{0} C. Peratusan pengurangan paling tinggi dengan menggunakan arang dan sabut kelapa mampu mengurangkan 50.38 % (6885 mg/L) dan 45.19 % (7605 mg/L) COD, 46.88 % (17 mg/L) dan 21.88 % (25 mg/L) OG, 55.13 % (35 mg/L) dan 45.51 % (42 mg/L) BOD_5, 60.05 % (5.15) dan 48.02 % (6.70) pH, 20.88 % (23 °C) dan 4.0 % (28 °C) suhu masing-masing. Jumlah berat optimum dalam skala yang besar dengan menggunakan arang dan sabut kelapa adalah 600 g dan 800 g berasaskan ejen gumpalan abu soda, aluminium sulfat dan ferum sulfat yang mempunyai purata 0.05:0.42:0.53 dengan karbon teraktif dan tanah liat yang mempunyai purata 0.74:0.26, mampu mengurangkan 91.78 % (1140 mg/L) dan 81.19 % (2610 mg/L) % nilai COD dengan mengulangi sebanyak lapan kali masing-masing. Ejen gumpalan digunakan dalam pra rawatan dan secara tidak langsung meningkatkan kecekapan kaedah penjerapan oleh bahan semulajadi. Oleh itu, bahan semulajadi dengan menggunakan arang lebih berkesan daripada sabut kelapa. Maklumat yang diperolehi daripada kajian ini amat berguna untuk peningkatan skala dalam industri penapisan petroleum yang memilih kaedah penjerapan dengan menggunakan bahan semulajadi berasaskan ejen gumpalan untuk merawat air sisa kaustik.

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LIST OF SYMBOLS

mg/L	milligram per liter
%	percentage
g/L	gram per liter
°C	degree celcius
g	gram
mL	mililiter
L	liter
mg	milligram
m^3	meter cubic
kg/m^3	kilogram per meter cubic
Kg	kilogram
RPM	Revolution Per Minute

LIST OF ABBREVIATIONS

AG25	Acid Green 25
APHA	American Public Health Association
BOD5	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CNS	Central Nervous System
DOE	Department of Environment
EPER	European Pollutant Emission Register
GAC	Granular Activated Carbon
HR	High Range
KTU	Kerosene Treating Unit
LPG	Liquefied Petroleum Gas
OG	Oil and Grease
PAC	Powdered Activated Carbon
TOC	Total Organic Carbon
TSS	Total Suspended Solid
USEPA	U.S. Environmental Protection Agency

1 INTRODUCTION

1.1 Motivation and statement of problem

Wastewater from the petroleum refining industry commonly has high chemical oxygen demand (COD), oil-grease (OG), Biochemical oxygen demand (BOD_5) concentration and pH. The wastewater can bring harm to the environment if it is released to the water bodies without treatment. Therefore, the wastewater needs to meet the specification and requirement of Malaysian's Department of Environment (DOE) before being release to environment. According to Environment Quality for Sewage and Industrial Effluent Regulations 1979 Third Schedule (2012), the acceptable conditions for discharge of Industrial Effluent of standard B, for COD concentration in wastewater is 100 mg/L, for OG concentration in wastewater is 10 mg/L, for BOD_5 concentration in wastewater is 50 mg/L, for pH in wastewater is 5.5 – 9.0 and temperature in wastewater is 40 °C.

Spent caustic is one sort of wastewater in the petroleum refining industry. Spent caustic is used caustic soda as well-known as sodium hydroxide. It is a made of sodium hydroxide or potassium hydroxide, water, and contaminants. Spent caustic is a waste industrial caustic solution that has become spent and is no longer useful (Harrafi et al., 2012). It is commonly used in petroleum refinery industry and petrochemical industry as scrubbing solutions for the removal of acid constituents such as hydrogen sulphide (H_2S), cresylic acids, naphthenic acid and mercaptans acids from the refined product stream (Kumfer et al., 2010). Spent caustic is produced from refinery units such as Kerosene Treating Unit (KTU) in the petroleum refining industry. Raw kerosene uses caustic soda to remove cresylic for gasoline, napthenic for commercial kerosene and jet fuel and hydrogen sulphide (H_2S) for Liquefied Petroleum Gas (LPG) spent caustic which is called refinery spent caustic when the acidic components are often mixed (Harrafi et al., 2012). Spent caustic from the KTU typically have high COD concentration, ranging from 50 000 to 150000 mg/L (Felch, Clark & Kumfer, n.d.). This is because wastewater that contains spent caustic has a high sulfide concentration which is known as strong oxidant and other chemicals such as cresylic acid, mercaptans, and sodium salts of napthenic (Kumfer et al., 2010). It is highly toxic to both environment and human as well. Spent caustic is highly corrosive due to the high pH because it typically has pH more than 12 and sulphide concentration exceeding in 2-3 wt. % (Heidarinasab & Hashemi, 2011). Furthermore, spent caustic from the KTU have high OG concentration, ranging from 59 to 72 mg/L (Hawari et al., 2014). Spent caustic also has high BOD_5 concentration from KTU, ranging 323-33426 mg/L (Attiogbe et al., 2002).

Releasing of untreated spent caustic can brings harm to the environment because the acids constituents in a spent caustic are hazardous and corrosive. According to European Pollutant Emission Register (EPER) and National encyclopaedia (2010), a high chemical oxygen demand (COD) concentration in the water may be sign of an oxygen lack, which can harm to fish and other aquatic species that need oxygen to live (as cited in Chemical Oxygen Demand (COD-Cr), n.d). Furthermore, if wastewater that contains high oil and grease (OG) concentration is discharged into water bodies, it can leads to the formation of oil layer which can bring major pollution problem such as reduction of photosynthesis and penetration. Besides that, it leads to decreased amount of dissolved oxygen at the bottom of the water and this will give affect the survival of aquatic life in the water because of there is no oxygen transfer from atmosphere to water bodies (Alade et al., 2011). Spent caustic has a high of organic matter content or biochemical oxygen demand (BOD) concentration. If the wastewater discharged into a river, the bacteria in the river will oxidize the organic matter by consuming oxygen from water. Therefore, the aquatic species will die because of oxygen deficiency (Attiogbe et al., 2002).

According to (Texas Technology, 2006), there are a tragedy happen in the Ivory Coast City of Abidjan about 500 metric tonnes (110000 gallons) of liquid spent caustic were illegally dumped in the city causing deaths and injuries to local residents. After the dumping of untreated spent caustic in various sites in the city of Abidjan, about 40000 people reported for medical help, from this tragedy also recorded ten people are died and 9000 people were injured. Since the incident began in 2006, about 197 million dollars have been spent on claims and remediation.

Thus, there are several treatment processes of spent caustic where it focuses on the reduction of COD and other harmful chemical have been developed such as wet air oxidation, chemical reagent oxidation, chemical reagent oxidation, catalytic oxidation, incineration, chemical precipitation and (Veerabhadraiah et al., 2011). This study aims to treat spent caustic by using adsorption method by using natural product based flocculants agent. Several methods in environmental treatment application throughout the world, adsorption is widely acceptable than the other methods. Among all type of adsorption materials, adsorption with activated carbon material has been regarded as an efficient and major technology, but the process is expensive. Therefore, more approaches have been investigated for the development of low cost adsorbents with a good sorption capacity to remove heavy metal ions from wastewater. Natural products have the advantages of large quantities, low cost, and good sorption capacity. They are always the unutilized materials but they have high potential to be used as adsorbents for heavy metals removal (Zhang et al., 2014). Besides that, this study also hoped to provide treatment alternatives and to widen the varieties for treatment of spent caustic in the petroleum refinery industry.

1.2 Objectives

The following are the objectives of this research:

- This study aims to determine the effectiveness of natural product based flocculants agent to treat the petroleum refinery industrial wastewater by using adsorption method.

1.3 Scope of Study

The following are the scope of this research:

i) To analyse the COD, OG, BOD_5 concentration, pH and temperature reading in wastewater that contains spent caustic from KTU at a petroleum refinery company by using spectrophotometer, liquid-liquid partition-gravimetric method, DO meter and pH meter respectively.

ii) To use adsorption method by using natural product based flocculants agent to treat the spent caustic wastewater samples.

iii) To compare the performance of the natural product based flocculants agent in terms of its effectiveness in reducing COD, OG, and BOD_5 concentration, pH and temperature reading.

iv) To analyse the COD, OG, BOD_5 concentration, pH and temperature reading in treated spent caustic wastewater.

1.4 Main contribution of This Study

The following are the contributions of this study:

i) The effectiveness of using chemical in flocculants agent and additional adsorbent to reduce COD, OG, BOD_5 concentration, pH and temperature in spent caustic wastewater.

ii) The best amount of natural product can be determined by treating spent caustic wastewater specifically from KTU tank.

iii) This work also will add some options varieties in treating spent caustic from KTU tank.

1.5 Organization of This Thesis

The structure of the rest of the thesis is outlined as follow:

Chapter 2 presents the literature review of this study. It started with the introduction of spent caustic where it generally describes the types of spent caustic, typical spent caustic composition, where does the spent caustic come from and effect spent caustic to health and environment. This chapter continues introduce the natural product used is charcoal that described charcoal processing and advantages of charcoal in reducing heavy metals. Secondly, natural product used is coconut husk that described the composition coconut husk, and the modification of coconut husk in treating wastewater. After that, this chapter also introduces COD, where it describes the major oxidants used in COD determination and the reactions behind the determination of COD. This chapter continues with the introduction of OG, BOD_5 and pH. This chapter continues with the treatment method of spent caustic, where the advantages and disadvantages of commonly used spent caustic treatment have been listed. After that, this chapter also introduced adsorption methods that have been used for the treatment of spent caustic in this study. Some brief review on the chemical in additional adsorbent and flocculants agent has been presented in this chapter.

Chapter 3 talks about material and methodology that have been used in this study. The chapter is started off with an overview of the chapter and brief introduction about the chapter. This chapter will brief about the chemicals, the additional adsorbent, the natural products, the spent caustic wastewater samples and also the analysis of the sample.

Method to prepare the flocculants agent as stock solution and also adsorption process will be explained as well.

This study continues with Chapter 4, where the results and discussions of this study are presented.

Last but not least, Chapter 5 presents about the conclusion and recommendation of this study.

2 LITERATURE REVIEW

2.1 Chapter Overview

This chapter introduces spent caustic wastewater. It also shows some previous study on spent caustic and the treatment method of spent caustic such as wet air oxidation. This chapter also reviews about the adsorption methods that are used to treat spent caustic wastewater from KTU tank.

2.2 Introduction to Spent Caustic

Caustic soda or commonly known as sodium hydroxide are used in the petroleum refining industry and the petrochemical industry as scrubbing solutions for the removal of acidic compounds. The spent caustic is produced continuously almost 85% by volume in the treatment of kerosene (Huaman et al., 2008). According to "Analysis of Oxygen in Wet Air Oxidation of Spent Caustic Effluents" (n.d.), spent caustic typically comes from the production of ethylene and the oil refining process, where aqueous sodium hydroxide was consumed for the scrubbing of cracked gas. Furthermore, sodium hydroxide also was used for the extraction or treatment of acidic impurities, such as hydrogen sulphide (H_2S), mercaptans and organic acids in hydrocarbon streams. Caustic soda generally was used in ethylene plants in the petrochemical industries to remove acid gases such as hydrogen sulphide (H_2S) and carbon dioxide (CO_2) from the ethylene gas (Maugans et al., 2010). In oil refinery, the spent caustic has a high pH which is more than 12 and sodium concentration in 5-12% by weight (Alnaizy, 2008). Caustic soda was generally used to remove hydrogen sulphide (H_2S) and organic sulphur compounds from hydrocarbon streams in the petroleum refining industry (Sipma et al., 2004). Therefore, spent caustic is generated once the caustic soda has reacted and removed undesired chemicals from the streams.

There are three types of spent caustic from petroleum refinery which are sulfidic spent caustics, cresylic spent caustic and naphthenic spent caustics. Ethylene or liquefied petroleum gas (LPG) produced sulfidic spent caustics that contain high concentrations of sulphides and mercaptans from the caustic scrubbing (Kumfer et al., 2010). Cresylic as well-known as phenolic spent caustics is generated when scrubbing of cracked gases or gasoline is produced by fluidized bed catalytic cracking process with caustic that contains phenols, cresols and xylenes with sulphides (Veerabhadraiah et al., 2011). Naphthenic spent caustic produced from the caustic scrubbing of kerosene and diesel products containing high concentrations of polycyclic organic compounds such as naphthenic acids (Kumfer et al., 2010). In this study, the main focus is naphthenic spent caustic which comes from the KTU. In the KTU, by using 1.5-2% solution of caustic soda the raw kerosene is pre-washed to neutralize both the hydrogen sulphide (H_2S) and the naphthenic acids that present in the raw kerosene (Prakash, 2003). The scrubbing process of raw kerosene by caustic soda are necessary to meet the acidity, mercaptan and other specifications required for upgrading raw kerosene to jet fuel products which is commercial kerosene, that are used by air transportations (Mohamadbeigy et al., 2006).

Generally, spent caustic have different compositions that depended on the scrubbing process. Table 2-1 shows the typical chemical characteristics of three types of spent caustic.

Table 2-1: Typical spent caustic composition by Huaman et al. (2008)

	Reported as (g/L)	Sulfidic Spent Caustics	Naphthenic Spent Caustics	Cresylic Spent Caustics
Chemical Oxygen Demand, COD	O_2	7-110	50-100	165-230
Total Organic Carbon, TOC	C	0.02-4	11-25	23-60
Sulfide	S	2-53	<0.001	0-64
Sulfite	S	0.002-0.48	0.004-0.009	0.8-1.6
Mercaptans	CH_3SH	0-28	<0.03	0-5.4
Thiosulfate	S_2O_3	0-3.7	0.07-0.13	10-12
Iron	Fe	0.005-0.025	0.025-0.03	0.025-0.03
Total Phenols	C_6H_6O	0.003-0.02	2-10	14-20

("Acids and Caustic from Petroleum Refining Category", 2009) described spent caustic solutions have high chemical oxygen demand as a result of all dissolved organics present in the spent caustic. Depending upon the type and the composition of spent caustic and for easy discussion, there are some effect of spent caustic to health and environment. Sulphides and mercaptans have very strong odours. The odour thresholds for these types of compound are generally in the order of magnitude of parts per billion. Furthermore, hydrogen sulphide is very insidious because at low concentration as 30 mg/L make it destroys the sense of smell. At low concentration of 700 mg/L, death can occur with a few breaths (Draper & Stark, 2012). Besides that, spent caustic wastewater can cause serious corrosion to the eyes and it also lead to corneal capacity. It may also cause serious irritation, redness and tearing, blurred vision and conjunctivitis and at last blindness. Inflammation and blistering can produce if skin contact occurs. Severe burns with deep ulcerations will happen. More than that, severe irritation of the respiratory such as characterized by coughing, choking or shortness of breath can produced from inhalation of mist or spray of spent caustic. In addition, inhalation of high concentrations may cause central nervous system (CNS) depression or chemical pneumonitis. In worst cases, it may cause immediate coma and death. It is fatal or harmful when swallowed. As shown in Figure 2-1 the pictures of effect of spent caustic dumped in city of Abidjan.

Figure 2-1: Effect of spent caustic dumped in city of Abidjan. (Source: Texas Technology Corporation, 2012)

There are some effects of spent caustic to environment. Spent caustic typically has high toxicity to aquatic organism if releasing to water bodies due to an increase in pH. If spent caustic is released to water or soil, constituents will remain in the soil because it is not likely to volatilize to the atmosphere. Fate in the soil will depend on the amount released of the receiving medium. Some constituents may display high mobility depend on the properties of soil. (Philips, 2010) stated at a slower rate, the higher chain alpha olefins may partition to the soil and sediment where degradation will occur. Therefore, spent caustic can cause issues in biological treatment process. According to (Heidarinasab & Hashemi, 2011) phenol in low concentrations as 400 mg/L have been shown to inhibit the removal of COD, phosphorous and ammonia as well as contribute negatively impact the settling characteristics of the sludge. As shown in Figure 2-2 dilution of a dead stream as a result of spent caustic.

Figure 2-2: Dilution of a dead stream as a result of spent caustic. (Source: Texas Technology Corporation, 2012)

The spent caustic solution has high alkalinity and corrosively that may contribute to health and environmental hazards. According to "Analysis of Oxygen in Wet Air Oxidation of Spent Caustic Effluents" (n.d.), spent caustic is highly corrosive, have high contaminants, have a significant odour source and therefore disruptive to the operation of any downstream bio treatment facility and an environmental hazard that needs processing. In this study, chemical oxygen demand (COD) concentration, oil-grease (OG) concentration, biochemical oxygen demand (BOD_5) concentration, pH and temperature of spent caustic are being emphasized.

2.3 Natural Product (Charcoal)

Charcoal is widely used solid to remove pollutants in wastewater due to its own characteristic such as high porosity, chemical structure and high surface area (Singh, U. & Khausal, R.K., 2013). Charcoal from mangrove barks (Rhizophora apiculata) is potential useful material as an adsorbent for removal of heavy metal. Charcoal as well-known as activated carbon is commonly used adsorbent in wastewater treatment. Generally, charcoal is provided from the factory making charcoal which is mangrove bark needs processing. wildshores (2009) stated that the logs are placed in a kiln usually in a shape like igloo. Then, the logs are smoked to remove the water from them. Other mangrove wood is burnt such as non-Rhizophora species like Bruguiera is used to create the smoke. As the mangrove timber are used for the production of charcoal, during the production of charcoal the mangrove wood was debarked to reduce the ash content of the charcoal produced (Rozaini C.A et al., 2010). Besides that, Rozaini C.A et al., (2010) stated bark has high content of polyhydroxy polyphenolic group and effectively to remove dye ions from water. Bark also contain carboxylic group which can bonding dye ions by ion- exchange mechanisms. According to (Rumidatul and Alfi, 2006) reported that charcoal from wood as an adsorbent in wastewater treatment can reduced 98.03% Biochemical Oxygen Demand (BOD_5), 97.66% total suspended solid and 76.92% oil and grease (OG). Charcoal mangrove bark as shown in Figure 2-3 can be used to treat heavy metal.

Figure 2-3: Charcoal mangrove bark

2.4 Natural Product (Coconut Husk)

Coconut husk is a one type of adsorbent has capacity for removal several of pollutant. Coconut husk is the mesocorp of coconut and it consists of 33-35% of husk. In Malaysia, the land was being used for coconut plantation in year 2001 is about 151000 ha. Almost 5280 kg of dry husk were become available per hectare per year (Tan, I.A.W. et al., 2008). The characteristic of coconut husk is 5-10 cm thick fibrous that covering coconut fruit which 3.5 mm thickness of shell structure. The average weight of coconut husk is 0.4 kg (Tejano, E.A, 1985). The composition of coconut husk is shown in Table 2-2.

Table 2-2: The composition of coconut husk (Balce, S., 1956)

Constituent	Percent (%)
Moisture	15.0
Lignin	43.0
Ash	8.26
Alkalinity	37.5

According to (Tan, I.A.W. et al., 2008) coconut husk is widely used as a fuel for coconut processing. Furthermore, it is used as a domestic fuel and also as a source of fibre for rope and mats. Coconut husk is cheap and abundant agricultural waste and proposed to convert coconut husk into activated carbon is better. Many researchers have done the research by using agricultural waste in adsorption of heavy metals. The coconut husk either treated or untreated was used as adsorbent to remove the Acid Green 25 (AG25) dye from aqueous solution (Abdul Halim, H. N. & Mohd Yatim, N.S, 2011). They reported that coconut husk treated is more effective in removing anionic dye (AG25) from synthetic wastewater. Other than that, activated carbon also can produce by coconut husk. According to Tan, I.A.W. et al., (2008) stated coconut husk based activated carbon can use in removal of 2, 4, 6-trichlorophenol (2, 4, 6-TCP) from aqueous solution. The performance of coconut husk based activated carbon is 97.52% of removal efficiency for 200 mg/L concentration of solution. As shown in Figure 2-4 is the coconut husk used as an adsorbent to treat wastewater.

Figure 2-4: Coconut husk used as adsorbent to treat wastewater

2.5 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) in spent caustic is one of the chemical characteristic that being tested in this study. COD has been one of the important parameters in the wastewater treatment. According to Boyles (1997), Chemical oxygen demand is defined as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. Boyles (1997) also described that the chemical oxygen demand test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to carbon dioxide (CO_2) and water (H_2O). The reaction mechanism can be summarized in equation (2.1):

$$\text{Organic carbon} + \text{Oxidant} \longrightarrow CO_2 + H_2O \quad (2.1)$$

There are many chemicals that have been used as a strong oxidant in COD test such as potassium permanganate ($KMnO_4$), cerium (IV) sulfate ($Ce(SO_4)_2$), potassium thiosulfate (K_2S_2O), potassium iodate (KIO_3), oxygen (O_2), potassium dichromate ($K_2Cr_2O_7$), manganese (III) sulfate ($Mn(SO_4)_3$). Each of the major oxidants used in COD determination have their own advantages and disadvantages, which can be summarized in Table 2-3.

Table 2-3: Advantages and disadvantages of major oxidants used in COD determination by Boyles (1997)

Oxidant	Advantages	Disadvantages
$KMnO_4$	• Stable for several months, MnO2 must be excluded • Is used in acidic, neutral and basic	• Relatively slow-acting and is not quantitative • Results may depend upon

	media • Manganese is a non-hazardous metal	sample size • Does not oxidize volatile acids or amino acids • Incomplete oxidation of organic compounds • Unstable in solution: Forms MnO2 precipitate which catalyzes reagent spending decomposition
Ce $(SO_4)_2$	• More complete oxidation of organic compounds • More stable than $KMnO_4$	• Incomplete oxidation of many organic compounds than $KMnO_4$ • Poor reproducibility • Photometric measurement at 320 NM where incompletely oxidized organic compounds interfere • Relatively expensive
K_2S_2O	• Oxidizes many organic nitrogen-containing • Widely used with TOC instrumentation	• Requires elaborate equipment compounds more completely than other oxidants • More labour intensive • Relatively unstable
KIO_3	• Strong oxidant	• Difficult to use • Questionable accuracy
O_2	• Oxygen consumption measured directly	• Elaborate equipment required
$K_2Cr_2O_7$	• Accomplishes a complete oxidation when used with a catalyst and a two-hour digestion period. • Stable at room temperature when protected from	• Some organic compounds are only partially oxidized • Some organic compounds such as pyridine are not oxidized • There can be interference from

$Mn(SO_4)_3$	exposure to light • One hour digestion period • Correlates very well with Dichromate COD and BOD test results • Is not photosensitive • Is stable at room temperature • Reagent contains no hazardous metals and generates no hazardous metal waste	inorganic pollutants, mainly chloride ions • Carcinogenic • Oxidizes approximately 80% oxidation of most organic compounds • Interference of most organic compounds, The reaction temperature is limited by thermal decomposition of the oxidant

The strong oxidants used in this work are potassium dichromate ($K_2Cr_2O_7$). The dichromate ions ($Cr_2O_7^{-2}$) form orange coloured solutions which will then reduce by organics to chromic ions (Cr^{3+}), forming a green solution (Roby, 2007). The reaction can be summarized in equation (2.2).

$$\underset{\text{(Orange)}}{\text{Organic} + Cr_2O_7^{-2}} \longrightarrow \underset{\text{(Green)}}{Cr^{3+}} \qquad (2.2)$$

Spent caustic wastewater specifically from KTU tank has high COD and possibly high OG concentration as well. (Felch, Clark & Kumfer, n.d.) have reported that spent caustic wastewater from the KTU tank have high COD concentration ranging from 50 000 to 150000 mg/L, which is very high when compared to the regulation of the Department of Environment, Malaysia that permits only 100 mg/L of COD concentration in wastewater to be released to water bodies. According to Sipma et al. (2004), the formation of elemental sulfur in spent caustic wastewater contributed to high COD concentration. Hariz et al., (2013) also stated that the high concentrations of sulfur compound resulting in high concentrations of COD in spent caustic wastewater.

COD is an important parameter for wastewater or surface water testing as it gives information about the degree of water pollution by organic material ("Chemical Oxygen Demand of Water", n.d.). Besides that, "Chemical Oxygen Demand" (n.d.) emphasized that COD measurements are extremely useful to those concerned with water quality since they represents the amount of oxygen necessary for the aerobic biological oxidation of the organics in water sample to carbon dioxide (CO_2) and water (H_2O) if it is assumed the organics are biodegradable. In addition, COD can be related to Total Organic Carbon (TOC) and its value is about 2.5 times Biological Oxygen Demand (BOD) value ("Experiment on Determination of Chemical Oxygen Demand", n.d.). Besides that, the determination of COD was preferred than the determination of BOD as it only takes about 3 hour to determine the COD concentration of water and wastewater, compare to usual 5 days required for the measurement of BOD (Nanyang Technological University, 2004).

2.6 Oil and Grease (OG)

Oil and Grease (OG) as one of the most important pollutants in the oil processing wastewater and are the most complicated to remove from the wastewater (Choong, Paul and Jay (n.d.)). The term "Oil and Grease" has become the popular term replacing the original term, which was "Fats, Oils and Grease", although both terms refer to the same wastewater constituents ("Understanding Laboratory Wastewater Tests: I. Organics", n.d.). OG is defined as any material recovered as a substance soluble in the solvent (*Standard Methods for The Examination of Water and Wastewater*, 2005). According to "Understanding Oil & Grease" (2012), the two main components of OG, which is petroleum based hydrocarbons, that being referred as nonpolar material and fatty compounds of animal or vegetable origin. (Irwin et al., 1997) have emphasized that OG includes not only petroleum oils but also vegetable oils, natural oils, some sediments, biota and decaying life forms that have high natural oils lipids. (Alade et al., 2011) have stated that the oil contaminated wastewater comes from varied sources such as crude oil production, oil refinery, petrochemical industry, metal processing, compressor condensates, lubricants and cooling agents, car washing and restaurants. Table 2-4 shows the OG concentration from several industries.

Table 2-4: Oil and grease concentration from several industries by Cheryan (1998)

Industrial Sources	Oil and Grease Concentration (mg/L)
Food processing	3800
Food processing (Fish)	13700
Can Production (Forming)	200000
Wool Scouring	12200
Tanning Waste, Hide Curing	40200
Metal Finishing	6000
Petroleum Refinery	3200
Steel-Rolling Coolant	48700