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 (BOD₅) 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 BOD₅ 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 (H₂S), 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, naphthenic for commercial kerosene and jet fuel and hydrogen sulphide (H₂S) 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.