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$FeCl_3$-Induced Oxidation of POME for Efficient Treatment: An Experimental Study

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Abstract

POME is a biomass waste product from cooking oil in the food industry which requires well treatment before discharge to the main stream. It becomes problematic cause POME contains a lot of organic compounds, suspended solids, lipids, and others which is hazard. Proper treatment is necessary in order to avoid adverse effects on the aquatic and fresh water quality. As that concerned, $FeCl_3$ was introduced to initiate the oxidation reaction and indirectly to degrade the organic compounds in the POME. Throughout the experiment, 0.005 M of $FeCl_3$ solution was mixed into each untreated POME. Besides POME, Glucose and lignin has been used for comparative study. Since POME is biomass waste, UV-Vis Spectroscopy instrumentation is the best to characterize the degradation behavior of organic compounds contained in POME, as well as in glucose and lignin. Based on Lamda, λ Max, the absorbance value as the indicator to measure the degradation level. The experiment done in room temperature (±25 °C) and catalyst optimization was done by Cyclic Voltammetry, CV with potential window from -0.1 to 1.5 V and for UV-Vis spectroscopy, the wavelength(nm) range between 200-600 nm was set throughout the analysis.

1. Introduction

In this study, the main scope is to develop novel approached of biomass degradation by using Ferric Chloride, $FeCl_3$ which is considering as an inexpensive metal and its ability to chelate with oxygen groups. In waste water treatment, $FeCl_3$ acts as a coagulant and some had been reported it working as catalyst for hydrolysis reaction in organic compounds. Ions Fe^{2+}/Fe^{3+} shows significant roles as promising catalytic capability in many organic transformations. For instances, its was involved in depolymerization of biomass such as hemi-cellulose, cellulose and lignin. Majority, the results after the catalyzed of organic compounds which are C-C bonds were synthesized from the aromatic C-H bonds [1]. Rather than that, ions Fe^{2+}/Fe^{3+} based catalyst plays as a co-catalyst which shows better efficiency compared with ions Cu^{2+}, Zn^{2+} and Mn^{2+} in hydrolysis cellulose in waste water treatments [2] [3]. Ferric chloride ($FeCl_3$) itself function not limits to coagulate yet used as degradation agent in waste water treatment. Instead of that, the usage of $FeCl_3$ is beyond and its capability to improve heavy metals removals [4].

Discussing about waste water and degradation of biomass, in Malaysia, Palm oil mill effluent (POME) is the major type of wastewater produced from in palm oil cooking industry [5][6]. During the palm oil production, the extraction process needs a lot of water and leads the properties of POME with oil-based and polluted effluent. Towards the end point of the waste water line, POME contributes to high COD values and will promote other hazardous substances [7]. This proves that the physicochemical properties of POME, contains a lot of cellulosic, holocellulose 65.5%, lignin 21.2% and the rest are organic compounds [8] [9].

Moreover, the food plant-based materials processes are the main food supply for life in the world to cater the demands. Due to this, caused hazardous by-product from industry. Relate to the topic, considering palm oil is one of the raw materials used in food and non-food industries contributes to the pollution at the end of pipeline waste discharged. Instead of that, it is widely utilized as a feedstock for biofuel production. Unfortunately, undesirable contaminants present in the effluent after the factory processed makes it unpleasant to the environment. To avoid further environmental problems, a proper treatment for POME is required before discharged [10]. This is because, the oily wastewater becomes one of the environmental issues when it will reach as high as 40,000 mg/l of oily wastewater from industries. As concerning to related problems, POME should be treated before discharged and suspectedly it hard to meet the limit required by Malaysia Department of Environment (DOE). Hoping that, $FeCl_3$ will able to demonstrate better organic degradation in order to clean up the waste water in POME before it will be discharge into the main stream.

2. Literature Review of Palm Oil Mill Effluent (POME) and Ferric Chloride ($FeCl_3$)

Malaysia boasts an expansive plantation land covering over 5 million acres, annually yielding approximately 30 million tons of waste in the forms of Empty Fruit Bunches (EFB), trunks, and oil palm fronds. Predominantly, the biomass waste in Malaysia originates from oil palm remnants. These biomass feedstocks are commonly utilized in the production of bio-based compounds. Through fractionation, sugars present in Palm Oil Mill Effluent (POME) can be extracted from cellulose, facilitating their utilization in the manufacturing of biobased products. Prior to discharge into the main stream, POME is typically deposited in a containment pond, as depicted in Fig.1

Fig. 1 *POME sludge in dumping pond [11]*

Palm Oil Mill Effluent (POME) constitutes a brownish colloidal water mixture derived from the extraction of palm fruit juice, encompassing both fiber and oil components. Extant literature suggests that its characteristics exhibit variability contingent upon factors such as the age of the fruit, the method of processing employed, and the specific batch under consideration. While POME possesses biodegradable properties, its acidic pH level of 5.0 poses significant environmental hazards, endangering ecosystems and organisms alike. Consequently, Malaysia has implemented pond systems for the treatment of POME waste prior to its dispersal, as documented by [12]. The annual production of waste palm oil is intricately linked to the demand for cooking oil derived from palm oil. This relationship is exemplified in Fig. 2.3, depicting a graphical representation of estimated POME generation based on Malaysia's Crude Palm Oil (CPO) output, as reported by [11].

The information presented has been critically analyzed, and the results highlight the necessity of taking proactive steps to manage Palm Oil Mill Effluent (POME) because of the potential hazards it presents to the environment. Beginning with the fact that the large amount of POME produced and expected increases in palm oil output make it important to put effective management techniques needs for this and upcoming environmental danger that results from releasing POME into the environment without sufficient treatment [13]. The severity of the problem is evident when one considers that each year more than 60 million tons of POME and about 94 million tons of fresh fruit bunches are produced. . Furthermore, POME's chemical makeup, which is marked by a high total solids content and elevated Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) values, highlights the material's potential to significantly contaminate the environment [14]. These measurements, in particular COD and BOD, indicate the organic load and oxygen requirement of POME, respectively, and if not monitored, may have adverse impacts on ecosystems and water bodies.

These outcomes make it evident that effective management strategies and policies are essential for reducing the environmental concerns related to POME. Further study is necessary to investigate novel treatment technologies and regulatory frameworks specifically designed to effectively handle this urgent environmental concern, even if the current research highlights the necessity of action and presents concerning data. Furthermore, for sustainable POME management methods to be implemented successfully, government authorities, the palm oil industry, and environmental organizations must collaborate and interact with beneficiaries.

2.1 Ferric Chloride As Catalyst ($FeCl_3$)

Iron(III) chloride, $FeCl_3$ is a good Lewis acid that has been widely and successfully employed as a catalyst in a variety of organic chemical processes. The $FeCl_3$-catalyzed electrophilic aromatic substitution (EAS) reactions are especially effective, and all $FeCl_3$-catalyzed procedures resulted in much higher percent yields [15] . In acidic ferric chloride solutions, the ion Fe^{3+} acts as an oxidant, whereas ion Cl^- acts as a complexant. The fact that adding $FeCl_3$ to the solutions accelerated metallic copper dissolution might be explained by the fact that $FeCl_3$ acts as both an oxidant and a complexant during metallic copper dissolution. While other variables remained constant, the effect of $FeCl_3$ concentration on copper dissolution was investigated at different $FeCl_3$ concentration levels ranging from 0 to 0.1 mol/L.

The presence of $FeCl_3$ in solutions speeds up the dissolution of copper by a large amount, and the fraction of copper that is dissolved increases as the concentration of $FeCl_3$ goes up. For example, the fraction of copper that is dissolved in 20 minutes is only 18.6% when $FeCl_3$ is not present, but it is 100% when $FeCl_3$ is present at a concentration of 0.02 mol/L. The other circumstances were the same in both cases [16]. Furthermore, ferric chloride has superior performance qualities and a much lower cost than other water treatment coagulants such as polyaluminum chloride, ferrous sulphate, and alum, which supports the $FeCl_3$ consumption and marketing requirements [17]. When ferrous chloride, $FeCl_2$ reacts with chlorine gas to form ferric chloride, $FeCl_3$ a portion of which is subsequently recycled to attack iron, iron dissolves more quickly into ferrous chloride, according to equation (1) and (2) [18].

$$Fe + 2FeCl_3 3FeCl_2 \tag{1}$$

The ferrous chloride solution is filtered and oxidized to ferric chloride with chlorine gas as follows:

$$3FeCl_2 + 1.5Cl_2 3FeCl_3 \tag{2}$$

The use of ferrous and ferric compounds as catalysts was investigated in the early 1980s. In 1982, according to a report by Habu and Yoshihro, a study of $FeCl_3$ with copper was initiated. On Habu and Yoshiro's study, an investigation was undertaken based on mass transfer theory and other elements such as the ferric ion's diffusion coefficient [19] . Other hypotheses corroborated this; Cakir et al. (2005) explored the high chemical etching rate from the standpoint of the ferric chloride mass transfer theory [20] .

Copper percentage decreases with increasing pH, as evidenced by $FeCl_3$ concentrations of roughly 0.1 mol/L with 1 mol/L NaCl at 25 ^oC. Because there are less active oxidants present, such as Fe^{3+}, this situation occurs. In the future, the reaction could be induced by $FeCl_3$ hydrolysis. To facilitate metallic copper dissolution, the oxidant and complexant $FeCl_3$ will be introduced. The Fe^{3+}/Fe^{2+} electrode potential in electrolysis is 0.77V, which is substantially higher than the Cu^{2+}/Cu electrode potentials of 0.34V or 0.52V [16].

Fe^{2+} and Fe^{3+} act as a simple catalyst in a redox pair. In addition, both serve as an oxidizing agent, a charge carrier, and a discharge agent. To illustrate the electro-catalytic properties of the catalyst, cyclic voltammetry was used to measure potential values less than 0.7 V. The Fe^{2+}/Fe^{3+} redox pair is somehow 0.77 V. After several hours, the redox reaction was observed, showing that the ferric ion solution gradually changed from yellow to red-brown. Fe^{3+} can be reduced to Fe^{2+} in biomass when the Fe^{2+} ion reacts with the biomass. By electrolyzing biomass to produce hydrogen, both Fe^{2+} and Fe^{3+} are employed as oxidation and charge transfer agents [21]. Other than that, underdeveloped countries frequently use $FeCl_3$ as a coagulant in drinking water. Market expansion is anticipated as a result of higher performance at comparatively low cost. When compared to polyaluminium chloride, ferrous sulphate, and alum, the role of $FeCl_3$ as a coagulant was found to be superior. [18] [22].

According to the research team Kim et al. 2019, referenced from the experimental research observation regarding the redox reaction for both ions Fe^{2+}/Fe^{3+} occurs at the opposing electrodes. The purpose of this study is to investigate the redox reaction at two distinct electrode temperatures, room temperature and increased temperature. According to the results, the ion Fe^{2+} is converted into the ion Fe^{3+} at the cold (room temperature) electrode, and the hot (elevated temperature) electrode reduces Fe^{3+} to Fe^{2+} [23].

3. Materials and Methods

This experimental study aims to comprehensively analyses the degradation of Palm Oil Mill Effluent (POME) utilizing ferric chloride ($FeCl_3$) as a catalyst. The scope of this research is specifically focused on evaluating the efficacy of $FeCl_3$ in degrading organic compounds present in POME. However, certain limitations are acknowledged, primarily pertaining to the experimental procedures and conditions. The preparatory phase of the experiment involves the meticulous pre-treatment of POME and the preparation of the ferric chloride catalyst. A 0.005 M solution of $FeCl_3$, adjusted to an acidic pH range of approximately 4.9-5.2, is meticulously prepared to ensure consistency throughout the experimental duration. The optimal molarity of $FeCl_3$, determined as 40 mg/L (w/v) based on prior research [24], serves as a reference point for this study. Considering the insights gleaned from previous preliminary investigations and guided by these established parameters, a decision is made to employ a lower molarity of $FeCl_3$, specifically set at 0.005 M, for the current experiment.

During the experimental procedure, approximately 10% (v/v) of the prepared $FeCl_3$ catalyst is added to the untreated POME, derived from the total volume of the effluent. Subsequently, the effects of ferric chloride on POME degradation are meticulously analyzed using a UV-Vis Spectrometer, specifically the Lambda (λ) 35 model. It is noteworthy that the scope of this study is confined to investigating the application of FeCl3 under ambient conditions, with a temperature maintained at approximately ±25°C.The spectroscopic analysis is conducted within the wavelength range of 200-600 nm using the Lambda (λ) Max feature of the UV-Vis spectrometer. This range enables the comprehensive assessment of the spectral characteristics of the treated POME samples, providing valuable insights into the degradation process facilitated by $FeCl_3$.Overall, this study aims to contribute to the understanding of POME treatment mechanisms, specifically highlighting the potential of ferric chloride as a catalyst for organic compound degradation, while acknowledging the specific experimental parameters and limitations inherent to the research design.

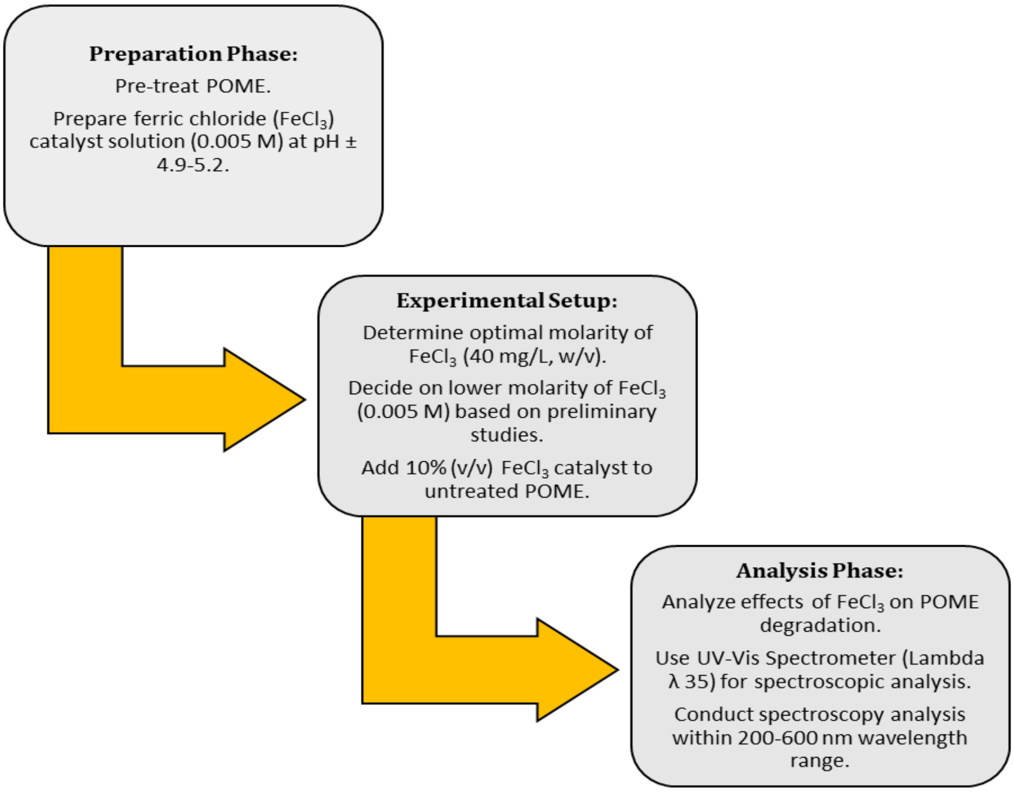


Fig. 2 *Flow chart of the experimental process*

3.1 Pre-treatment of POME

After conducting in-situ sampling of Palm Oil Mill Effluent (POME), the raw effluent was carefully collected and transferred into Schott bottles, known for their durability and resistance to chemical reactions. These bottles were then placed inside a thermal insulated box to maintain the temperature stability of the samples during transportation to the laboratory for further analysis. POME is categorized as an organic biomass, characterized by its composition of various organic compounds and materials. However, the presence of existing microbes in POME can lead to microbial oxidation, which can compromise the freshness and integrity of the effluent. To mitigate this issue, it is essential to subject all POME samples to autoclaving, a sterilization process that eliminates microbial activity by exposing the samples to high-pressure steam. Following autoclaving, the sterilized POME samples were stored in a chiller at a controlled temperature of approximately ≤ 4°C. This refrigeration step is crucial for preserving the stability of the samples and preventing any potential microbial growth or degradation of organic compounds before the commencement of further analysis in the laboratory. By adhering to these rigorous sample handling procedures, the integrity of the POME samples is maintained, ensuring accurate and reliable physiochemical analysis results.

3.2 Catalyst Preparation

The process begins by weighing approximately ±0.33793 g of ferric chloride ($FeCl_3$) and dissolving it in 250 ml of distilled water. To this solution, 5 ml of hydrochloric acid (HCl) with a concentration of 0.1M is added to adjust the pH value. The mixture is then heated to approximately ±60-70°C to facilitate the dissolution of the solid ferric chloride. Once the solution is prepared, it is transferred to a chiller and stored at a temperature of ± ≤4°C until it reaches room temperature (RT) before further analysis. It is noteworthy that the solution of $FeCl_3$ exhibits a yellow-greenish color. pH value of the ferric chloride solution is carefully monitored and maintained within the range of 3.5 to 4.5 to ensure its stability and freshness. Special attention is paid to storing the $FeCl_3$ solution in an amber glass bottle at ≤ 4°C to prevent further oxidation of Fe^{2+} ions to Fe^{3+} ions, which could occur due to exposure to free oxygen and stray light. This oxidation process is indicated by a change in color from yellow-greenish (indicative of Fe^{2+} ions) to a deep dark yellowish hue (indicative of Fe^{3+} ions). Additionally, equation (3) represents the reaction that occurs during the preparation of the $FeCl_3$ catalyst. This meticulous process ensures the stability and effectiveness of the $FeCl_3$ solution, critical for its role as a catalyst in subsequent analyses.

$$Fe^{3+} + HCl\ (0.1M) \rightarrow Fe^{2+} \tag{3}$$

The redox analysis was conducted utilizing a Pontentiostat-Galvalostat instrument from Metrohm, a renowned manufacturer of analytical instrumentation. Prior to running the cyclic voltammetry analysis, the potential window for the redox reaction was carefully set within the range of -0.1 to 1.5 V, with a scan rate of 0.05 v/s. The results of the redox analysis were interpreted based on the response of the current (μA) observed on the y-axis, which corresponded to the redox reaction of the 0.005 M ferric chloride solution. The voltammetry data were graphically represented, with the plot typically exhibiting two distinct parts: the upper part corresponding to the anodic reaction and the lower part corresponding to the cathodic reaction. In the cyclic voltammogram, the current values (μA) observed in the lower part consistently displayed negative notation, indicating the occurrence of cathodic reactions. This graphical representation provided valuable insights into the behaviour of the $FeCl_3$ catalyst solution during redox processes. Fig. 3 provides a visual depiction of the preparation process of the $FeCl_3$ catalyst, offering a comprehensive overview of the experimental setup and methodology employed in the redox analysis. This detailed approach ensured accurate characterization and understanding of the redox behaviour of the $FeCl_3$ catalyst solution, essential for its application in subsequent analytical procedures.

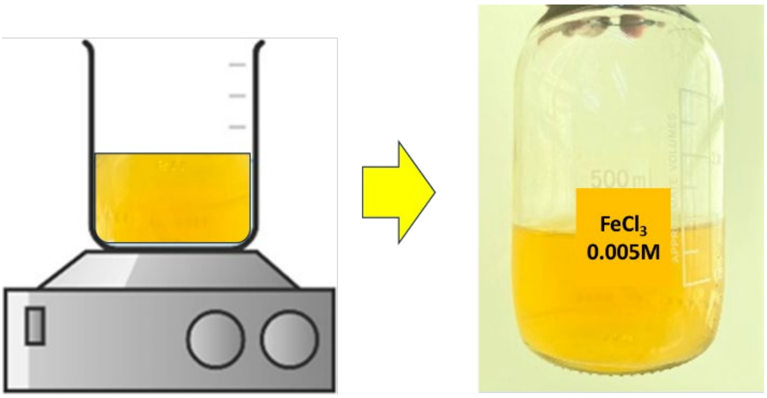


Fig. 3 *$FeCl_3$ catalyst preparation*

3.3 UV-Vis Spectrometer

The spectroscopic analysis was executed utilizing a UV-Vis Spectrometer of the Lambda (λ) 35 model, operating at room temperature (RT), with each analysis consisting of three cycles of scans. The resultant data were presented in the form of absorbance spectra (A%) plotted against wavelength. Fig. 4 provides a visual representation of the comprehensive setup of the UV-Vis instrumentation, wherein one cuvette accommodated the blank sample, comprising distilled water, while the other contained the POME samples under scrutiny. Integral to the instrumentation was the Tungsten lamp, serving as the radiation source during analysis. The blank sample, composed of distilled water, served as a critical benchmark for comparison with the POME samples. The selection of the appropriate spectrum for analysis was paramount, with wavelength or spectrum values measured in nanometers. Prior to analysis, the determination of spectrum values was imperative to ensure the reliability and accuracy of the results. This meticulous methodology facilitated the precise evaluation of POME absorbance characteristics, thereby enabling informed conclusions regarding its composition and properties.

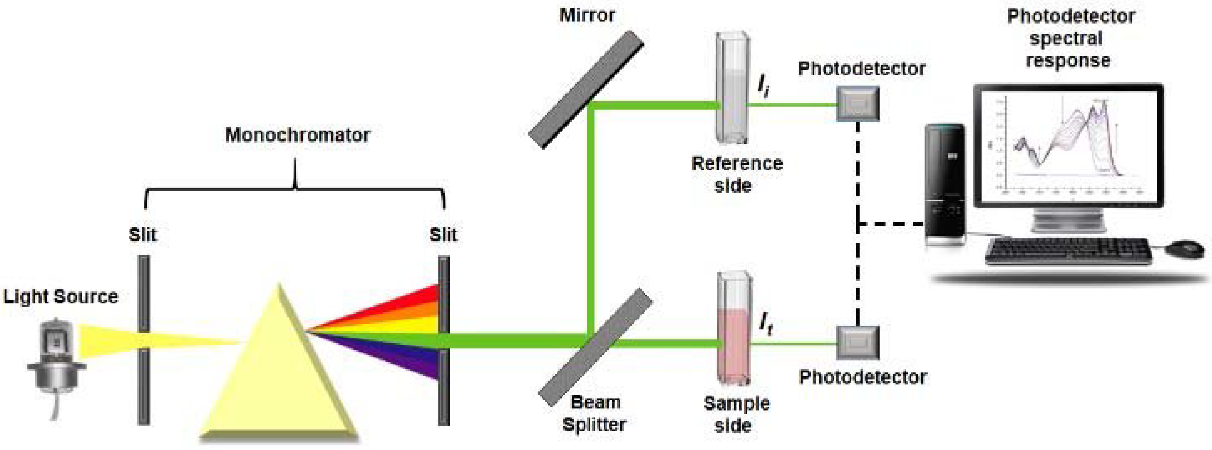


Fig. 4 *Schematic diagram of UV-Vis double beam [12]*

4. Results and Discussion

The physical properties of Palm Oil Mill Effluent (POME) primarily comprise water along with various organic materials that accumulate at the conclusion of the oil palm processing. Additionally, it is crucial to recognize that POME is classified as hazardous material due to its potential adverse effects on living organisms. Consequently, direct discharge into the main stream or reuse without proper treatment poses significant risks. The primary objectives of this study revolve around addressing these concerns by focusing on the treatment and degradation of organic materials present in POME. By doing so, these organic components can be rendered safe for subsequent use or other applications in the future. To achieve this, various technologies for wastewater treatment can be considered and implemented. In this experimental investigation, particular emphasis is placed on the utilization of a metal complex catalyst such as ferric chloride ($FeCl_3$). The selection of $FeCl_3$ is significant due to its potential effectiveness in catalyzing the degradation of organic compounds presents in POME.

By employing $FeCl_3$ as a catalyst, it is anticipated that the efficiency of the treatment process can be enhanced, leading to the successful removal or transformation of hazardous organic materials in POME. The integration of metal complex catalysts like $FeCl_3$ into the treatment process represents a promising approach towards mitigating the environmental risks associated with POME and facilitating its safe utilization for various applications. Through rigorous experimental analysis, this study aims to contribute valuable insights into the effectiveness of $FeCl_3$ as a catalyst for POME treatment, thereby advancing the development of sustainable wastewater management practices in the palm oil industry. The primary objective of this study is to investigate the chemical oxidation process facilitated by the catalyst $FeCl_3$ with the compounds present in Palm Oil Mill Effluent (POME). This oxidation process relies on the reversible reaction between Fe^{2+} and Fe^{3+} ions, which assists in degrading the raw POME into more manageable forms. The qualitative assessment of the degraded POME is conducted using UV-Vis spectroscopy, while the redox behaviour of the $FeCl_3$ catalyst is examined through cyclic voltammetry (CV).

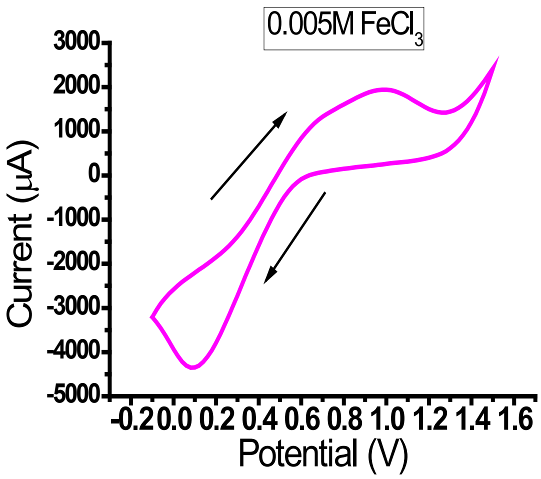
CV is a powerful electrochemical technique used to study redox reactions, providing valuable insights into the behaviour of the catalyst $FeCl_3$ during oxidation processes. The voltammetry curve obtained from this analysis allows for the interpretation of the redox behaviour based on the chosen potential window and scan rate parameters. In Fig. 5, the voltammetry curves of $FeCl_3$, raw POME, and POME treated with $FeCl_3$ are described. Remarkably, each sample exhibits distinct responses in terms of the observed current values on the y-axis. Positive curves indicate oxidation reactions occurring at the anodic part of the curve, while negative curves represent reduction reactions at the cathodic part. These observations highlight the differential responses of each sample to the redox processes initiated by the $FeCl_3$ catalyst. Through the interpretation of the voltammetry curves, the efficacy of $FeCl_3$ in promoting oxidation reactions and facilitating the degradation of POME compounds can be assessed. This comprehensive analysis sheds light on the mechanistic aspects of the oxidation process and provides valuable insights into the potential applications of $FeCl_3$ in POME treatment and remediation efforts.

In cyclic voltammetry (CV), both the anodic and cathodic reactions occur within a single completed cycle, constituting what are known as redox reactions. The speed at which each cycle occurs is determined by the scan rate (V/s), with higher scan rates resulting in wider voltammograms. The behaviour of the species presents in the electrolyte, particularly supporting electrolytes, significantly influences the response current (μA) observed in both the anodic and cathodic curves. Supporting electrolytes enhance electron transfer and diffusion processes, thereby contributing to increased current responses. Fig. 5 illustrates individual voltammograms for the catalyst $FeCl_3$, POME, and the combination of POME with $FeCl_3$. Notably, the voltammogram for the catalyst $FeCl_3$ (Fig. 5a) exhibits distinct peak values for the anodic and cathodic currents, measuring 1.943x103 μA and -4.351x103 μA, respectively. These values suggest the presence of Fe^{3+} ions in the anodic curve and Fe2+ ions in the cathodic curve. In CV analysis, the different types of species present in the sample can be easily distinguished through the plotted curves in the anodic and cathodic parts. These curves provide valuable insights into the specific oxidation or reduction reactions occurring within the sample. By interpreting the voltammograms, the nature of the redox processes involved, thereby gaining a deeper understanding of the chemical interactions within the system.

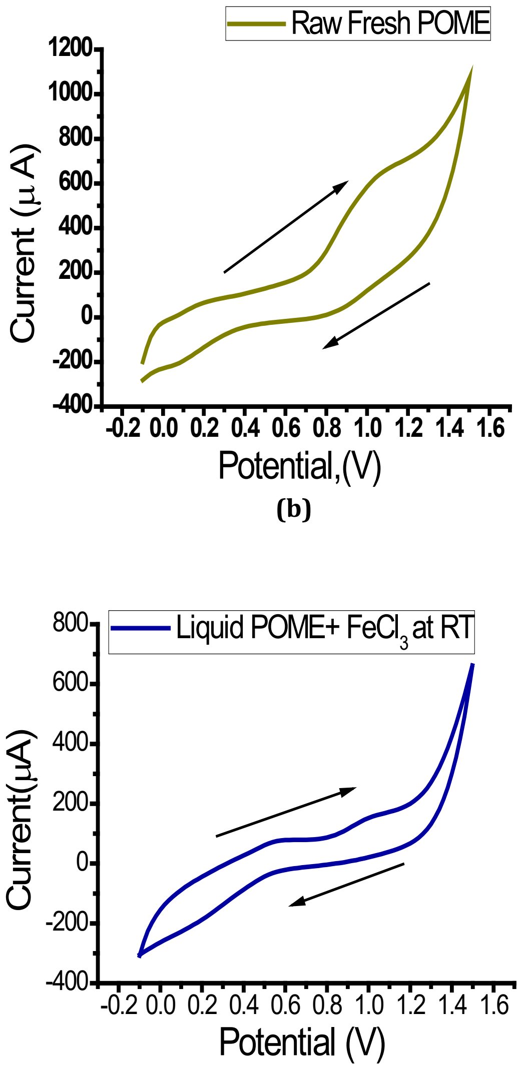
Each voltammogram represents the response current (μA) generated during redox reactions, and the specific values observed depend on the presence of species participating in these reactions. In Fig. 5(b), the voltammogram corresponding to the fresh or raw POME exhibits distinctive characteristics that suggest the possibility of an irreversible reaction. This observation arises from the absence or limited presence of electrolyte species in the raw POME sample, which may hinder the initiation of redox reactions within the cell. As a result, the voltammogram may lack well-defined redox reaction peaks, leading to a broader or less pronounced curve. This phenomenon, commonly referred to as a "duck-curve" or broad peak, poses challenges in analysis, as the peaks at both the anodic and cathodic regions may appear ambiguous or less discernible. The ambiguous nature of the peaks in the raw POME voltammogram complicates the interpretation of the redox behaviour of the sample. Without clear peak distinctions, it becomes challenging to determine the specific oxidation or reduction reactions occurring within the system. Consequently, additional analytical techniques or modifications to the experimental setup may be necessary to elucidate the redox processes involved in the raw POME sample accurately.

Palm Oil Mill Effluent (POME) itself lacks the electrolyte species necessary to support redox reactions, making it insufficient for inducing oxidation and reduction processes within a cell. Consequently, the addition of a catalyst, such as $FeCl_3$, is essential to initiate these reactions. Upon the introduction of $FeCl_3$ into the POME sample, an increase in current (μA) is observed, as evidenced by the voltammogram depicted in Fig. 5(c). The addition of $FeCl_3$ alters the electrochemical behaviour of the system, leading to changes in the specific current values observed in both the raw POME (Fig. 5b) and $FeCl_3$-treated POME (Fig. 5c) voltammograms. The increased current values observed in Fig. 5c compared to Fig. 5b indicate that $FeCl_3$ is capable of facilitating oxidation reactions within the POME sample, particularly at the anodic parts of the voltammogram.

To further elucidate the degradation and oxidation processes occurring in POME, UV-vis spectrometry can be employed to characterize the absorbance of $FeCl_3$, POME, and the mixture of POME with $FeCl_3$ within the UV-vis range. This spectroscopic analysis provides valuable insights into the chemical transformations and interactions occurring between $FeCl_3$ and POME constituents, complementing the information obtained from cyclic voltammetry. The addition of $FeCl_3$ serves to catalyse oxidation reactions within the POME sample, as evidenced by the increase in current observed in the voltammogram. UV-vis spectrometry further enhances our understanding of the degradation and oxidation processes in POME, offering valuable information for the development of effective treatment strategies.



(a)



(b)

(c)

Fig. 5 *Cyclic voltammetry,CV of a) FeCl3; b) Raw+FeCl3; c)POME +FeCl3 with potential window range at -0.1 to 1.5 V*

UV-vis spectroscopy operates within a wavelength range of 200-600 nm, making it suitable for analysing the absorbance of various compounds. Before conducting a scan, the targeted absorbance, known as Lambda (λ) Max, is determined to optimize the analysis conditions. UV-vis spectroscopic analysis is particularly effective for samples containing chromophore species. Chromophores are chemical structures within organic compounds that contain conjugated double bonds (π bonds), which serve as indicators in UV-vis spectrophotometry by causing changes in absorbance values. Fig. 6 displays UV-vis spectra of various samples, including the catalyst $FeCl_3$, Ferrocyanide, and Ferroin (1,10-Phenanthrolineferrous). Each sample, including the 0.005M $FeCl_3$ catalyst, was freshly prepared on the same day as the analysis. According to the principles of spectroscopy, each species reacts differently to UV energy. This discrepancy in response is based on the species' emittance energy, resulting in varying absorbance values in the UV region. The species exhibiting the highest absorbance will generate the highest peak at a specific wavelength (nm). By analysing the UV-vis spectra, researchers can gain valuable insights into the composition and properties of the samples. The distinctive absorbance peaks at specific wavelengths provide information about the presence and concentration of various compounds, enabling the characterization and identification of target molecules. This detailed analysis enhances our understanding of the chemical behaviour and interactions occurring within the samples, facilitating their comprehensive characterization and further investigation.

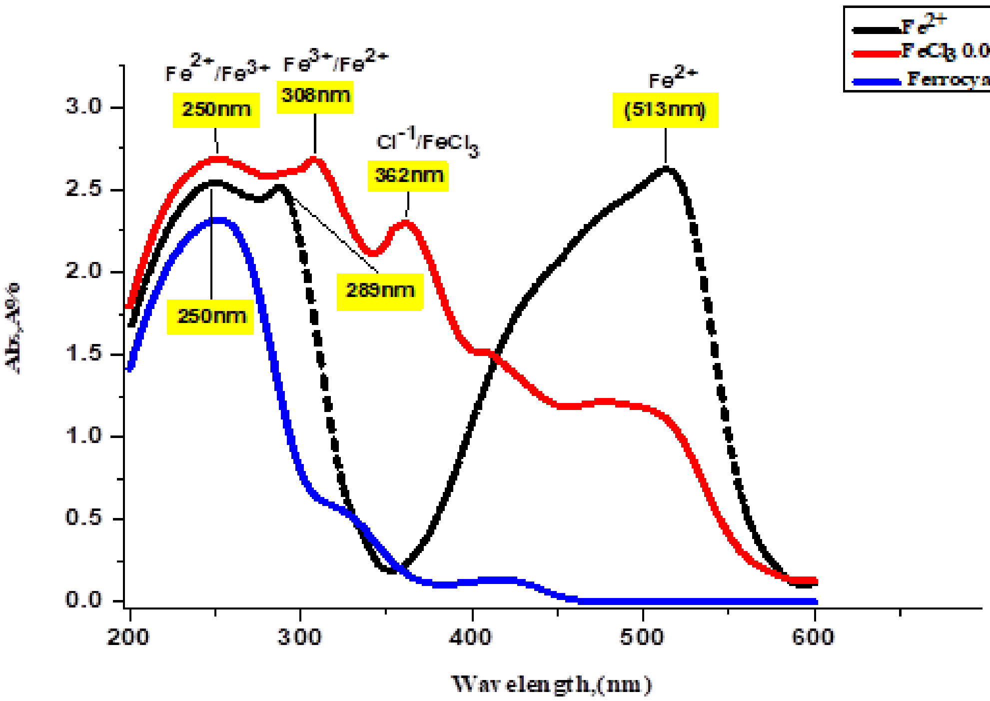


Fig. 6 *Lamda Max of ions Fe^{3+}, $Cl^{-1}/FeCl_3$ and Fe^{2+} wavelength at 250,308, 362 and 513 nm*

Fig. 6 illustrates the UV-vis spectra of $FeCl_3$ catalyst, showcasing three prominent peaks at absorbance wavelengths of 250, 308, 362, and 513 nm respectively. The spectrum reveals distinctive features, particularly the peak at 362 nm, which exhibits a striking resemblance by Rigas and Friends. Their research identified an absorbance peak at 360 nm, indicative of Fe^{3+} ions [25]. Further examination of the $FeCl_3$ spectrum reveals a peak at 308 nm, suggesting the presence of a significant concentration of Fe^{3+} ions, potentially influenced by a mixture of Fe^{3+} and Fe^{2+} ions. Similarly, the peak observed at 250 nm may signify the prevalence of Fe^{2+} ions, influenced by a combination of Fe^{2+} and Fe^{3+} ions. This observation suggests the presence of an oxidizing agent, with a concurrent occurrence of simple redox ion pairs between Fe^{2+} and Fe^{3+} ions during the reaction. Additionally, the UV-vis spectrum of Fe^{2+} derived from a Ferrous Cyanide solution exhibits a broad peak at 513 nm, further corroborating the presence of Fe^{2+} ions in the sample. These findings provide valuable insights into the composition and behaviour of $FeCl_3$, shedding light on the redox processes involving Fe^{2+} and Fe^{3+} ions. By analysing the UV-vis spectra, researchers can gain a deeper understanding of the chemical interactions and transformations occurring within the $FeCl_3$ catalyst, facilitating its characterization and application in various processes [26].

The UV-Vis spectrum depicted in Fig. 6 reveals discernible changes in the peaks corresponding to specific wavelengths. This observation aligns with the anticipated behaviour of $FeCl_3$, which is expected to participate in hydrolysis and oxidation processes by reducing the sugar molecules present in organic biomass. Regardless of the degradation temperatures applied, it is anticipated that the degradation of biomass would occur. Notably, this experimental study was conducted under room temperature conditions (approximately ±25 °C), with no elevation or increment in the digestion temperature. This choice was made to assess the catalytic role of $FeCl_3$ in degrading and oxidizing carbohydrates effectively, even at ambient temperatures. Through redox reactions, $FeCl_3$ is hypothesized to facilitate the oxidation of the majority of organic polymer structures within biomass, particularly those containing double bonds. This oxidation process leads to the transformation of organic polymers into smaller fragments, predominantly hydroxyl groups, eventually yielding carboxylic acids during cellulose hydrolysis. It is important to note that POME, being a type of biomass, contains lignin, characterized by a helical polymer structure comprising three phenylpropanoid monomer units. These monomers are interconnected through ether (-O-) and carbon-carbon (C-C) linkages, contributing to the complex composition and structure of lignin. The insights gained from this UV-Vis analysis provide valuable information regarding the potential mechanisms underlying the catalytic activity of $FeCl_3$ in degrading and oxidizing biomass components, particularly carbohydrates and lignin, at ambient temperatures. This understanding is critical for optimizing the utilization of $FeCl_3$ as a catalyst in various applications, including biomass conversion processes and environmental remediation efforts [27].

The application of different digestion temperatures plays a significant role in influencing the degradation rate of organic biomass, particularly at temperatures below or equal to 180°C. Studies have demonstrated that variations in digestion temperature can lead to observable increases in the degradation rate, with certain temperatures yielding more pronounced effects. For instance, research focusing on the by-products of sugar obtained from switchgrass has identified a reduction in the number of aromatic rings in the analysis sample when subjected to specific temperature conditions [28]. This phenomenon is attributed to the Fenton process, a well-known hydrolysis reaction involving the utilization of iron ions, specifically Fe^{3+} and Fe^{2+}. In wastewater treatment applications, the Fenton process is commonly employed due to its efficacy in reducing chemical oxygen demand (COD) by degrading and coagulating organic matter. The process relies on the interconversion of Fe^{3+} and Fe^{2+} ions, facilitating redox reactions that lead to the efficient reduction of organic pollutants. Studies have highlighted the significance of the Fenton process, particularly in achieving high-efficiency reduction of organic matter. This efficiency has been attributed to the favourable redox potential (Eo = 2.80 V) associated with the process, which enables effective degradation and oxidation of organic compounds. Collectively, these findings underscore the ability of $FeCl_3$ to degrade organic biomass in wastewater through chemical hydrolysis and oxidation reactions. By leveraging the Fenton process and harnessing the catalytic properties of $FeCl_3$, wastewater treatment processes can achieve significant reductions in organic pollutant levels, contributing to improved water quality and environmental sustainability.

The research conducted by Hou Y and colleagues has shed light on the comparative effectiveness of various metal salts, including $AlCl_3$, $CaCl_3$, $CrCl_3$, and $MgCl_3$, in degrading biomass samples. Their findings indicate that while these metal salts are capable of facilitating electron transfer reactions, they do not possess the capability to effectively degrade biomass. In contrast, $FeCl_3$ has emerged as a standout performer, demonstrating superior efficacy in biomass degradation, with formic acid production reaching 48.3%. The role of catalysts such as $FeCl_3$ in the degradation and oxidation of cellulose warrants further investigation, particularly due to the extended time required for the degradation process compared to lignin and other biomass components [29]. Fig. 7 provides a comparative analysis of the spectra of fresh lignin, glucose, POME, $FeCl_3$, and ferrous cyanide (Fe^{2+}), serving as a reference before the degradation of all samples by $FeCl_3$ catalyst.

The UV-Vis spectrum presented in Fig. 7 reveals λ Max values for lignin at wavelengths of 249, 308, 359, and 513 nm. Notably, significant peaks are observed in the wavelength range of 249 to 308 nm, attributed to $FeCl_3$, particularly under a mixture of Fe^{2+} and Fe^{3+} ions. This observation suggests the potential involvement of $FeCl_3$ in the degradation and oxidation processes of lignin and other biomass components. Moreover, the spectrum indicates a notable increase in λ Max absorption within the wavelength range of 250 to 290 nm, corresponding to the degradation of cellulose. This observation underscores the importance of $FeCl_3$ as a catalyst in promoting the degradation and oxidation of cellulose, thereby facilitating the breakdown of biomass components into smaller, more manageable fragments. Comprehensive analysis presented in Fig. 7 highlights the potential of $FeCl_3$ as a catalyst for biomass degradation and oxidation, underscoring its significance in advancing our understanding of biomass conversion processes and promoting sustainable utilization of biomass resources.

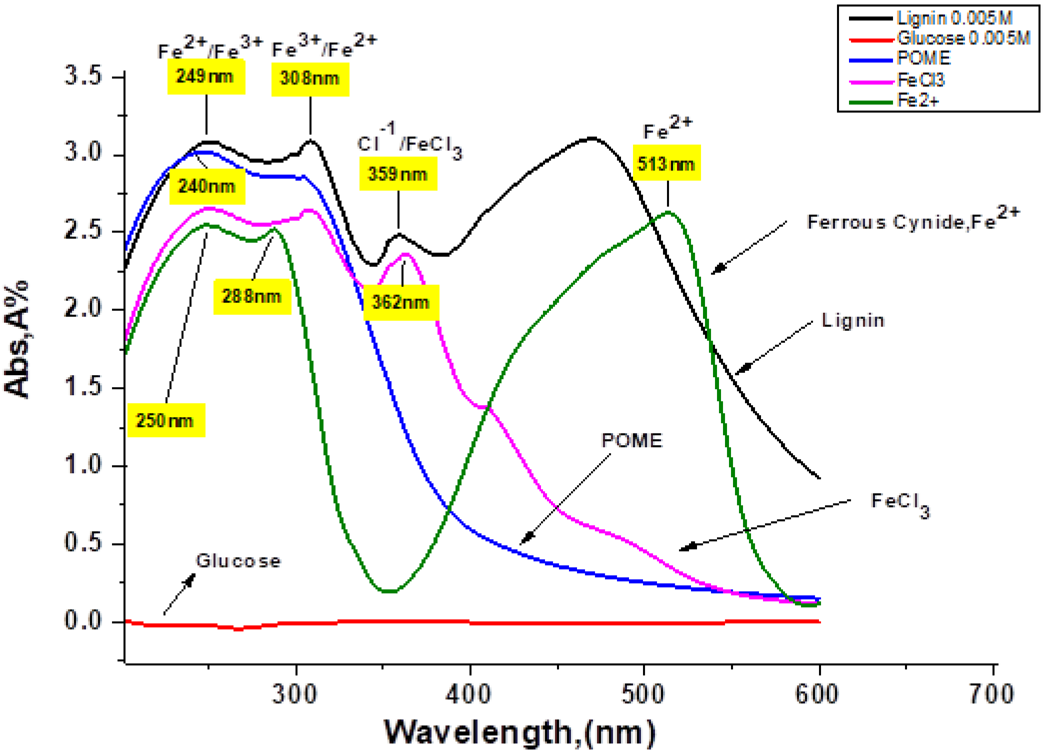


Fig. 7 *Fresh POME, lignin, glucose, $FeCl_3$ and ferrous cyanide (ion Fe^{2+})*

The ions Fe^{2+} and Fe^{3+} formed $Fe(H2O2)$ complexes due to ions of H_2O attached with circulated by octahedron. In aqueous solution, $FeCl_3$ will be dissociated into the ions Fe^{2+} and Fe^{3+} which cause by hydrating reaction into single crystals. Thus, the UV-Vis spectra will detect the present of the ions Fe^{2+}/Fe^{3+} free in the aqueous solution or in the sample. Through the crystal field and electron transfer transition of ions species Fe^{2+}/Fe^{3+}, the interactions make it can be evaluated qualitatively by UV-Vis spectroscopy and CV analysis.

Fig. 8 illustrated the organic sample known as lignin to be analysis and compare between fresh and degrade by 0.005M of $FeCl_3$ solution. The reaction condition is in room temperature and maintain in acidic condition pH between ±4.5-5.5. From the UV spectrum in Fig. 8, fresh lignin 0.005M shows the higher absorbance comparing with treated lignin which mixture of lignin with catalyst $FeCl_3$. The increasing the absorbance value is due to the hydrolysis chemical reactions and induced the formation of double bounds in biomass. Contradict observation was investigated on treated lignin with $FeCl_3$ which gives a significant different on absorbance value. This indicates that, the λ Max value at 260 nm shows fresh lignin experienced shifting in the absorption band. This phenomenon clearly can be explained that the absorbance increased with the number of chromophore species increased. Due to this reasons, highest absorbance value in UV range was observed for ions Fe^{2+}/Fe^{3+}. Rather than that, the hypochromic shifting of absorbance band (moved to left) for fresh lignin wavelength at λ Max 308 nm changed to the λ Max at 287 nm for lignin + $FeCl_3$.

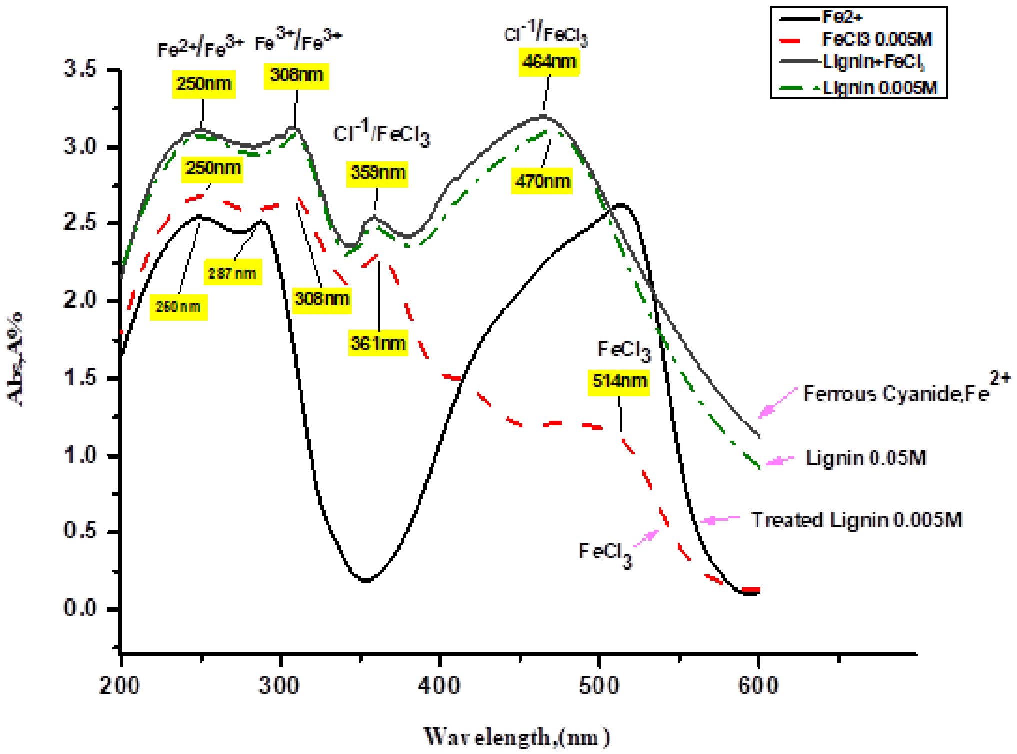


Fig. 8 *UV-Vis spectrum of lignin towards $FeCl_3$ oxidation*

The spectrum produced between fresh lignin and degraded lignin was compared with catalyst $FeCl_3$. Whereases, ions Fe^{2+} complex spectrum was observed from 0.1M of ferrocyanide solution. To confirm the present of ions Fe^{2+}/Fe^{3+}, the indicator known as 1,10-phenanthroline ($[Fe(o\text{-}phen)_3]SO_4$) was used. This indicator commonly functions based on the redox reaction in the sample solution. From the reactions, the color changes were observed from dark red to dark blue. Indicates that, the changes of the solution color from dark red to dark blue represent oxidation reaction from ion Fe^{2+} to Fe^{3+}. So, the majority of ions present in the solution was converted to more ion Fe^{3+} compared to ion Fe^{2+}. Regardless to the concentration, the ability of $FeCl_3$ is to perform hydrolysis and oxidation in biomass sample had been proved based on the study by Xu and friends. Other than hydrolysis and oxidation, ion Fe^{2+}/Fe^{3+} also took part in electron shuttle. Consideration the $FeCl_3$ catalyst is a Lewis acid which acts as co-catalyst for oxidation biomass. Meaning that, $FeCl_3$ has significant potential to replace 80% from the portion amount of polyoxometalates (POM) in the oxidation reactions of biomass in liquid catalyst fuel cell (LCFC)[30] . In this study not going to cover the study of replacement oxidizer POM in biomass oxidation but only to observe the potential of $FeCl_3$ act as oxidizing agent. Lignin is complex cross-linked derived produced from the degradation process of lignocellulose which required specific method for extraction. Event though, lignin considered as part of biomass and it is a waste product. Lignin will produce phenolic compounds after depolymerization via hydrolysis chemical reaction[27].

Fig. 9 represents the spectrum of fresh POME with treated POME. The effluent from palm oil-based cooking oil factory usually contains a lot of organic matters which suspended in the liquid. Fresh POME properties contain 4000 mg/L and grease, 40 000 mg/L of Total Solids (TS) 750 mg/L of Total Nitrogen (TN). Due to these reasons, POME compulsory to be well treated before its available discharge to the river or drainage water system [31]. The conventional method to treat POME is not capable to cope with high volume of POME every day. The pond cooling system is the most common practice seems not very effectively to solve this phenomenon. Other than that, as looking for the better and cheaper ways are by applying the non-Nobel metal such as $FeCl_3$ as oxidation agent. The optimize of coagulant $FeCl_3$ ranging between 20 to 50 mg/L for 1 minute at 160 r/min as a coagulant in waste water treatment [32]. The spectrum of fresh POME shows the significant difference in term of the λ Max values compared to treated POME (POME+$FeCl_3$). When catalyst 0.005M of $FeCl_3$ was added into fresh POME, the changes in term of absorbance, A value was observed.

As shown in Fig. 9, according to λ Max value at 247nm which indicates the present of ion Fe^{2+} in the sample of fresh POME. Somehow while comparing to treated POME, the Lamda, λ Max at some degree it moves to 250nm. This indicates that, the phenomenon of hypochromic had been observed and it happens for threes samples on treated POME, $FeCl^3$ and Ferrocyanide. These happen when the sample have same Lamda λ Max value but shifting down and increasing the wavelength to right side due to decreasing in absorption intensity. Theoretically, the hypochromic happen and detected by UV range indicates the sample experienced the reducing the concentration of chromophore species. The fresh POME to be revealed have some existing amounts of ions Fe^{2+}/Fe^{3+} in sample. Due to this circumstances, λ Max at 247 nm indicates as Fe^{2+} and Lamda, λ Max at 308nm as the present of ion Fe^{3+} were observed at highest absorption value is due to the corrodes from the steel container of factory [33] [34][35].

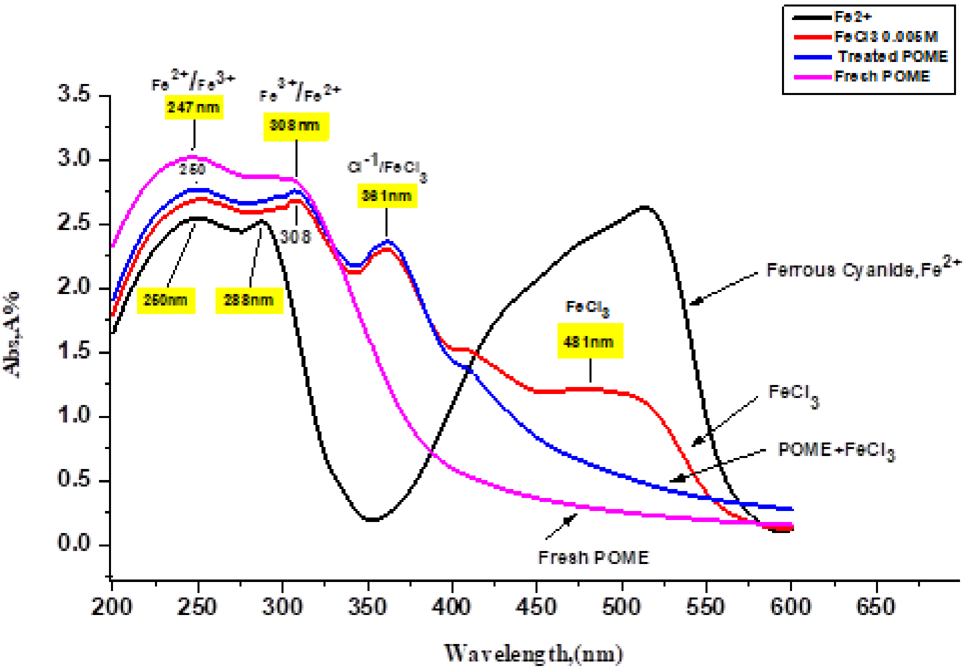


Fig. 9 *UV-Vis spectrum of POME with present of catalyst FeCl³*

The interactions of catalyst $FeCl_3$ can be briefly discussed because based on the spectra of UV-Vis, indicates that, when addition of $FeCl_3$, the absorption value of treated POME was changed to the lower absorption compared to fresh POME which displayed highest absorption among others sample. Highest absorbance demonstrates less degradation occurred on fresh POME. Meaning that, $FeCl_3$ enhancing the degradation process on POME compared to the fresh POME. So that, the reducing of absorption in UV range indicates the treated POME had been reduced the total concentration of organic compounds may due to the oxidation and hydrolysis by $feCl_3$ catalyst. In the reactions, the process of degradation by $FeCl_3$ takes part for reducing the molecular weight by adding the aromatic as by products. After cellulose, lignin was the second abundant in biomass and always present in waste water. As this concrete reason, in POME should be contained abundant lignin which can be used in future potentially as renewable source of aromatic chemicals. In the present of the catalyst $FeCl_3$, not only can be oxidized but also cleaved the ether bonds. Thus, $FeCl_3$ has ability to improve the degradation process by the process of depolymerization via hydrolysis and oxidation reactions of the biomass[36].

5. Conclusion

Ferric Chloride ($FeCl_3$) exhibits remarkable catalytic properties in the degradation of chromophores, which are chemical structures found in polymer biomass, such as in Palm Oil Mill Effluent (POME). Beyond its role as a coagulant, FeCl3 serves as an initiator for hydrolysis reactions, including the synthesis of galvanic acid from glucose. These findings highlight the multifaceted nature of $FeCl_3$, which not only coagulates organic polymers but also actively degrades and hydrolyses organic compounds present in POME. Through UV-Vis analysis spanning the range of 200 to 600 nm, significant insights into the chemical behaviour of POME, lignin, and glucose can be gleaned, particularly with respect to Lambda (λ) max values and Cyclic Voltammetry (CV) analyses. $FeCl_3$, acting as a catalyst, demonstrates its capability to hydrolyse organic compounds suspected to be present in POME, glucose, and lignin. The presence of hydrolysed compounds is corroborated by the results obtained from CV and UV-Vis analyses. In this experimental study, the investigation was limited to the fundamental stages of degradation and hydrolysis of POME. However, it is evident that further research is warranted to delve deeper into the mechanisms and end products resulting from the degradation reactions. Understanding these processes in greater detail is crucial for optimizing the utilization of $FeCl_3$ as a catalyst in biomass conversion processes and environmental remediation efforts. Additionally, elucidating the intricate pathways and products of degradation will contribute to the development of more efficient and sustainable waste treatment strategies.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Mohd Hafiz Md Ali, Mohammad Noor Jalil,* ***data collection:*** *Mohd Hafiz Md Ali;* ***analysis and interpretation of results:*** *Mohd Hafiz Md Ali, Mohammad Noor Jalil, Zainiharyati Mohd Zain, Tay Chia Chay, Hamizah Mohd Zaki;* ***draft manuscript preparation:*** *Mohd Hafiz Md Ali, Mohammad Noor Jalil. All authors reviewed the results and approved the final version of the manuscript.*

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