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Photocatalytic Degradation of Synthetic Sulfur Pollutants in Petroleum Fractions under Different pH and Photocatalyst

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Abstract: Thiophene is one of the sulfur compounds in the petroleum fraction that can be harmful to living things and lead to a critical effect on the ecosystem. Photocatalytic degradation is one of the promising methods in treating wastewater as it can mineralization of pollutants into carbon dioxide and water. Other than that, this method is non-toxic and relatively low cost. The production of hydroxyl radicals playing a vital role in the degradation of organic pollutants. It has been claimed that the usage of zinc oxide (ZnO) nanoparticles could give an excellent degradation process as this photocatalyst have high photosensitivity, low cost and chemically stable. However, the preparation method of ZnO nanoparticles will affect the agglomeration, particle size, shape and morphology of particles and lead to influence the photocatalytic activity in degrading thiophene. Therefore, this study focused on the effectiveness of ZnO nanoparticles in the presence of fibrous nanosilica (KCC-1) and polyethylene glycol (PEG) as the capping agent to degrade synthetic thiophene. ZnO/KCC-1 had been synthesized via the precipitation method and characterized by using Fourier Transform Infrared (FTIR). The chemical bond and nature of the photocatalyst from the FTIR results proved that the synthesis process to produce the ZnO/KCC-1 was succeed. The large surface area of KCC-1 increases the effectiveness of ZnO which is supported by the experimental data. Accordingly, the optimum condition for photocatalytic degradation of thiophene is under pH 7 by using ZnO/KCC-1 as photocatalyst. Hence, it is believed that this research could be implemented to remove the thiophene in petroleum fraction from the actual industrial effluents and this can preserve nature in the future.

Keywords: Thiophene, photocatalytic degradation, zinc oxide, nanoparticles, precipitation

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1. Introduction

The petroleum industry nowadays plays a big role in the development of a country. This industry is getting bigger as this world has become more advanced. However, this industry producing its own wastewater that contained organic pollutants which can harm the living things such as plant, aquatic life, microbes and human. This industry will produce polluted wastewater as it may consist of toxic pollutants. Other than that, petroleum industrial wastewater consists of organic and inorganic matters in various concentration and contain heavy metals, surfactants, grease, oils and distinct salts. Moreover, petroleum wastewater can lead to a critical problem for the environmental due to the existence of a large amount of suspended organic compounds, the toxicity of coloring material and high chemical oxygen demand (COD) [1]. Therefore, the pollutants in the petroleum wastewater needs to be treated before being released into the environment.

Sulfur-containing compounds (SCCs) are the most abundant heteroatom-containing component that presents in petroleum where could lead to environmental problems. There are six classifications of the SCCs based on their functional groups which are hydrogen sulfide (H_2S), elemental sulfur, mercaptans (thiols), sulfides (acyclic and cyclic), polysulfides (disulfides, trisulfides, etc.) and thiophenes [2].

There are many approaches that have been used to treat petroleum wastewater. Coarse screening of petroleum wastewater is the least effective to be because of its complexity [3]. Although the membrane technologies had come out with reverse osmosis, this wastewater produced a huge amount of residual concentrated and membrane fouling where involve high cost of chemical cleaning is needed and lead to reduce the membrane lifetime and its efficiency. Excessive sludge and consumption of time is the problem if petroleum wastewater is treated with an anaerobic biological process [4]. The latest technique to treat the wastewater that consists of sulfur-containing component especially thiophene is hydrodesulfurization (HDS) technology. However, this process consumes high temperature, pressure and a large amount of hydrogen. Thus, it will result in high operation-cost and large octane loss especially for gasoline [5].

Recently, the other method to treat the wastewater by using the advanced oxidation process (AOPs) such as photocatalytic degradation has received a lot of attention. Photocatalytic degradation is a promising method and has been claimed as low cost and non-toxicity method. Moreover, it has been found that this method can be done under an aqueous system to treat the organic pollutant [6]. One of the most vital elements that affect the performance of the degradation process is a type of photocatalyst. Zinc oxide with a large bandgap, low cost and non-toxicity is claimed as the most preferred photocatalyst in the degradation process. However, the synthesizing of ZnO nanoparticles via precipitation method lead agglomeration problem. Therefore, this research tries to fill the gap by addition of polyethylene glycol (PEG) and fibrous nanosilica (KCC-1) in synthesizing ZnO. This research was aimed to synthesis, characterize ZnO/KCC-1 and study the effectiveness of ZnO/KCC-1 photocatalyst in order to degrade thiophene and compared to ZnO-PEG.

The objectives of this research are (1) to synthesize and characterize ZnO/KCC-1 nanoparticles; (2) to investigate the photocatalytic degradation of synthetic sulfur-pollutant in petroleum fractions (thiophene) under various initial pH and different photocatalyst; (3) to elucidate the kinetic study of photocatalytic degradation of sulfur-pollutant in petroleum fractions (thiophene). The scopes of study in this research are (1) ZnO/KCC-1 had been synthesized via precipitation method and characterized using Fourier Transform Infrared Spectroscopy (FTIR) in order to identify the chemical bonding of ZnO/KCC-1; (2) investigation of the photocatalytic degradation of synthetic sulfur-pollutant in petroleum fractions (thiophene) under various initial pH (5, 7, 9) and different types of photocatalyst (ZnO-PEG, ZnO/KCC-1 and KCC-1).

2. Materials and Methods

2.1 Synthesis of ZnO/KCC-1 and ZnO-PEG

ZnO/KCC-1 and ZnO-PEG were synthesized via precipitation method and the chemical substances were purchased from R&M Marketing, Essex, United Kingdom (UK) and used without further purification [9][20].

The preparation of ZnO/KCC-1, 0.2 M solution of oxalic acid dehydrated was mixed slowly with 0.1 M solution of zinc acetate dehydrated under room condition at the temperature of 25 °C. Then, 2 g/L of KCC-1 was added into the mixture after 5 minutes of the reaction. Next, the mixture was stirred for 12 hours to enhance the production of nanoparticles. The precipitate obtained was filtered and consequently dried in an oven of less than 100 °C for 1 hour to remove the excessive water. Then, the precipitate was undergone the calcination process in the furnace (Nabertherm model, Germany) at 550 °C for 3 hours to remove all the unwanted impurities. After the calcination process, the white powder of ZnO/KCC-1 was formed and ready to be characterized and applied as photocatalyst.

While for ZnO-PEG, 0.15 M of oxalic acid dehydrate solution was slowly added into 0.1 M of zinc acetate dehydrates solution under room temperature (25 °C). After 5 minutes of reaction, 0.015 g/L of PEG was added into the mixture and it was stirred for 12 hours to enhance the production of nanoparticles. Next, the precipitate formed was filtered and collected to dry in an oven of less than 100 °C for 1 hour. Lastly, the precipitate was calcined at 550 °C via furnace for 3 hours. After the calcination process, the white powder of ZnO-PEG was formed and ready to be applied for photocatalytic of Thiophene.

2.2 Characterization of ZnO/KCC-1

The characterization of ZnO-KCC-1 and KCC-1 nanoparticles was done by using Fourier Transform Infrared Spectroscopy (FTIR) with wavelength range from range from 3000 to 4000 cm^{-1} in order to observe the functional group of ZnO in the compound.

2.3 Photocatalytic Degradation of Thiophene

The maximum capacity of the photocatalytic reactor was 2 L where it can be operated either using batch or continuous methods. Inside the reactor, a UV lamp (253.7 nm, 18 W, GPH295T5L 4PSE, USA) was inserted for activated of the photocatalyst.

Synthetic thiophene solutions were prepared by dissolving 0.1429 μl of synthetic thiophene in 500 mL of acetonitrile solution. Then, 0.05 gL^{-1} of photocatalyst either ZnO/KCC-1, ZnO-PEG or KCC-1 was added into 500 mL of thiophene solution. The initial pH of the solution was adjusted to 5, 7 and 9 by adding the solution of sodium hydroxide, NaOH and hydrochloric acid, HCl. The mixture solution was fed into the reactor and mixed thoroughly by turning on the agitator at 300 rpm for 30 minutes in the dark condition before the photocatalytic process to achieve adsorption-desorption equilibrium between the solution and photocatalyst. Next, the temperature of the reaction was maintained at 25 $^{\circ}\text{C}$ by using the water chiller where it controlled the flow of cooling water. Then, 10 mL of degraded thiophene had been sampled at interval of 15 minutes for 1 hour and the samples had been centrifuged (Eppendorf, 5804 model) within 20 minutes to separate the photocatalyst from the reaction system. Then, the samples that had been separated were used for further analysis.

2.4 Proposed Photocatalytic Degradation Mechanism of Thiophene

In order to understand the photocatalytic degradation of thiophene in the photocatalytic reactor, Figure 1 is shown the illustration of the photocatalytic process to degrade thiophene. Firstly, the photocatalytic process was started as the photocatalyst which is ZnO was absorbed the UV light. Then, an electron-hole pair was generated only if the energy is more than the bandgap energy of the material. Band gap is the energy difference between the valence band (VB) and the conduction band (CB). The exposure to the illuminated light energy was the reason the conduction band electron of the photocatalyst gets excited. This phase was called the photo-excitation state. The photo generated electron was negatively charged while the hole is positively charged ($h\nu B^+$) or known as the high oxidative potential of the hole in ZnO due to the direct oxidation of thiophene [11].

Then, the reaction of the hole and hydroxide ion form very reactive hydroxyl radicals. The formation of the hydroxyl radical was an unstable state and the thiophene is being degraded. In the conduction band, the molecular oxygen was reduced to superoxide anion by electron. Due to the presence of organic scavengers or hydrogen peroxide (H_2O_2), the radical may form organic peroxide. After that, the H_2O_2 will be reacted with the hydroxyl radical and holes to generate (HO_2). The production of hydroxyl radicals due to the electrons in the conduction band and being showed that the main reason for the thiophene mineralization [9].

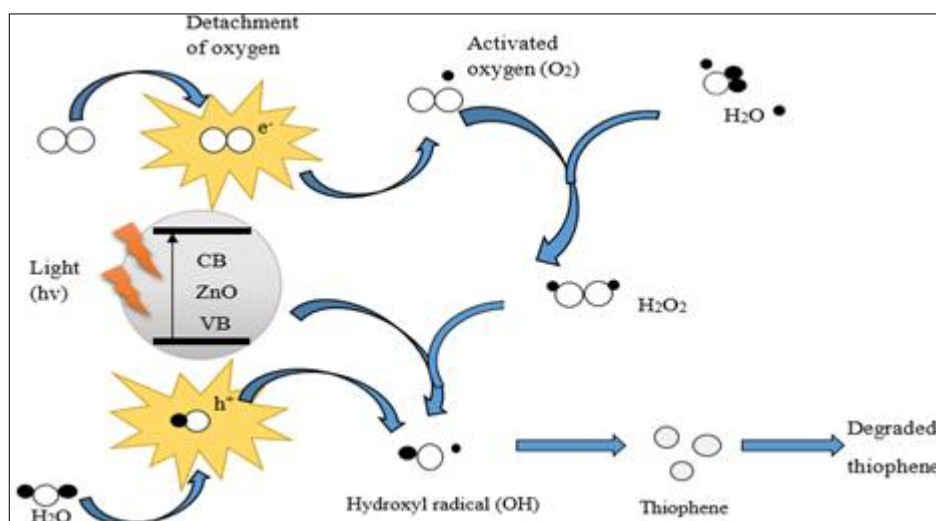


Fig. 1 - Photocatalytic degradation mechanism of thiophene

2.5 Analysis of Degraded Thiophene

For the quality of treated water analysis, the concentration of the samples was measured by using UV-Vis Spectrophotometer (LABOMED, INC, Spectro UV-2650). Then, the pH of the sample was taken by using a pH meter (EUTECH Instruments, pH 700).

2.6 Kinetic Study of Photocatalytic Degradation

The reaction rate or chemical kinetics of a chemical reaction can be defined as the concentration change of the reactant or product during the process meanwhile a rate law is the relationship between the rate of a chemical reaction and the reactant concentration [12]. In addition, the exponential in the rate law is the reaction order which means the effect of the reactant concentration.

Several factors that control the reaction kinetic including the ionic or molecular nature of the reactants, concentration of the reactant, the temperature of the reactants and availability of catalyst [13]. The importance of the study on the kinetics is to permit the reaction condition of the selected process to produce maximum products. Other than that, the study allows the prediction of time-dependent system. In addition, the most significant to study the kinetic will enhance the understanding of the mechanism of the reaction [8].

It can be predicted that the initial step in the reaction is the ability to adsorb the pollutant molecule and their degradation products on the surface of the photocatalyst while the second step is where the substrate is adsorbed to be decomposed under the condition in the experiment. Thus, the prediction was followed as below after consideration above process.

As the hydroxyl groups adsorbed on the surface of the photocatalyst, the photocatalytic process is completed. This occurs when the organic compounds and related intermediates on the catalyst surface and lead to the rate limiting step for photocatalytic degradation. From the adsorbed H₂O molecules, the combination of H₂O /OH⁻ with the photo-induced holes h⁺ to form hydroxyl groups and the OH radicals need to be formed. The rate formation for the hydroxyl is less compared to the combination rate of h⁺/e⁻ of the reaction between h⁺, H₂O and OH⁻. Following to the Bodenstein steady state assumption, the hydroxyl radical concentration is constant. Following to the Bodenstein steady state assumption, the h⁺ is constant at steady state [15].

First-order reaction where A → B can be expressed in terms of the reactant concentration:

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = k[A]^1 \quad (1)$$

This form of the rate law is sometimes referred to as the differential rate law. It can perform a mathematical procedure known as an integration to transform the rate law to another useful form known as the integrated rate law:

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (2)$$

Where ln is the natural logarithm, [A]₀ is the initial concentration of A and [A]_t is the concentration of A at another time. Other literature reported that the equation for the pseudo first order reaction is $\ln \frac{[C]_0}{[C]} = k_{app} t$ [16]. The most useful aspect of the integrated rate law is that it can be rearranged to have the general form of a straight line.

$$\ln [A]_t = -kt + \ln [A]_0 \quad (3)$$

Therefore, graph of the natural logarithm of the concentration of a reactant (ln) versus time, a reaction that has a first-order rate law had yield a straight line, while a reaction with any other order had not yield a straight line. The slope of the straight line corresponds to the negative rate constant, -k, and the y-intercept corresponds to the natural logarithm of the initial concentration. If the photocatalytic degradation shows the first order it assume that the mass transport as the rate limiting mechanism [17].

The rate for second-order reactions depends either on two reactants raised to the first power or a single reactant raised to the second power. This was examined a reaction that is the latter type: C → D. The differential rate law can be written:

$$\text{Rate of reaction} = -\frac{\Delta[C]}{\Delta t} = k[C]^2 \quad (4)$$

The integrated rate law can be written in the form of a straight line as:

$$\frac{1}{[C]_t} = kt + \frac{1}{[C]_o} \tag{5}$$

From the equation above, it stated that the equation for pseudo second order reaction is $\left(\frac{1}{[C]} = \frac{1}{[C]_o} + k_{obs2} t\right)$ [18]. Therefore, if the reaction is second order, a plot of $1/[C]t$ versus t had produce a straight line with a slope that corresponds to the rate constant, k , and a y-intercept that corresponds to the inverse of the initial concentration, $1/[C]_o$ [19]. The chemical adsorption as the rate limiting mechanism as the process shows the second order [17].

3. Results and Discussions

3.1 Fourier Transform Infrared Radiation Analysis

Characterization of KCC-1 and ZnO/KCC-1 were conducted by using Fourier Transform Infrared Spectroscopy (FTIR) to identify the purity, nature and chemical bonds in KCC-1 and ZnO/KCC-1 nanoparticle due to the production of an infrared absorption spectrum. The chemical bonds that present in the two types of photocatalyst that being used in this study were shown in Figure 2 and Figure 3 respectively. The photocatalyst was observed at the wavelength range from 3000-4000 cm^{-1} . Figure 2 shows the transmittance pattern of KCC-1. Firstly, primary amine which N-H bond was found at peak 3400 to 3332 cm^{-1} which attributed to antisymmetric stretching. The broad peaks at 3400 to 3200 cm^{-1} indicate the stretching mode for the O-H bond while the deformation appears at the range of 1480 to 1410 cm^{-1} . Other than that, silicon compound which was Si-O-Si detected at the range of 1080 to 1050 cm^{-1} where corresponds to the mode of stretching. Previous study has reported the existence of the silicon compound which was Si-O-Si vibration of the supported KCC-1 by using FTIR [21].

Figure 3 shows the transmittance pattern of ZnO/KCC-1 nanoparticles. The prominent absorption peak at 3400 to 3200 cm^{-1} was appeared to be the O-H component that indicated the stretching mode while indication for deformation at peak 1350 to 1260 cm^{-1} . The O-H component that presents in the sample due to the adsorption of the water vapor from the surrounding and the moisture residue during the synthesizing of the photocatalyst [10]. Next, the formation carboxylic group (C=O) was also detected at peak 1770 to 1720 cm^{-1} that correspond to the stretching. Moreover, peak at 1300 to 1000 cm^{-1} that corresponds to the stretching mode of the C-O-C component. This being reported that the presence of CO₂ complex bond is due to the oxidative decomposition of the organic species [22]. Besides, the prominent peak was at 3400 to 3332 cm^{-1} that detect the N-H component which indicates the antisymmetric stretching same as the N-H in the KCC-1. In addition, the peak at 600 until 700 cm^{-1} indicated the Zn-O stretching and deformation vibration. Therefore, it can be said that ZnO nanoparticles had successfully loaded on KCC-1 as the silicon compound which is Si-O-Si at the peak 1080 to 1050 cm^{-1} which correspond to the mode of stretching.

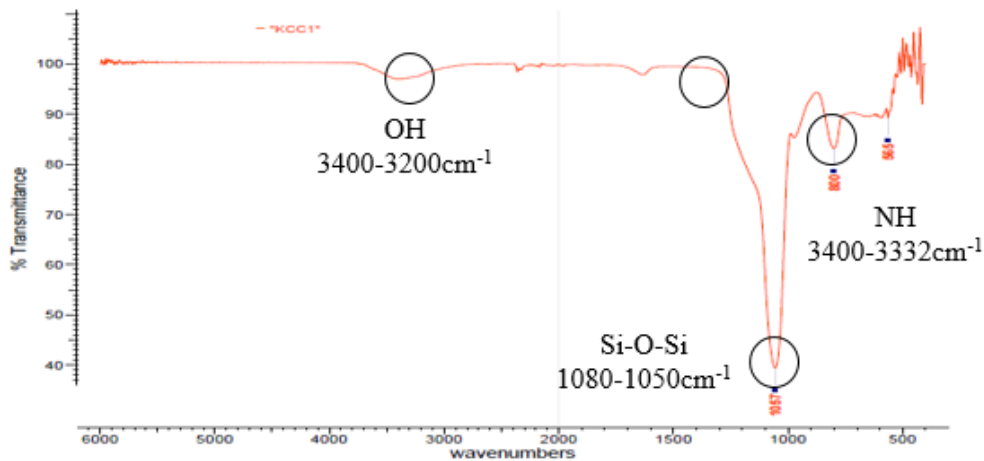


Fig. 2 - FTIR Spectra of KCC-1

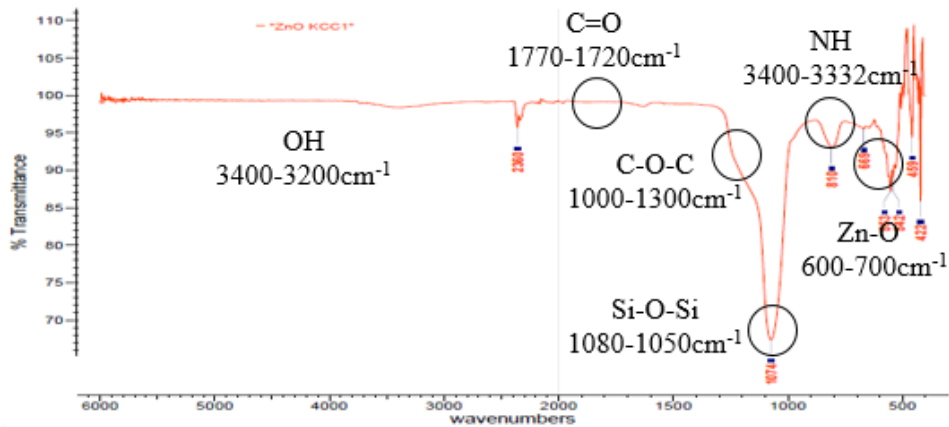


Fig. 3 - FTIR Spectra of ZnO/KCC-1

3.2 Effect of pH on Percentage of Thiophene Degradation

Based on the result obtained from Figure 4, it showed that degradation of thiophene under pH 7 and pH 9 are the highest performance in photocatalytic activity which is 88.89% after 60 minutes. For acidic conditions at pH 5, the performance in thiophene degradation is only at 33.33% after 30 minutes. Point zero charge (pH_{zpc}) of the catalyst can be used to consider the pH optimum for the reaction [20]. Previous literature reported that the point of zero charge for the ZnO is 8.19 [23]. In this study, the pH_{zpc} for ZnO/KCC-1 was considered as 8.19. This is because ZnO has involved more in the degradation reaction while the presence of KCC-1 was recognized as a supported catalyst to ZnO and did not involve in the reaction. Different catalyst has variation in adsorption capacities, and it is highly dependent on the zero-point charges [24]. Semiconductor oxides have amphoteric behavior, an important parameter in the reaction taking place on the semiconductor particles surfaces is the pH dispersion since it influences the surface charge properties of the photocatalyst.

The higher pH_{zpc} of the catalyst than the pH of the solution indicated that the catalyst surface is positively charged while the smaller pH_{zpc} of the catalyst than the pH of the solution indicated to negatively charged catalyst surface [20]. Thus, for this study, the surface of the ZnO/KCC-1 was considered positively charged due to the higher pH_{zpc} than the pH of the solution. From the result obtained, it can be said that the enforcement of the reaction to undergo under alkaline conditions could be attributed to the increase of hydroxyl ions which induce more hydroxyl radical formation. The hydroxyl radical ($\bullet OH$) is the main oxidizing agent that playing important role in the degradation of thiophene and the organic compound to carbon dioxide (CO_2) and water (H_2O) [7]. Thus, it can be said that degradation of thiophene was better at neutral and alkaline compared to the acidic condition. However, the most preferred pH in this research is neutral which at 7 because no addition of chemicals is required to increase the pH of the solution.

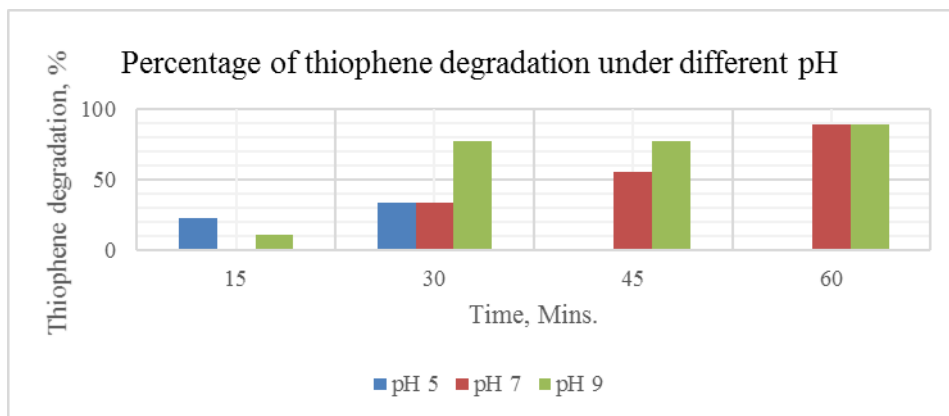


Fig. 4 - Percentage of thiophene degradation under different pH

3.3 Effect of Different Photocatalyst on Percentage of Thiophene Degradation

Different types of photocatalysts also playing a crucial role in the degradation of thiophene. Figure 5 shows the percentage degradation of thiophene via photocatalytic treatment by using different types of photocatalyst which were

ZnO-PEG, KCC-1 and ZnO/KCC-1. From the obtained result, it clearly shows that degradation of thiophene by using ZnO loaded on KCC-1 as support catalyst is very significance which achieved at 88.89%. Meanwhile, the usage of ZnO-PEG only achieved 66.67% at 15 minutes. However, beyond 30 minutes declination of thiophene degradation can be seen. In addition, 25% of degradation of thiophene as the lowest photocatalytic activity by using bare KCC-1.

Zinc oxide has a larger energy gap which is 3.4 eV and it had been reported that ZnO has high efficiency in the photocatalytic degradation process. In addition, ZnO loaded on the large surface area of KCC-1 which is $641\text{m}^2/\text{g}$ leading to the high accessibility of the active site and enhance the efficiency of the adsorption process [25]. The greater surface area of KCC-1 has made the greater number of ZnO particles reside on the surface thus, improves the performance of adsorption ability of the photocatalyst towards organic pollutant. The activity of photocatalyst is linked with the time required for electrons and holes to get the surface of the particles. When particles are in nano-sized, their diameter becomes miniature, so it is then very straight forward for the charge carrier to move from the inside to the surface and starting a redox reaction. The greater surface to volume ratio, the smaller diameter of the particle and the smaller time may be used up by charge carriers diffusing to the surface from inside. This can provide the lesser probability of electron and hole recombination [22]. Other than that, the greater surface area also contributes to greater exposure to a light source such as UV radiation. As much as the surface availability that interacts with the light, there had more oxidizing species produced like hydroxyl radical.

KCC-1 gave the lowest percentage of thiophene degradation. This is because KCC-1 is modified silica catalyst where it does not have the ability like metal-oxide semiconductor that can allow light absorption that can induce charge separation process and form positive hole that allow the oxidation of organic pollutant [8]. Therefore, it is believed that the ZnO/KCC-1 had given the best performance in the degradation of thiophene.

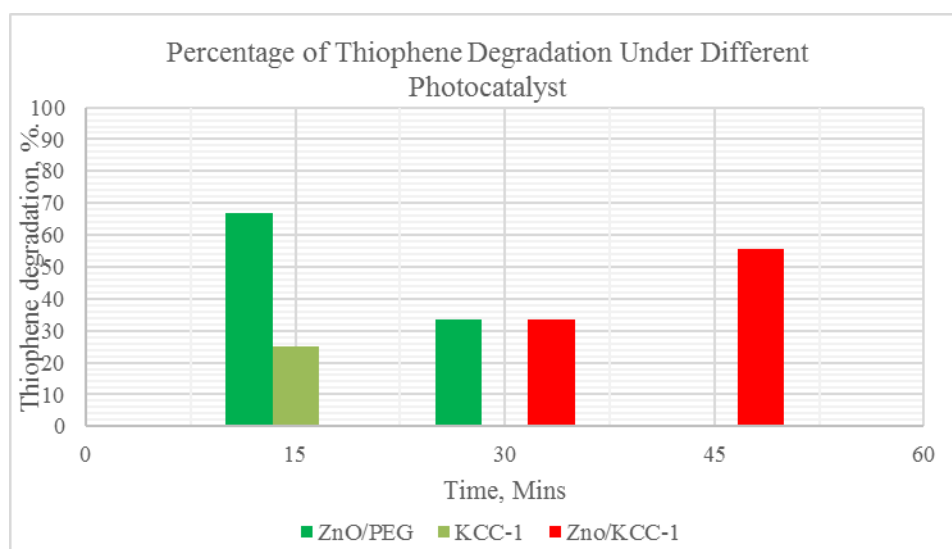


Fig. 5 - Percentage of thiophene degradation under different photocatalyst

3.4 Kinetic Study of Photocatalytic Degradation

Figure 6 shows the relationship of the $\ln [C_0/C]$ of thiophene against degradation time in the presence of ZnO/KCC-1 photocatalyst in 60 minutes illumination. The figures also represent the kinetic order of photocatalytic degradation. The concentration of thiophene solution before and after adsorption was estimated using UV-visible spectroscopic at a absorbance of 233nm. From the result obtained, the pseudo-first-order equation was the model that gave the best fit to the experimental data. From the graph that had been plotted, the correlation coefficient, (R_1^2) for the pseudo-first order is nearest to 1 compares to the correlation coefficient, which was 0.8163. It had been reported that the correlation coefficient is a good criterion for the selection of a kinetic model [16]. Photocatalytic degradation was found to follow pseudo-first order revealed the mass transport as the rate-limiting mechanism [17].

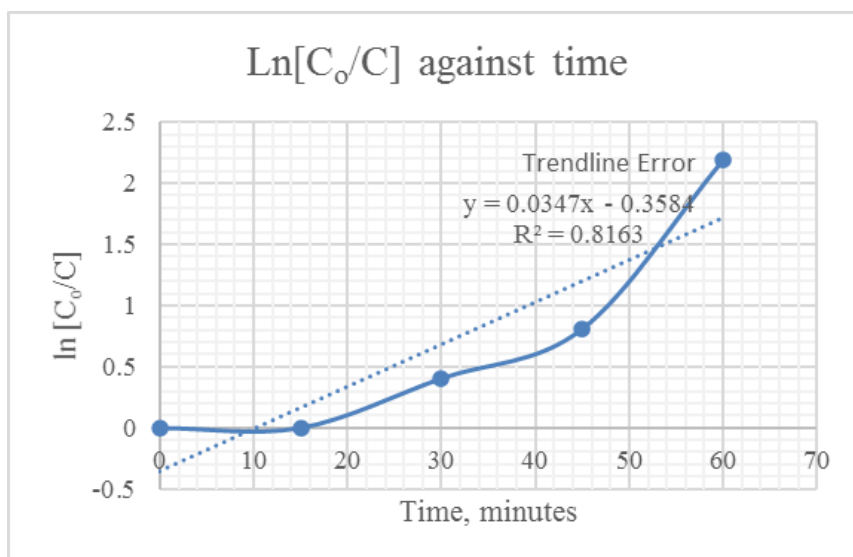


Fig. 6 - The plot of $\ln [C_0/C]$ against time.

4. Conclusions

Thiophene known as a sulfur pollutant in petroleum fraction was successfully treated via photocatalytic degradation. The photocatalyst ZnO/KCC-1 had successfully synthesis via precipitation method and the characterization show that ZnO and silicon compound were found by using FTIR. Degradation of thiophene has the best condition under pH 7 by using ZnO/KCC-1 as a photocatalyst. ZnO loaded on KCC-1 as support catalyst lead to the greater surface area of photocatalyst and resulted in better performance in the degradation of thiophene. In addition, photocatalytic degradation of thiophene had the rate-limiting mechanism is the mass transport as this photocatalytic degradation follow pseudo-first order.

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