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Photodegradation of Different Wastewater Using Modified Fibrous Silica (KCC-1) Catalysts Under Different Duration Time

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ABSTRACT

Persistent Organic Pollutants (POPs) commonly found in industrial wastewater have an ability to bio-accumulate and bio-magnify naturally which make it resistance towards simple chemical and biological degradation processes. Example of commonly found POPs are polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbon (PAHs), aliphatic or heterocyclic compound, etc. Therefore, photodegradation had become the alternative in treating industrial wastewater containing POP. Textile industry uses raw materials from animal fibres such as silk and wool and also from synthetic materials such as acrylics, nylon or polyester that contains formaldehyde which will affect human's stimulus and mucous membrane. It is compulsory for the formaldehyde to be eliminated before being discharge into the environment. In the other hand, POMSE is a biological treated wastewater from palm oil mill effluent (POME) that still have high turbidity level and able to induce eutrophication. The pollutant content in POMSE come from a non-humic organic matter that come from organisms. The objectives of this research are to formulate ZnO-KCC-1 nanoparticles via precipitation method as well as to investigate the photocatalytic degradation of organic pollutant in POMSE and textile wastewater under different duration time via ZnO-KCC-1. Last but no least is to elucidate the kinetic study of photocatalytic degradation activity of organic pollutant by using synthesized ZnO-KCC-1 catalyst. ZnO-KCC-1 have the ability to reduce 30.77% colour intensity of POMSE at 15 minutes and reduced 40.82% colour intensity in textile wastewater. Besides, the use of ZnO-KCC-1 also reduce the DO consumption into 12.09% in POMSE and only 20.88% DO was consumed in textile wastewater. This proved that ZnO-KCC-1 have the ability to become one of the future alternatives photocatalyst in photodegradation of industrial wastewater due to its promising abilities in reducing the colour intensity, turbidity, COD and BOD of the wastewater.

Key words: Photocatalytic, photodegradation, POMSE, ZnO-KCC-1

1. INTRODUCTION

Wastewater mainly from industrial sources contain high number of organic pollutants that could pose numerous effects if being directly discharged to the environment with no authorization. Nowadays, industries prefer to replace the conventional microbial degradation process with heterogeneous photodegradation process which also known as an Advanced Oxidation Process (AOP) [1]. In photocatalytic system, they figured out that light from the light sources activates the catalyst at certain wavelength depend on the types of catalyst used. Then, the activated photocatalyst will tend to induce the formation of strong oxidation agent that will trigger redox reaction that have the ability to decompose the unwanted organic pollutant away from the wastewater. Zinc Oxide (ZnO) nanoparticles have become a widely favourable catalyst due to its stability, persistency, having wide band gap and most importantly high photo sensitivity. This research aimed to study the effectiveness of Modified

Fibrous Silica (KCC-1) embedded withZnO forming ZnO-KCC-1 that act as the photocatalyst to replace the conventionally used photocatalyst such as ZnO/PEG or TiO_2.

Industries such as textile and palm oil industries produced numbers of wastewater every day. Wastewater produced from textile industries used dye that resist to biodegradation and cannot be degrade through simple biological treatment, aeration and oxidation due to its complex cyclic structure [2].The released of dyes directly to the environment will cause eutrophication and will definitely disturb the ecology system [3]. Besides that, wastewater from a palm oil industry emit POMSE containing high number or organic pollutant that is very turbid and contained high colour intensity [4]which will block the sunlight from penetrating the water that reduce the aquatic growth due to interruption of photosynthesis process. Due to the rising demand of photodegradation process in sustaining greener environment, the effective photocatalyst to replace or substitute the common photocatalyst such as titanium oxide should be identified so that the photodegradation can widely being use in industries around the world. Therefore, this research investigated the effectiveness and usability of ZnO-KCC-1 as the photocatalyst to replace the common photocatalyst.

The objectives of this research are to formulate ZnO-KCC-1 nanoparticles via precipitation method as well as to investigate the photocatalytic degradation of organic pollutant in POMSE and textile wastewater under different duration time via ZnO-KCC-1. Last but no least is to elucidate the kinetic study of photocatalytic degradation activity of organic pollutant by using synthesized ZnO-KCC-1 catalyst.

1.1 Modified Fibrous Silica (KCC-1)

Porous solids fabrication is one of the common industrial applications that had widely being use in the microelectronic development and diagnosis application in medical area since past few decades. One of the commonly used material would be silica. Conventionally, mesoporous silica material (MSM-41) with surfactant as its organic agent had become the earliest porous solid fabrication to aid the industry [5], the structures, morphology as well as the pore sizes of the MSM-41 can be controlled, hence modified fibrous silica (KCC-1) was introduced to resolve the issue, replacing MSM-41 [6]. Besides, the KCC-1 could also increase the catalytic sites of the catalyst through their fibrous structure and will then improves the catalytic process. The improvement had become an initiator to the synthesis of nanoscale and mesoporous silica with various morphology type. The synthesis of modified fibrous silica (KCC-1), its physical and chemical characteristic as well as its advantages in photodegradation process will be explain further.

Previously, production of KCC-1 was made from urea, cetylpyridium bromide and water with the aid of microwave for the hydrothermal process in obtaining the KCC-1. Based on their study, it is said that KCC-1 have the ability to exhibit a uniform spherical structure as well as having a unique porous silica dendrimer. It is also proven that the KCC-1 possessed a high surface area at 634m^2/g and having a pore with diameter of 4.7nm [7].

KCC-1 was synthesized by using a microwave assisted hydrothermal techniques that run at short period of time. This method [6]would be the most common and typical synthesis method in order to produce the modified fibrous silica hydrothermally. First, 30 ml of cyclohexane was added with 1.5ml pentanol to produce the solvent. The mixture (solvent) was let to dissolve with 2.4g of 0.012mol of tetraethyl orthosilicate (TEOS) which become the precursor in this process. The solvent-precursor mixture was labelled as mixture A. Meanwhile, the solution B was prepared by mixing up 1g of 0.0026mol of cetylpyridinium bromide (CPB) with 0.6g of 0.01mol of urea in 30ml water. CBP initiated the formation of micro emulsion that help to fabricate a fibrous nanosilica sphere while the urea controlled the hydrolysis speed of the TEOS. Both mixture A and B were mixed at room temperature and stirred for about 30 minutes. The mixture was placed inside a Teflon-sealed microwave reactor and further exposed to microwave irradiation for 4 hours under 120°C with not more than 400W power.

The radiated mixture was let to cool to room temperature and the silica was formed. To extract the silica, the mixture was centrifuged, washed and dried for about 24 hours. The pure silica was calcined or desiccated for 6 hours under 550°C to extract the modified fibrous silica. KCC-1 have a colloidal sphere shape with diameter in the range between 250nm to 450nm that can be seen under a scanning electron microscope (SEM), while the structural criteria of the KCC-1 are said to be in order and presence of disperse (dendrimer) fibres that uniformly distributed from the centre of the particle. The fibrous nanostructure of the KCC-1 is the result from the formation of micro emulsion by cetylpyridinium bromide.

1.2 Synthesis of ZnO/KCC-1

To synthesis the ZnO-KCC-1, the ZnO and KCC-1 were made on the first hand. The KCC-1 was synthesized by using method stated in the previous subchapter and was added into the ZnO during the mixing process. The ZnO was synthesized by using oxalic acid and zinc acetate with mass of 13.505g and 18.348g respectively. The calculated mass of oxalic acid and zinc acetate is to be dissolved in 1 litre distilled water in order to achieve 0.15M of oxalic acid and 0.1M of zinc acetate. The suitable concentration of oxalic acid and zinc acetate was then mixed up at 60°C until it reaches homogeneity and forming ZnO. According to Hanis et al,[8]the mechanisms of the synthetization of ZnO from zinc acetate and oxalic acid were as follows:

$$Zn(CH_3COO)_2 . 2H_2O + H_2C_2O_4 . 2H_2O \rightarrow ZnC_2O_4 . 2H_2O + 2CH_3COOH + 2H_2O \quad (1)$$

From the reaction above, the intermediate zinc oxalate was formed directly. After that, the intermediate zinc oxalate was calcined to form ZnO as below:

$$ZnC_2O_4.2H_2O + \tfrac{1}{2}O_2 \rightarrow ZnO + 2CO_2 + H_2O \quad (2)$$

Next, 2g of synthesized KCC-1 was added into the mixture for 4 minutes under 60°C. This to allow the KCC-1 to embed with the ZnO. Then, the mixture was let to cool at room temperature for at least 1 to 2 hours before proceeding to the next steps. The next coming steps aim to form the ZnO-KCC-1 into powder form. First and foremost, the liquid mixture of ZnO/KCC-1 was filtered using a 110mm filter paper to remove the undissolved and impurities away. This process is prominent in order to prevent unwanted particles and impurities from presence in the powder as well as to increase the purity of the ZnO/KCC-1 formed. The filtered mixture was then placed in oven for about 1 hour under 100°C to remove the water content in the mixture. Next, the mixture was placed into furnace for 3 hours under 500°C to extensively remove water content and turn the mixture into powder form. After 3 hours in the furnace, the mixture was already be in powder form. The powder mixture was then grinded by using mortar to form a smooth powder and also to prevent clumpy powder. That is all the required steps to form the ZnO-KCC-1. However, the powder was then be characterized by using FTIR (Carry 630 AU13040047, Agilent Cross Lab) in order to identify the presence of ZnO and KCC-1 in the powder by analysing its functional groups.

1.3Organic pollutant in wastewater

Organic pollutant in wastewater are commonly categorized as a Persistent Organic Pollutant (POPs) which contain a cluster of organic compounds that resist and unable to easily being degraded through either chemical, biological or photolytic processes. A POPs have the ability to exist in the environment at long time which become one of the reasons why it is very important to be able to eliminate away the POPs content in the wastewater. POPs also have the ability to bio-accumulated and bio-magnify throughout its existence in the environment. The undegradable pollutant become a highly concern problems that require solutions to prevent pollutions. There are many types of organic pollutant that exist in the world [9]few examples of it are formaldehyde, PAHs, PCBs, and pesticide. Textile industry are one of industry that discharge high volume of wastewater every day, the raw materials in textile industry are mainly from animal fibres such as silk and wool, and also from synthetic materials such as acrylics, nylon or polyester [10]. The use of these materials high formaldehyde content which pose effect on humans' stimulus and mucous membrane. The formaldehyde requires to be eliminated from the wastewater before discharge into the environment. Besides, textile wastewater also tends to show high chemical oxygen demand value due to the use of dye which proves to show low degradability in water and have the ability to induce sludge accumulation that definitely will threat the aquatic sustainability.

In the other hand, POMSE is a biological treated wastewater from palm oil mill effluent (POME) that still have high turbidity and have an ability to induce eutrophication. The pollutant contained in POMSE come from a non-humic organic matter that come from organisms and also contained organophosphorus and atrazine pollutant due to the use of pesticides and herbicides in the palm orchard. Hence, this study meant to analyse the effect of photodegradation process via ZnO-KCC-1 towards the organic pollutant presence in POMSE and textile wastewater.

1.4Photocatalytic degradation of organic pollutant via ZnO-KCC-1

ZnO-KCC-1 will act as an accelerator of oxidation process which already active in nature. Silica is a semiconductor that presence in the KCC-1 changes the rate of chemical reaction through the action of light. The silica has a band structure on its molecular orbital that consist of largely vacant conduction band (CB) and valance band (VB) which become the bands of interest in this photocatalytic process. The bands will have its specific band gap energy that will characterize them. Due to the presence of light, the semiconductor which is silica in KCC-1 will be photo-excite to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidising sites) that will trigger the redox reaction to happen. When the silica is illuminated with light that strikes higher energy to overcome the band gap energy between the CB and VB, it will tend to promote the free electron in the valence band towards the conduction band. The electron promotion will leave a positive hole in the VB and CB will contain electron that had been promoted from the VB before. The formation of this redox sites in the silica will then triggered the redox process between the KCC-1 with the organic pollutant presence in the wastewater to happen [11]. Figure 1 illustrates the valence band (VB) as well as the conduction band (CB) as well as the reducing and oxidising sites triggered with the presence of light.

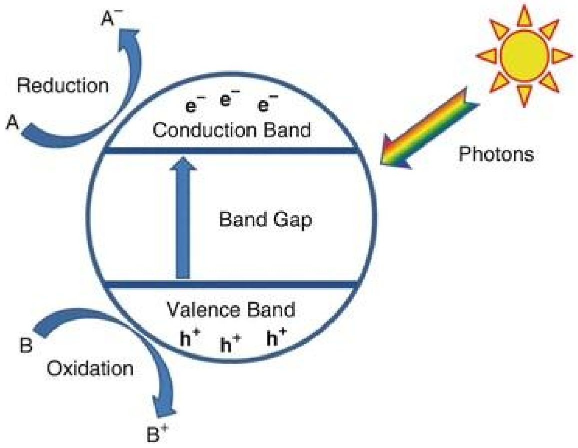

Figure 1: Formation of reduction and oxidation sites in silica photoexcitation process [12]

2. MATERIALS AND METHODS

The photo-catalysis process was conducted by using Zinc Oxide embedded with a modified fibrous silica (ZnO-KCC-1). The effectiveness of the ZnO-KCC-1 was studied in two different types of wastewater which obtained from palm oil (POMSE) and textile industries. Textile wastewater containing dye was collected from the effluent tank from a clothing manufacturer located in BatuPahat,Johor and the palm oil secondary effluent (POMSE) was collected from the palm oil mill located in Kluang, Johor. The degraded wastewater quality was analysed based on their colour intensity, pH, biological oxygen demand (BOD), chemical oxygen demand (COD) as well as its turbidity reduction percentages.

Figure 2 shows the laboratory-scale schematic diagram of photocatalytic reactor that was used in this study. UV lamp with wavelength of 365nm was placed parallel to the reactor containing wastewater which act as the light source. Sodium chloride (NaCl) and sodium hydroxide (NaOH) were added in order to adjust the pH via probe attached in the reactor. The ZnO-KCC-1 at specific loading was added into the reactor and the agitator was set to be at 150 rpm speed to allow the catalyst to fully distribute in the wastewater. The temperature in the reactor was let to remain constant under room temperature throughout the process. For each selected time interval, 45ml of treated wastewater was drawn into 50ml centrifuge tube. The drawn sample containing treated wastewater and ZnO-KCC-1 had been centrifuged under 4°C for 20 minutes at 5000 rpm speed to separate the mixture. The following procedure was repeated for every sample at different parameter in order to study the effectiveness of the ZnO-KCC-1 to degrade the sample.

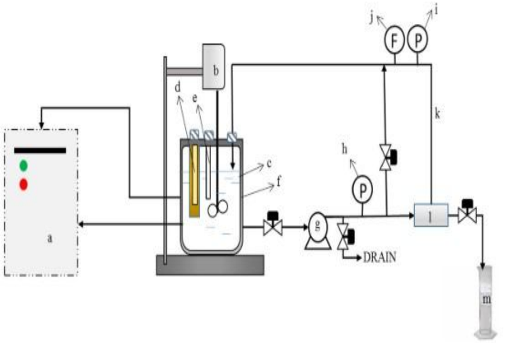

Figure 2: Laboratory-scale schematic diagram of membrane photocatalytic reactor (MPR) a) water chiller, b) overhead stirrer with stand, c) photocatalytic reactor, d) UV lamp, e) feed, f) cooling jacket, g)pump, h &i) pressure gauge, j) flow meter, k) recycle flow, l) membrane filtration system and m) measuring cylinder [13]

Chemical Oxygen Demand (COD) was determined via Reactor Digestion method [14]. In this method, the sample was inserted into COD vials and placed in a COD reactor for approximately one hour before it being analyse under DR6000 spectrophotometer.

Biochemical Oxygen Demand (BOD) was examined via two analytical method which are dilution method (EPA method 405.1 and Standard method 5210 B) as well as the respirometric method (using BOD Trak apparatus provided from Hach company).

The turbidity reduction was determined by using turbidity meter (EUTECH Instrument, TN100, 1000NTu) while the pH of the sample was analyzed via pH meter (EUTECH Instrument, pH700) and the color intensity was analyzed by DR6000 spectrophotometer.

3. RESULTS AND DISCUSSIONS

The performance of ZnO-KCC-1 to photodegrade organic pollutants in two different types of wastewater were identified through the effect it possesses on the colour intensity, pH changes and the turbidity change. From all those analyse, sample at the most compatible time taken for the ZnO-KCC-1 to perform was selected to undergo the chemical and biological oxygen demand test and the effects were observed.

3.1 Characterization of ZnO-KCC-1

The ZnO-KCC-1 was characterized to identify their component by using FTIR. Figure 3 and Figure 4 indicated the IR spectra of KCC-1 and ZnO-KCC-1. The two different spectra were recorded to identify the successfulness of the embedding process. In the following Figure 4, the IR spectra of compound in KCC-1 were analysed. The silicon compound (Si-O-Si) present in the KCC-1 at range between 1050- 1080 cm^{-1} due to the stretching of the KCC-1, while the second most prominent peak in KCC-1 was the amine groups (NH) which appeared in the range in between 750-850 cm^{-1}. This broad peak was the result of the wagging of the KCC-1 which appeared in the spectra. Besides that, the alcohol groups compound (OH) present in the range between 3200-3400 cm^{-1} indicated the stretching of KCC-1 in the sample.

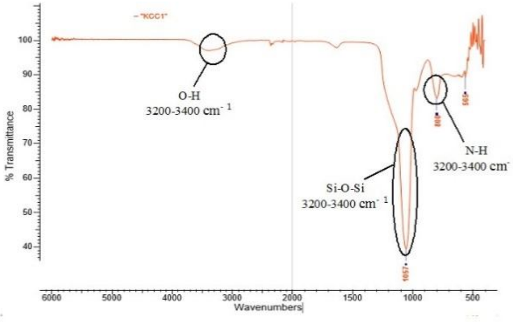

Figure 3:IR spectra of KCC-1

In Figure 4, the IR spectra of compound in ZnO-KCC-1 was analysed. The silicon compound (Si-O-Si) present in the spectra indicated the presence of KCC-1 at range between 1050-1080 cm^{-1} while the amine groups (NH) appeared in the range in between 750-850 cm^{-1} as the result of the wagging of the KCC-1. Besides that, the alcohol groups compound (OH) was also present in the range between 3200-3400 cm^{-1} indicated the stretching of KCC-1 in the sample. The peaks in between 500-700 cm^{-1} indicated the presence of ZnO in the ZnO-KCC-1 sample. Based on research from [15], the presence of ZnO can also be characterized from the appearance of peak between the range of 1000-1300 cm^{-1} which indicated the presence of ester compound (C-O-C). Therefore, the characterization process of ZnO-KCC-1 via FTIR proved the presence of ZnO and KCC-1 in the sample.

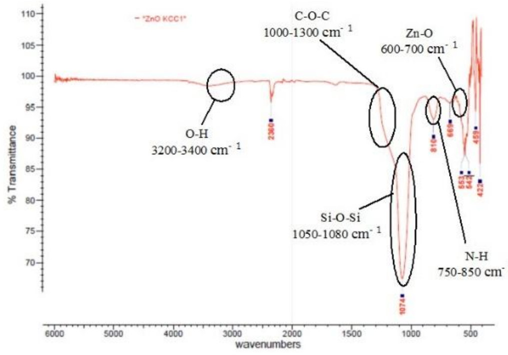

Figure 4:IR spectra of ZnO-KCC-1

3.2Effect of photodegradation of textile wastewater using ZnO-KCC-1

The photodegradation of textile wastewater via ZnO-KCC-1 had been conducted under different duration time. 0.050g/L of ZnO-KCC-1 loading was used to photodegrade the textile wastewater and was analysed in term of the colour intensity, pH, turbidity and the chemical and biological oxygen demand (COD & BOD). The reading was taken every 15 minutes up till 90 minutes.

3.3Analysis of colour intensity

As recorded in Table 1 and Figure 5, the colour intensity was compared under different exposure time of the ZnO-KCC-1 with the sample. The initial sample before treatment was set to be the standard and blank. Initially in the first 15 minutes, the colour intensity reduction percentage was at the highest value where at 0 minutes, 18.09% colour was reduced and in the 15 minutes, the highest percent of reduction was recorded at 30.77%. As the time continues up till 90 minutes, the colour reduction percent decreases which indicate that the ZnO-KCC-1 reduced the colour intensity of the textile wastewater effectively at 15 minutes exposure whilst as the longer the exposure time, the colour intensity reduction decreases. The reduction of colour intensity in textile wastewater was due to the degradation of organic compound in the sample which mainly consist of dye depending on their chemical structure and functional groups. The ZnO-KCC-1 produced free radical OH^+ that hydrogenated and oxidized the dye compound into CO_2 and H_2O. The degradation of dye compound will definitely reduce the colour intensity of the wastewater.

Table 1: Colour intensity of textile wastewater sample of ZnO-KCC-1

Time (min)	ADMI Reading (DF:20)	Reduction (%)
Initial	8840	
0	7240	18.09
15	6120	30.77
30	6140	30.54
45	6280	28.90
60	6360	28.05
75	6320	28.51
90	6320	28.51

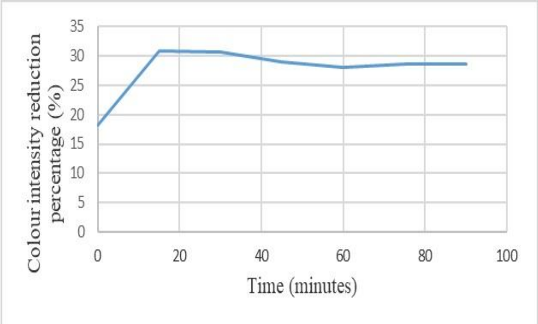

Figure 5: Graph of colour intensity reduction (%) against time (minutes)

3.4Analysis of pH

As tabulated in Table 2, the pH values for textile wastewater sample after treated with ZnO-KCC-1 under series of different duration time were studied. From the data recorded, it can be analysed that the exposure of textile wastewater with ZnO-KCC-1 does not show any significant reduction. The longer the exposure time of the ZnO-KCC-1 in the sample, the more the pH were reduced at slight value only. The textile wastewater had an initial pH value of 10.72 which determined as a high basicity type of wastewater. High basic wastewater causes by excess hydroxide ions, through photodegradation via ZnO-KCC-1, oxygen containing radical attacked the excess hydroxide ions presence in the high basicity textile wastewater and H_2O was formed.

Table 2:pH of treated textile wastewater sample of ZnO-KCC-1

Time (min)	pH value	Reduction (%)
Initial	10.72	
0	10.59	1.21
15	10.57	1.40
30	10.74	-0.19
45	10.63	0.84
60	10.58	1.31
75	10.46	2.43
90	10.42	2.80

3.5Analysis of turbidity

As tabulated in Table 3, the turbidity for textile wastewater sample after treated with ZnO-KCC-1 under series of different duration time were studied. At 0 minutes, the turbidity of the sample shows a highest reduction percent from 51.4 Ntu to 8.47 Ntu, this was calculated to be at 83.52% turbidity reduction which was also the highest reduction recorded in this experiment. However, the reduction percentage drops as the exposure time increases. This data was analysed that on the 0 minutes, the highest reduction value was probably due to the inhomogeneous mixture of sample with the ZnO-KCC-1, as the mixing continues, the reduction drops as the prolong reaction with the ZnO-KCC-1 induce the turbidity of the sample. Even though the reduction reduced as the time continues, the turbidity of the treated sample was still far low from the untreated sample. Which means, the ZnO-KCC-1 still has the ability to reduce the sample turbidity but require extensive studies on its effect during the mixing upon reaching the homogeneity.

Table 3: Turbidity value of treated textile wastewater sample of ZnO-KCC-1

Time (min)	Turbidity (Ntu)	Reduction (%)
Initial	51.4	
0	8.47	83.52
15	8.79	82.89
30	10.64	79.29
45	9.52	81.47
60	17.12	66.69
75	22.20	56.80
90	39.90	22.37

3.6Analysis of chemical and biological oxygen demand (COD & BOD)

From the previous parameter, selection of sample at most effective exposure time was selected to undergo the COD and BOD test. From all the analysed parameter, 15 minutes was the best time required for the ZnO-KCC-1 to photodegrade the textile wastewater, therefore the COD and BOD for textile wastewater sample will be conducted on sample at 15 minutes exposure time. Based on Table 4, the COD value was initially high at value of 574 mg/L while COD value for treated sample at 15 minutes in ZnO-KCC-1 reduced into 439 mg/L only. This can be said that the treatment of textile wastewater successfully reduced the chemical oxygen demand of the sample up to 23.52% reduction.

Table 4:COD value of treated textile wastewater in ZnO-KCC-1

Sample	Initial	15 Minutes
COD value (mg/L)	574	439

From the COD value, the sample size for BOD testing was calculated. As recorded in Table 5, initially, the treated sample showed lowest DO value probably due to the oxygen consumption for the degradation process to occur put the oxygen level in the treated water to be less than the untreated sample. After 3 days, the DO value in the samples were measured once again. The untreated sample show lower DO value compare to the sample at 15 minutes treatment. The percentage of DO reduction in untreated sample was 27.52% while only 12.09% DO was reduced in the treated sample. This showed that the treatment of the sample with ZnO-KCC-1 had the ability to kill and reduced the potential microbial growth in the wastewater.

Table 5:BOD value of treated textile wastewater in ZnO-KCC-1

Sample	Initial pH	Dissolve Oxygen (mg/L)		Dissolved Oxygen Consumption (%)
		Day 0	Day 3	
Initial	7.62	6.25	4.53	27.52
15 Minutes	6.55	5.46	4.80	12.09

3.7Effect of photodegradation of POMSE wastewater using ZnO-KCC-1

The photodegradation of palm oil wastewater via ZnO-KCC-1 had been conducted under different duration time. 0.050g/L of ZnO-KCC-1 loading was used to photodegrade the POMSE wastewater and the parameter analysed were in term of the colour intensity, pH, turbidity and the chemical and biological oxygen demand (COD & BOD). The reading was taken every 15 minutes up till 120 minutes.

3.8Analysis of colour intensity

As recorded in Table 6 and Figure 6, colour intensity of POMSE samples after undergo series of photodegradation were analysed under the DR6000 spectrophotometer. The colour intensity was compared under different exposure time. The initial sample before treatment was set to be the standard and blank. Initially, at 0 minutes before the mixing process, the colour intensity was reduced to 10.71% and continue to peak up at the 15 minutes exposure where the colour intensity was then reduced up to 40.82% which was also the highest reduction percentage of the colour intensity. As the time continues, the reduction showed inconsistent pattern whilst still successfully reduced the colour intensity from its initial untreated sample. The reduction of colour intensity in POMSE was due to the degradation of organic compound in the sample. The ZnO-KCC-1 produced free radical OH^+ that hydrogenated and oxidized the organic compound in POMSE into CO_2 andH_2O. The degradation of organic compound will definitely reduce the colour intensity of the wastewater.

Table 6: Colour intensity of textile wastewater sample of ZnO-KCC-1

Time (min)	ADMI Reading (DF:20)	Reduction (%)
Initial	3920	
0	3500	10.71
15	2320	40.82
30	2560	34.69
45	2860	27.04
60	2400	38.77
75	2540	35.20
90	2500	36.22
105	2520	35.71
120	2520	35.71

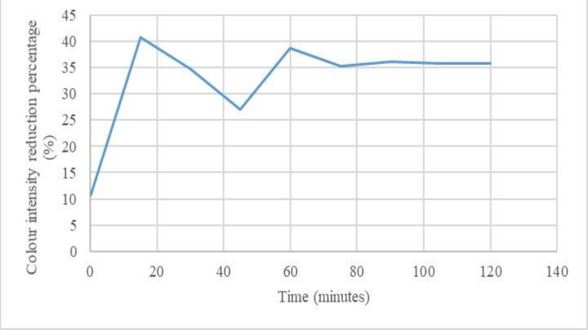

Figure 6: Graph of colour intensity reduction (%) against time

3.9Analysis of pH

As tabulated in Table 7, the pH values for POMSE wastewater sample after treated with ZnO-KCC-1 under series of different duration time were studied. From the data recorded, it can be analysed that the exposure of POMSE wastewater with ZnO-KCC-1 does not show any significant reduction as the highest reduction was recorded at the 120 minutes exposure where 3.03% pH had been reduced. The longer the exposure time of the ZnO-KCC-1 in the sample, the more the pH were reduced.

Table 7: pH of treated textile wastewater sample of ZnO-KCC-1

Time (min)	pH value	Reduction (%)
Initial	8.90	
0	8.81	1.01
15	8.74	1.80
30	8.72	2.02
45	8.72	2.02
60	8.71	2.14
75	8.71	2.14
90	8.68	2.47
105	8.66	2.70
120	8.63	3.03

3.10Analysis of turbidity

As tabulated in Table 8, the turbidity for textile wastewater sample after treated with ZnO-KCC-1 under series of different duration time were studied. From the recorded data, initially the untreated sample show high value of turbidity at 81.0 Ntu, as the sample was treated with ZnO-KCC-1, the turbidity value started to significantly reduced, which the highest reduction was recorded at 90 minutes exposure with value of 80.44% of reduction. The pattern of turbidity reduction was inconsistent as the value drops and rises at each different point. However, the treatment with ZnO-KCC-1 to the POMSE wastewater successfully able to reduce the turbidity of the sample. The turbidity reduction was due to the degradation of organic compound in POMSE which also similar to the effect it possessed on the colour intensity of POMSE after treatment.

Table 8: Turbidity value of treated textile wastewater sample of ZnO-KCC-1

Time (min)	Turbidity (Ntu)	Reduction (%)
Initial	81.0	
0	22.0	72.84
15	20.1	75.19
30	31.1	61.60
45	32.0	60.49
60	18.4	77.29
75	15.9	80.33
90	15.8	80.44
105	17.6	78.28
120	17.5	78.37

3.11Analysis of chemical and biological oxygen demand (COD & BOD)

From the previous parameter, selection of sample at most effective exposure time was selected to undergo the COD and BOD testing. From all the analysed parameter, 15 minutes was the best time required for the ZnO-KCC-1 to photodegrade the POMSE wastewater, therefore the COD and BOD for POMSE wastewater sample will be conducted on sample at 15 minutes exposure time. Based on Table 9, the COD value was initially high at value of 632 mg/L while COD value for treated sample at 15 minutes in ZnO-KCC-1 reduced into 514 mg/L only. This can be said that the treatment of POMSE wastewater successfully reduced the chemical oxygen demand of the sample up to 18.67% reduction.

Table 9:COD value of treated textile wastewater in ZnO-KCC-1

Sample	Initial	15 Minutes
COD (mg/L)	632	514

From the COD value, the sample size for BOD testing was calculated. As recorded in Table 10, both samples before and after 15 minutes treatment were placed into the BOD bottles for 3 days. Initially both samples were control to be at pH in the range of 6.5 -8.0 as this is the best pH for the possible microbes to grow in 3 days. The initial dissolved oxygen value was measured and recorded. Initially, the treated sample showed lowest DO value probably due to the oxygen consumption for the degradation process to occur put the oxygen level in the treated water to be less than the untreated sample. After 3 days, the DO value in the samples were measured once again. The untreated sample show the lowest value of DO which almost reaching 0mg/L oxygen left. The DO in untreated sample after 3 days incubation was 0.97 which means 83.22% of DO was consumed by the microbes in the untreated sample. In the other hand, only 20.88% of DO was consumed in the 15 minutes sample treatment with ZnO-KCC-1. The data could be analysed that the ZnO-KCC-1 had the ability to reduce the BOD up to 60% in the POMSE wastewater.

Table 10: BOD value of treated textile wastewater in ZnO-KCC-1

Sample	Initial pH	Dissolve Oxygen (mg/L)		Dissolve Oxygen Consumption (%)
		Day 0	Day 3	
Initial	7.86	5.78	0.97	83.22
15 Minutes	7.41	5.56	4.79	20.88

The wastewater treatment via ZnO-KCC-1 have the ability to attack and further destroyed the microorganisms. The higher the value of oxygen consumption indicated higher value of microbes' presence that consume away remaining dissolve oxygen presence in the samples. The free radical of oxygen and hydroxide attacked the peptidoglycan layer of the microbes that was further denatured the microbes.

3.12 Kinetic study of photodegradation using ZnO-KCC-1

Kinetic is a study of how fast a complete reaction would take and also the study of the reaction rate. Reaction rate can definitely be measure in several ways based on the substance properties. Despite what method being done, the aim of reaction rate still to measure the changes of concentration per unit of time. Concentration can be measured in many ways depend on the nature of the substances involve. Which in this experiment, the kinetic study of the ZnO-KCC-1 was calculated by the used of ADMI values from DR6000 as the concentration against the time as portrayed in the following Table 11 and 12. There are 3 types of kinetic order reaction rate which are the zero order, first order and second order. The zero order was directly been terminated on consideration as the zero order was defined at where the reaction rate was independent on the concentration of the reactant and shall not show any effect on the product. That is where the zero-order theory did not compatible with this experimental result as the used of ZnO-KCC-1 did showed effect on the end product as well as altering the concentration of the catalyst will definitely affect the reaction rate of the processes. To identify the order of reaction between a first and second order of reaction, extensive calculation and graph was done to find the best fits result.

Table 11: The concentration- time data for the reaction of ZnO-KCC-1 in POMSE wastewater sample

Time (min)	Concentration (ADMI value)	First Order	Second order
		ln (Ca)	**1/Ca**
0	3500	8.160518	0.000286
15	2320	7.749322	0.000431
30	2560	7.847763	0.000391
45	2860	7.958577	0.00035
60	2400	7.783224	0.000417
75	2540	7.839919	0.000394
90	2500	7.824046	0.0004
105	2520	7.832014	0.000397
120	2520	7.832014	0.000397

From the Figure 7 and 8. the highest value of R² was at the first order reaction graph at value of 0.2095. Therefore, the reaction order of photodegradation of POMSE wastewater via ZnO-KCC-1 was at the first order of kinetic reaction. This means that the product of the degradation process was proportional to the loading of the reactant.

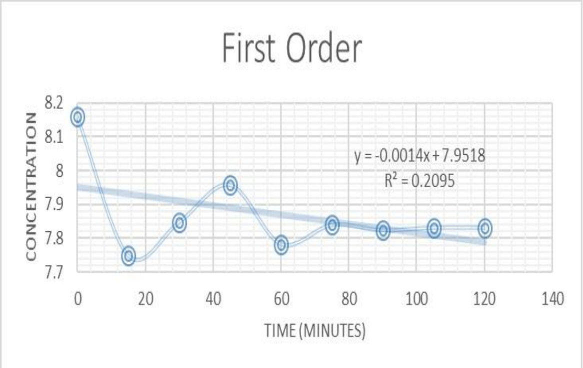

Figure 7: The concentration against time graph for First order reaction of ZnO-KCC-1 in POMSE wastewater samples

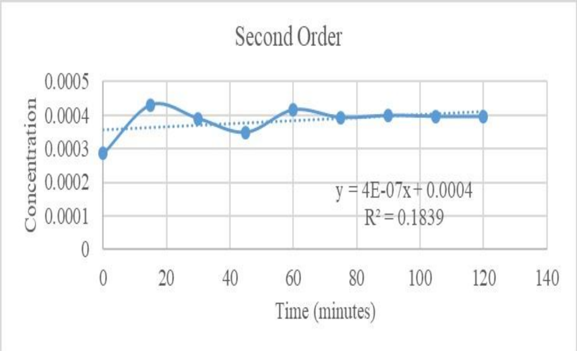

Figure 8: The concentration against time graph for second order reaction of ZnO-KCC-1 in POMSE wastewater samples

From the Figure 9 and 10, the highest value of R² was at the first order reaction graph at value of 0.1729. Therefore, the reaction order of photodegradation of textile wastewater via ZnO-KCC-1 was at the first order of kinetic reaction where the product of the degradation process was proportional to the loading of the reactant. Doubling the ZnO-KCC-1 will double the rate of photodegradation of organic compound in the textile wastewater.

Table 12: The concentration- time data for the reaction of ZnO-KCC-1 in textile wastewater sample

Time (minutes)	Concentration (ADMI value)	First Order	Second order
		ln (Ca)	**1/Ca**
0	7240	8.887376	0.000138
15	6120	8.719317	0.000163
30	6140	8.72258	0.000163
45	6280	8.745125	0.000159
60	6360	8.757784	0.000157
75	6320	8.751474	0.000158
90	6320	8.751474	0.000158

Figure 9: The concentration against time graph for first order reaction of ZnO-KCC-1 in textile wastewater samples

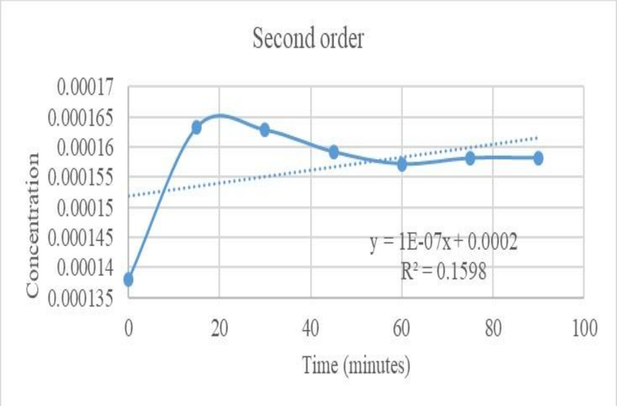

Figure 10: The concentration against time graph for second order reaction of ZnO-KCC-1 in textile wastewater samples

4. CONCLUSION

Based on the findings and results of the research, all the objectives were successfully achieved. It was proved that ZnO-KCC-1 has high potential in treating wastewater from palm oil mill and textile industry. This research successfully achieved the following objectives:

- The ZnO-KCC-1 was successfully synthesized via precipitation method
- FTIR results show that the ZnO-KCC-1 contained ZnO stretching and deformation while it also shows the presence of silica compound which indicated the KCC-1 in the synthesized ZnO-KCC-1
- The best results for both type of wastewater after been treated with ZnO-KCC-1 was identified to be at first 15 minutes and it had abilities to degrade chemical compound and microbe presence in the wastewater by examining through COD and BOD test. The value of DO consumption was reduced after 3 days treatment with the ZnO-KCC-1.
- The kinetic study of photodegradation using ZnO-KCC-1 was identified to be at first order of reaction for both type of wastewater. The elucidation of first order reaction defined as when doubling the ZnO-KCC-1 will double the degraded product. Altering the loading of ZnO-KCC-1 will affect the rate of degradation process.

Therefore, it was believed that photodegradation in the presence of ZnO-KCC-1 is appropriate to be used in industrial wastewater treatment applications. The use of modified fibrous silica had attracted many attentions from researchers and scientist globally as the benefits it possess to the environment has always been the prior concern for sustainable development.

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