LEACHATE TREATMENT THROUGH FENTON REACTION-AIDED-CHEMICAL TREATMENT

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Petrochemical Engineering

Faculty of Engineering and Green Technology
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DECLARATION

I hereby declare that this project is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this report entitled **“LEACHATE TREATMENT THROUGH FENTON REACTION-AIDED-CHEMICAL TREATMENT”** was prepared by **THONG HUI SHAN** has mat the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Petrochemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : ___________________

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Date : 12nd May 2022

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ABSTRACT

As landfill leachate consists a lot of hazardous compounds that will contaminate the water nearby, leachate treatment must be carried out in order to prevent water pollution and other health problems. There are several techniques developed can be used for leachate treatment, while the Fenton reaction using heterogeneous iron oxide catalyst can conquer the shortcomings of conventional homogeneous Fenton reaction. Therefore, this project is to investigate the performance of leachate treatment using heterogeneous Fenton reaction under different conditions and parameters, i.e. the presence of light, the presence of hydrogen peroxide, the size of iron oxide particles as well as the iron oxide concentration. The effect of other parameters such as pH, reaction time, hydrogen peroxide concentration was studied prior to the experiment. The optimal pH, reaction time and hydrogen peroxide concentration that are used in this study is pH 3.0, 120 minutes and 3 g/L respectively. The results indicated that the optimal conditions and parameters is nano-sized iron oxide particles at concentration of 150 mg/L in the presence of light and hydrogen peroxide. The opacity and COD removal efficiency is reported as 25.4% and 72.3% respectively. Other than that, the reaction kinetics of Fenton reaction was also studied and results show that second-order kinetic model could explain the data very well with a R^2 of 0.9138. The reusability of iron oxide catalyst was also studied in this project. The COD removal of Fenton reaction decreases from 68.49% to 45.21% after iron oxide catalyst was reused for 5 cycles. Hence, the iron oxide particles could be considered good in the term of reusability.

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LIST OF SYMBOLS / ABBREAVIATIONS

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
TOC	Total organic carbon
NO_2-N	nitrite-nitrogen
TDS	Total dissolved solids
TN	Total nitrogen
TSS	Total suspended solids
EDTA	Ethylenediaminetetraacetic acid
EDDS	Ethylenediamine-N,N’-disuccinic acid
UV-Vis spectroscopy	Ultraviolet-visible spectroscopy
ABS	Absorbance intensity

$\bullet OH$, $HO_2\cdot$	Hydroxyl radicals
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
NaOH	Sodium hydroxide
$\equiv Fe^{III}$-OH	Goethite surface
hv	Light

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, control of water pollution is attracting extensive attention worldwide, and one of the contributors to the water pollution is leachate production. Leachate is a by-product liquid produced and drained from solid waste disposal sites due to their physical, chemical and biological changes (Zhao, 2018) which contains several organic and inorganic matters such as heavy metals, inorganic salts, ammonia nitrogen (Li, Tang, Xu and Xie, 2021), making it hard to be treated (Warmadewanthi et al., 2021). The composition, flowrate (Salem, Mohammed and Fattah, 2021) and characteristic of the leachate can vary due to the landfill site age, the type of waste it contains (Japperi et al., 2021), stabilization level of the disposed waste as well as the leachate collection system (Wdowczyk and Szymańska-Pulikowska, 2020). Moreover, the characteristic of leachate can be also affected by the weather and hydrogeological condition (Warmadewanthi et al., 2021), where the high rainfall area will produce leachate with higher organic substances (Ilhami Firiyal Imtinan, Purwanto and Yulianto, 2020). The characteristic of leachate is high values of BOD, COD, high concentrations of ammonia nitrogen, heavy metals and humic substances (Mojiri et al., 2020), dark colour due to oxidation of ferrous to ferric form (Nagarajan, Thirumalaisamy and Lakshumanan, 2012) and smelly odour, which make the leachate treatment becomes troublesome and complicated (Raghab, Abd El Meguid and Hegazi, 2013). **Table 1.1** below shows the landfill leachate constituent concentration ranges.

Table 1.1: Landfill leachate constituent concentration ranges (Yusmartini and Setiabudidaya, 2013).

Leachate constituent	Transition phase (0 – 5 years)	Acid formation phase (5 – 10 years)	Methane fermentation (10 – 20 years)	Final maturation phase (> 20 years)
BOD	100 – 11000	1000 – 5700	100 – 3500	4 – 120
COD	500 – 22000	1500 – 71000	150 – 10000	30 – 900
TOC	100 – 3000	500 – 28000	50 – 2200	70 – 260
Ammonia	0 – 190	30 – 3000	6 – 430	6 – 430
NO_2-N	0.1 – 500	0.1 – 20	0.1 – 1.5	0.5 – 0.6
TDS	2500 – 14000	4000 – 55000	1100 – 6400	1460 – 4640

Other than that, leachate has contributed a lot to the wastewater treatment issues. There are many methods available to treat the leachate produced from landfill sites categorized into four steps including preliminary, primary, secondary and tertiary treatment. Different treatment process removes or reduces certain contaminants in the leachate such as large suspended solids, organic matters, toxic chemicals, and improve the leachate processability as well as the quality. The purpose of preliminary treatment process is to remove large solids by capturing them using nets and deposition which the heavy solids will accumulate at the bottom of the station before proceeding to next stage of treatment process. Primary treatment process removes settable organic solids by sedimentation process and some chemicals, such as coagulant and flocculant are added in this stage to help the substances to float on the water surface and the solids to settle at the bottom. After the sedimentation process is done, the effluent is sent for secondary treatment process. This treatment process reduces the BOD value, biodegradable organic substances contamination level by more than 20 – 30%, as well as the total suspended solids by more than 50 – 60% (Jasim, 2020).

Then, the leachate undergoes secondary treatment process to eliminate soluble organic substances that are not be able to be removed from primary treatment process as well as the remaining suspended solids. This secondary treatment is considered as biological treatment which conducted by microorganisms that consume organic substances and turn it into the final products. This stage can remove more than 85% of the organic substances, but the low level of nitrogen, heavy metals, non-biodegradable organic substances, bacteria and viruses is eliminated (Jasim, 2020). Hence, tertiary or advanced treatment process such as filtration, activated carbon adsorption, nitrification as well as chemical precipitation is needed for higher quality effluent produced from secondary treatment. The purpose of filtration is to reduce suspended solids and BOD, and activated carbon adsorption is to remove stubborn organic substances. Nitrification followed by denitrification is used to reduce ammonia and nitrogen concentration, while microbial uptake or chemical precipitation is used to eliminate phosphorus (National Research Council., 1996). **Table 1.2** shows the standard conditions for discharge of leachate by the Department of Environment Malaysia.

Table 1.2: Acceptable conditions for discharge of leachate (Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009).

	(1) **Parameter**	(2) **Unit**	(3) **Standard**
(i)	Temperature	°C	40
(ii)	pH value	-	6.0 – 9.0
(iii)	BOD_5 at 20°C	mg/L	20
(iv)	COD	mg/L	400
(v)	Suspended Solids	mg/L	50
(vi)	Ammoniacal Nitrogen	mg/L	5
(vii)	Mercury	mg/L	0.005
(viii)	Cadmium	mg/L	0.01
(ix)	Chromium, Hexavalent	mg/L	0.05
(x)	Chromium, Trivalent	mg/L	0.20
(xi)	Arsenic	mg/L	0.05
(xii)	Cyanide	mg/L	0.05
(xiii)	Lead	mg/L	0.10
(xiv)	Copper	mg/L	0.20
(xv)	Manganese	mg/L	0.20

(xvi)	Nickel	mg/L	0.20
(xvii)	Tin	mg/L	0.20
(xviii)	Zinc	mg/L	2.0
(xix)	Boron	mg/L	1.0
(xx)	Iron	mg/L	5.0
(xxi)	Silver	mg/L	0.10
(xxii)	Selenium	mg/L	0.02
(xxiii)	Barium	mg/L	1.0
(xxiv)	Fluoride	mg/L	2.0
(xxv)	Formaldehyde	mg/L	1.0
(xxvi)	Phenol	mg/L	0.001
(xxvii)	Sulphide	mg/L	0.50
(xxviii)	Oil and Grease	mg/L	5.0
(xxix)	Colour	ADMI*	100

**ADMI- American Dye Manufacturers Institute*

According to previous study, the types of toxic chemicals found in leachate produced from municipal waste landfill sites is reported to be 133, which is much higher than the industrial waste landfills that is reported to be 72 (Banch, M. Hanafiah, Alkarkhi and Abu Amr, 2019). Even though there are many physical, chemical or biological treatments used to treat leachate before it is discharged or recycled, a lot of challenges still be faced in source reduction and pollutants removal (Zhao, 2018). If the related authority did not put attention and take proper actions to enclose landfill sites, drain off leachate and undergo leachate treatment, it can result in serious soil and water pollution, affecting the plant growth as well as health issues to the user. When the water contained in the waste or rain water flows through the waste and leaches to the ground, the groundwater will be contaminated with the hazardous compounds and heavy metals (Kannan, 2016). The landfill leachate will also cause a serious impact to the aquatic life due to the dangerous substances contained in the leachate (Hassani et al., 2016). This is due to the reason that the major microorganisms found in the leachate are bacteria, viruses, fungi as well as algae, and most of them can spread diseases when consumed (Rajasulochana and Preethy, 2016).

Although there are many new technologies and techniques invented and implemented in order to treat leachate produced from landfill sites, challenges are still be faced in maximizing and enhancing the performance of the biochemical treatment, improving the total nitrogen (TN) removal rate as well as reducing the total processing cost. First and foremost, the treatment process for a leachate that has high organic compound and toxic substances using only one physicochemical or biochemical treatment process is unable to achieve the standard conditions of discharge leachate permitted by the government. Hence, the physicochemical and biochemical treatment process as well as nanofiltration and reverse osmosis has to be combined, resulting in high processing cost. Besides, the leachate quality and quantity inconsistency due to the rainfall volume, landfill age as well as waste disposed also becomes a difficulty to determine and operate a standard leachate treatment method as the contaminants and composition of the leachate may vary (Wang, Li, Tan and Wu, 2018).

1.2 Problem Statement

Solid waste management has become a serious problem faced by many countries due to the increasing trend of population and urbanization, resulting in high annual waste generation (Idris, Inanc and Hassan, 2004). In Malaysia, the total volume of leachate produced from landfill sites is estimated to be approximately 3 million litre/day due to heavy rainfall (Banch, M. Hanafiah, Alkarkhi and Abu Amr, 2019) and the average pH value of the leachate was 6.7 (Abd El-Salam and I. Abu-Zuid, 2015). However, fluctuations in leachate volume and pollutant concentration often occur and the performance of the leachate treatment process will be affected. The efficiency of secondary treatment will be affected significantly especially when the concentration of leachate is too high. In secondary treatment which utilise biological treatment process, bacteria are used to decompose organic substances either aerobically or anaerobically depending on the leachate condition. However, the high pH value condition of the leachate which attributed to the high concentration of contaminants cannot be accepted and adapted by the bacteria. Hence, the growth of bacteria is inhibited and the leachate treatment efficiency is affected (Haslina et al., 2021).

From literature review, an advanced oxidation technique, Fenton reaction is reported to be an effective and environmentally friendly treatment process that can be used to undergo oxidation reaction to degrade organic pollutants (Wu, Chen, Gu and Li, 2021; Chen, et al.,2020). This method is proposed to be included in the primary treatment process of the leachate treatment system in order to reduce the concentration of the contaminants in the leachate before it was sent for the biological treatment in secondary treatment process. However, even though Fenton reaction has been studied to improve the biodegradability of leachate, but the Fenton reaction that was commonly used is homogeneous Fenton reaction, which utilise iron salts, Fe^{2+} as the catalyst. In this study, the heterogeneous catalyst, iron oxides particles (Fe_3O_4) are proposed due to its novelty, low-cost synthesis (Litter and Slodowicz, 2017), and it can be removed easily from the treated effluent by sedimentation or filtration. The use of heterogeneous catalyst can also reduce the amount of iron sludge produced during Fenton reaction and prolong the catalyst lifetime without regeneration or replacement.

The iron oxide particles are proposed as it is heterogeneous and due to its magnetic property, which allows easy removal from the treated effluent for catalyst recovery and reuse in multiple stage by applying magnetic field. In addition, the reaction stops after Fe^{2+} ions were converted to Fe^{3+} completely in dark condition, and it is reported that the UV or UV-visible light can improve the oxidizing power of Fenton reaction (Rodríguez et al., 2005). This may due to more amount of $\cdot OH$ radicals are formed and Fe^{2+} regenerated by photo-reduction. As sunlight are available in Malaysia for the entire year, solar irradiation is also applied in this project to study the effect of light on the Fenton reaction rate using fluorescent light as light source. The performance and feasibility of heterogeneous Fenton reaction in leachate treatment will be investigated in the perspective of the reduction in leachate opacity and COD removal efficiency. From the economic perspective, the reusability of the iron oxide catalyst in Fenton reaction is also need to be identified in order to save cost and maintain the efficiency of Fenton reaction.

1.3 Aims and Objectives

i. To study the performance of Fenton reaction onto the opacity and COD removal of leachate.

ii. To study the reaction kinetics of heterogeneous Fenton reaction.

iii. To investigate the reusability of iron oxide particles in leachate treatment.

1.4 Outline of Study

In the first chapter, the background of landfill leachate is studied. There are also problem statements on the use of iron oxide particles as heterogeneous Fenton reaction to solve the problem of fluctuations in leachate volume and pollutant concentrations. The objectives of this project are also listed out.

In chapter two, the Fenton reaction is introduced. The effect of various parameters i.e. pH level, reaction time, Fe^{2+} ion concentration, H_2O_2 concentration, presence of light, on the pollutant removal rate was studied. In addition, the optimized Fenton reaction such as heterogeneous Fenton, photo-Fenton and electrochemical Fenton reaction was studied. In order to enhance the Fenton reaction, the effect of iron oxide particles as the catalyst and its reusability was investigated. Last but not least, the application of Fenton reaction in various industry such as textile dyes, pharmaceutical wastewater, olive mill wastewater was reviewed.

In chapter three, a research flowchart is prepared to outline the flow of the experiment which includes characterization or iron oxide particles, the performance study of Fenton reaction, the reaction kinetic study and lastly the reusability study of iron oxide particles. The materials, chemicals and equipment used in this project is listed out and the methodology to carry out the experiment are described in details.

In chapter four, the characterization or iron oxide particles such as zeta potential and absorption wavelength are showed and discussed. The opacity and COD removal Fenton reaction using different size of iron oxide particles under different condition is compared and discussed. Moreover, the reaction kinetics of heterogeneous Fenton reaction is studied by carrying out the Fenton reaction until it reaches equilibrium. Lastly, the reusability of iron oxide particles in Fenton reaction is discussed after the iron oxide particles were reused for 5 cycles.

In the last chapter, it concludes all the findings and analysis of this project. In order to optimized the project, some recommendations are proposed for further improvement.

CHAPTER 2

LITERATURE REVIEW

2.1 Fenton Reaction Introduction

The Fenton reaction is an oxidation process to enhance the oxidative potential of hydrogen peroxide (H_2O_2) which is activated by aqueous ferrous ions (Fe^{2+}) in the presence of H_2O_2, and hydroxyl radicals ($\bullet OH$, $HO_2\cdot$) are produced (Vasquez-Medrano, Prato-Garcia and Vedrenne, 2018; Ameta, K. Chohadia, Jain and Punjabi, 2018). Hydroxyl radicals can oxidize refractory organic pollutants in the wastewater, and convert them into carbon dioxide, water and inorganic salts effectively. At the same time, the iron produced by Fenton reaction will act as a flocculant. The Fenton reaction was named after Henry John Horstman Fenton who firstly discovered the specific electron transfer in the metals (Sillanpää and Shestakova, 2017) to oxidize tartaric acid in 1894. However, the first application of Fenton reaction to destroy hazardous organic compounds was implemented until the late 1960s (Xu, Wu and Zhou, 2020). The Fenton reaction mechanisms (**Equation 2.1–2.6**) is shown below (Ameta, K. Chohadia, Jain and Punjabi, 2018).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (2.1)$$

$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (2.2)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad (2.3)$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (2.4)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (2.5)$$

$$\text{Organic compound} + \bullet OH \rightarrow \text{Degraded products} \quad (2.6)$$

Where **Equation 2.1** shows the initiation step by Fe^{2+} ions to catalyse the decomposition of H_2O_2 and produce $\bullet OH$ radicals, while **Equation 2.3** shows the termination of $\bullet OH$ radical production. The Fe^{3+} ions formed from the reaction may catalyse H_2O_2 and convert it into water and oxygen, which is undesired (Pawar and Gawande, 2015). The Fe^{2+} ion production can be enhanced by some catalysts such as iron-oxide based catalysts, ferrites and magnetite, other iron minerals as well as iron supported on other materials (Thomas, Dionysiou and Pillai, 2021).

The advantages of using Fenton reaction in treating wastewater are it offers high degradation efficiency and it is easy to be operated and maintained. Besides, Fenton reaction does not require any complicated equipment and it is environmentally friendly as hydrogen peroxide can be break down into water and oxygen (Xu, Wu and Zhou, 2020; Domingues et al., 2018). Other than that, the Fenton reagent is also cheaper and easy to handle. The reaction does not require any energy to activate H_2O_2 as it takes place at room temperature and atmospheric pressure. Fenton reaction offers shorter reaction time compared to other advanced oxidation reactions. Due to the homogeneity of the catalyst used in Fenton reaction, there is no problem exist in the mass transfer of the water, and no energy formation from catalyst (Nidheesh and Gandhimathi, 2012; Pawar and Gawande, 2015). Therefore, Fenton reaction was reported to be a feasible method as the pre-treatment for polluted water to oxidize organic pollutants, improve the biodegradability, solubility and coagulation, which are useful for further treatment (Xu, Wu and Zhou, 2020).

However, Fenton reaction also has some drawbacks at which the dissolved iron in the treated effluent needs to be removed before discharging as the amount of catalyst required is always higher than the standard of iron permitted for effluent discharge. Hence, the treated effluent will be neutralized by adding alkaline after the oxidation reaction, because insoluble $Fe(OH)_3$ complexes will be produced and removed as iron sludge. This method requires more spaces and higher capital cost; hence a new integrated rapid system is preferred for industrial application (Chen et al., 2019). The conventional Fenton reaction is shown in **Figure 2.1** below, which includes acid regulation, catalyst mixing, oxidation reaction, neutralization and solid-liquid separation. Moreover, Fenton reaction also has a narrow pH range (pH 2 – 3), where the reaction is easy to be operated on the laboratory scale, but not cost effective when applied on the industrial scale (Rueda-Márquez, Levchuk, Manzano and Sillanpää, 2020). The consumption of Fe^{2+} ions during the Fenton reaction is also occur more rapidly than their regeneration (Nidheesh and Gandhimathi, 2012). The high hydrogen peroxide consumption and the accumulation of Fe^{3+} sludge will also affect the oxidation efficiency. Therefore, both heterogeneous and homogeneous catalyst such as ferric oxide, iron minerals and nano zero-valent iron were used to replace Fe^{2+} ions, and the light and/or electro-driven Fenton reaction can be used. This method can also reduce the amount of iron catalyst required. (Xu, Wu and Zhou, 2020; Domingues et al., 2018).

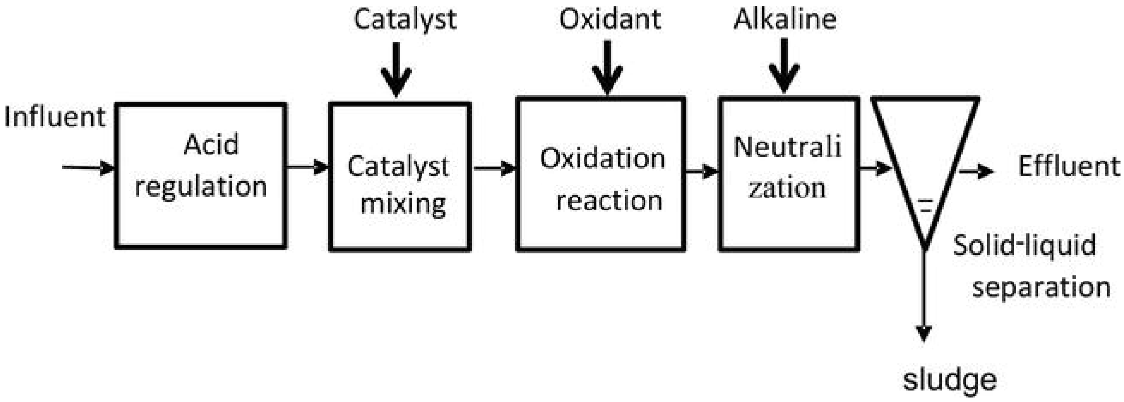

Figure 2.1: Schematic diagram of Fenton reaction process (Xu, Wu and Zhou, 2020; Domingues et al., 2018).

2.2 Kinetic Study of Leachate Treatment by Fenton Reaction

In order to design a Fenton reactor, the reaction rates in the reactor must be determined as it can directly affect the size of the reactor. Hence, the reaction kinetics need to be studied and the pollutant removal rates must be predicted for designing and modelling of Fenton treatment process. The kinetics for COD, TSS, TOC and colour removal of Fenton reaction in leachate treatment also need to be determined in order to predict the required reaction time. The study used leachate sample with COD value of 3895±180 mg/L and homogeneous catalyst, Fe^{2+} salts without solar irradiation (Ahmadian et al., 2013). **Table 2.1 and 2.2** shows the kinetic analysis conducted by fitting the time-course performance data with zero-, first- and pseudo-second-order kinetic equations as well as the results.

Table 2.1: Equations and linear forms of kinetic models (Ahmadian et al., 2013).

Kinetic Model	Equation	Linear Form
Zero-order	$r_c = \frac{dC}{dt} = k_0$	$C_t - C_0 = -k_0 t$
First-order	$r_c = \frac{dC}{dt} = k_1 C$	$\ln \frac{C_t}{C_0} = -k_1 t$
Second-order	$r_c = \frac{dC}{dt} = k_2 C^2$	$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t$

Table 2.2: Results of kinetic models (Ahmadian et al., 2013).

Kinetic Model	Parameter	COD	TOC	TSS	Colour
Zero-order	K_0	27.93	4.48	9.04	18.58
	R^2	0.93	0.88	0.94	0.76
First-order	K_1	0.012	0.004	0.009	0.013
	R^2	0.98	0.92	0.99	0.91
Second-order	K_2	6×10^{-6}	4×10^{-6}	1×10^{-5}	1×10^{-5}
	R^2	0.97	0.91	0.95	0.94

Where r_c represents the conversion rate, k_0, k_1, and k_2 represents the reaction rate constant, t represents reaction time, while C_0 and C_t represents the initial and final pollutant concentration in the solution respectively. From **Table 2.1 and 2.2**, it is shown that the first-order kinetic model offers higher R^2, which can simulate COD, TSS, TOC and colour removal in Fenton reaction successfully. It is also shown that the COD, TSS, TOC and colour removal efficiency is highly related to the initial pollutant concentration (Ahmadian et al., 2013). **Figure 2.2 to 2.4** shows the zero-, first- and second-order kinetic study results on COD, TOC, TSS and colour removal efficiency respectively. However, the experiment was carried out using homogeneous catalyst without sunlight, hence the reaction kinetics of Fenton reaction using heterogeneous catalyst under light will be studied in this project.

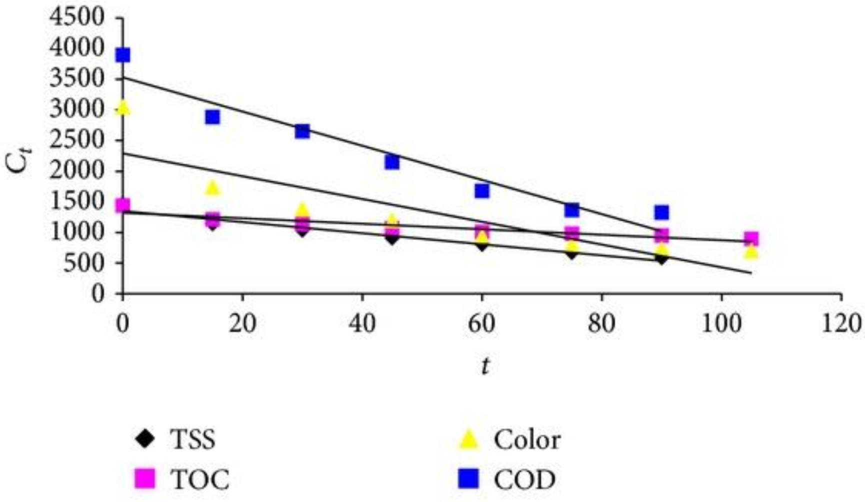

Figure 2.2: Zero-order kinetic study results on COD, TOC, TSS and colour removal efficiency (Ahmadian et al., 2013).

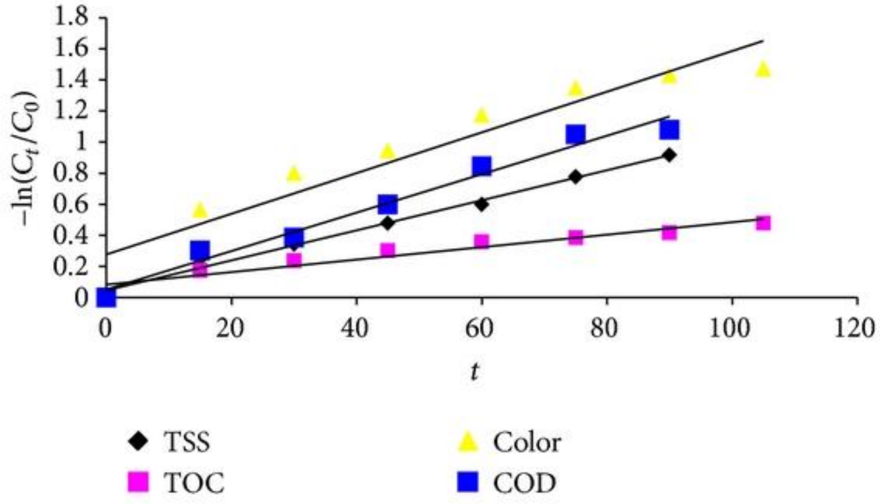

Figure 2.3: First-order kinetic study results on COD, TOC, TSS and colour removal efficiency (Ahmadian et al., 2013).

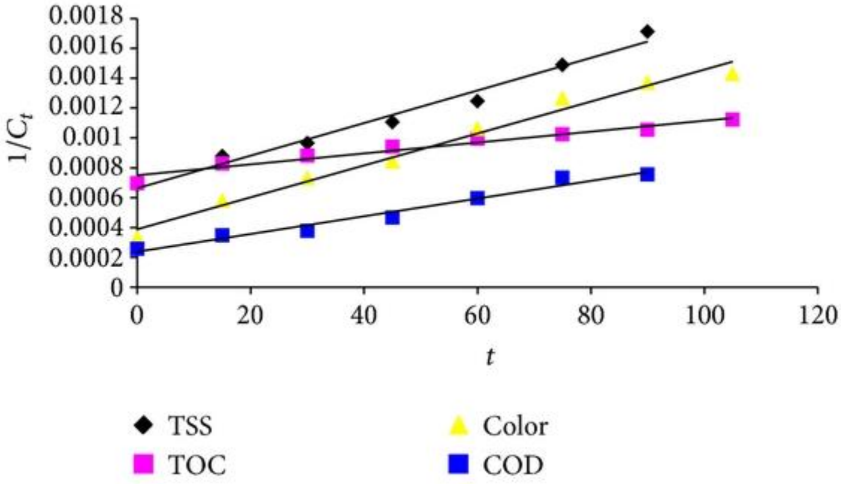

Figure 2.4: Second-order kinetic study results on COD, TOC, TSS and colour removal efficiency (Ahmadian et al., 2013).

2.3 Operating Parameters

2.3.1 Effluent pH Level

The degradation efficiency of •OH radical for COD, TOC, TSS and colour removal is related to the pH level of the water. **Figure 2.5** below shows the effect of pH level in water on COD, TOC, TSS and colour removal efficiency in 90 minutes reaction time. The optimum pH range of Fenton reaction reported is approximately 3.0. At that pH level, the efficiency of Fenton reaction is high due to higher solubility of Fe^{3+} ions in water. However, when the pH falls below 3.0, iron complexes such as $[Fe(H_2O)_6]^{2+}$ may be formed, and slow down the reaction of iron with H_2O_2, leading to lesser amount of •OH radicals generated. On the other hand, if the water is basic, the reaction between iron and hydroxide ions (OH^-) will produce iron hydroxide $Fe(OH)_2$ or $Fe(OH)_3$, which precipitates and does not react with H_2O_2 (Rueda-Márquez, Levchuk, Manzano and Sillanpää, 2020; Ahmadian et al., 2013). Therefore, Fenton reaction under acidic condition is preferred compared to basic condition. In the pH range of 1 – 7, pH 3 is most preferred in this study as it offers the highest COD, TOC, TSS and colour removal efficiency.

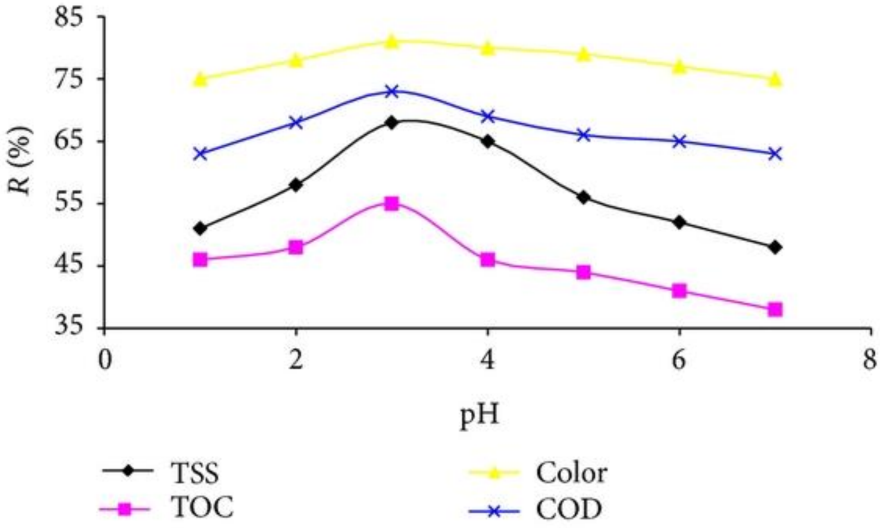

Figure 2.5: Effect of pH level in water on COD, TOC, TSS and colour removal efficiency in leachate treatment (90 minutes reaction time) (Ahmadian et al., 2013).

2.3.2 Reaction Time

The reaction duration can also affect the COD, TOC, TSS and colour removal efficiency for Fenton reaction. **Figure 2.6** below shows the effect of reaction time on COD, TOC, TSS and colour removal efficiency when pH level is fixed at 3. When the reaction time is increased, the COD, TOC, TSS and colour removal efficiency will also increase. The removal efficiency of Fenton reaction increases until the reaction time reaches 105 minutes. The effect of further increase in reaction time on the removal efficiency is not significant. This means that the reaction between iron salts and H_2O_2 to produce •OH radicals is almost complete. Based on some studies on electro-Fenton reaction, the optimal reaction time is reported to be less than 30 minutes (Ahmadian et al., 2013). Hence, the preferred reaction time for Fenton reaction in this study is 120 minutes.

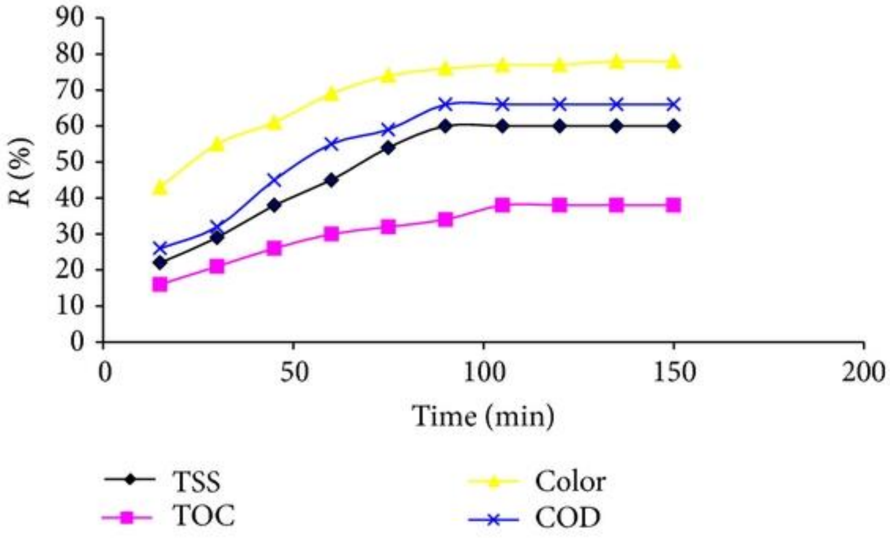

Figure 2.6: Effect of reaction time on COD, TOC, TSS and colour removal efficiency in leachate treatment (pH level: 3) (Ahmadian et al., 2013).

2.3.3 Fe^{2+} Concentration

The effect of iron salt concentration also plays an important role on the Fenton reaction efficiency. Iron salts can act as catalyst in Fenton reaction, at which its increasing concentration can improve the removal efficiency of COD, TOC, TSS and colour. However, it is still limited to its reasonable concentration. When amount of iron salt is excessive, the •OH radicals produced will be consumed by the excess iron salts through **Equation 2.3**, and decrease the efficiency of oxidation. **Figure 2.7** below shows the effect of Fe^{2+} concentration on COD, TOC, TSS and colour removal efficiency. According to Ahmadian et al. in 2013, the optimal Fe^{2+} concentration for highest COD, TOC, TSS and colour removal is 1600 mg/L when the H_2O_2 dosage is 2500 mg/L and the pH level is 3.0 in reaction time of 105 minutes.

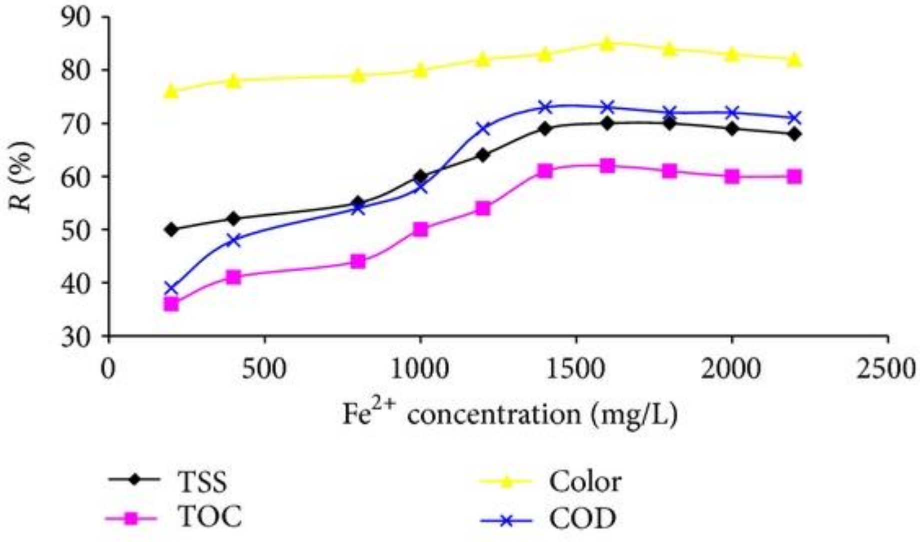

Figure 2.7: Effect of Fe^{2+} concentration on COD, TOC, TSS and colour removal efficiency in leachate treatment (H_2O_2: 2500 mg/L, pH level: 3, 105 minutes reaction time) (Ahmadian et al., 2013).

2.3.4 H_2O_2 Dosage

The dosage of H_2O_2 is also an important factor that can affect the COD, TOC, TSS and colour removal of Fenton reaction. This is due to H_2O_2 dosage depends heavily on the initial COD concentration of the effluent, and it will affect the amount of •OH radicals produced. At low H_2O_2 concentration relative to initial COD concentration, the efficiency of Fenton reaction may be more than 100% as the organic substances is oxidized by •OH radicals produced instead of H_2O_2. On the other hand, when H_2O_2 dosage is increased, the efficiency drops to below 100% because the •OH radicals produced will be consumed by excess H_2O_2 through **Equation 2.2**. The theoretical mass ratio of removable COD to H_2O_2 is 470.6/1000 which 1000 mg/L H_2O_2 removes 470.6 mg/L COD by oxidation theoretically (Deng and Englehardt, 2006). **Figure 2.8** below shows the effect of H_2O_2 concentration on COD, TOC, TSS and colour removal efficiency. Based on the study proposed by Ahmadian et al. (2013), when the Fe^{2+} concentration of 1800 mg/L, pH level of 3 and reaction time of 105 minutes was fixed in the Fenton reaction process, the removal efficiencies increased gradually with the increasing of H_2O_2 concentration from 500 mg/L to 3000 mg/L, and no significant change was observed upon the further increasing of H_2O_2 concentration. Since the highest removal efficiencies were observed at 3000 mg/L of H_2O_2 concentration, hence the H_2O_2 concentration that will be used in this study is 3 g/L.

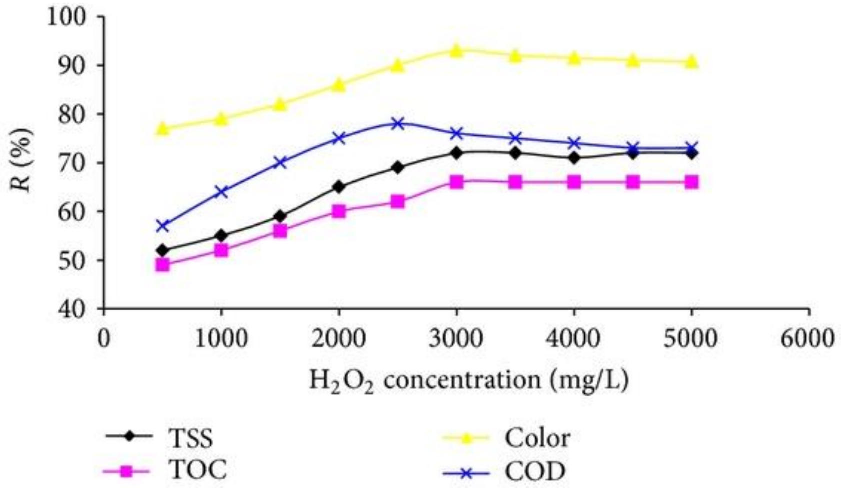

Figure 2.8: Effect of H_2O_2 concentration on COD, TOC, TSS and colour removal efficiency in leachate treatment (Fe^{2+}: 1800 mg/L, pH level: 3, 105 minutes reaction time) (Ahmadian et al., 2013).

2.3.5 Presence of Sunlight

Due to the effect of solar irradiation in leachate was not commonly studied, the effect of solar irradiations on the COD removal in Metronidazole (MTZ) synthetic solutions was studied by Ammar, Brahim, Abdelhédi and Samet in 2016 in order to evaluate the effect of solar irradiation on the Fenton reaction efficiency. **Figure 2.9** below shows the effect of sunlight on COD removal in MTZ synthetic solutions using (i) H_2O_2, (ii) H_2O_2 + solar irradiations, (iii) $H_2O_2 + Fe^{2+}$ (dark Fenton) and (iv) $H_2O_2 + Fe^{2+}$ + solar irradiations (photo-Fenton). According to Ammar, Brahim, Abdelhédi and Samet in 2016, the COD removal efficiency of process (i) was increased from 19% to 36% upon solar irradiations (ii) after 30 minutes of reaction time, and the reactor performance was improved for 47%. Moreover, the same trend was observed when comparing the process (iii) and (iv). The COD removal efficiency of process (iii) was increased from 72% to 86% when the reaction was enhanced by the sunlight. From the results evaluated, it can be summarised that solar irradiations can improve the Fenton reaction efficiency as more amount of $\bullet OH$ radicals are formed and Fe^{2+} regenerated from $[FeOH]^{2+}$ by photo-reduction.

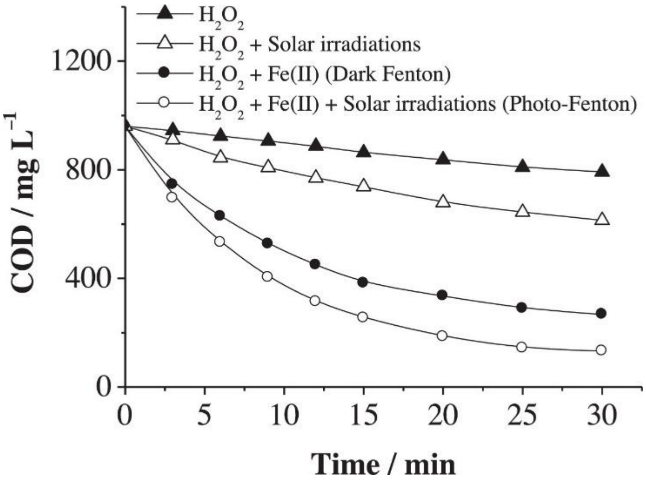

Figure 2.9: Effect of sunlight on COD removal in MTZ synthetic solutions ($[Fe^{2+}]_0$: 1 mmol/L, $[H_2O_2]$: 2 mmol/min, T = 35 °C) (Ammar, Brahim, Abdelhédi and Samet, 2016).

2.4 Optimized Fenton Reaction

2.4.1 Heterogeneous Fenton Reaction

Heterogeneous Fenton reaction is a method that can produce $^{\bullet}OH$ radicals by pure heterogeneous catalytic mechanism, or homogeneous Fenton reaction due to leached iron from the solid catalyst. The application of a heterogeneous catalyst can reduce the amount of iron sludge formed in Fenton reaction, and prolong the catalyst lifetime without regeneration or replacement as well as remove the catalyst from the treated wastewater easily by sedimentation or filtration (Bolobajev et al., 2014). The iron-based materials used in the Fenton reaction are commonly considered as excellent heterogeneous Fenton reaction catalyst because they are cheap, have insignificant toxicity levels, high catalytic activity as well as easy to be recovered. The mechanism of heterogeneous Fenton reaction on the reaction between H_2O_2 and solid iron oxide catalyst (goethite) is shown below (Thomas, Dionysiou and Pillai, 2021):

$$\equiv Fe^{3+}\text{-}OH + H_2O_2 \leftrightarrow (H_2O_2)_s \tag{2.7}$$

$$(H_2O_2)_s \leftrightarrow (\equiv Fe^{2+\bullet}O_2H) + H_2O \tag{2.8}$$

$$(\equiv Fe^{2+\bullet}O_2H) \rightarrow \equiv Fe^{2+} + HO_2^{\bullet} \tag{2.9}$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+}\text{-}OH + {}^{\bullet}OH \tag{2.10}$$

where $\equiv Fe^{3+}$ represents the iron on the surface. H_2O_2 reacts on the goethite surface ($\equiv Fe^{III}$-OH) and produce complex $(H_2O_2)_s$ (**Equation 2.7**). Then, a charge is transferred from ligand to metal and a transition state complex ($\equiv Fe^{2+\bullet}O_2H$) is formed (**Equation 2.8**). The complex ($\equiv Fe^{2+\bullet}O_2H$) is then separated to form $\equiv Fe^{2+}$ and $HO_2^{\bullet}$ radicals (**Equation 2.9**). Finally, $\equiv Fe^{2+}$ reacts with H_2O_2 to generate $^{\bullet}OH$ radicals and $\equiv Fe^{3+}$-OH (**Equation 2.10**). This mechanism demonstrates the continuous cycle of Fe^{2+} and Fe^{3+} ions on the surface, which caused goethite a heterogeneous catalyst (Thomas, Dionysiou and Pillai, 2021). As a conclusion, heterogeneous system is preferred than homogeneous system as it can reduce the iron sludge production and the catalyst can be removed more easily. Hence, heterogeneous iron oxide catalysts will be used in this study.

2.4.2 Photo-Fenton Reaction

During the conventional Fenton reaction, Fe^{3+} ions are formed and accumulated due to slower reduction of Fe^{3+} to Fe^{2+} (**Equation 2.4**) compared to $\cdot OH$ radical generation (**Equation 2.1**). However, Fe^{2+} ions have better performance compared to Fe^{3+} ions on the conversion of H_2O_2 into $\cdot OH$ radicals, and hence the accumulation of Fe^{3+} ions will lower down the reaction efficiency (Domingues et al., 2018). In order to improve the efficiency of Fenton reaction, light is introduced to the Fenton reaction to promote the in-situ circulation from Fe^{3+} to Fe^{2+} ions, which produces more $\cdot OH$ radicals compared to the conventional Fenton reaction. The hydroxy-Fe^{3+} complexes formed after Fenton reaction which exist as $Fe(OH)^{2+}$ complexes, will undergo regeneration to Fe^{2+} ions by photo-reduction of Fe^{3+} ions in the photo-Fenton reaction (**Equation 2.11**). The regenerated Fe^{2+} ions will continue the cycle to react with H_2O_2 to produce $\cdot OH$ radicals and Fe^{3+} ions. Moreover, the direct photolysis of H_2O_2 will also produce $\cdot OH$ radicals (**Equation 2.12**), which will degrade the organic substances, and improve the degradation rate of the organic substances. The mechanisms of photo-reduction of Fe^{3+} ions and direct photolysis of H_2O_2 is shown below (Xu, Wu and Zhou, 2020).

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + \cdot OH \qquad (2.11)$$

$$H_2O_2 + hv \rightarrow 2\ \cdot OH \qquad (2.12)$$

However, photo-Fenton reaction only offers better performance when degrading organic substances with low concentrations. This is due to the light absorptivity of $Fe(OH)^{2+}$ ions could be affected by the high concentration organic substances, resulting in longer time is required for the light radiation and greater amount of H_2O_2 needed. By adding some organic ligands such as EDTA, EDDS, oxalate and other carboxylic acid to Fe^{3+} ions using photocatalysis, the efficiency of photo-Fenton reaction can be improved. The use of these ligands may enhance the photo-reduction of Fe^{3+} ions to Fe^{2+} ions as well as the regeneration of $\cdot OH$ radicals, as iron-ligands have higher photosensitivity to capture light in wider wavelength and utilise all the useful solar radiation spectrum. In addition, iron-ligands can also improve H_2O_2 activation, $\cdot OH$ radical production as well as broaden the operating pH range of Fenton reaction as iron will dissolve and no iron will precipitate in the basic water during the reaction (Xu, Wu and Zhou, 2020; Domingues et al., 2018).

When photo-Fenton reaction is implemented, the concentration of iron in the water is lower than the conventional Fenton reaction without light, due to the rapid photo-reduction of iron complexes. If the iron concentration in the treated effluent is below the standard discharge limit permitted by the government, the iron removal process can be also eliminated. The iron concentration in effluent changes dramatically, depending on the type of effluent or industry. From literature review, photo-Fenton reaction can even take place at very low concentrations of dissolved iron (μg/L) in water. It was reported that 50–90 μg/L of natural iron content was adequate for an efficient photo-Fenton reaction (Rueda-Márquez, Levchuk, Manzano and Sillanpää, 2020). Yet, the photo-Fenton reaction still has limited efficiency due to low photoactivity of the produced iron complexes under UV-visible light and slow photo-reduction on the iron complexes surface through ligand-to-metal charge mechanism (Gutierrez-Mata et al., 2017).

In addition, **Table 2.3** below shows the comparison of Fenton reagent dosage and COD removal in photo-Fenton reaction of landfill leachate. The UV radiation is reported to offer a positive effect to the photo-Fenton reaction in mature leachate. The TOC removal is observed to be 51% when an energy of 80 kW/m^3 was input into the reaction, which is three times higher than the removal efficiency in dark condition (Deng and Englehardt, 2006). According to literature, the removal rate of TOC by UV/H_2O_2 system could reach 95% within 150 minutes, showing strong oxidation capacity of UV-Fenton reaction. However, UV-Fenton reaction has only short working lifespan, high energy consumption, high risk for environmental pollution as well as high cost. Hence, solar is used as an alternative free and renewable energy source in order to overcome the drawbacks in UV-Fenton reaction. The removal rate of TOC by solar photo-Fenton reaction is increased by 2.46 times to 90% compared with conventional Fenton reaction process, also showing the great oxidation capacity of solar photo-Fenton reaction (Zhang et al., 2019). Therefore, due to fast Fe^{2+} ion regeneration by photo-reduction and $\bullet OH$ radical generation, photo-Fenton is concluded to be better than conventional Fenton in dark condition., which will also be applied in this study.

Table 2.3: Comparison of Fenton reagent dosage and COD removal in photo-Fenton reaction of landfill leachate (Deng and Englehardt, 2006).

Leachate Characteristic	Fenton Type	Initial COD (mg/L)	Reagent Dosage		Molar H_2O_2:Fe^{2+}	COD removal efficiency	Consumed reagent	
			H_2O_2 (mg/L)	Fe^{2+} (Fenton), Fe^{3+}(Fenton-like) (mg/L)			H_2O_2 (mg/mg COD)	Fe^{2+} (Fenton) Fe^{3+}(Fenton-like) (mg/mg COD)
Pre-treated biologically	Photo-Fenton	1150	1150	72	26.2	70	1.43	0.09
Pre-treated biologically	Photo-Fenton-like	440	660	31	35.0	80	1.88	0.09
Mature	Photo-Fenton	1150	2438	56	1	70	3.03	0.07
Pre-treated biologically	Photo-Fenton	513	800	N/A	N/A	71	2.19	N/A

N/A: Not available.

2.4.3 Electrochemical Fenton Reaction

The electrochemical Fenton reaction is the combination of electrochemical process with conventional Fenton (CF) reaction to produce Fe^{2+} and H_2O_2 by electrochemical process and form $\bullet OH$ radicals more efficiently, improving the Fenton reaction performance (Xu, Wu and Zhou, 2020). During the electrochemical Fenton reaction, H_2O_2 is generated continuously in an acidic medium (Rueda-Márquez, Levchuk, Manzano and Sillanpää, 2020) from the two-electron oxygen reduction at cathodes (**Equation 2.13**), while the Fe^{2+} is regenerated at cathodes (**Equation 2.14**) or at iron anodes (**Equation 2.15**) at the same time. The types of electrochemical Fenton reaction include Fered-Fenton (EF-FeRe), electrochemical peroxidation/anodic Fenton (EF-FeOx), electro-Fenton (EF- H_2O_2-FeRe), and peroxi-coagulation (EF-H_2O_2-FeOx). The CF involves only the addition of H_2O_2 and Fe^{2+} in the water, EF-FeRe involves the addition of both reagents and regeneration of Fe^{2+}, EF-FeOx involves the addition of H_2O_2, generation of Fe^{2+} from iron anode and regeneration of Fe^{2+}, EF-H_2O_2-FeRe involves the addition of Fe^{2+}, generation of H_2O_2 and regeneration of Fe^{2+}, and EF-H_2O_2-FeOx involves the generation of H_2O_2 and Fe^{2+}. **Figure 2.10** below shows the schematic diagram of CF reaction and various types of EF reaction (Gutierrez-Mata et al., 2017).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2.13)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (2.14)$$

$$Fe - 2e^- \rightarrow Fe^{2+} \quad (2.15)$$

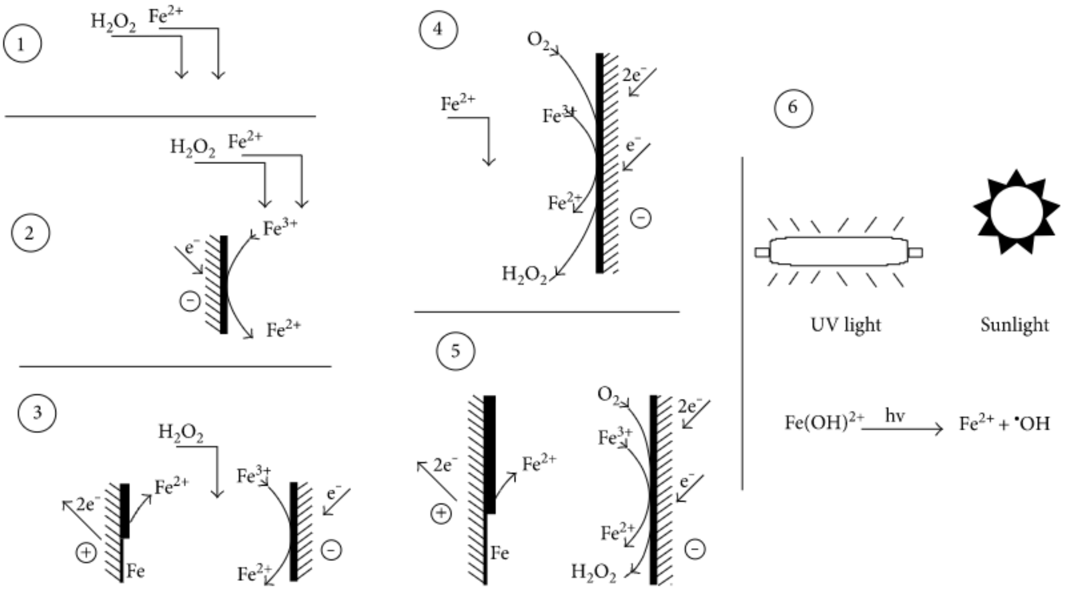

Figure 2.10: Schematic diagram of (1) conventional Fenton, (2) Fered-Fenton, (3) electrochemical peroxidation/anodic Fenton, (4) electro-Fenton, (5) peroxi-coagulation, and (6) combination of CF and EF with UV or sunlight radiation.

In fact, electro-Fenton reaction is the most common electrochemical Fenton reaction which offers better degradation performance of the organic substances compared to conventional Fenton reaction. It can generate H_2O_2 via an electrochemical process during the reaction, increasing the degradation efficiency of Fenton reaction, reducing the cost and the risks arise during transportation at one time. This is due to the reduction of Fe^{3+} ions by regeneration of Fe^{2+} ions on the cathode, which reduces the formation of iron sludge. The organic substances degradation method is also diversified into Fenton oxidation, anodic oxidation, flocculation as well as electric adsorption. However, the main drawback of electro-Fenton is the slow generation of H_2O_2 due to the low solubility of oxygen in the water. Furthermore, the efficiency of electro-Fenton is also depending on the electrode characteristic, pH level, concentration of the catalyst used, electrolytes, dissolved oxygen level, density and the temperature. When the pH level of water is lower than 3, the degradation efficiency is low (Xu, Wu and Zhou, 2020). Therefore, electrochemical Fenton reaction is not being studied in this project due to its slow H_2O_2 generation rate.

2.5 Iron Oxides as Fenton Reaction Catalyst

When the pollutant concentrations in water are high, the oxidation of the organic pollutants by H_2O_2 alone is not effective. This is due to the low reaction rate of H_2O_2 at its reasonable concentration. By adding iron oxides which act as the catalyst, H_2O_2 can be activated to produce $\bullet OH$ radicals which are strong oxidants. There are some iron oxides that can be used as Fenton reaction catalyst such as magnetite, ferrihydrite, hematite, goethite, schwertmannite, lepidocrocite, and maghemite. Iron oxides has high biodegradability, and it is non-toxic and environmentally friendly (Pawar and Gawande, 2015; Thomas, Dionysiou and Pillai, 2021). The degrees of structural order and crystallinities of iron oxides vary depending on the conditions for crystal formation. Low crystallinity iron oxides produce more iron ions than high crystallinity iron oxides especially in acidic condition (Wang, Liu and Sun, 2012).

Iron oxides are also semiconductors which have the potential to act as photocatalysts. Upon light irradiation, the production of Fe^{2+} from the reduction of Fe^{3+} in heterogeneous Fenton reaction is enhanced. As a result, the amount of $\bullet OH$ radicals generated on the catalyst surface by the reaction between Fe^{2+} and H_2O_2 is also increased. In the iron oxide systems, Fe^{2+} ion is part of the crystal system of oxides. It enhances the stability of the catalyst towards the division of H_2O_2, and reduces Fe^{2+} ions leaching from the catalyst (Thomas, Dionysiou and Pillai, 2021). In addition, the nanosized iron oxides can increase their catalytic activity but good catalyst reusability is also needed. Solid iron oxides can also overcome the disadvantages of homogeneous catalyst to remove the iron sludge after the oxidation reaction. However, the separation of the nanosized particles from the mixture after reaction is complicated. Hence, iron oxides that can settle down at the bottom of the reactor aided by a magnetic field under the reactor for easy separation (Wang, Liu and Sun, 2012). As a conclusion, iron oxide is chosen as the catalyst to be used in this study because it is semiconductors which can play as photocatalysts, and it has good magnetic property which can be removed easily using magnetic field after the reaction.

2.6 Reusability of Iron-containing Sludge after Fenton Reaction

During the Fenton reaction, iron sludge is produced due to the accumulation of iron complexes after neutralization process. The iron sludge produced could be hazardous due to the residual organic substances may be adsorbed from treated wastewater, so it requires adequate treatment and disposal method or it may lead to secondary pollution. Based on literature, the iron sludge could be reused as a coagulant for pre-treatment of wastewater before the Fenton reaction treatment, reducing up to 50% in the amount of coagulant required. However, the iron-containing sludge could be only be reused one time for this method. The iron sludge formed is also reported to be reusable as an iron source for new Fenton reaction catalyst synthesis or as a Fenton reaction catalyst after some regeneration process. The iron sludge can be regenerated by thermal regeneration and further re-dissolution of iron-containing substances by acid, chemical regeneration with reducing agent as well as electrochemical reduction. Yet, the regeneration of iron sludge will increase the overall cost of leachate treatment process, hence the reuse of the iron sludge without regeneration is preferable (Bolobajev et al., 2014; Zhou and Zhang, 2017).

Figure 2.11 below shows the iron sludge reusability and the COD removal of Nonylphenol ethoxylates (NPEOs) wastewater using the reduced iron sludge. According to Zhou and Zhang in 2017, the iron sludge can be reused by reduction to produce Fe^{2+} ions using ferrous sulfide (FeS) under a strongly acidic condition. When the FeS dosage of 5 g/L, 25 g/L and 50g/L, the Fe^{2+} ion concentration in the sludge is 140.7 mg/L, 278.1 mg/L and 367.6 mg/L respectively. From **Figure 2.11**, it can be seen that the Fe^{2+} ion concentration in the iron sludge is slowly increasing, and the Fe^{3+} ion concentration only shows a slight increase. This is due to the dissolution rate of FeS in the sludge is slower as it is limited by the Fe^{2+} produced from reduction of iron sludge. The reduced iron sludge is then reused for Fenton reaction in NPEOs wastewater treatment, and the COD removal achieved was approximately 80%.

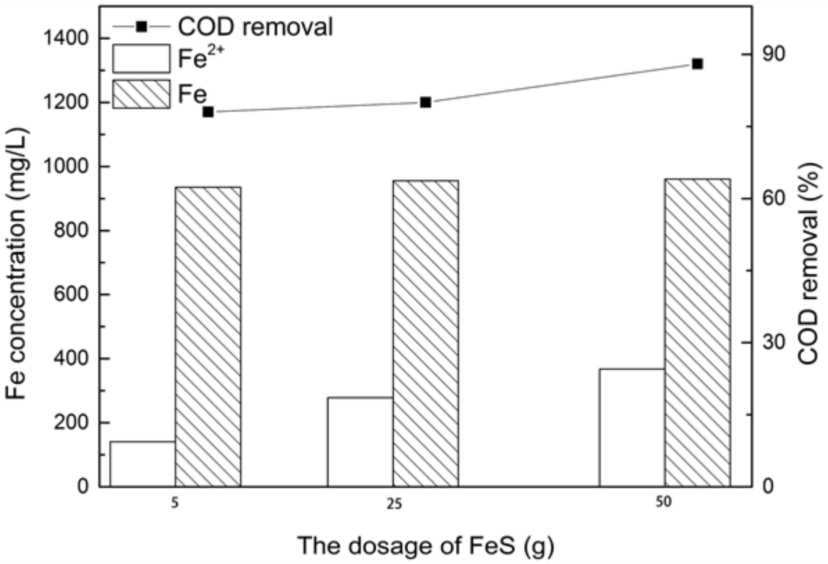

Figure 2.11: Effect of FeS concentration in iron sludge on its reusability and the COD removal of NPEOs wastewater (Zhou and Zhang, 2017).

On the other hand, Cao et al. had studied the feasibility of reusing iron sludge obtained from the reaction directly as the Fenton-like catalyst in chemical wastewater after it is dewatered and dried in 2009. The effect of the reused time of the iron sludge on the COD removal and TOC content is shown in **Figure 2.12 and 2.13**. The COD removal of the Fenton-like reaction decreases with each sludge reuse, from 58% to 45% approximately, while the TOC content in the sludge increases from around 14.5 mg TOC/g solid to 18 mg TOC/g solid. This is because the adsorbed organics on the iron sludge would dissolves in the reaction solution when it is reused directly as the Fenton-like reaction catalyst without any treatment. Hence, the increased organic substances loading leads to lower COD removal and higher TOC content in the iron sludge obtained. Therefore, the reuse of iron sludge directly as a catalyst after the reaction is reported to be not feasible for Fenton-like reaction. However, if the iron sludge is baked at an elevated temperature, the organic substances content can be burned off, and the bad effect of the adsorbed organics on the Fenton-like reaction efficiency can be eliminated.

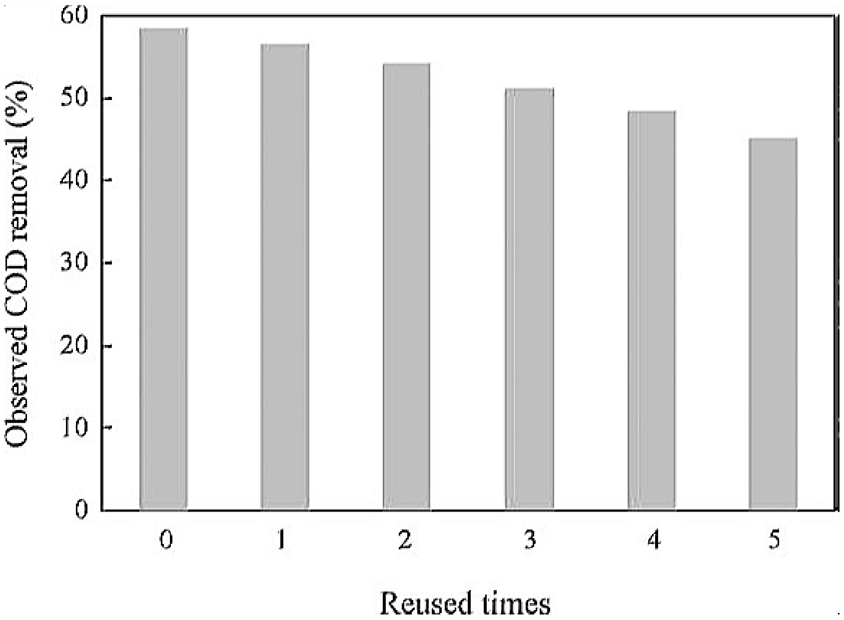

Figure 2.12: Effect of iron sludge reuse time on the COD removal efficiency in chemical wastewater (pH: 3.0, COD_0 = 1200 mg/dm^3, $[H_2O_2]_0$ = 10 mM, $[Fe^{3+}]_0$ = 1.0 mM, t = 480 min) (Cao et al., 2009).

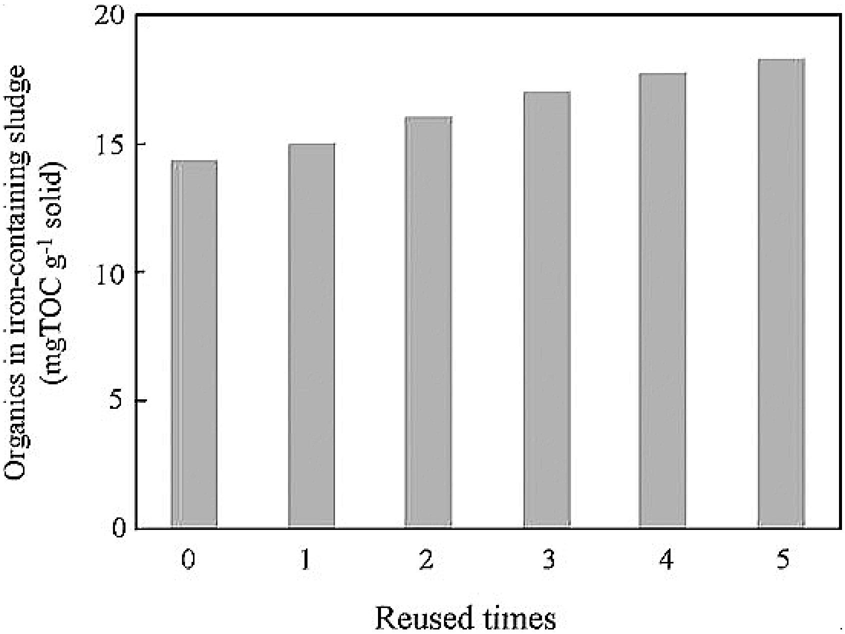

Figure 2.13: Effect of iron sludge reuse time on the TOC content in the iron sludge from chemical wastewater (pH: 3.0, COD_0 = 1200 mg/dm^3, $[H_2O_2]_0$ = 10 mM, $[Fe^{3+}]_0$ = 1.0 mM, t = 480 min) (Cao et al., 2009).

Cao et al. further study on the reusability of the regenerated catalyst produced from iron sludge with 20 minutes baking at 400°C in the multi-cycle Fenton-like process. **Table 2.4** below shows the COD removal and BOD_5/COD for each iron sludge reuse. The iron sludge produced from the reaction is collected, regenerated and reused as the Fenton-like reaction catalyst for the next cycle. Before adding H_2O_2 to start the reaction, the iron concentration of the reaction mixture is measured by atomic absorption. Lastly, $Fe_2(SO_4)_3$ solution is added prior to the reaction to make up for the iron loss in regeneration and reuse process to ensure constant iron concentration used in all reaction runs. In summary, the reusability of iron sludge is dependent on the regeneration method, adsorbed organics that will leached from the sludge and so on. Hence, the reusability of iron sludge in Fenton reaction will be further studied in this project.

Table 2.4: Effect of reuse time of the iron sludge catalyst on COD removal and BOD_5/COD (Cao et al., 2009).

Reused times	**1**	**2**	**3**	**4**	**5**	**6**
COD removal (%)	59.0	64.2	63.8	65.0	64.5	64.0
BOD_5/COD	0.38	0.40	0.41	0.39	0.39	0.42

2.7 Application of Fenton Reaction

Fenton reaction is widely implemented in wastewater treatment for textile dyes, pharmaceutical wastewater, landfill leachate, olive mill wastewater, agrochemicals and so on (Chen et al., 2020). The COD removal or degradation rate is highly dependent on the Fenton reaction condition. **Table 2.5 to 2.8** below shows the Fenton reaction performance for different effluent treatment under different reaction condition.

Table 2.5: Studied works of methylene blue (MB) degradation using Fenton reaction.

Author	Catalyst	Reaction Condition	Findings
(Zhang et al., 2020)	$NiFe_2O_4$	[Catalyst] = 0.2 g/L, [H_2O_2] = 5 mM, [MB] = 30 mg/L, t = 50 min, light irradiation	98.5% degradation rate
(Zhang et al., 2020)	α- Fe_2O_3	[Catalyst] = 0.025 g/L, [H_2O_2] = 1.10 mM, [MB] = 40 mg/L, t = 80 min, UV irradiation	94.7% degradation rate
(Zhang et al., 2020)	$CuFe_2O_4$	[Catalyst] = 0.1 g/L, [H_2O_2] = 20 mM, [MB] = 30 mg/L, t = 80 min, light irradiation	80% degradation rate
(Zhang et al., 2020)	$K_2Fe_4O_7$	[Catalyst] = 0.03 g/L, [H_2O_2] = 5 mM, [MB] = 20 mg/L, t = 35 min, light irradiation	100% degradation rate
(Giwa et al., 2020)	$FeSO_4.7H_2O$	[Fe^{2+}] = 4mM and [H_2O_2] = 70 mM, [MB] = 20 mg/L, Fe^{2+}/H_2O_2 ratio = 0.05, pH = 3, t = 30 min	98.8% degradation rate
(Rahim Pouran, Abdul Raman and Wan Daud, 2014)	Niobia/iron oxide composite–1:1	[Catalyst] = 30 mg, [H_2O_2] = 2 mL/10 mL, [MB] = 100 mg/L (10 mL), t = 120 min	~ 90% degradation rate

Table 2.5 shows the methylene blue degradation rate using different catalyst under different Fenton reaction condition. It is shown that the degradation of methylene blue using Fenton reaction can achieve good efficiency (> 80%) when $NiFe_2O_4$, α - Fe_2O_3, $CuFe_2O_4$, $K_2Fe_4O_7$, $FeSO_4.7H_2O$ and niobia/iron oxide composite catalyst was used. Among them, $K_2Fe_4O_7$ shows the highest methylene blue degradation rate of 100% when catalyst concentration, H_2O_2 concentration and methylene blue concentration of 0.03 g/L, 5 mM, and 20 mg/L, respectively was used. The reaction was carried out for 35 minutes under light irradiation. On the other hand, the methylene blue degradation rate of 98.8% was also reached without light irradiation using Fenton reaction. The reaction was carried out using Fe^{2+} concentration, H_2O_2 concentration and methylene blue concentration of 4mM, 70 mM and 20 mg/L respectively, under pH = 3 for 30 minutes.

Table 2.6: Studied works of pharmaceutical wastewater treatment using Fenton reaction.

Author	Catalyst	Reaction Condition	Findings
(Tekin et al., 2006)	$FeSO_4·7H_2O$	[Catalyst] = 0.033 M, $[H_2O_2]$ = 5 M, t = 30 min, T = 50°C	85% COD removal
(Nithyanandam and Saravanane, 2013)	$FeSO_4·7H_2O$	$[Fe^{2+}]/[H_2O_2]$ = 1:10, $[FeSO_4]$ = 0.3 M, t = 30 min	65% COD removal
(Cheng et al., 2018)	$FeSO_4·7H_2O$	$[H_2O_2]/ [Fe^{2+}]$ = 1:1, $[H_2O_2]$ = 120 mg/L, t = 10 min	62% COD removal
(Shetty and Verma, 2015)	$FeSO_4·7H_2O$	$[FeSO_4]$ = 3675 mg/L, $[H_2O_2]$ = 900 mg/L, $[FeSO_4]/[H_2O_2]$ ratio = 1:2	85% COD removal
(Behfar and Davarnejad, 2019)	$FeSO_4·7H_2O$	H_2O_2/Fe^{2+} = 4.29, H_2O_2/PhW = 1.67 ml/L, pH = 2.91, UVA light, t = 54.24 min	93% COD removal
(Su, Wang, Jiang and Gu, 2010)	$FeSO_4·7H_2O$	H_2O_2/ Fe^{2+} = 1:1, $[FeSO_4]$ = 7.8mmol/L, pH = 3, solar ray radiation	78.9% COD removal

Table 2.6 the COD removal efficiency of pharmaceutical wastewater treatment using homogeneous Fenton reaction under different reaction condition. The COD removal efficiency fluctuated between 62% and 100%. The catalyst used for the reactions are $FeSO_4 \cdot 7H_2O$. Among them, the study performed by Behfar and Davarnejad in 2019 shows the highest COD removal (93%) of pharmaceutical wastewater. The reaction was conducted using H_2O_2/Fe^{2+} ratio of 4.29, H_2O_2/PhW volume ratio of 1.67 ml/L under pH of 2.91 and UVA light for 54.24 minutes. On the other hand, a 62% of COD removal is also achieved. H_2O_2/Fe^{2+} molar ratio of 1:1, H_2O_2 concentration of 120 mg/L was used in this reaction for 10 minutes reaction time without light irradiation.

Table 2.7: Studied works of leachate treatment using homogeneous Fenton reaction.

Author	Catalyst	Reaction Condition	Findings
(Maslahati Roudi, Chelliapan, Wan Mohtar and Kamyab, 2018)	$FeSO_4 \cdot 7H_2O$	$[Fe^{2+}]$ = 1000 mg/L, $[H_2O_2]$ = 6000 mg/L, pH = 3, t = 32.5 min	94.41% COD removal
(Badawy, El-Gohary, Gad-Allah and Ali, 2013)	$FeSO_4 \cdot 7H_2O$	H_2O_2/Fe^{2+} = 50, H_2O_2/COD = 4.4, 3300 mgO_2/L, pH = 3	83% COD removal
(Jegan Durai, Gopalakrishna, Padmanaban and Selvaraju, 2020)	$FeSO_4 \cdot 7H_2O$	$[H_2O_2]$ = 29.12 mM, $[FeSO_4]$ = 14.44 mM, pH 3	97.83% COD removal
(Deng and Englehardt, 2006)	$FeSO_4 \cdot 7H_2O$	$[Fe^{2+}]$ = 300 mg/L, $[H_2O_2]$ = 200 mg/L	70% COD removal
(Deng and Englehardt, 2006)	$FeSO_4 \cdot 7H_2O$	$[Fe^{2+}]$ = 2500 mg/L, $[H_2O_2]$ = 2500 mg/L	79% COD removal
(Deng and Englehardt, 2006)	$FeSO_4 \cdot 7H_2O$	$[Fe^{2+}]$ = 294 mg/L, $[H_2O_2]$ = 200 mg/L	70% COD removal
(Deng and Englehardt, 2006)	$FeSO_4 \cdot 7H_2O$	$[Fe^{2+}]$ = 1500 mg/L, $[H_2O_2]$ = 600 mg/L	69% COD removal

From **Table 2.7**, it shows the COD removal efficiency of landfill leachate treatment using $FeSO_4·7H_2O$ catalyst using homogeneous Fenton reaction. The COD removal is reported to reach 69% to 97.83% under different reaction condition. The reaction using Fe^{2+} concentration of 1500 mg/L, H_2O_2 concentration of 600 mg/L can only reach 69% of COD removal. However, the reaction using $FeSO_4$ concentration of 14.44 mM, H_2O_2 concentration of 29.12 mM at pH 3 can achieve 97.83% of COD removal. Under the same pH level used, 94.41% of COD removal is also achieved by using Fe^{2+} concentration of 1000 mg/L and H_2O_2 concentration of 6000 mg/L for 32.5 minutes. Since $FeSO_4·7H_2O$ homogeneous catalyst is used in most of the study proposed, the Fenton reaction performance using iron oxide heterogeneous catalyst will be evaluated in this project.

Table 2.8: Studied works of olive mill wastewater treatment using Fenton reaction.

Author	Catalyst	Reaction Condition	Findings
(Domingues et al., 2018)	$FeSO_4·7H_2O$	$H_2O_2/Fe^{2+} = 15$, $H_2O_2/COD = 1.75$, pH = 3.5, T = 30°C	70% COD removal
(Domingues et al., 2018)	$FeSO_4·7H_2O$	$[Fe^{2+}] = [H_2O_2] = 2000$ mg/L	80% COD removal
(Domingues et al., 2018)	Fe–Ce–O	$[H_2O_2] = 224$ mM, [Fe-Ce-O] = 1.0 g/L, pH = 3	31% COD removal
(Domingues et al., 2018)	$FeCl_3$	$[H_2O_2] > 8$ g/L, $[FeCl_3] = 3$ g/L, pH = 3, t = 5–30 min T = 20°C, UV irradiation	90% COD removal
(Agabo-García, Calderón and Hodaifa, 2021)	$HfeO_2$	$[HfeO_2] = 50$ g/L, pH = 3, T = 20°C	62.8% COD removal
(Esteves, Morales-Torres, Maldonado-Hódar and Madeira, 2021)	OSAC-Fe-IWI	$[H_2O_2] = 0.5$ g/L, [Cat] = 2.0 g/L, T = 25°C	37% COD removal

From **Table 2.8**, it shows the olive mill wastewater treatment using different catalyst for Fenton reaction. Low COD removal of 31% compared to other catalyst used, was reached when using Fe-Ce-O as the Fenton reaction catalyst. The Fe-Ce-O concentration of 1.0 g/L, H_2O_2 concentration of 224 mM was used under pH = 3. The reaction using OSAC-Fe-IWI as the catalyst also achieved low COD removal of 37%. The catalyst concentration and H_2O_2 concentration used in this reaction was 2.0 g/L and 0.5 g/L, respectively. However, 90% of COD removal is reported when using $FeCl_3$ as the catalyst. The $FeCl_3$ solution concentration used was 3 g/L while the H_2O_2 concentration used was more than 8 g/L. The reaction is conducted in pH 3 under UV irradiation for 5 to 30 minutes.

CHAPTER 3

METHODOLOGY

3.1 Research Flowchart

All the materials, apparatuses, equipment, chemicals that are required in this study is specified in this chapter. The outline of the experimental methodology in this study is demonstrated in **Figure 3.1**.

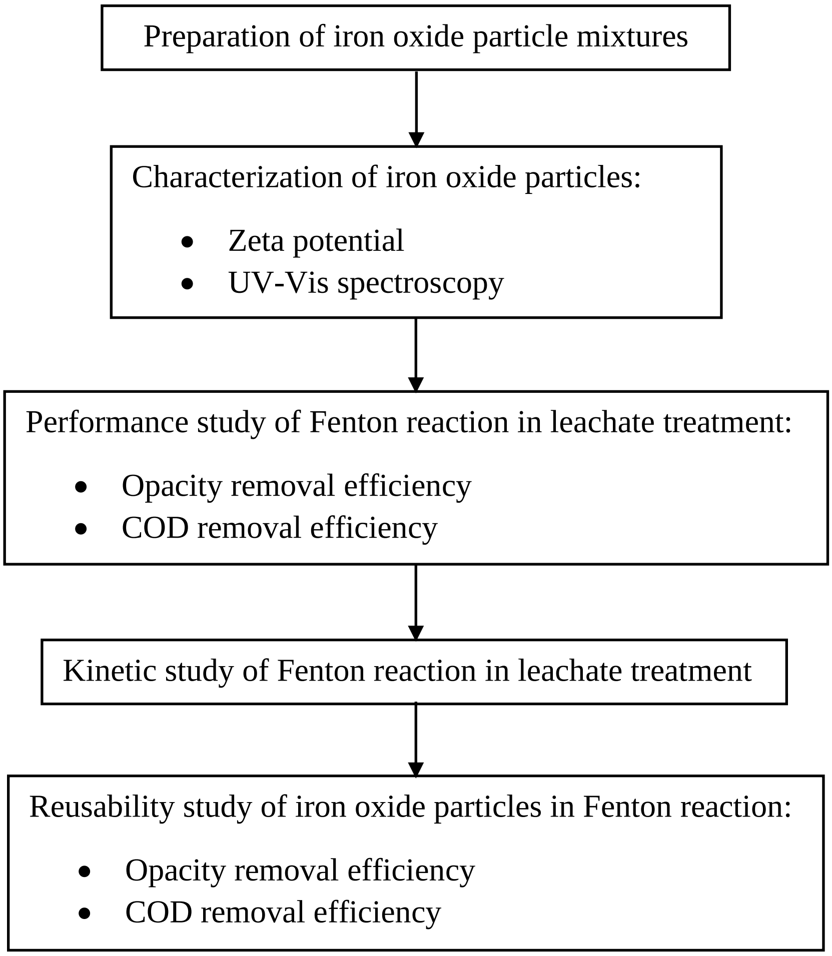

Figure 3.1: Research flowchart for the leachate treatment through Fenton reaction.

3.2 Materials, Chemicals and Equipment

All the materials and chemicals required were prepared prior to the experiment. The required materials, chemicals and equipment are tabulated in **Table 3.1**.

Table 3.1: List of materials, chemicals and equipment.

Material/Chemical	Equipment
Iron (II) oxide microparticles ($5 \times 10^{-6}\ m$)	Electronic balance
Iron (II) oxide nanoparticles ($50 \times 10^{-9}\ m$)	Magnetic stirrer plate
Hydrogen peroxide (H_2O_2)	pH meter

Sulphuric acid (H_2SO_4)	UV-Vis spectroscopy
Sodium hydroxide (NaOH)	Ultrasonicator bath
Deionized water	End-to-end rotator
Distilled water	

3.3 Preparation of Iron Oxide Particle Mixtures

A mixture for both bare-iron oxide microparticles and nanoparticles was prepared in a concentration of 10 mg/L, which is 0.1 mg iron oxide particles in 1 mL deionized water and 9 mL leachate. In order to have a well dispersion of iron oxide particles, the particles were dispersed into deionized water and sonicated for 1 hour. Then, the steps were repeated to produce samples with different concentration of iron oxide particles and hydrogen peroxide based on **Table 3.2 and 3.3.**

Table 3.2: Mass of iron oxide particles and volume of deionized water used to produce different concentration of iron oxide particle mixtures.

Mass of iron oxide particles (mg)	Volume of leachate (mL)	Volume of deionized water (mL)	Concentration of iron oxide particle mixtures (mg/L)
0.10	9	1	10
0.25	9	1	25
0.50	9	1	50
1.00	9	1	100
1.50	9	1	150

Table 3.3: Mass of iron oxide particles and volume of deionized water used to produce different concentration of iron oxide particle mixtures (with H_2O_2).

Mass of iron oxide particles (mg)	Volume of leachate (mL)	Volume of deionized water (mL)	Volume of H_2O_2 (mL)	Concentration of H_2O_2 (g/L)	Concentration of iron oxide particle mixtures (mg/L)
0.10	9	0.5	0.5	3	10
0.25	9	0.5	0.5	3	25
0.50	9	0.5	0.5	3	50
1.00	9	0.5	0.5	3	100
1.50	9	0.5	0.5	3	150

3.4 Characterization of Iron Oxide Particles

The Fenton reaction efficiency is highly dependent on the reaction activity of iron oxide. Hence, the zeta potential of iron oxide particles was measured by Malvern Instruments Zetasizer. Moreover, the absorption wavelength was also measured by the UV-Vis spectroscopy.

3.5 Performance Study of Fenton Reaction in Leachate Treatment

Batch experiments were conducted on Fenton reaction of landfill leachate using 20 mL vial. 0.1 M H_2SO_4 and 0.1 M NaOH was used to adjust the leachate pH level. The iron oxide concentration used was based on **Table 3.2 and 3.3**, while H_2O_2 concentration used in the experiment was 3 g/L. The parameters of the experiment were the presence of light and H_2O_2 in the reaction, size of iron oxide particles used ($5 \times 10^{-6}\ m$ and $50 \times 10^{-9}\ m$) as well as iron oxide concentration (10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L, 150 mg/L), as shown in **Table 3.4**. In this experiment, the light source used is fluorescent light. All experiments were carried out at atmospheric pressure and room temperature. First, H_2SO_4 was added into landfill leachate to adjust the pH to 3.0. Then, 9 mL of landfill leachate was poured into the vial. 0.5 mL of iron oxide mixture was added to the landfill leachate as the Fe^{2+} ion source. Finally, the reaction was started after the addition of 0.5 mL of H_2O_2. The sample is attached to an end-to-end rotator to stir the sample continuously for 120 minutes of reaction time to ensure complete reaction.

Table 3.4: Parameters of leachate treatment using Fenton reaction.

Run	Presence of light	Presence of H_2O_2	Size of iron oxide	Iron oxide concentration (mg/L)
1	Yes	Yes	$5 \times 10^{-6}\ m$	10
2	Yes	Yes	$5 \times 10^{-6}\ m$	25
3	Yes	Yes	$5 \times 10^{-6}\ m$	50

4	Yes	Yes	$5 \times 10^{-6}\ m$	100
5	Yes	Yes	$5 \times 10^{-6}\ m$	150
6	Yes	Yes	$50 \times 10^{-9}\ m$	10
7	Yes	Yes	$50 \times 10^{-9}\ m$	25
8	Yes	Yes	$50 \times 10^{-9}\ m$	50
9	Yes	Yes	$50 \times 10^{-9}\ m$	100
10	Yes	Yes	$50 \times 10^{-9}\ m$	150
11	Yes	No	$5 \times 10^{-6}\ m$	10
12	Yes	No	$5 \times 10^{-6}\ m$	25
13	Yes	No	$5 \times 10^{-6}\ m$	50
14	Yes	No	$5 \times 10^{-6}\ m$	100
15	Yes	No	$5 \times 10^{-6}\ m$	150
16	Yes	No	$50 \times 10^{-9}\ m$	10
17	Yes	No	$50 \times 10^{-9}\ m$	25
18	Yes	No	$50 \times 10^{-9}\ m$	50
19	Yes	No	$50 \times 10^{-9}\ m$	100
20	Yes	No	$50 \times 10^{-9}\ m$	150
21	No	Yes	$5 \times 10^{-6}\ m$	10
22	No	Yes	$5 \times 10^{-6}\ m$	25
23	No	Yes	$5 \times 10^{-6}\ m$	50
24	No	Yes	$5 \times 10^{-6}\ m$	100
25	No	Yes	$5 \times 10^{-6}\ m$	150
26	No	Yes	$50 \times 10^{-9}\ m$	10
27	No	Yes	$50 \times 10^{-9}\ m$	25
28	No	Yes	$50 \times 10^{-9}\ m$	50
29	No	Yes	$50 \times 10^{-9}\ m$	100
30	No	Yes	$50 \times 10^{-9}\ m$	150
31	No	No	$5 \times 10^{-6}\ m$	10
32	No	No	$5 \times 10^{-6}\ m$	25
33	No	No	$5 \times 10^{-6}\ m$	50
34	No	No	$5 \times 10^{-6}\ m$	100
35	No	No	$5 \times 10^{-6}\ m$	150

36	No	No	$50 \times 10^{-9}\, m$	10
37	No	No	$50 \times 10^{-9}\, m$	25
38	No	No	$50 \times 10^{-9}\, m$	50
39	No	No	$50 \times 10^{-9}\, m$	100
40	No	No	$50 \times 10^{-9}\, m$	150

After each run of the experiment, all the samples were allowed to settle down over a permanent magnet for 5 minutes to collect the iron oxide particles, and the supernatant was then collected for absorbance intensity measurement using UV-Vis spectrophotometer. The opacity removal efficiency was calculated using **Equation 3.1**.

$$Opacity\ removal\ efficiency\ (\%) = \frac{ABS_i - ABS_f}{ABS_i} \times 100\% \tag{3.1}$$

Where ABS_i represents initial absorbance intensity of leachate recorded from UV-Vis spectrophotometer and ABS_f represents final absorbance intensity of leachate recorded from UV-Vis spectrophotometer.

In order to measure the COD level of the leachate, HACH Company method on COD level determination was applied. The DRB 200 reactor was switched on and preheated to 150°C. 2 mL of the stirred sample was added into test vial. The vial was closed tightly and cleaned. Afterwards, the vial was inverted gently for several times for well mixing before it was placed into the DBR 200 reactor for 2 hours. After 2 hours, the DBR 200 reactor was switched off and the sample was allowed to cool down to room temperature. Finally, each vial was cleaned and then inserted into the COD spectrophotometer to analyse the COD level. The COD reduction efficiency was calculated by using **Equation 3.2.**

$$COD\ removal\ efficiency\ (\%) = \frac{COD_i - COD_f}{COD_i} \times 100\% \tag{3.2}$$

Where COD_i represents initial COD concentration and COD_f represents final COD concentration. At the end of this experiment, the opacity and COD removal efficiency for each reaction were tabulated and evaluated.

3.6 Kinetic Study of Fenton Reaction

The reaction rates in the reactor must be identified in order to obtain the information and design of a reactor system as well as the direct effect on the reactor size. Therefore, the study of reaction kinetics plays an important role to predict the pollutant removal rates, designing and modelling of the treatment process (Ahmadian et al., 2013). After getting the optimal performance of Fenton reaction in **Section 3.5**, the reaction was carried out until the final COD reaches equilibrium, and the reaction kinetics of Fenton reaction was studied. The Fenton reaction was repeated using the optimal parameter such as presence of light and H_2O_2 in the reaction, size of iron oxide particles used as well as iron oxide mixture concentration in **Section 3.5**. In this experiment, the light source used is fluorescent light. The iron oxide concentration used was the optimal concentration obtained from **Section 3.5**, while H_2O_2 concentration used in the experiment was fixed at 3 g/L. 0.1 M H_2SO_4 and 0.1 M NaOH was used to adjust the leachate pH level. The experiment was carried out at atmospheric pressure and room temperature. First, 9 mL of landfill leachate was added into 20 mL vial. H_2SO_4 was added into landfill leachate to adjust the pH to 3.0. Then, 0.5 mL of iron oxide mixture was added to the reaction mixture. Finally, the reaction was started after the addition of 0.5 mL of H_2O_2. The sample is attached to an end-to-end rotator to stir the sample continuously, and the sample was collected for every 30 minutes until 240 minutes. Each sample were allowed to settle down over a permanent magnet for 5 minutes to collect the iron oxide particles, and the supernatant was then collected for final COD measurement. The COD reduction efficiency was calculated by using **Equation 3.2.**

3.7 Reusability Study of Iron Oxide Particles in Fenton Reaction

After getting the optimal performance of Fenton reaction in **Section 3.5**, the reusability of iron oxide particles was studied. The Fenton reaction was repeated using the optimal parameter results such as presence of light and H_2O_2 in the reaction, size of iron oxide particles used as well as iron oxide mixture concentration in **Section 3.5**. In this experiment, the light source used is fluorescent light. The iron oxide particles can be collected easily by introducing a magnetic field using a permanent magnet, due to its magnetic property. 0.1 M H_2SO_4 and 0.1 M NaOH was used to adjust the leachate pH level. The Fe_3O_4 concentration used was the optimal concentration obtained from **Section 3.5**, while H_2O_2 concentration used in the experiment was fixed at 3 g/L. The size of iron oxide particles used and the reaction time was also the optimum point obtained from **Section 3.5**. The experiment was carried out at atmospheric pressure and room temperature. First, 9 mL of landfill leachate was added into 20 mL vial. H_2SO_4 was added into landfill leachate to adjust the pH to 3.0. Then, 0.5 mL of iron oxide was added to the reaction mixture. Finally, the reaction was started after the addition of 0.5 mL of H_2O_2. The sample is attached to an end-to-end rotator to stir the sample continuously.

After the first cycle was done, the sample was allowed to settle down over a permanent magnet for 5 minutes to collect the iron oxide particles, and the supernatant was then collected for absorbance intensity measurement using UV-Vis spectrophotometer. The opacity removal efficiency was calculated using **Equation 3.1**, and the COD reduction efficiency was calculated by using **Equation 3.2.** Afterwards, the reaction was repeated for 4 times using the recycled iron oxide particles as the Fenton reaction catalyst. At the end of this experiment, the opacity and COD removal efficiency for each cycle of iron oxide particles reused were tabulated and the reusability of iron oxide particles was evaluated.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Iron Oxide Particles

4.1.1 Zeta Potential

The zeta potential of a substance is used as a parameter for the prediction of its colloidal stability. **Table 4.1** shows the zeta potential measured for bare-iron oxide microparticles and nanoparticles. An empirical rule says that the zeta potential values ≤|±30| mV indicates instability of colloidal dispersions. Hence, the results states that the bare-iron oxide microparticles and nanoparticles are instable in solution. Due to the negligible repulsive force between the iron oxide particles and its good magnetic properties, hence the agglomeration of iron oxide particles would happen and it can be assumed as catalyst agglomerates instead of catalyst nanoparticles (Rusevova, Kopinke and Georgi, 2012).

Table 4.1: Zeta potential of bare-iron oxide microparticles and nanoparticles.

Sample	Zeta Potential (mV)
Bare-iron oxide nanoparticles	-15.8±0.36
Bare-iron oxide microparticles	-19.0±0.10

4.1.2 UV-Vis Spectroscopy

UV-Vis spectroscopy is a technique which utilise the UV and visible light spectrum in order to measure the amount of light absorbed by the sample. By obtaining the light absorption wavelength of a sample, the constituents in the solution sample can be determined (Lozinski, Bolyard, Reinhart and Motlagh, 2019). The absorption wavelength of the leachate sample is 221 nm, which indicates the sample contains lead (Pb^{2+}) and copper (Cu^{2+}) (Tan, Moo, Mat Jafri and Lim, 2014).

4.2 Performance Study of Fenton Reaction in Leachate Treatment

The performance of Fenton reaction was investigated using 5 micrometre and 50 nanometre of iron oxide at different concentration ranging from 10, 25, 50, 100 and 150 mg/L under different condition. Besides, the reported optimal pH of 3.0 for Fenton reaction is also used. This is because when the pH is lower than the optimal pH, the reaction between Fe^{3+} with H_2O_2 was inhibited and the production of OH radical was limited due to slow reaction. When the pH is higher than the optimal pH, especially pH 7.0 to 14.0, H_2O_2 will decompose itself to water and oxygen, the ferrous catalyst will be deactivated due to the ferric oxyhydroxide formation and the OH radical will have decreasing oxidation potential at high pH (Deng and Englehardt, 2006).

4.2.1 Opacity Removal using Fenton Reaction

Figure 4.1 below shows the opacity removal of Fenton reaction using different size of iron oxide at different concentration under different condition. Overall, the opacity removal using iron oxide nanoparticles are higher than microparticles only in the presence of light only and in the presence of H_2O_2 only. From **Figure 4.1 (a)** the opacity removal using iron oxide nanoparticles is slightly lower than iron oxide microparticles in the presence of light and H_2O_2.

However, from **Figure 4.1 (b) and (c)**, the removal rate of iron oxide nanoparticles possesses a higher opacity removal. The nano-sized iron oxide in **Figure 4.1 (b)** illustrate 12.5%, 18.6%, 30.7%, 25.8%, 31.5% and 23.2%, while in **Figure 4.1 (c)** the removal rate was 17.2%, 34.3%, 30.1%, 34.7%, 42.3% and 34.6% for 0, 10, 25, 50, 100 and 150 mg/L iron oxide concentration, respectively. Generally, iron oxide nanoparticles have greater catalytic activity as it has relatively larger surface area and more active sites compared to microparticles (Wang, Liu and Sun, 2012). Hence, the opacity removal of nano-sized iron oxide is higher than micro-sized iron oxide.

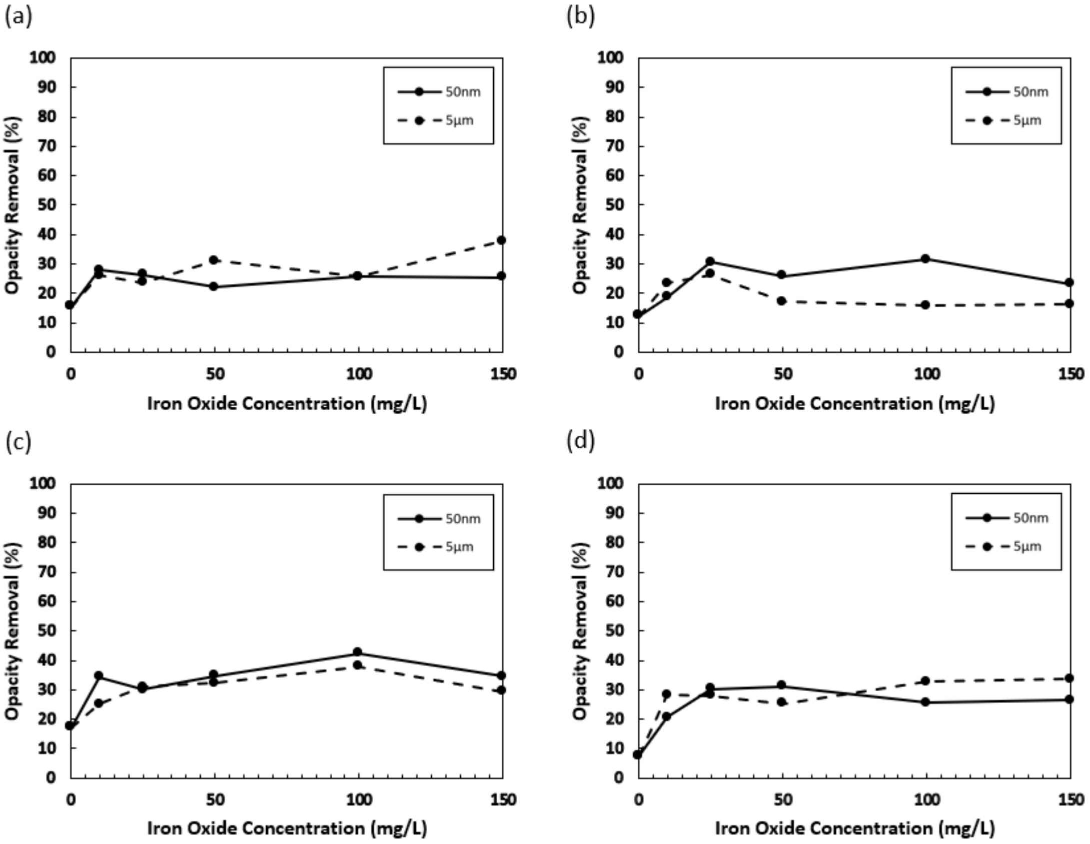

Figure 4.1: Opacity removal using different size of iron oxide under different concentration: (a) in the presence of light and H_2O_2, (b) in the presence of light only, (c) in the presence of H_2O_2 only, and (d) in the absence of light and H_2O_2.

Figure 4.2 (a) and (b) shows the opacity removal using iron oxide microparticles and nanoparticles under different concentration and condition. From the results, it is shown that the opacity removal of Fenton reaction in the presence of H_2O_2 only for both size of iron oxide particles is the highest, followed by Fenton reaction without light and H_2O_2. The probably reason of high opacity removal rate in Fenton reaction without light and H_2O_2 could be the leachate sample was contaminated by copper ion as the absorption wavelength of the sample is 221 nm. This reason can be supported by the study performed by Tan, Moo, Mat Jafri and Lim (2014) that the copper ions can be detected by UV spectroscopy from 0.2 mg/L to 10mg/L at a wavelength of 205 nm to 225 nm. Due to iron oxide particles have large surface area, more active sites as well as good magnetic properties, it has shown its outstanding potential as the solid adsorbent for copper removal using adsorption technique (Jadidian, Parham, Haghtalab and Asrarian, 2013). Hence, the opaque copper ion is removed more effectively by iron oxide adsorption than Fenton reaction, and its opacity removal is also higher compared to other reaction condition. However, there is no study reported on the opacity removal using Fenton reaction. Hence, the effect of Fenton reaction on leachate opacity is yet to be studied.

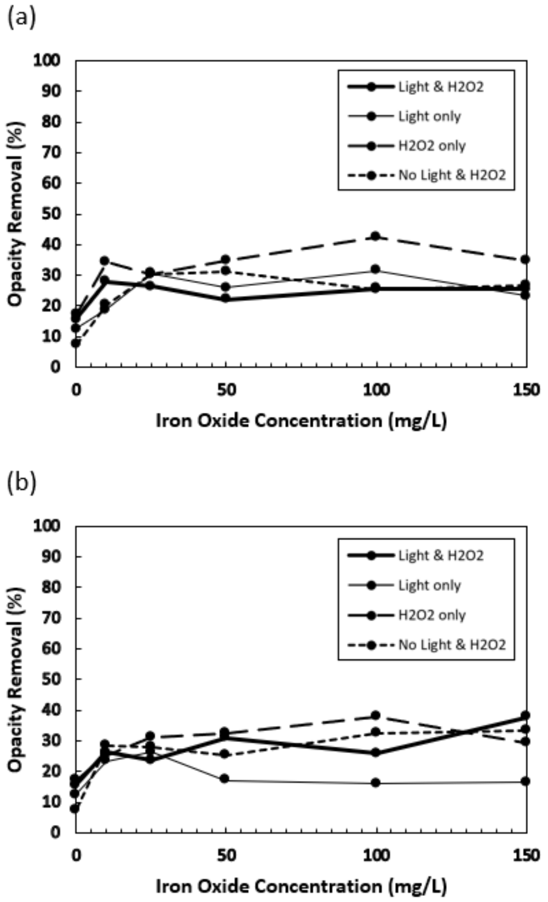

Figure 4.2: Opacity removal using (a) micro-sized and (b) nano-sized iron oxide under different concentration and condition.

4.2.2 COD Removal using Fenton Reaction

Figure 4.3 below shows the COD removal of Fenton reaction using different size of iron oxide at different concentration under different condition. Overall, the COD removal of Fenton reaction using iron oxide nanoparticles is higher only in the presence of light and H_2O_2, and in the presence of light only. However, both of the condition shows similar COD removal rate, even though there is no H_2O_2 in **Figure 4.3 (b)**. The possible reason is anaerobic digestion occur in the sample. The leachate sample may contain fruit waste, brown sugar and water, which can be fermented to become anaerobic organism activated solution (AOAS) (Kamaruddin, Yusoff, Aziz and Basri, 2013).

From **Figure 4.3 (c) and (d)**, it shows that micro-sized iron oxide has higher COD removal than nano-sized iron oxide. The possible reason of iron oxide microparticles having higher COD removal rate is the agglomeration of nano-sized iron oxide, resulting in lower surface area and active sites compared to micro-sized iron oxide. This can be supported by the zeta potential measured for both sized of iron oxide. Nano-sized iron oxide has smaller zeta potential of -15.8 mV, while micro-sized iron oxide has larger zeta potential of -19.0 mV. These results indicate that nano-sized iron oxide is more unstable and more likely to form agglomerates compared to micro-sized iron oxide.

On the other hand, negative COD removal is also observed for Fenton reaction in the presence of H_2O_2 only and in the absence of light and H_2O_2 when the iron oxide concentration is 0 mg/L in both **Figure 4.3 (c) and (d).** This result indicates that the COD increases after the experiment when there are no iron oxide particles added into the sample. According to Barber and Stuckey (2000), an increase in the COD is a typical defence mechanism by bacteria to provide a diffusion barrier against toxic materials. Hence, there might be a reaction between H_2O_2 and other pollutants that produce toxic matter in **Figure 4.3 (c)**. However, the reason why the COD increases in **Figure 4.3 (d)** when no H_2O_2 and iron oxide added is yet to be investigated.

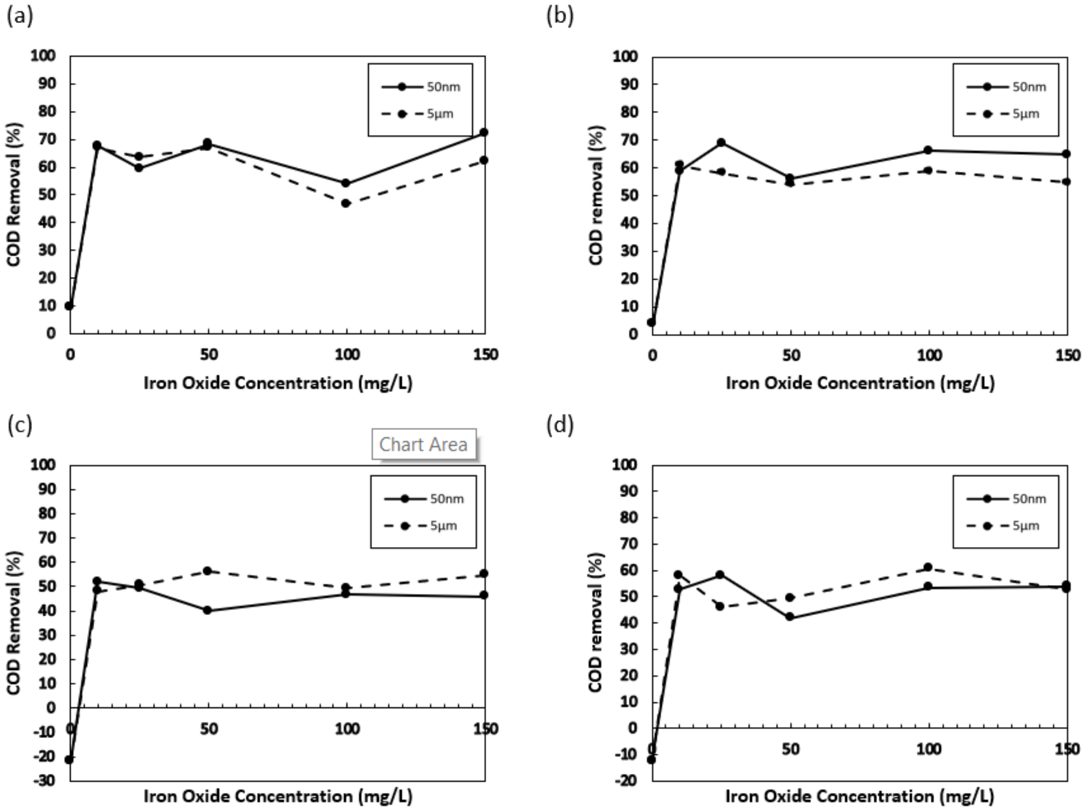

Figure 4.3: COD removal using different size of iron oxide under different concentration: (a) in the presence of light and H_2O_2, (b) in the presence of light only, (c) in the presence of H_2O_2 only, and (d) in the absence of light and H_2O_2.

Figure 4.4 (a) and (b) shows the COD removal using iron oxide microparticles and nanoparticles under different concentration and condition. From the results, it is shown that the Fenton reaction in the presence of light and H_2O_2 has highest COD removal for both size of iron oxide catalyst. This is because iron oxides will be under go reduction process and dissolve into Fe^{2+} ions under UV radiation (Wang, Liu and Sun, 2012). Hence, the presence of light can increase the amount of Fe^{2+} ions, and thus increase the organics degradation rate.

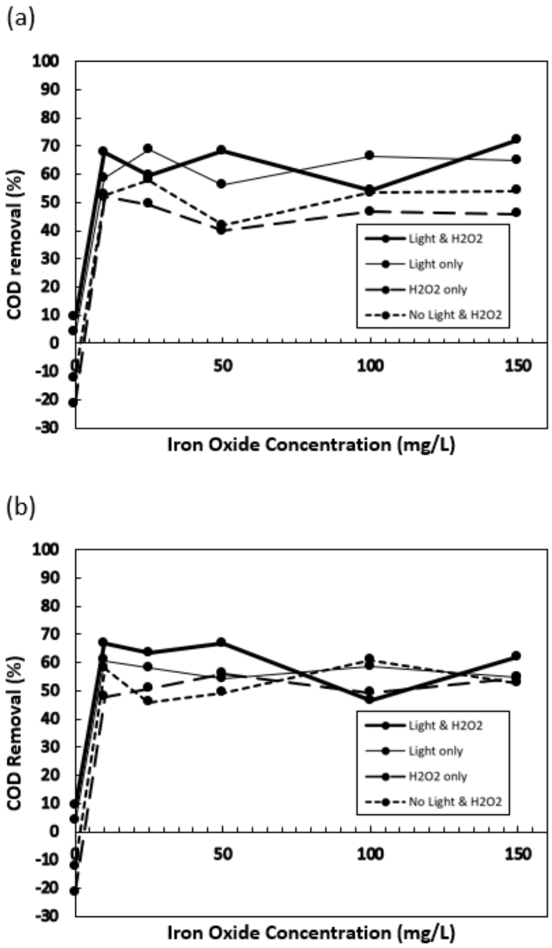

Figure 4.4: COD removal using (a) micro-sized and (b) nano-sized iron oxide under different concentration and condition.

4.3 Kinetic Study of Fenton Reaction

After the determination of the optimal size and concentration of iron oxide catalyst, Fenton reaction in leachate treatment was tested for 240 minutes until the COD removal reaches equilibrium. The Fenton reaction takes place using 50 nanometre iron oxide particles at concentration of 150 mg/L in the presence of light and H_2O_2. **Figure 4.5** shows the COD removal of Fenton reaction in leachate treatment over 240 minutes. It is shown that the COD removal reaches around 45% in the first 30 minutes and then rise slowly for the subsequent 180 minutes and reaches constant after 240 minutes. The high COD removal rate in the first 30 minutes is due to the rapid reaction between iron oxide catalyst and H_2O_2, which can produce •OH radicals immediately after the reaction starts. After 30 minutes, the •OH radicals were consumed, and the recycling as well as regeneration of Fe^{2+}, Fe^{3+}, H_2O_2 and •OH radicals is the rate-determining step. Due to the relatively slow regeneration, the reaction take place at lower rate, and hence slight increase in the COD removal (Rusevova, Kopinke and Georgi, 2012).

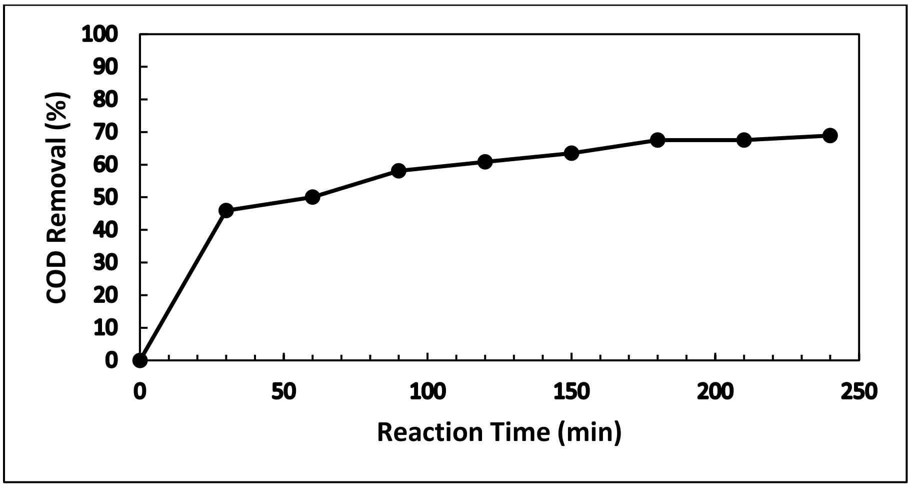

Figure 4.5: COD removal of Fenton reaction for 240 minutes.

Table 4.2 below shows the kinetic study results for zero-order, first-order and second-order, where r_c represents the conversion rate, k_0, k_1, and k_2 represents the reaction rate constant, t represents reaction time, while C_0 and C_t represents the initial and final pollutant concentration in the solution respectively. The Fenton reaction kinetics for leachate treatment was investigated at different reaction time from 0 to 240 minutes using 50 nanometre iron oxide at concentration of 150 mg/L in the presence of light and H_2O_2. From **Table 4.2**, the R^2 obtained is increasing from zero-, first- to second-order kinetic model with a R^2 of 0.9138. Hence, it can be summarised that the data were explained smoothly by second-order kinetic model, and the simulation of COD removal efficiency in Fenton Reaction using second-order kinetic model is very well. These results also show a good relationship between the COD removal efficiency and the initial COD concentration in Fenton reaction. According to Aljuboury and Palaniandy (2017), many researchers also reported that COD degradation kinetic by Fenton reaction can follow second-order kinetic model with a high R^2. **Figure 4.6** shows the kinetic study results for zero-, first- and second-order.

Table 4.2: Equations, linear forms and results of kinetic models.

Kinetic model	Equation	Linear Form	$\boldsymbol{k_0}$	$\boldsymbol{R^2}$
Zero-order	$r_c = \frac{dC}{dt} = k_0$	$C_t - C_0 = -k_0 t$	7.8333	0.6472
First-order	$r_c = \frac{dC}{dt} = k_1 C$	$\ln \frac{C_t}{C_0} = -k_1 t$	0.004	0.7966
Second-order	$r_c = \frac{dC}{dt} = k_2 C^2$	$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t$	2×10^{-6}	0.9138

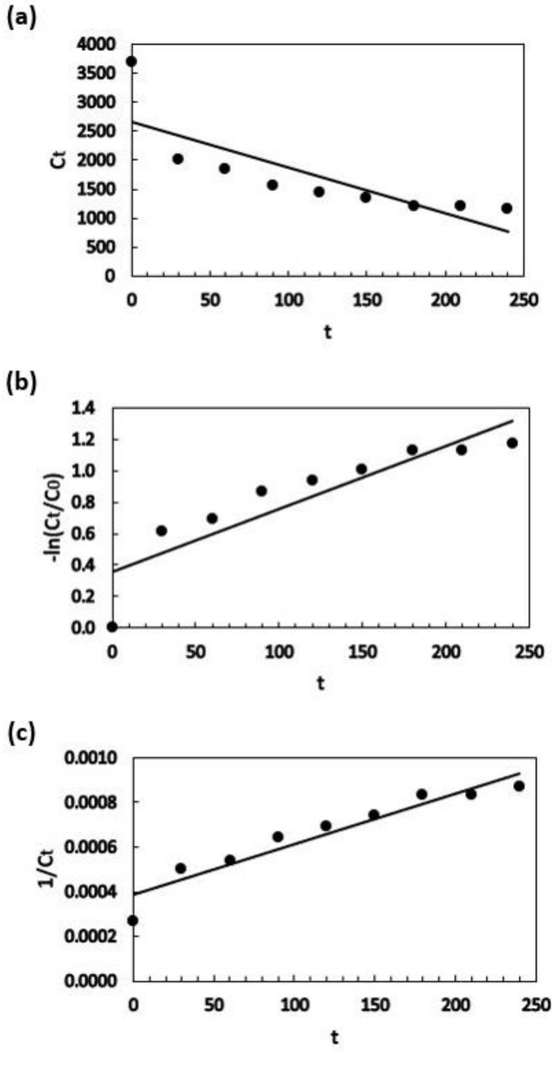

Figure 4.6: Kinetic study results for (a) zero-order, (b) first-order and (c) second-order.

4.4 Reusability Study of Iron Oxide Particles in Fenton Reaction

After obtaining the optimal reaction time of 180 minutes, Fenton reaction was repeated using 50 nanometre iron oxide at 150 mg/L in the presence of light and H_2O_2. The iron oxide catalyst was reused for 5 times under same condition to study the catalyst reusability. The iron oxide catalyst was removed from the effluent after 5 minutes of settling over a magnet. **Figure 4.7 and 4.8** shows the opacity and COD removal when the iron oxide catalyst was reused for 5 times. Both opacity and COD removal shows a decreasing trend when the iron oxide was reused for 5 times. The opacity removal decreasing from 28.19% to 9.69% after 5 cycles. On the other hand, the COD removal decreasing from 68.49% to 45.21% after 5 cycles, in which small drop in removal efficiency of 4.11%, 5.48%, 5.48% and 8.21% were observed after reusing for second, third, fourth and fifth time respectively.

From the results, it is shown that the decreases in COD removal after each cycle is getting bigger and this may be due to the H_2O_2 decomposition rate was decreased with the increasing of iron oxide catalyst reused time, and less OH radical was produced (Rusevova, Kopinke and Georgi, 2012). In addition, the drop in removal efficiency may also due to the iron leaching from the iron oxide nanoparticles through the pores in the effluent. According to Briton et al. (2019), the leached iron dosage after 4 cycles was reported as 0.507 mg/L, 0.476 mg/L and 0.4 mg/L after reusing for second, third and fourth time, which equals to 15.7% loss of iron from the first cycle to fourth cycle. Moreover, the deactivation of catalytic sites or could also cause the decrease in both opacity and COD removal efficiency (Briton et al., 2019). According to Ferroudj et al. (2017), the characterization of the γ-Fe_2O_3 nanoparticles supported on the surface of the SiO_2 microsphere catalyst have proved the presence of little number of organics on the catalyst surface after reused for 5 times. Hence, the decrease of catalytic activity could be due to the contamination of other organic substances on the catalyst surface.

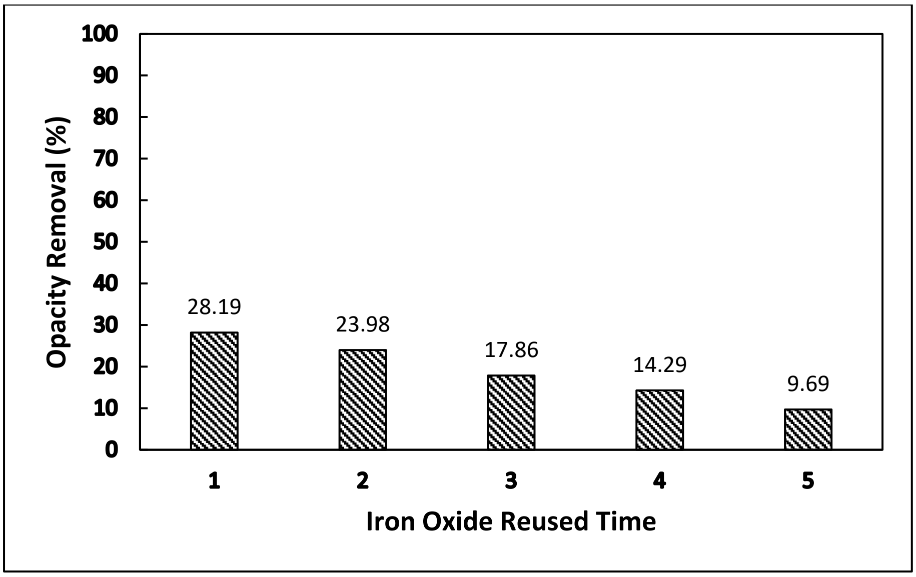

Figure 4.7: Opacity removal against iron oxide catalyst reused time.

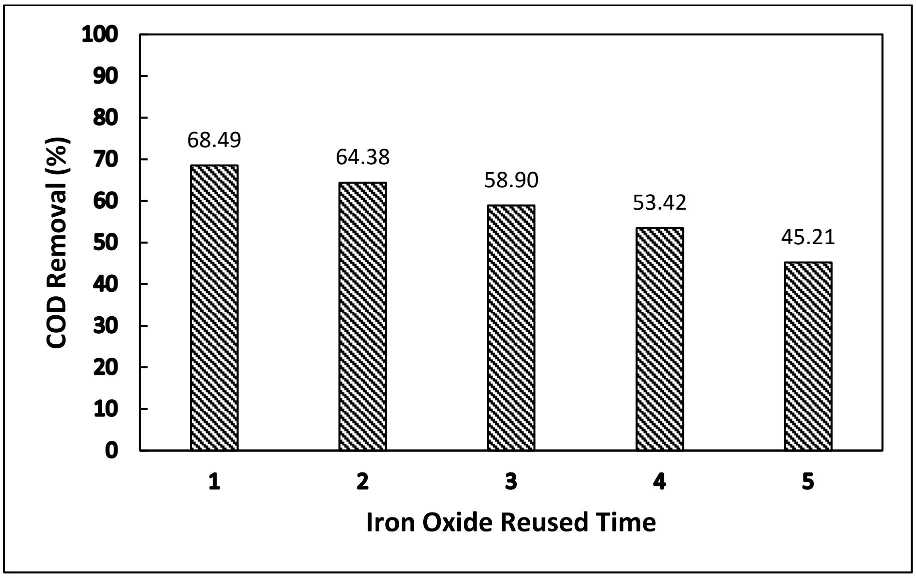

Figure 4.8: COD removal against iron oxide catalyst reused time.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, this study shows that leachate treatment using Fenton reaction offers a COD removal rate of 68.5% using iron oxide nanoparticles at concentration of 150 mg/L in the presence of light and H_2O_2. In contrast, the opacity removal rate of leachate is 25.4% under the same condition. Fenton reaction is an advanced oxidation technique which can be used in wastewater treatment and it brings many benefits because it offers high degradation efficiency, convenient operation and maintenance. Iron oxide particles as the heterogeneous catalyst also solve the shortcoming of homogeneous Fenton reaction, which is additional treatment is required to eliminate the dissolved iron in the treated effluent before discharge. Due to the good magnetic properties of iron oxide particles, it can be removed easily after Fenton reaction using magnetic field.

Other than that, in the designing of Fenton reactor, the reaction rate in the reactor is essential as it affects the reactor size. Hence, the kinetic model of Fenton reaction in leachate treatment using heterogeneous iron oxide catalyst was also been investigated in this project to have an adequate prediction on the reaction rate. The data explained by second-order kinetic model is very appropriate with a high R^2 of 0.9138. Lastly, the reusability of iron oxide is also studied in order to reduce the use of fresh iron oxide particles and replace it with the recycling and regeneration of catalyst. From the results, the opacity removal decreased from 28.19% to 9.69%, while the COD removal decreases from 68.49% to 45.21%.

5.2 Recommendations

The use of heterogeneous iron oxide microparticles and nanoparticles as catalyst in Fenton reaction can overcome the shortcomings of homogeneous Fenton reaction, which additional treatment is not required in order to remove the dissolved iron ions in the treated effluent. This is because iron oxide particles offer good magnetic properties and thus it can be eliminated from the effluent by applying magnetic field. However, the zeta potential of iron oxide microparticles and nanoparticles of -15.8±0.36 mV and -19.0±0.10 mV respectively indicates that they are unstable in solution and would agglomerate to form large clusters. The form of iron oxide agglomerates will reduce the efficiency of hydroxyl radical production, therefore the Fenton reaction rate drops. The recommendation to enhance the Fenton reaction rate is additional functionalization of iron oxide particles prior to the experiment. Besides, modification can be made on the iron oxide surface such as addition of organic or inorganic matters. By the surface functionalization of iron oxide particles, the colloidal stability of iron oxide could be enhanced and aggregations could be avoided.

Moreover, solar irradiation is reported to have good impact in Fenton reaction, which it can improve the Fenton reaction rate and pollutant removal efficiency. Fluorescent light is considered to be similar with sunlight as it emits light with a wavelength that is close to sunlight, thus it is used to simulate sunlight in this project. The use of the fluorescent light instead of sunlight is due to the weather instability in Malaysia. By using a fluorescent light to simulate sunlight, the Fenton reaction can be carried out for 24 hours without worrying for the weather condition. However, due to only one florescent light was used in the experiment, the distance between each sample and the light was different. It can cause the Fenton reaction rate in the sample under same condition to vary due to different amount of light is absorbed to enhance the reaction performance. Hence, it is recommended to have more fluorescent light to ensure the distance between each sample and the light is same.

REFERENCES

Abd El-Salam, M. and I. Abu-Zuid, G., 2015. *Impact of landfill leachate on the groundwater quality: A case study in Egypt*.

Agabo-García, C., Calderón, N. and Hodaifa, G., 2021. Heterogeneous Photo-Fenton Reaction for Olive Mill Wastewater Treatment—Case of Reusable Catalyst. *Catalysts*, 11(5), p.557.

Ahmadian, M., Reshadat, S., Yousefi, N., Mirhossieni, S., Zare, M., Ghasemi, S., Rajabi Gilan, N., Khamutian, R. and Fatehizadeh, A., 2013. Municipal Leachate Treatment by Fenton Process: Effect of Some Variable and Kinetics. *Journal of Environmental and Public Health*, 2013, pp.1-6.

Aljuboury D.A.D. and Palaniandy P. 2017. Kinetic study of inorganic carbon (IC) removal and COD removal from refinery wastewater by solar Photo-Fenton. *Global NEST Journal*, 19(4), 641-649.

Ameta, R., K. Chohadia, A., Jain, A. and Punjabi, P., 2018. Fenton and Photo-Fenton Processes. *Advanced Oxidation Processes for Waste Water Treatment*, pp.49-87.

Ammar, H., Brahim, M., Abdelhédi, R. and Samet, Y., 2016. Enhanced degradation of metronidazole by sunlight via photo-Fenton process under gradual addition of hydrogen peroxide. *Journal of Molecular Catalysis A: Chemical*, 420, pp.222-227.

Badawy, M., El-Gohary, F., Gad-Allah, T. and Ali, M., 2013. Treatment of landfill leachate by Fenton process: parametric and kinetic studies. *Desalination and Water Treatment*, 51(37-39), pp.7323-7330.

Banch, T., M. Hanafiah, M., Alkarkhi, A. and Abu Amr, S., 2019. *Statistical Evaluation of Landfill Leachate System and its Impact on Groundwater and Surface Water in Malaysia*.

Barber, W. and Stuckey, D., 2000. Effect of Sulfate Reduction on Chemical Oxygen Demand Removal in an Anaerobic Baffled Reactor. Water Environment Research, 72(5), pp.593-601.

Behfar, R. and Davarnejad, R., 2019. Pharmaceutical wastewater treatment using UV-enhanced electro-Fenton process: Comparative study. *Water Environment Research*, 91(11), pp.1526-1536.

Bolobajev, J., Kattel, E., Viisimaa, M., Goi, A., Trapido, M., Tenno, T. and Dulova, N., 2014. Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment. *Chemical Engineering Journal*, 255, pp.8-13.

Briton, B., Duclaux, L., Richardson, Y., Yao, K., Reinert, L. and Soneda, Y., 2019. Effectiveness of the dispersion of iron nanoparticles within micropores and mesopores of activated carbon for Rhodamine B removal in wastewater by the heterogeneous Fenton process. Applied Water Science, 9(7).

Cao, G., Sheng, M., Niu, W., Fei, Y. and Li, D., 2009. Regeneration and reuse of iron catalyst for Fenton-like reactions. *Journal of Hazardous Materials*, 172(2-3), pp.1446-1449.

Chen, Y., Cheng, Y., Guan, X., Liu, Y., Nie, J. and Li, C., 2019. A Rapid Fenton treatment of bio-treated dyeing and finishing wastewater at second-scale intervals: kinetics by stopped-flow technique and application in a full-scale plant. *Scientific Reports*, 9(1).

Chen, Y., Fan, T., Wang, L., Cheng, T., Chen, S., Yuan, M., & Cheng, S., 2020. Application of Fenton Method for the Removal of Organic Matter in Sewage Sludge at Room Temperature. *Sustainability*, 12(4), p.1518.

Cheng, Y., Chen, Y., Lu, J., Nie, J. and Liu, Y., 2018. Fenton treatment of bio-treated fermentation-based pharmaceutical wastewater: removal and conversion of organic pollutants as well as estimation of operational costs. *Environmental Science and Pollution Research*, 25(12), pp.12083-12095.

Deng, Y. and Englehardt, J., 2006. Treatment of landfill leachate by the Fenton process. *Water Research*, 40(20), pp.3683-3694.

Deng, Y. and Englehardt, J., 2006. Treatment of landfill leachate by the Fenton process. Water Research, 40(20), pp.3683-3694.

Domingues, E., Gomes, J., Quina, M., Quinta-Ferreira, R. and Martins, R., 2018. Detoxification of Olive Mill Wastewaters by Fenton’s Process, *Catalysts*, 8(12), p.662

Esteves, B., Morales-Torres, S., Maldonado-Hódar, F. and Madeira, L., 2021. Integration of olive stones in the production of Fe/AC-catalysts for the CWPO treatment of synthetic and real olive mill wastewater. *Chemical Engineering Journal*, 411, p.128451.

Ferroudj, N., Talbot, D., Michel, A., Davidson, A. and Abramson, S., 2017. Increasing the efficiency of magnetic heterogeneous Fenton catalysts with a simple halogen visible lamp. Journal of Photochemistry and Photobiology A: Chemistry, 338, pp.85-95.

Giwa, A., Bello, I., Olabintan, A., Bello, O. and Saleh, T., 2020. Kinetic and thermodynamic studies of fenton oxidative decolorization of methylene blue. *Heliyon*, 6(8), p.e04454.

Gutierrez-Mata, A., Velazquez-Martínez, S., Álvarez-Gallegos, A., Ahmadi, M., Hernández-Pérez, J., Ghanbari, F. and Silva-Martínez, S., 2017. Recent Overview of Solar Photocatalysis and Solar Photo-Fenton Processes for Wastewater Treatment. *International Journal of Photoenergy*, 2017, pp.1-27.

Haslina, H., NorRuwaida, J., Dewika, M., Rashid, M., Md Ali, A., Khairunnisa, M. and Afiq Daniel Azmi, M., 2021. Landfill Leachate Treatment Methods and Its Potential for Ammonia Removal and Recovery - A Review. *IOP Conference Series: Materials Science and Engineering*, 1051(1), p.012064.

Hassani, G., Alinejad, A., Sadat, A., Esmaeili, A., Ziaei, M., Bazrafshan, A. and Sadat, T., 2016. Optimization of Landfill Leachate Treatment Process by Electrocoagulation, Electroflotation and Sedimentation Sequential Method. *International Journal of Electrochemical Science*, 11(8), pp.6705-6718.

Idris, A., Inanc, B. and Hassan, M., 2004. Overview of waste disposal and landfills/dumps in Asian countries. *Journal of Material Cycles and Waste Management*, 6(2), pp.104-110.

Ilhami Firiyal Imtinan, S., Purwanto, P. and Yulianto, B., 2020. The biological treatment method for landfill leachate. *E3S Web of Conferences*, 202, p.06006.

Jadidian, R., Parham, H., Haghtalab, S. and Asrarian, R., 2013. Removal of Copper from Industrial Water and Wastewater Using Magnetic Iron Oxide Nanoparticles Modified with Benzotriazole. *Advanced Materials Research*, 829, pp.742-746.

Japperi, N., Mohd Asri, Z., Wan Bakar, W., Dollah, '., Ahmad Fuad, M. and Che Mohamed Hussein, S., 2021. *Review on landfill gas formation from leachate biodegradation*.

Jasim, N., 2020. The design for wastewater treatment plant (WWTP) with GPS X modelling. *Cogent Engineering*, 7(1), p.1723782.

Jegan Durai, N., Gopalakrishna, G., Padmanaban, V. and Selvaraju, N., 2020. Oxidative removal of stabilized landfill leachate by Fenton's process: process modeling, optimization & analysis of degraded products. *RSC Advances*, 10(7), pp.3916-3925.

Kamaruddin, M., Yusoff, M., Aziz, H. and Basri, N., 2013. Removal of COD, ammoniacal nitrogen and colour from stabilized landfill leachate by anaerobic organism. *Applied Water Science*, 3(2), pp.359-366.

Kannan, R., 2016. *What contaminated ground water can do to your health*. [online] The Hindu. Available at: <https://www.thehindu.com/news/cities/chennai/what-contaminated-ground-water-can-do-to-your-health/article5019514.ece> [Accessed 23 July 2021].

Li, Y., Tang, F., Xu, D. and Xie, B., 2021. *Advances in Biological Nitrogen Removal of Landfill Leachate*.

Litter, M. and Slodowicz, M., 2017. An overview on heterogeneous Fenton and photoFenton reactions using zerovalent iron materials. *Journal of Advanced Oxidation Technologies*, 20(1).

Lozinski, D., Bolyard, S., Reinhart, D. and Motlagh, A., 2019. Treatment of leachate organic matter through sunlight driven processes. Waste Management, 94, pp.18-26.

Maggi, F., Dossi, S., Paravan, C., Galfetti, L., Rota, R., Cianfanelli, S. and Marra, G., 2019. Iron oxide as solid propellant catalyst: A detailed characterization. *Acta Astronautica*, 158, pp.416-424.

Maslahati Roudi, A., Chelliapan, S., Wan Mohtar, W. and Kamyab, H., 2018. Prediction and Optimization of the Fenton Process for the Treatment of Landfill Leachate Using an Artificial Neural Network. *Water*, 10(5), p.595.

Mojiri, A., Zhou, J., Ratnaweera, H., Ohashi, A., Ozaki, N., Kindaichi, T. and Asakura, H., 2020. Treatment of landfill leachate with different techniques: an overview. *Journal of Water Reuse and Desalination*, 11(1), pp.66-96.

Nagarajan, R., Thirumalaisamy, S. and Lakshumanan, E., 2012. Impact of leachate on groundwater pollution due to non-engineered municipal solid waste landfill sites of erode city, Tamil Nadu, India. *Iranian Journal of Environmental Health Science & Engineering*, 9(1).

National Research Council. 1996. *Use of Reclaimed Water and Sludge in Food Crop Production.* p.49.

Nidheesh, P. and Gandhimathi, R., 2012. Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination*, 299, pp.1-15.

Nithyanandam, R., & Saravanane, R., 2013. Treatment of Pharmaceutical Sludge by Fenton Oxidation Process. *International Journal of Chemical Engineering and Applications*, 4(6), pp.359-364.

Pawar, V., & Gawande, S., 2015. An overview of the Fenton Process for Industrial Wastewater.

Raghab, S., Abd El Meguid, A. and Hegazi, H., 2013. Treatment of leachate from municipal solid waste landfill. *HBRC Journal*, 9(2), pp.187-192.

Rahim Pouran, S., Abdul Raman, A. and Wan Daud, W., 2014. Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions. *Journal of Cleaner Production*, 64, pp.24-35.

Rajasulochana, P. and Preethy, V., 2016. Comparison on efficiency of various techniques in treatment of waste and sewage water – A comprehensive review. *Resource-Efficient Technologies*, 2(4), pp.175-184.

Rodríguez, M., Malato, S., Pulgarin, C., Contreras, S., Curcó, D., Giménez, J. and Esplugas, S., 2005. Optimizing the solar photo-Fenton process in the treatment of contaminated water. Determination of intrinsic kinetic constants for scale-up. *Solar Energy*, 79(4), pp.360-368.

Rueda-Márquez, J., Levchuk, I., Manzano, M. and Sillanpää, M., 2020. Toxicity Reduction of Industrial and Municipal Wastewater by Advanced Oxidation Processes (Photo-Fenton, UVC/H2O2, Electro-Fenton and Galvanic Fenton): A Review. *Catalysts*, 10(6), p.612.

Rusevova, K., Kopinke, F. and Georgi, A., 2012. Nano-sized magnetic iron oxides as catalysts for heterogeneous Fenton-like reactions—Influence of Fe(II)/Fe(III) ratio on catalytic performance. Journal of Hazardous Materials, 241-242, pp.433-440.

Salem, A., Mohammed, Z. and Fattah, M., 2021. Leachate Properties of Municipal Solid Waste in Laboratory Landfill. *Advances in Mechanics,* 9(3), pp.143-150.

Shetty, R., & Verma, S., 2015. Fenton’s Reagent for the Treatment of Pharmaceutical Industry Wastewater.

Sillanpää, M. and Shestakova, M., 2017. Emerging and Combined Electrochemical Methods. *Electrochemical Water Treatment Methods*, pp.131-225.

Su, R., Wang, P., Jiang, L. and Gu, F., 2010. Study on Treatment of Acetylspiramycin Pharmaceutical Wastewater by the Photo-Fenton Oxidation Process. *Advanced Materials Research*, 113-116, pp.512-515.

Tan, C., Moo, Y., Mat Jafri, M. and Lim, H., 2014. UV spectroscopy determination of aqueous lead and copper ions in water. SPIE Proceedings,.

Tekin, H., Bilkay, O., Ataberk, S., Balta, T., Ceribasi, I., Sanin, F., Dilek, F. and Yetis, U., 2006. Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *Journal of Hazardous Materials*, 136(2), pp.258-265.

Thomas, N., Dionysiou, D. and Pillai, S., 2021. Heterogeneous Fenton catalysts: A review of recent advances. *Journal of Hazardous Materials*, 404, p.124082.

Vasquez-Medrano, R., Prato-Garcia, D. and Vedrenne, M., 2018. Ferrioxalate-Mediated Processes. *Advanced Oxidation Processes for Waste Water Treatment*, pp.89-113.

Wang, C., Liu, H. and Sun, Z., 2012. Heterogeneous Photo-Fenton Reaction Catalyzed by Nanosized Iron Oxides for Water Treatment. *International Journal of Photoenergy*, 2012, pp.1-10.

Wang, C., Liu, H. and Sun, Z., 2012. Heterogeneous Photo-Fenton Reaction Catalyzed by Nanosized Iron Oxides for Water Treatment. International Journal of Photoenergy, 2012, pp.1-10.

Wang, K., Li, L., Tan, F. and Wu, D., 2018. Treatment of Landfill Leachate Using Activated Sludge Technology: A Review. *Archaea*, 2018, pp.1-10.

Warmadewanthi, I., Zulkarnain, M., Ikhlas, N., Kurniawan, S. and Abdullah, S., 2021. *Struvite precipitation as pretreatment method of mature landfill leachate*.

Wdowczyk, A. & Szymańska-Pulikowska, A., 2020. Differences in the Composition of Leachate from Active and Non-Operational Municipal Waste Landfills in Poland. *Water*, 12(11), p.3129.

Wu, C., Chen, W., Gu, Z. and Li, Q., 2021. A review of the characteristics of Fenton and ozonation systems in landfill leachate treatment. *Science of The Total Environment*, 762, p.143131.

Xu, M., Wu, C. and Zhou, Y., 2020. *Advancements in the Fenton Process for Wastewater Treatment*.

Yusmartini, E. and Setiabudidaya, D., 2013. Characteristics of Leachate at Sukawinatan Landfill, Palembang, Indonesia. *Journal of Physics: Conference Series*, 423, p.012048.

Zhang, M., Dong, H., Zhao, L., Wang, D. and Meng, D., 2019. A review on Fenton process for organic wastewater treatment based on optimization perspective. *Science of The Total Environment*, 670, pp.110-121.

Zhang, X., Geng, Z., Jian, J., He, Y., Lv, Z., Liu, X. and Yuan, H., 2020. Potassium Ferrite as Heterogeneous Photo-Fenton Catalyst for Highly Efficient Dye Degradation. *Catalysts*, 10(3), p.293.

Zhao, Y., 2018. Summary. *Pollution Control Technology for Leachate from Municipal Solid Waste*, p.xxiii.

Zhou, R. and Zhang, W., 2017. Reuse of Ferric Sludge by Ferrous Sulfide in the Fenton Process for Nonylphenol Ethoxylates Wastewater Treatment. *Computational Water, Energy, and Environmental Engineering*, 06(01), pp.89-96.

APPENDICES

Table A: Results of opacity and COD for Fenton reaction in different conditions.

Table A.1: Results of opacity and COD for Fenton reaction in the presence of light and H_2O_2.

Presence of light	Presence of H_2O_2	Size of iron oxide	Iron oxide concentration (mg/L)	Initial opacity (Abs)	Final opacity (Abs)	Opacity removal (%)	Initial COD (mg/L)	Final COD (mg/L)	COD removal (%)
Yes	Yes	-	0	0.918	0.775	15.58	7400	6700	9.46
		5µm	10	0.863	0.637	26.19	7400	2450	66.89
			25	0.863	0.659	23.64	7400	2700	63.51
			50	0.863	0.595	31.05	7400	2450	66.89
			100	0.863	0.641	25.72	7400	3950	46.62
			150	0.863	0.537	37.78	7400	2800	62.16
		50 nm	10	0.863	0.623	27.81	7400	2400	67.57
			25	0.863	0.635	26.42	7400	3000	59.46
			50	0.863	0.672	22.13	7400	2350	68.24
			100	0.863	0.641	25.72	7400	3400	54.05
			150	0.863	0.644	25.38	7400	2050	72.30

Table A.2: Results of opacity and COD for Fenton reaction in the presence of light only.

Presence of light	Presence of H_2O_2	Size of iron oxide	Iron oxide concentration (mg/L)	Initial opacity (Abs)	Final opacity (Abs)	Opacity removal (%)	Initial COD (mg/L)	Final COD (mg/L)	COD removal (%)
Yes	No	-	0	0.918	0.803	12.53	7400	7100	4.05
		5μm	10	0.863	0.661	23.41	7400	2900	60.81
			25	0.863	0.636	26.30	7400	3100	58.11
			50	0.863	0.715	17.15	7400	3400	54.05
			100	0.863	0.726	15.87	7400	3050	58.78
			150	0.863	0.722	16.34	7400	3350	54.73
		50nm	10	0.863	0.702	18.66	7400	3050	58.78
			25	0.863	0.598	30.71	7400	2300	68.92
			50	0.863	0.64	25.84	7400	3250	56.08
			100	0.863	0.591	31.52	7400	2500	66.22
			150	0.863	0.663	23.17	7400	2600	64.86

Table A.3: Results of opacity and COD for Fenton reaction in the presence of H_2O_2 only.

Presence of light	Presence of H_2O_2	Size of iron oxide	Iron oxide concentration (mg/L)	Initial opacity (Abs)	Final opacity (Abs)	Opacity removal (%)	Initial COD (mg/L)	Final COD (mg/L)	COD removal (%)
No	Yes	-	0	0.918	0.76	17.21	7400	9000	-21.62
		5µm	10	1.003	0.75	25.22	7400	3850	47.97
			25	1.003	0.692	31.01	7400	3650	50.68
			50	1.003	0.678	32.40	7400	3250	56.08
			100	1.003	0.622	37.99	7400	3750	49.32
			150	1.003	0.709	29.31	7400	3350	54.73
		50nm	10	1.003	0.659	34.30	7400	3550	52.03
			25	1.003	0.701	30.11	7400	3750	49.32
			50	1.003	0.655	34.70	7400	4450	39.86
			100	1.003	0.579	42.27	7400	3950	46.62
			150	1.003	0.656	34.60	7400	4000	45.95

Table A.4: Results of opacity and COD for Fenton reaction in the absence of light and H_2O_2.

Presence of light	Presence of H_2O_2	Size of iron oxide	Iron oxide concentration (mg/L)	Initial opacity (Abs)	Final opacity (Abs)	Opacity removal (%)	Initial COD (mg/L)	Final COD (mg/L)	COD removal (%)
No	No	-	0	0.918	0.848	7.63	7400	8300	-12.16
		5μm	10	1.014	0.727	28.30	7400	3100	58.11
			25	1.014	0.729	28.11	7400	4000	45.95
			50	1.014	0.756	25.44	7400	3750	49.32
			100	1.014	0.683	32.64	7400	2900	60.81
			150	1.014	0.674	33.53	7400	3500	52.70
		50nm	10	1.014	0.805	20.61	7400	3500	52.70
			25	1.014	0.706	30.37	7400	3100	58.11
			50	1.014	0.697	31.26	7400	4300	41.89
			100	1.014	0.755	25.54	7400	3450	53.38
			150	1.014	0.745	26.53	7400	3400	54.05

Table B: Results of opacity and COD for Fenton reaction for 240 minutes.

Presence of light	Presence of H_2O_2	Size of iron oxide	Iron oxide concentration (mg/L)	Time (min)	Initial opacity (Abs)	Final opacity (Abs)	Opacity removal (%)	Initial COD (mg/L)	Final COD (mg/L)	COD removal (%)
Yes	Yes	50 nm	150	0	0.937	0.937	0.00	7900	7900	0.00
				15	0.937	0.753	19.64	7900	3850	51.27
				30	0.937	0.698	25.51	7900	3800	51.90
				45	0.937	0.601	35.86	7900	3500	55.70
				60	0.937	0.56	40.23	7900	3100	60.76
				75	0.937	0.636	32.12	7900	2350	70.25
				90	0.937	0.605	35.43	7900	2250	71.52
				105	0.937	0.664	29.14	7900	1950	75.32
				120	0.937	0.598	36.18	7900	1650	79.11

Table C: Results of opacity and COD for Fenton reaction after reused for 5 cycles.

Presence of light	Presence of H_2O_2	Size of iron oxide	Iron oxide concentration (mg/L)	Reused cycle	Initial opacity (Abs)	Final opacity (Abs)	Opacity removal (%)	Initial COD (mg/L)	Final COD (mg/L)	COD removal (%)
Yes	Yes	50 nm	150	1	0.784	0.563	28.19	3650	1150	68.49
				2	0.784	0.596	23.98	3650	1300	64.38
				3	0.784	0.644	17.86	3650	1500	58.90
				4	0.784	0.672	14.29	3650	1700	53.42
				5	0.784	0.708	9.69	3650	2000	45.21