PEROXIDE ASSISTED ADSORPTION FOR TREATING PALM OIL MILL EFFLUENT USING PALM SHELL BASED ACTIVATED CARBON

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FACULTY OF ENGINEERING UNIVERSITI MALAYA KUALA LUMPUR

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KWONG CHIA JUN

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PEROXIDE ASSISTED ADSORPTION FOR TREATING PALM OIL MILL EFFLUENT USING PALM SHELL BASED ACTIVATED CARBON

ABSTRACT

In Malaysia, palm oil production is one of the major agricultural industries, attributing 37.9 % of the agricultural contribution to Gross domestic product (GDP). Among them, POME is the largest wastes generated from the palm oil mills production with high BOD, COD, TS, TSS, colour more than 500 ADMI. Since POME is considered as highly recalcitrant, the Department of Environment is started to be more stringent in standard discharge limits to control water pollution. Therefore, this study aimed to develop green hybrid adsorbent from activated PKS by integrating iron oxide and zeolite to treat POME. Palm kernel shell-based activated carbon (PKSAC) was incorporated with zeolite and iron oxide (Fe) to synthesize Zeolite-Fe/PKSAC and Fe/PKSAC adsorbents. The adsorbents have been prepared using co-precipitation and ultrasonic-assisted mixing processes and analyzed for surface functional group, morphology, N₂ adsorption porosity, magnetic properties, and stability. The result showed that Zeolite-Fe/PKSAC and Fe/PKSAC have predominant mesoporous structures with a high surface area up to 619 m²/g for Fe/PKSAC and 573 m²/g for Zeolite-Fe/PKSAC. Both adsorbents also illustrated a high magnetic saturation of 16.6 emu/g and 10.6 emu/g for Fe/PKSAC and Zeolite-Fe/PKSAC, respectively.

The adsorption efficiency of both adsorbents was investigated with and without the addition of H_2O_2 for POME removal. The effects of operating parameters that include H_2O_2 dosage, adsorbent dosage, contact time and initial pH of solution on the adsorption process, were investigated. The adsorption study using Fe/PKSAC without H_2O_2 showed that Fe/PKSAC had higher colour removal (93 %) than Zeolite-Fe/PKSAC (88 %) 5 g/L

of adsorbent was used at pH 3 for 40 min of contact time. However, Zeolite-Fe/PKSAC revealed a higher chemical oxygen demand removal of 63 % compared to Fe/PKSAC (58 %). The reusability analysis also indicated that Zeolite-Fe/PKSAC has higher stability as it maintains its adsorbent capacity over five cycles, with just a decrease of 6 % compared to Fe/PKSAC. The adsorption of POME using Zeolite-Fe/PKSAC and H₂O₂ had successfully removed 83 % colour and 67 % COD using a lesser amount of adsorbent of 4 g/L and H₂O₂ of 68 mM, within a shorter reaction time of 30 minutes compared to Fe/PKSAC. Besides, Zeolite-Fe/PKSAC+H₂O₂ found to maintain its adsorbent potential up to the 5th cycle with a reduction of just 3 % of adsorption efficiency compared to Fe/PKSAC+H₂O₂ (7 %). Zeolite-Fe/PKSAC+H₂O₂ (55 mg/g), Zeolite-Fe/PKSAC (48 mg/g) and Fe/PKSAC (44 mg/g).

In conclusion, the study has proven that the incorporation of iron oxide and zeolite into palm kernel shell activated carbon enhances the stability, separability and surface area of the adsorbents. The peroxide-assisted adsorption process using Zeolite-Fe/PKSAC greatly improved the reusability and adsorption efficiency of the adsorbent, minimizing the dosage of the adsorbent while reducing contact time.

Keywords: Biomass; Activated Carbon; Adsorption; Zeolite; Iron Oxide; Wastewater Treatment

PENJERAPAN TERBANTU PEROKSIDA BAGI RAWATAN EFLUEN KILANG KELAPA SAWIT MENGGUNAKAN KARBON AKTIF BERASAS TEMPURUNG KELAPA SAWIT

ABSTRAK

Di Malaysia, pengeluaran minyak sawit adalah salah satu industri pertanian utama dan menyumbang 37.9% daripada sumbangan pertanian kepada Keluaran Dalam Negara Kasar (KDNK). Walaubagaimanapun, Efluen Kilang Kelapa Sawit (EKKS) juga adalah sisa terbesar yang dihasilkan daripada pengeluaran kilang sawit dengan BOD, COD, TS, TSS dan warna yang tinggi. Oleh itu, Jabatan Alam Sekitar mula lebih ketat dalam had pelepasan standard untuk mengawal pencemaran air. Dalam penyelidikan ini, Tempurung Kelapa Sawit (TKS) diperkembangkan dengan besi oksida (Fe) dan zeolit untuk menghasilkan dua jenis penjerap biomas, Zeolit-Fe/TKS dan Fe/TKS untuk rawatan EKKS. Kedua-dua penjerap biomas ini berjaya disintesis dengan kaedah pemendakan dan process pencampuran panduan ultrasound dan telah dianalisis dari segi kumpulan fungsi permukaan, morfologi, keliangan penjerapan N₂, sifat magnetik, dan kestabilan. Hasilnya menunjukkan bahawa kedua-dua penyerap biomas mempunyai luas permukaan yang tinggi sehingga 619 m²/g untuk Fe/TKS dan 573 m²/g untuk Zeolit-Fe/TKS dan struktur mesopori yang dominan. Penyerap biomas ini menggambarkan magnetisasi tepu yang tinggi dengan 16.6 emu/g untuk Fe/TKS dan 10.6 emu/g untuk Zeolit-Fe/TKS. Pengaruh hidrogen peroksida (H₂O₂) terhadap kecekapan penjerapan penyerap biomas juga telah disiasatkan. Perisian Design Expert 10 digunakan untuk menentukan bilangan eksperimen vang optimum dan perlu dilaksanakan dalam penyelidikan ini. Kesan-kesan pelbagai parameter operasi juga telah dikaji, iaitu merangkumi dos H₂O₂, dos penjerap, masa kontak, pH permulaan larutan pada proses penjerapan.

Bagi kajian penjerapan tanpa H₂O₂, Fe/TKS didapati lebih efektif dengan mengurangkan 5 % lebih banyak warna (93 %) berbanding dengan Zeolit-Fe/TKS (88 %) pada keadaan operasi yang optimum dengan menggunakan 5 g/L dos penjerap dan pH 3 sebagai pH permulaan dalam 40 minit. Walaubagaimanapun, Zeolit-Fe/TKS menunjukkan kecekapan degradasi 63 % lebih tinggi bagi penyingkiran COD berbanding dengan Fe/TKS (58 %). Tahap penggunaan semula analisasi ini juga menunjukkan kestabilan yang lebih tinggi di Zeolit-Fe/TKS. Hal ini disebabkan ia mengekalkan kapasiti penyerapnya selama lima kitaran dengan sedikit penurunan 6 % berbanding dengan Fe/TKS. Bukan itu sahaja, hasilnya juga disokong oleh kajian penjerapan dengan bantuan peroksida (H₂O₂). Kombinasi H₂O₂ dan Zeolit-Fe/TKS berjaya menyingirkan 83 % warna dan 67 % COD dengan 4 g/L dos penjerap yang lebih kurang dan 68 mM H₂O₂ dalam 30 minit masa kontak yang minima berbanding dengan Fe/TKS. Selain itu, Zeolit-Fe/TKS+H₂O₂ dapat mengekalkan stabiliti hingga kitaran ke-5 dengan penurunan 3 % sahaja berbanding dengan Fe/TKS+H₂O₂ (7 %). Tambahan pula, Zeolit-Fe/TKS+H₂O₂ juga mencapai kapasiti penjerapan tertinggi 73 mg/g berbanding dengan Fe/TKS+H2O2 (55 mg/g), Zeolit-Fe/TKS (48 mg/g) dan Fe/TKS (44 mg/g).

Kesimpulannya, kajian ini telah membuktikan bahawa penggabungan besi oksida dan zeolit ke dalam tempurung kelapa sawit dapat meningkatkan kestabilan, keterpisahan dan luas permukaan penjerap. Penjerapan yang dibantu oleh peroksida bagi Zeolit-Fe/TKS juga dapat meningkatkan prestasi penjerapan secara signifikan dan penggunaan semula, serta mengurangkan dos penyerap dan masa kontak.

Kata kunci: Biomas; Tempurung Kelapa Sawit; Penjerapan; Zeolit; Besi Oksida; Rawatan Air Kumbahan

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LIST OF ABBREVIATIONS

AOPs	:	Advanced Oxidation Processes
BOD	:	Biological Oxygen Demand
CCD	:	Central Composite Design
COD	:	Chemical Oxygen Demand
CR	:	Colour Removal
F-value	:	Fisher's Value
POME	:	Palm Oil Mill Effluent
RSM	:	Response Surface Methodology
СТ	:	Contact Time
рН	:	pH Value
FTIR	÷	Fourier Transform Infrared Spectroscopy
SEM	:	Scanning Electron Microscopy
EDX	:	Energy Dispersive X-Ray
VSM	:	Vibrating Sample Magnetometer
XRD	:	X-Ray Diffraction
RSM	:	Response Surface Methodology
CCD	:	Central Composite Design
ANOVA	:	Analysis Of Variance
PKS	:	Palm Kernel Shell

PKSAC	:	Palm Kernel Shell Activated Carbon
Fe/PKSAC	:	Iron Oxide Palm Kernel Shell Activated Carbon
Zeolite-Fe/PKSAC	:	Zeolite Iron Oxide Palm Kernel Shell Activated Carbon
ТР	:	Total Phosphorus
TN	:	Total Nitrogen

LIST OF NOMENCLATURE AND SYMBOL

k	:	Reaction rate constant Zero Order (M s-1), First-order (s-1), Second-
		order (M-1 s-1)
Т	:	Temperature (⁰ C)
t	:	Time (min)
+COD-	:	Chemical oxygen demand (mg/L)
K_L	:	Constant of Langmuir isotherm
K_{f}	:	Constant of Freundlich isotherm
K_T	:	Constant of Temkin isotherm
Ct	:	Contact time (min)
[Dye]	:	Dye concentration (mol/L)
[Dosage]	:	Adsorbent dosage (g)
CR	:	Colour Removal (ADMI)

CHAPTER 1: INTRODUCTION

1.1 Background

Approximately 1500 million tons of agricultural waste is produce and dispose annually in the landfills in the world (S. Li & Chen, 2020). Landfilling of agricultural waste cost about USD 55 per ton and also release different type of pollutants into the environment which might lead to harmful impacts on human health (Vaverková et al., 2019). Hence, researchers have recently devoted much attention in converting agricultural waste into useful products such as green adsorbents, biofuels, enzymes, vitamins, antioxidants, animal feed, antibiotics, and other chemicals (Munir et al., 2018). The agricultural waste can be developed into an efficient adsorbent due to its chemical properties such as availability of functional group such hydroxyl, amino and carboxylic groups which lead to higher surface area, more active sites, and high adsorption efficiency (Anastopoulos et al., 2019).

Adsorption is one of the most efficient treatment technologies for the removal of extremely recalcitrant pollutants especially from chemical and pharmaceutical effluents due to its high feasibility and workability. But there is a limitation of adsorption which is high retention time. Hence, in order to address the limitation, additional of oxidants in adsorption process might be the effective method for wastewater treatment application. Adsorbents developed from agricultural waste have several benefits over conventional commercial adsorbents such as activated carbons, ion-exchange resins and inorganic materials such as activated alumina, silica gel and molecular sieves due to its better biodegradability, high abundancy and reusability (Crini, Lichtfouse, Wilson, & Morin-Crini, 2018). Agricultural waste such as peanut shell, coconut shell, banana peel, palm kernel shell, garlic peel and rice husks have been used to developed an efficient bio

adsorbent for the removal of various heavy metal, anionic and cationic dyes, and persistent organic pollutants (Asfaram, Fathi, Khodadoust, & Naraki, 2014; Hameed & Ahmad, 2009; Indera Luthfi, Jahim, Harun, Tan, & Mohammad, 2017; Kaman, Tan, & Lim, 2016; Zainal et al., 2018).

In Malaysia, Palm oil production is one of the major agricultural industries, attributing 37.9 % of the agricultural contribution to gross domestic product (GDP) (MAHIDIN, 2019). However, palm kernel shell (PKS) is one of the significant wastes discharged from the palm oil mill industry, producing approximately 2 million tons annually (Mohammad Razi, Al-Gheethi, Al-Qaini, & Yousef, 2018; R. R. Mohammed & Chong, 2014). The characteristics of PKS, such as large cavities, porosity, and adsorption affinity, may make it one of the excellent organic sorbents (Ezzuldin, Rahim, Wan Yussof, Olalere, & Habeeb, 2019; F. Zhao et al., 2017). In addition, PKS also readily available in the market and inexpensive raw materials. However, the researcher identified that raw PKS, does not pose adequate adsorption efficiency, stability, good separation, and relevant use in real wastewater application. Hence, suitable modification needed to address all the limitation of raw PKS adsorbent.

The adsorption properties of the raw PKS adsorbent can be modified by various methods such as chemical modification, physical modification, biological modification, mineral impregnation, and magnetic modifications to improve the efficiency of raw biomass adsorbent (Gautam, Mudhoo, Lofrano, & Chattopadhyaya, 2013; P. Zhang et al., 2020). PKS composite adsorbent can also increase their adsorption performance by combining or hybridizing with other powerful adsorbents, inorganic compounds, and organic compounds such as iron oxide, titanium dioxide (Fazal et al., 2020), graphene oxide (Z. Wang et al., 2020), magnesium oxide (Oginni et al., 2020), zeolite, polymer (J.-X. Yu,

Li, Sun, Yuan, & Chi, 2009), and sulfone (Nejadshafiee & Islami, 2019) to increase its active sites for better adsorbent performance (I. A. W. Tan, Ahmad, & Hameed, 2008; Xie, Lin, Wu, & Kong, 2017; P. Zhang et al., 2020).

Therefore, a study is required to develop hybrid magnetite biomass-based adsorbents from activated PKS by incorporating with iron oxide and zeolite to treat, biologically treated POME through adsorption process with peroxide assisted. Biomasscoprecipitating iron oxide can improve the magnetic properties of the adsorbent, ease magnetic separation, excellent biocompatibility and relatively cheaper compared to other materials (Jain et al., 2018; L. C. A. Oliveira et al., 2002; Suresh Kumar et al., 2017). On the other hand, Zeolite is an inorganic material that is known for its ion exchange power, high porosity, large surface area, high regeneration potential, strong acidic stability, readily available and low cost (Al-Jubouri & Holmes, 2020). In addition, the present of H₂O₂ in adsorption process able to improve the adsorption efficiency, shorten the contact time, steady reusability, and facile separability (H. Li et al., 2020). This study would provide a promising choice for a low cost, high performance, and eco-friendly treatment of POME with peroxide assisted as well as opens a new renew to utilize by-product of palm oil processing.

1.2 Problem Statement

Adsorption process has been widely used in wastewater treatment because this process proved to be more effective than other wastewater treatment technologies in terms of cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Ahmed, Yaakob, Akhtar, & Sopian, 2015). However, the use of conventional commercial adsorbents has limited the application of the process due to its high cost and low regeneration cycle (Pyrzynska, 2019). The conventional commercial adsorbents include in activated carbons, ion-exchange resins and inorganic materials such as activated alumina, silica gel and molecular sieves (Crini et al., 2018). These materials are expensive and non-renewable, which is unjustified in pollution control applications. Therefore, recent interest of the researchers has moved towards to discover a better substitute or a superior source for the creation of low cost and effective adsorbent for the treatment of wastewater.

In Malaysia, the most vital agricultural industry is the palm oil mill industry (MAHIDIN, 2019). Starting from 2020, the production rate of palm oil mill is likely to increase rapidly due to the demand of crude palm oil internationally and locally. In the dark side, large production will eventually generate a large amount of solid waste such as trunks, empty fruit bunches, shells, and fibres which leads to environmental issues. There are no significant commercial applications for the palm kernel shell (PKS), unlike trunk, empty fruit bunches (EFB) and mesocarp fibre (MF); are used as construction materials. Annually, 2 million tons of palm kernel shell (PKS) were generated (Mohammad Razi et al., 2018). One possibility of managing the waste is to convert it into a useful product such as activated carbon. This approach will reduce the problem of managing waste during fresh fruit bunches (FFB) processing and also helpful in removing pollutants from industrial wastewater.

POME is among the major environmental problems facing Malaysia. Approximately, 5 to 7.5 tons of POME discharge of every ton of fresh fruit bunches (FFB) processed (Mustapha Mohammed Bello & Abdul Raman, 2017). Although Malaysian palm oil mills have adopted biological treatment through open ponding system, the effluent from most of these mills still fail to satisfy the discharge standard. Previous studies have shown that the discharged POME contains high COD, nutrients and very colourful (Khalida Muda1,

2016; W. J. Ng, Goh, & Tay, 1987; Y. Y. Tan, Bello, & Abdul Raman, 2021). Consequently, the Malaysian DoE is putting more stringent discharge limits for POME. Thus, there is a need to developed effective treatment process that can be used as polishing stage for the biologically treated POME. Adsorption processes has been investigated as a possible technology for polishing of POME. However, practical application of adsorption processes has faces drawback due to longer contact time, cost of adsorbent and difficult to separate after the treatment.

1.3 Research Questions

- 1. Does the incorporation of iron oxide and zeolite improve the adsorption of PKS activated carbon?
- 2. Can the hybrid magnetite biomass-based adsorbent able to treat POME wastewater more efficiently compared to palm kernel shells activated carbon?
- 3. Does the present of H_2O_2 oxidants enhance the adsorption efficiency?
- 4. How does the pH, adsorbent, contact time and H₂O₂ dosages affect the adsorption efficiency?
- 5. How to determine the type of adsorption and illustrate the mechanism of adsorption?

1.4 Aim and Objectives of the Study

The aim of this study is to develop an abundantly available waste based high performance biomass adsorbent for POME treatment. Based on the problem statement, few main objectives are identified as follows:

1. To synthesize and characterize hybrid magnetite biomass-based adsorbent developed using palm kernel shell activated carbon, Iron oxide and Zeolite.

- 2. To evaluate the adsorption characteristics of the hybrid magnetite biomass-based adsorbent for the treatment of real palm oil mill effluent (POME) with and without H₂O₂.
- 3. To determine the kinetics and mechanism of adsorptions for the newly developed biomass adsorbents.

1.5 Scope of the Study

The scopes of this study are as follows:

- Palm Kernel Shell activated carbon (PKSAC), which is prepared from abundantly available palm kernel shell has been utilized as the adsorbent for the removal of pollutants from biological treated POME.
- 2. To enhance the characteristic of biomass adsorbent by coprecipitating iron oxide and zeolite into PKSAC as an effective adsorbent.
- 3. The characterization of the newly synthesized adsorbent (Zeolite-Fe/PKSAC) is limited to textural, morphological, chemical composition and surface properties.
- 4. To determine the effect of the operational parameters including initial pH of solution, adsorbent dosage, contact time and oxidant dosages on the adsorption.
- 5. The adsorption kinetic and isotherm studies is conducted to evaluate the adsorption capacity of Zeolite-Fe/PKSAC and Fe/PKSAC for biological treated POME.

1.6 Significance of the Study

The significance of the research is in providing a new alternative and know-how for developing a simple, cheaper, stand-alone, and efficient adsorbent that suitable for industries with recalcitrant wastewater generation. This study can help in minimizing the environmental impact by usage of palm kernel shell-based adsorbent to treat POME through adsorption process assisted by peroxide. This study is timely since there is a need to develop effective technologies for POME. The use of palm kernel shell, which is a solid waste generated by the palm oil mills and have a dual benefit. It will lower the costs of POME treatment and ensures the management of the solid waste. However, so far in the literature, the application of iron oxide and zeolite for the modification of activated carbon-PKS has not been carried out yet. Additionally, literature also confirms that the studies have been conducted on adsorption processes with oxidants using real wastewater were limited, particularly POME wastewater. Therefore, the significance of this study is to synthesis hybrid magnetite biomass-based adsorbent and use it to treat real wastewater, with the aid of oxidant. The significant of study for this research are as follows:

a) Aquatic environment

When POME wastewater containing organic matters, heavy metals and other pollutants were discharged from industry, this will create water pollution to aquatic environment. The aquatic ecosystem will also be damaged. So, this research will protect aquatic environment by the removal of pollutants from POME.

b) Convert palm kernel shell into useful products

Palm oil mills in Malaysia produces about 2 million tons of palm kernel shell annually and the significant problems in the palm fruit processing is managing the wastes generated during the process. This palm kernel shell can be converted into useful products such as activated carbon. So, this approach will reduce the problem of managing waste during palm fruit processing and helpful in removing pollutant from POME wastewater.

c) Industrial purposes

The methods that developed in this research will therefore be useful to the palm oil mill industry or any others industry that were having wastewater issue. Besides, the treated wastewater can be reused in the industry for other applications such as cooling and cleaning. As those application does not require high quality of water.

1.7 Thesis Outline

This thesis starts with an abstract followed by five chapters dealing with different aspects of the current study and ending with references and appendixes.

Chapter 1: Introduction

The introduction chapter provides a background of the study which covers overview of agricultural waste, biomass-based adsorbent, palm oil mill effluent (POME) and various type of biological treatment for POME, particularly on adsorption. It also includes the drawbacks of adsorption process with highlighting the importance of developing a sustainable, high stability and cost-effective adsorbent for the treatment of POME from agricultural sectors in Malaysia. Justification of choosing adsorption process and hybrid palm kernel shell with zeolite and iron oxide as an adsorbent based on literature study also briefly discussed. Based on the problem statement, research questions, aim and objectives, scope, and significance of the study are defined. The outline of the thesis is also included in this chapter.

Chapter 2: Literature Review

This chapter establishes the literature review which includes topic extensively researched of agricultural waste, type of adsorbent in the market, challenges and limitation of biomass-based adsorbent, characteristics of palm oil mill effluent (POME) and various type of POME treatment technologies specially on physical and oxidation method. Develop an effective and high stability adsorbent was found to be the sustainable and cheap method for degrading POME and literature about this type of adsorbent was also reviewed. The justification for the selected on the adsorbent was given in this section as well. Lastly, this chapter also discussed the effect of operational parameter on adsorption process and adsorption kinetic and isotherm.

Chapter 3: Methodology

An overview of the methodology of the research activities is described in this chapter. The characteristics of newly developed hybrid magnetite biomass-based adsorbent based on palm kernel shell, zeolite and iron oxide (Zeolite-Fe/PKSAC) adsorbent and the procedures of the experiments and method of analyses are presented in this chapter. In addition, UV spectrophotometer are the equipment used for the determination of degradation efficiency of POME using COD and colour removal. The detailed information on the response surface methodology, a statistical used in this work also briefly explained.

Chapter 4: Results and Discussion

Chapter 4 contains the results and discussion on the analysis of characterization of newly synthesized biomass-based adsorbent by using SEM/EDX, VSM, FTIR, BET and XRD analysis. Hence, the results and discussion on the removal efficiency of adsorption on treatment of biological POME with and without the aids of oxidants also present in this chapter. The detailed information of the effects of the operating parameters were also described. The kinetic study, adsorption isotherm and the reusability of adsorbent were also presented in this chapter. In addition, the comparison between both adsorbent

Fe/PKSAC and Zeolite-Fe/PKSAC also presented in this chapter. The comparison of adsorption process with and without oxidants and both biomass-based adsorbent in terms of degradation efficiency, economic analysis and environmental implication are presented.

Chapter 5: Conclusion

Chapter 5 provides a summary and concluding remarks of the main findings of this research. The significance and potential application of the work are also provided in this chapter.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter provides an overview on agricultural waste, type of biomass-based adsorbent in the market, limitation of adsorbent, modification of adsorbent, and various type of treatment technologies especially on adsorption method. Besides, the most suitable materials to use to modify the adsorbent also have been reviewed in this chapter. The effect parameters such as pH, adsorbent dosage, oxidants dosage and contact time on adsorption also have been discussed based on the previous studies. The adsorption mechanism, kinetic and isotherms of various adsorption process using biomass adsorbent is summarized as well in the chapter. The characteristics of palm oil mill effluent (POME), and the advantages and limitation of various POME treatment technologies also included in this chapter. Finally, a summary is included to conclude the key information of the whole chapter.

2.2 Adsorbents that developed from Agricultural Waste

The rapid rise in global agricultural waste is due to the development of the agricultural sector, population growth, and the country's social economy over time. About 998 million tons of agricultural waste are produced and disposed of annually in landfills worldwide (Agamuthu, 2009; S. Li & Chen, 2020). Malaysian landfills receive approximately 1.2 million tons of agricultural waste per year (Abdel-Shafy & Mansour, 2018). If agricultural waste is not correctly disposed of, many nitrous oxide, methane, sulfur dioxide, and other gases are released, resulting in air pollution. (K. He, Zhang, & Zeng, 2019). Furthermore, water pollution may occur if livestock and animal waste are disposed of directly into the water supply without proper treatment.

Agricultural-based adsorbents have been used to remove various contaminants, including dyes, organic pollutants, and heavy metal ions, in the past years (V. K. Gupta, Carrott, Ribeiro Carrott, & Suhas, 2009). Biodegradability, abundant supply, low cost, regeneration ability, and high adsorption capacity are all advantages of agricultural wastebased adsorbents. Agricultural waste also has better surface area active sites. Various functional groups such as hydroxyl, methoxy, amino and carboxylic groups lead to high adsorption efficiency, essential in adsorbent development (Anastopoulos et al., 2019; Khan et al., 2016). Based on the previously published results, peanut shells (J. Liu, Wei, Xue, & Su, 2020), coconut shell (Indera Luthfi et al., 2017; Kaman et al., 2016), banana peel (R. R. Mohammed & Chong, 2014), palm kernel shell (Zainal et al., 2018), garlic peel (Asfaram et al., 2014; Hameed & Ahmad, 2009) have been used to remove of various heavy metal, anionic and cationic dyes, and persistent organic pollutants via electrostatic interactions, cheating, completing, coordinating, H-bonding interactions, $n-\pi$ interactions and others. Hence, the development of adsorbents from agricultural waste is recognized as a sustainable solution for wastewater treatment for the removal of extremely recalcitrant industrial wastewater and minimize waste simultaneously (Patterson, 1985). Agricultural waste has a natural porous structure and a functional group with an affinity to specific material, leading to excellent adsorption efficiency. As shown in table below, many different types of high-performance adsorbents had been developed from agricultural waste such as grape vines, fruit bearing trees, vegetables, eggshell, coconut, green tea, husks, and others to remove the pollutants in industrial waste. The parameters that commonly investigated were pH (2 - 12), Dosage of adsorbent (0.02 g - 40 g), Contact time (3 min – 2880 min) and Temperature (293 K – 323 K). In addition, the removal rate for most of the pollutants by using biomass adsorbents were achieved at 80 % and above. Lastly, the details of recent reported studies on using biomass adsorbent to treat various types of pollutants had been summarised in Table 2.1.

No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
1.	Coconut adsorbent (DCWC)	Pb (II)	 pH: 6 [dye]: 0.15 mM [Dosage]: 25 mg Temp.: 303 K C_t: 2 days 	 DCWC500: 3.51 mmol/g DCWC500: 134.640 m²/g Pb (II) removal DCWC500: 99 % > 80 % after 5th cycles Kinetic: Second order Isotherm: Langmuir 	(Abd ul Rahi m et al., 2020)
2.	Green tea (GT)	Pb (II)	 pH: 5.5 Temp.: 298 K C_t: 12 hrs 	 GT: 584.8 mg/g Pb (II) removal GT: 90% Kinetic: Second order Isotherm: Langmuir 	(Den g et al., 2021)
3.	Lathyrus sativus husk untreated (UHLS) H ₂ SO ₄ treated (SHLS) H ₃ PO ₄ treated (PHLS)	Methylene blue (MB)	UHLS • pH: 4 • [dye]: 75 mg/L SHLS • pH: 6 • [dye]: 150 mg/L PHLS • pH: 5 - 9 • [dye]: 200 mg/L	 UHLS: 98.33 mg/g SHLS: 104.28 mg/g PHLS: 113.25 mg/g Kinetic: Second order Isotherm: Langmuir and Temkin Spontaneous adsorption and exothermic 	(Ghos h, Kar, Chatt erjee, Bar, & Das, 2021)
4.	Macroalgal Eucheuma spinosum biochar (ES- BC)	Azo dye (RR-120)	 pH: 4 [dye]: 100 mg/L Temp.: 313 K [Dosage]: 0.25 g/L 	 ES-BC: 331.97 mg/g CR%: 97.06 % Kinetic: Second order Isotherm: Langmuir Max. Monolayer ads 	(Gura v et al., 2021)

Table 2. 1: Type of	of biomass	adsorbents
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No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
5.	Oscillatoria (ODOB) + Polyaniline (PANI- ODOB) + Sodium alginate (Na-Alg- ODOB)	Basic blue 41	 pH: 9 Temp.: 303 K [Dosage]: 0.05 g C_t: 120 min 	 ODOB: 700 mg/g Na-Alg-ODOB: 634.4 mg/g PANI-ODOB: 786.6 mg/g COD: 93.7 % TP: 80.8 % TN: 85.5 % Kinetic: Second order Isotherm: Freundlich 	(Maqbo ol, Bhatti, Sadaf, Mana Al- Anazy, & Iqbal, 2020)
6.	Palm Kernel Shell Activated Carbon (PKSAC) + Silver (Ag- NPs- PKSAC)	Phenol	 [dye]: 200 mg/L Temp.: 298 K [Dosage]: 0.25 g Ct: 74 min Agitation rate: 156 rpm 	 Phenol removal PKSAC: 85.64 % Ag-NPs-PKSAC: 90.29 % commercial adsorbent: 91.70 % Kinetic: Second order Isotherm: Langmuir 	(Aremu , Arinko ola, Olowon yo, & Salam, 2020)
7.	Graphene shell composite from oil palm frond juice	Methylene blue (MB)	 [dye]: 20 mg/L [Dosage]: 20 g C_t: 20 h 	 CR%: 75.45 %– 99.13 % Kinetic: Second order Isotherm: Freundlich 	(Teow, Tajudin , Ho, & Moham mad, 2020)
8.	Egg Shells (ES) Spent Tea Leaves (STL)	Copper ions	 pH: 6 [dye]: 20 ppm [Dosage]: 1:25 (S: L) Ct: 120 min 	 ES: 422.5 mg/g STL: 447.5 mg/g Copper removal ES: 84.5% STL: 91% Kinetic: ES: First order STL: Second order Isotherm: Freundlich 	(Bashir, Tyagi, & Annach hatre, 2020)

Table 2. 1: (Continued
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No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
9.	Soya waste + Silica coated (CSW)	Neutral red (NR) Methylene blue (MB)	 pH: 7 Temp.: 298 K [Dosage]: 2 g/L C_t: 15 min 	 CSW-MB: 97.1 % CSW-NR: 93.8 % CSW-MB: 90 mg/g CSW: > 80% after 3th cycle Kinetic: Second order Isotherm: Langmuir 	(Batoo 1 & Valiya veettil, 2020)
10.	Coconut shell + carbon dioxide (CCS) + Ozone (OCS) + Steam and carbon dioxide (CSCS)	Hexavalen t chromium	 pH: 2 [dye]: 10 ppm Temp.: 298 K [Dosage]: 1 g/L Ct: 140 min Agitation rate: 300 rpm 	 CSCS: 26 mg/g Hexavalent chromium removal CSCS: 78 % CCS: 71 % OCS: 61 % Kinetic: Second order Isotherm: Langmuir 	(Chan dana, Krush namurt y, Suryak ala, & Subrah manya m, 2020)
11.	Persimmon tannins + Graphene oxide (PT- GO) Hawthorn	Methylene blue (MB)	 pH: 8 [dye]: 35 mg/L [Dosage]: 20 mg Ct: 180 min pH: 10 	 PT-GO: 256.58 mg/g Methylene blue removal PT-GO: 92 % Kinetic: Second order Isotherm: Freundlich 88.3 % after 5th cycles HK: 49.5 mg/g 	(Z. Wang et al., 2020) (Akkö
	kernel (HK) + Sulphonic acid groups (SHK)	blue (MB)	 [dye]: 100 mg/L Temp.: 298 K [Dosage]: 2 g/L Ct: 6 hrs 	 SHK: 151.5 mg/g Methylene blue removal HK: 80 % removal with 5 g/L adsorbent SHK: 100 % removal with25 g/L adsorbent SHK lost 1 % after the fifth cycles Kinetic: Second order Isotherm: Langmuir 	z, Coşku n, & Deliba ş, 2019)

Table 2. I: Continue

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No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
16.	Corn cobs + Carbon dioxide (CCC) + Steam (SCC)	Methylene blue (MB)	 pH: 7 [dye]: 100 mg/L Ct: 15 min 	 CCC: 100 mg/g SCC: 75.5 mg/g Kinetic: Second order Isotherm: Langmuir Max. Monolayer ads 	(Redd y, Verm a, & Subra hman yam, 2016)
17.	Sludge from the textile industry + Chemical (PC) + Biological (BIO)	Reactive Red 2	 pH: 2 Temp.: 298 K [dye]: 500 mg/L [Dosage]: 5 g/L 	 PC: 213.9 mg/g BIO: 159.3 mg/g Kinetic: Second order Isotherm: Langmuir Max. Monolayer ads Spontaneous adsorption and exothermic 	(Sona i, de Souza , de Olive ira, & de Souza , 2016)
18.	Walnut shell (LMWS)	Lead (Pb)	 pH: 5 [dye]: 23 mg/L [Dosage]: 2 g/L Ct: 4 min 	 Lead removal LMWS: 98 % LMWS: 75 % after 10th cycle Kinetic: Second order Isotherm: Langmuir Max. Monolayer ads 	(Safin ejad, Cham jangal i, Goud arzi, & Bagh erian, 2017)
19.	Corn straw core + Graphene oxide (CSC- GO)	Methylene blue (MB)	 pH: 12 Temp.: 298 K [dye]: 500 mg/L [Dosage]: 0.221 g/L 	 CSC-GO: 414.03 mg/g Methylene blue removal CSC-GO: 98.76% CSC-GO: >90 % after 5th cycle Kinetic: Second order Isotherm: Temkin Spontaneous adsorption and exothermic 	(S. Liu, Ge, Wang , Zou, & Liu, 2018)

No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
20.	Tea waste (TW)	Cr (VI)	pH: 3.9 Temp.: 303 K [Dosage]: 6 g/L C _t : 240 min	 Cr (VI) removal TW: 97 % TW: 90.5 % after 5th cycle COD: 74.8 %, TDS: 55 % TS: 71 % Kinetic: Second order Isotherm: Langmuir Max. Monolayer ads 	(Nigam , Rajoriy a, Rani Singh, & Kumar, 2019)
21.	Wheat straw + Fe (NO ₃) ₃ (WFE)	Se (VI)	pH: 5 [dye]: 100 mg/L	 WFE: 14.3 mg/g Kinetic: Second order Isotherm: Freundlich 	(Godle wska, Bogusz , Dobrzy ńska, Dobro wolski, & Oleszcz uk, 2020)
22.	Banana peel + Iron oxide (BP-Fe)	Methylene blue (MB)	pH: 6.1 [dye]: 500 mg/L Temp.: 313 K	 BP-Fe: 862 mg/g Kinetic: Second order Isotherm: Freundlich BP-Fe: High adsorption capacity after 5th cycle 	(P. Zhang et al., 2020)
23.	Sugarcan e bagasse + Iron (ISCB)	Dye removal	pH: 8.4 [dye]: 8.6 mg/L [Dosage]: 0.7 g/L	 ISCB: 7 mg/g Dye removal: 93.7 % CR%: 88.8 % Kinetic: Second order Isotherm: Langmuir Magnetic Properties 	(Buthiy appan, Gopala n, & Abdul Raman, 2019)
24.	Garlic peel (GP)	Direct Red 12B	pH: 2 [dye]: 50 mg/L [Dosage]: 4 g/L	 GP: 37.96 mg/g Dye removal: >99 % Kinetic: Second order Isotherm: Langmuir 	(Asfara m et al., 2014)

No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
25.	Banana peels (BP) + Orange peels (OP)	Reactive red dye (RRD)	 pH: 4 [dye]: 25 mg/L [Dosage]: 10 g/L Temp.: 303 K 	 BP: 21.456 m²/g OP: 336.224 m²/g Reactive red dye removal BP: 89.41 % OP: 70.25 % Kinetic: Second order Isotherm: Langmuir and Freundlich 	(Tem esgen , Gabbi ye, & Sahu, 2018)
26.	Garlic peel (GP)	Methylene blue (MB)	 [dye]: 100 mg/L [Dosage]: 0.3 g Temp.: 323 K C_t: 210 min 	 303 K: 82.64 mg/g 313 K: 123.45 mg/g 323 K: 142.86 mg/g Dye removal: >99 % Kinetic: Second order Isotherm: Freundlich Max. monolayer adsorption 	(Ham eed & Ahma d, 2009)
27.	Passion fruit peel (PFP)	Methylene blue (MB)	 pH: 9 [dye]: 0.09 mmol/L [Dosage]: 1 g Temp.: 298 K Ct: 50 hrs 	 PFP: 0.0068 mmol/g 	(Pava n, Mazz ocato, & Gushi kem, 2008)
28.	Banana peel (BP) + Orange peels (OP)	Methyl orange Methylene blue Rhodamin e B Congo red Methyl violet Amido black	 pH: 6 - 7 [dye]: 100 mg/L [Dosage]: 1 g/L Temp.: 303 K 	 BP: 7.9 - 17.2 mg/g OP: 3.8 - 15.8 mg/g Density BP: 1.72 g/ml Density OP: 1.47 g/ml Isotherm: Freundlich (BP) Langmuir (OP) BET: 20.6-23.5 m²/g 	(Ann adura i, Juang , & Lee, 2002)

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No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
29.	Grape pomace (GP)	Brown KROM KGT dye	 pH: 2 [dye]: 100 mg/L Temp.: 298 K Ct: 12 hrs Agitation rate: 90 rpm 	 GP: 180.2 mg/g Size: 0.14–1.4 mm Kinetic: First order Isotherm: Langmuir Spontaneous adsorption and exothermic 	(A. P. d. Oliveir a et al., 2018)
30.	Korean cabbage Korean cabbage (KC) + Rice straw (RS) + Wood chip (WC) + Activated carbon (AC)	Congo red Crystal violet	 pH: 7 [dye]: 500 mg/L Temp.: 303 K 	 KC: 1304 mg/g RS: 620.3 mg/g WC: 195.6 mg/g AC: 271.0 mg/g Kinetic: Second order Isotherm: Langmuir 	(Sewu, Boakye , & Woo, 2017)
31.	Almond shell (CAS) + Orange peel (COP)	Methylene blue Congo red Methyl violet Amido black	 pH: > 5 [dye]: 100 mg/L [Dosage]: 2 g/L Temp.: 298 K C_t: 120 min Agitation rate: 150 rpm 	 COP: 166.7 mg/g CAS: 288.57 mg/g Kinetic: Second order Isotherm: Langmuir 	(Hashe mian, Salari, & Yazdi, 2014)
32.	Cucumis sativus peel (CSP)	Methylene blue	 pH: 8 [dye]: 100 mg/L [Dosage]: 4 g/L Ct: 1hrs 	 CPS: 122.4 mg/g Kinetic: Second order Isotherm: Freundlich Desorption: 63.62 % 	(Shako or & Nasar, 2017)

No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
33.	Banana peel powder (BPP)	Rhomine- B	 [Dye]: 25 mg/L [Dosage]: 0.3 g Ct: 60 min 	 Rhomine-B removal BPP: 81.01 % Isotherm: Langmuir 	(Singh, Parveen, & Gupta, 2018)
34.	Bottle gourd peel + Formaldehy de (FBGP) + Acetic acid (ABGP)	Reactive red 195-A (RRD) Reactive blue 222 (RBD)	 pH: 2 [Dosage]: 1 g/L Temp.: 300 K Ct: 60 min Agitation rate: 200 rpm 	 FBGP: 245.5 mg/g ABGP: 242.4 mg/g RRD and RBD removal FBGP: >98 % ABGP: >98 % RRD removal after 6th cycles FBGP: 98.2 to 84.9% ABGP: 97.9 to 83.2% Kinetic: Second order Isotherm: Temkin 	(Palamt hodi & Lele, 2016)
35.	Potato leaves powder (PLP) + Potato stem powder (PSP)	Methylene blue (MB) Malachite green (MG)	 pH: 7 [Dye]: 10 mg/L [Dosage]: 2 g/L Temp.: 303 K Ct: 3 min 	 PLP-MB: 52.6 mg/g PSP-MB: 41.6 mg/g PLP-MG: 33.3 mg/g PSP-MG: 27 mg/g Kinetic: Second order Isotherm: Langmuir and Freundlich 	(N. Gupta, Kushwa ha, & Chattop adhyaya, 2016)
36.	Pomelo peel (PP)	Methylene blue (MB)	 pH: 2 - 10 [Dye]: 250 mg/L [Dosage]: 0.25 g Ct: 5 hrs 	 PP: 7041.52 mg/g Isotherm: Dubinin-Radushkevich 	(Low & Tan, 2018)

No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
37.	Cashew nutshell (CNS)	Methylene blue (MB)	 pH: 10 [Dye]: 50 mg/L [Dosage]: 2.19 g/L Ct: 63 min 	 Methylene blue removal CNS: 99.97 % 2⁴ full factorial central composite design 	(Subra mania m & Kumar Ponnu samy, 2015)
38.	Activated banana peel (ABP) + Natural banana peel (NBP)	Cationic dye	 pH: 4 - 8 [Dye]: 100 mg/L [Dosage]: 0.5 g/L Temp.: 293 K 	 ABP =19671 mg/g NBP =18647 mg/g Kinetic: Second order Isotherm: Freundlich (ABP) Langmuir (NBP) 	(Amel a, Hasse n, & Kerrou m, 2012)
39.	Banana peel (BP)	Cr (VI)	 pH: 8 [Dye]: 1.92 × 10⁻⁵ M Temp.: 313 K Ct: 60 min 	 BP: 35.52 mg/g Cr (VI) removal BP: 97 % within 10 min BP: Lost 1–3% after 10th cycle Kinetic: First order Isotherm: Langmuir 	(Mem on et al., 2008)
40.	Banana Peel Powder	Reactive Black 5 (RB5) Congo Red (CR)	 pH: 3 [dye]: 300 mg/L Temp.: 298 K [Dosage]: 0.03g 	 RB5: 49.2 mg/g CR: 164.6 mg/g Kinetic: Second order Isotherm: Langmuir Max. Monolayer ads 	(Muna gapati, Yarra muthi, Kim, Lee, & Kim, 2018)
41.	Banana peels + Acrylonitrile (GBPs)	Hexavalen t chromium Cr (VI)	 pH: 3 [dye]: 400 mg/L Temp.: 298 K [Dosage]: 4 g/L Ct: 120 min 	 Cr (VI)%: 96 %. Kinetic: Second order Isotherm: Freundlich and Langmuir Spontaneous adsorption and exothermic 	(Ali, Saeed, & Maboo d, 2016)

No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
42.	Oil palm kernel shell (OPKS) carbonisatio n-activation	POME	 [dye]: POME [Dosage]: 40 g/L Ct: 30h 	 TSS 90% COD 68% CR%: 97% BOD: 83% OPKS surface area increase from 305 m²/g to 935 m²/g 	(Zainal et al., 2018)
43.	Potato peels charcoal (PPC)	Copper (II)	 pH: 6 [Dye]: 150 mg/L [Dosage]: 1 g Temp.: 303K 	 Copper (II) removal PPC: 99.8 % Isotherm: Langmuir and Freundlich Spontaneous adsorption and exothermic 	(Aman, Kazi, Sabri, & Bano, 2008)
44.	Banana peel (BPP)	Strontium (II) Sr (II)	 pH: 7 [Dye]: 100 mg/L Temp.: 323 K Ct :10 min Agitation rate: 120 rpm 	 BPP: 41.5 mg/g Desorption: 66.7 % Regeneration up 5th cycles. Kinetic: Second order Isotherm: Freundlich Spontaneous adsorption and endothermic 	(Mahin drakar & Rathod, 2018)
45.	Banana peel + Acrylonitril e + Cellulosic (BPAC)	Mn (II)	 pH 8 [Dye]: 100 mg/L [Dosage]: 4 g Temp.: 303 K 	BPAC: 94 %Isotherm: Langmuirco-polymerization	(Ali, 2017)
46.	Overripe Cucumis sativus (OCS)	Acid Blue 113	 pH: 11 [Dye]: 750 mg/L Temp.: 323 K Ct :3 hrs 	 OCS: 59.81 mg/g Kinetic: Second order Isotherm: Langmuir Spontaneous adsorption and endothermic 	(L. Y. Lee et al., 2016)

No.	Biomass	Pollutants	Optimized	Main Findings	Ref.
			condition		
47.	Oak acorn peel (OP)	Methylene blue (MB) Acridine orange (AO) Malachite green (MG)	 pH: 2-10 [Dye]: 600 mg/L [Dosage]: 5 g/L Ct: 3 hrs 	 MB: 109.43 mg/g AO: 115.92 mg/g MG: 111.85 mg/g Dye removal OP: 60 – 97% Kinetic: Second order Isotherm: Langmuir and Freundlich Coagulated-coupled adsorption 	(Kuppu samy et al., 2017)
48.	Banana peels + Hierarchical ly porous carbon (BPCA) + Porous carbon oxide (BPCAO)	Methylene blue (MB) Co (II)	 pH: 7 [Dosage]: 1 g/ml Temperat ure: 298 K Ct:1 hr Ultrasoun d: 40 kHz 	 BPCA-MB: 744.39 mg/g BPCA-Co (II): 80.89 mg/g BPCAO-MB: 986.89 mg/g BPCAO-Co (II): 122.4 mg/g MB and Co (II) BPCAO Kinetic: Second order Isotherm: Langmuir 	(D. Yu, Wang, & Wu, 2018)
49.	Carbonized pomegranate peel (CPP)	Malachite green (MG)	 pH: 6 [Dye]: 30 mg/L [Dosage]: 0.1 g Temp.: 323 K Ct: 90 min 	 CPP: 31.45 mg/g MG removal CPP: 99.10% Kinetic: First order Isotherm: Langmuir Spontaneous adsorption and endothermic 	(Gündü z & Bayrak, 2017)
50.	Litchi peel (LP) + Mercapto- acetic acid (MLP)	Cr (VI)	 pH: 1- 4 [Dosage]: 8 g/L Ct: 80 min Temp.: 303 K 	 LP: 7.05 mg/g MLP: 9.55 mg/g Kinetic: Second order Isotherm: Langmuir Spontaneous adsorption and endothermic 	(Yi, Lv, Liu, & Wu, 2017)

2.3 Limitation of Biomass Adsorbents

Biomass wastes can be used as raw material to synthesize high-value adsorbent as it contains components like carbohydrates, lipids, and proteins. However, low regeneration capacity, less stability, low adsorption performance, smaller surface area, and poor separability are all limitations of raw biomass adsorbent. (Y. Yang et al., 2011). Modification of the adsorbent could be made to overcome the limitation of biomass adsorbent (Thomas & Alexander, 2020; Zhuang, Liu, Chen, & Fei, 2020).

According to the literature review in Table 2.1, modified raw biomass adsorbents show excellent properties such as broad surface area, high porosity, and more excellent adsorption performance (Van Thuan, Quynh, Nguyen, Ho, & Bach, 2017). The study of CS Lee and others (2013) reported that the activated carbon-based on palm kernel shell with sterically hindered amines (C. S. Lee, Ong, Aroua, & Daud, 2013) and FeCl₃ (Mubarak, Kundu, Sahu, Abdullah, & Jayakumar, 2014) shows enhancement in adsorption capacity, surface area, porosity compared to the unmodified adsorbent. In addition, activated carbon-zeolite composite (ACZ) prepared from waste macadamia nut shell and synthetic faujasite (Wongcharee, Aravinthan, & Erdei, 2019) for the removal of methylene blue (MB) also reported that the hybrid adsorbent shows high adsorption ability, and high regeneration compared to the unmodified adsorbent.

2.4 Modification of Biomass Adsorbent

The adsorbent could be modified using chemical, physical, or biological methods. The literature study shows that biomass adsorbent mostly modified using iron oxide, titanium dioxide (Fazal et al., 2020), graphene oxide (Z. Wang et al., 2020), magnesium oxide (Oginni et al., 2020), zeolite, polymer (J.-X. Yu et al., 2009), spent shiitake substrate (Dong & Lin, 2015), sulfone (Nejadshafiee & Islami, 2019).

2.4.1 Zeolite Based Adsorbent

Generally, the organic compound contains carbon and hydrogen or other non-metal elements such as oxygen, nitrogen, sulfur, and phosphorus. Whereas inorganic compound consists of ions, metal oxide and inorganic salt (Mei et al., 2020). Organic compounds such as sodium alginate, anthocyanin, citric Acid, tartaric Acid, lignin, and inorganic compound such as iron oxide, zeolite, Copper (II), Mn (II), cobalt-iron are commonly used to hybrid with biomass adsorbents (W. Huang et al., 2018; Maqbool et al., 2020; Shavandi, Haddadian, Ismail, Abdullah, & Abidin, 2012)

Zeolite is an inorganic material known for its ion exchange power, high porosity, large surface area, high regeneration potential, strong acidic stability, readily available and low cost (Al-Jubouri & Holmes, 2020). Zeolite is made up of aluminium (Al), oxygen (O), carbon (C) and metals like Titanium (Ti), Tin (Sn), and Zinc (Zn) (Montalvo, Huiliñir, Borja, Sánchez, & Herrmann, 2020). It also has a unique feature that allows other molecular dimensions to move through and shows cations selectivity (Al-Jubouri & Holmes, 2020; Andraka, Dzienis, Myrzakhmetov, & Ospanov, 2017; Montalvo et al., 2020). Previous studies also reported that zeolite is very effective for removal of the organic compound and heavy metals from wastewater (Erdem, Karapinar, & Donat, 2004; Hun Kwak, Zhu, Lee, Peden, & Szanyi, 2012; Motsi, Rowson, & Simmons, 2009; Pitcher, Slade, & Ward, 2004; H. Zhang, Li, Zhang, & Shuang, 2016). Shavandi and others (2012) reported that zeolite shows great adsorption capacity to adsorb heavy metals from POME obtained from the aerobic pond (Shavandi et al., 2012). Furthermore, previous studies have shown that zeolite is a suitable material to combine with commercial or biomass activated carbon as it possessed micropores and mesopores properties and it acts as high value-added environmental materials (Gao, Kume, & Watari, 2005; Z. Li et al., 2014; Min Wang et al., 2018). Ma and others (2008) have successfully synthesized zeoliteactivated carbon extrudates (ZEOAC) (Ma, Sun, Su, Cheng, & Li, 2008). On the other hand, Khanday and others (2017) reported that zeolite in chitosan composite could increase the stability of the adsorbent in an acidic medium and impart mechanical strength (Khanday, Asif, et al., 2017). The study shows that zeolite able to enhance the surface area of the adsorbent and increase adsorption capacity.

In short, many articles have discussed the adsorption performance of zeolite-based adsorbent in term of it costing, characteristic, adsorption and desorption capacity (Khalil, Thomas, Jabraoui, Bazin, & Maugé, 2020; Khanday, Asif, et al., 2017; Khanday, Marrakchi, Asif, & Hameed, 2017; Min Wang et al., 2018). Combining zeolite with adsorbent derived from agricultural waste may act as a strong capping adsorbent for cationic and anionic ions in the adsorption process. In summary, the hybrid adsorbent provides excellent adsorption efficiency, regeneration capacity, and treatment cost-effectiveness.

2.4.2 Iron Oxide Based Adsorbent

Magnetically modified biomass adsorbents have attracted much attention because of their advantages, including cost-effectiveness, environmentally friendly, high reactivity, facile availability, and good recovery (Jain et al., 2018; L. C. A. Oliveira et al., 2002; Suresh Kumar et al., 2017). In recent years, iron species such as zero-valent iron Fe₃O₄, Fe₂O₃, and FeS, have been extensively used for adsorbent modification. Magnetic particles can be used to adsorb pollutants from aqueous or gaseous effluents and then separated from the medium using a simple magnetic process after adsorption (L. C. A. Oliveira et al., 2002). Furthermore, iron oxides have been suggested as anti-fouling agents and have been successfully tested in the adsorption process by Choo and Kang (2010) (Choo & Kang, 2003; Kang & Choo, 2010).

Besides, wheat straw (Wei Yang et al., 2019), macroalgae biomass (Angelova et al., 2016), and sugarcane bagasse (Noor, Othman, Mubarak, & Abdullah, 2017) have been incorporated with iron oxides to remove both organic and inorganic pollutants. According to the study conducted by Hua and others (2018), containing iron oxide in the biomass adsorbent can increase the efficiency of the adsorbent's separation process and adsorption capacity (Hua, 2018; Kharissova, Dias, & Kharisov, 2015). Lompe and others (2017) reported that iron oxide nanoparticles did not produce sludge after adsorption (Lompe, Menard, & Barbeau, 2017). Hence, combining iron oxide with other biomass adsorbents will maximize the characteristic of the adsorbent. The magnetic properties help solve the separation issue at the end of the adsorption treatment. The presence of an oxidant in combination with iron oxide, on the other hand, helps to initiate the Fenton reaction, which produces hydroxyl radicals and aids the adsorption process (Azmi Aris, 2008). As a result, in this analysis, zeolite and iron oxide were chosen to hybridize biomass to improve the stability, surface area, and adsorption potential of biomass.

2.5 Adsorption

In comparison with other wastewater treatment methods or techniques, the adsorption process has been proved to be one of the most efficient and attractive methods due to high efficiency, biodegradability, low investment cost, no sludge generation, simplicity of design, ease of operation and the ability to treat organic and inorganic pollutants (Bulca, Palas, Atalay, & Ersöz, 2020). On the other hand, the conventional adsorption method has several drawbacks, including low stability, extended retention period, high capital, and inefficient performance. Previous research has shown that adding oxidants to wastewater treatment will increase degradation and reduce COD and colour (Chung, Wang, Wang, Huang, & Chang, 2017; Huling, Huling, & Ludwig, 2017). Chung and others (2017) has concluded that the presence of oxidants such as H_2O_2 , $S_2O_8^{2-}$, and KMnO₄, able to increase the rate of caffeine adsorption in the reaction from water by using a facile modification of graphite sheet (Chung et al., 2017). The presence of oxidants in others reaction like photocatalytic (Habibi & Shojaee, 2020) and Fenton oxidation (Bokare & Choi, 2014) also able to increase the rate of COD and TOC removal. Habibi and others (2019) have studied the effect of oxidants on enhanced degradation of Indo light blue dye (Habibi & Shojaee, 2019). In contrast to no oxidants, oxidants like K₂S₂O₈, KBrO₃, and H₂O₂ can have a much faster degradation rate. Huling and colleagues (2017) confirmed that adsorption could remove arsenic from ground water and could be used as a treatment method to protect human health (Huling et al., 2017). In addition, H. Li and colleagues (2020) indicated that adsorption with oxidants could provide a fast oxidation rate, strong adsorption, consistent reusability, and easy separation (H. Li et al., 2020). In conclusion, oxidants can improve the adsorption process by reducing retention time and increasing adsorption capability.

Advantages	Limitations
 Biodegradability 	 Low stability and selectivity
 Low investment cost 	 Extended retention period
 No sludge generation 	 High capital
• Simplicity of design	 Inefficient performance depending adsorbent
• Ease of operation	 Disposal of exhausted adsorbents

Table 2. 2: Advantages and limitations of adsorption

2.6 Effect of Parameters on Adsorption Process

2.6.1 Effect of pH

One of the most critical parameters that affect adsorption is pH (Nandi, Goswami, & Purkait, 2009). Adsorbent charge and the degree of ionization of pollutants are affected by the solution pH (Asfaram et al., 2014). Changes in pH affect the kinetics of the reaction as well as the equilibrium properties of adsorption. Increases in pH causes a negative charge to increase in the cationic dye such as methylene blue (MB), safranine T (ST) and crystal violet (CV), resulting in increased dye adsorption (Padmavathy, Madhu, & Haseena, 2016). As the pH drops, the adsorbent's surface has a higher positive charge, attracting anionic molecules to the surface, increasing adsorption for anionic dye such as methyl orange (MO), Congo red (CR), direct blue 71 (DB71) and Eriochrome black T (EBT) (Asfaram et al., 2014).

Adeleke and others (2017) have reported that adsorption flavor in pH 10 gives an 89.6% COD removal in POME compared to acidic condition (A. O. Adeleke, Latiff, Al-Gheethi, & Daud, 2017). On the other hand, Ying He and others (2019) have reported that when biochar is used as an adsorbent for removal of ionizable organic contaminants, efficient adsorption happened at pH 2 to 5 (Y. He et al., 2019). The majority of studies found that adsorption processes work best in an acidic environment (M. M. Bello et al., 2013; Ge et al., 2018; R. R. Mohammed & Chong, 2014; Padmavathy et al., 2016; J. Zhao, Wang, Wang, Zhang, & Zhang, 2019). R. R. Mohammed and others (2014) reported that treating Palm Oil Mill Effluent (POME) with banana peel favors acidic conditions (R. R. Mohammed & Chong, 2014).

On the other hand, the removal of Hexavalent Chromium (Cr (VI)) from wastewater by magnetite nanoparticles also shows that the most optimum pH for the adsorption process

is at pH 3.0 ± 0.1 . Besides, the COD removal is most efficient at the pH range of 3 - 4 for the adsorption of the organic substances with recyclable magnetic Ni_{0.6}Fe_{2.4}O₄ nanoparticles. However, the removal is drastically decreased when the pH value is increased above 5 (J. Zhao et al., 2019).

Moreover, Keran Li and others (2021) have also reported that best performance for the removal of cation dye such as methylene blue (MB) and safranine T (ST) happened at pH 10 - 11 (K. Li, Yan, Zhou, Li, & Li, 2021). On the others hands, anionic azo dye was evaluated where the highest removal of direct blue 71 (DB71) was achieved at pH 3 by using bipyridinium-based polyhydrazone adsorbent (El Malah et al., 2021). Lastly, Chen and others (2021) have stated that cationic methylene blue preferred to adsorb on negatively charges adsorbent under alkaline conditions, whereas anionic Congo red easily adsorbed on positively charges adsorbent under acidic conditions (Chen, Feng, Ma, & Huang, 2021). In summary, effect of pH is strongly depending on type of adsorbents, type of dyes and type of wastewater.

2.6.2 Effect of Adsorbent Dosage

The adsorption rate is also affected by the adsorbent dosage and particle size of the adsorbent or adsorbate. The surface area of the adsorbent increases as the dose is increased, making it more available for adsorption (Padmavathy et al., 2016). However, the adsorbent dose will increase until maximum removal is achieved, after which it will remain constant or decrease (Akköz et al., 2019). This is due to the interaction between adsorbate and adsorbent in the solution.

Buthiyappan and others (2019) have reported that adsorbent dosage plays an essential role in the adsorption efficiency of POME and dye overs the activated carbon developed

from biomass waste (Buthiyappan et al., 2019; R. R. Mohammed & Chong, 2014). The adsorption was significantly affected by the higher dose because more surface area was available for adsorption, enabling the adsorbate to penetrate the adsorption sites easily.

Nejadshafiee and others (2019) also reported that the adsorption efficiency of heavy metal ions increased with increasing the dosage of bio-adsorbent (Nejadshafiee & Islami, 2019). Reddy and others (2016) reported that increasing the adsorbent dosage will increase surface area and availability of more adsorption sites. Still, some of the sites present on the surface of the adsorbent will be left unoccupied, which accounts for the decrease in adsorption capacity (Reddy et al., 2016). In summary, the adsorbent dose has a significant impact on the removal rate, and it is also one of the most important characteristics of industrial applications. (Tri et al., 2020).

2.6.3 Effect of Oxidants Dosage

Some of the most widely used oxidants include sodium persulfate (Na₂S₂O₈), sodium permanganate (Na₂MnO₄), hydrogen peroxide (H₂O₂), $S_2O_8^{2-}$ and KMnO₄. Huling and others (2017) discussed the characteristic and cost of the oxidants (Huling et al., 2017). The study found that sodium persulfate is costlier (\$4.20/mole) and that it must be activated by Fe²⁺, a base (KOH), or thermally (>30 °C), which adds to the expense. On the other hand, although Na₂MnO₄ is less expensive (\$2.69/mol), it is still not economically feasible. MnO₂, one of the residuals from Na₂MnO₄, is non-toxic, highly stable, and capable of providing different adsorptive surfaces on the adsorbent. H₂O₂, on the other hand, is less expensive (\$0.04/mol) and least limitation as compared to most other oxidants.

The present of H_2O_2 will react with Fe^{2+} from the adsorbent to form hydroxyl radical (OH·). Whereas when there is excess amount of H_2O_2 , Fe^{3+} will react with H_2O_2 to regenerate Fe^{2+} with hydroperoxyl radical (HO₂) and hydron (H⁺) (Bokare & Choi, 2014). During the reaction, radicals, and others potential reactive complex such as Fe (OH)⁺, Fe (OH)²⁺, Fe (OH)²⁺, and Fe (OH)(OOH)⁺ have high potential to be actively participate in degrading organics pollutants in wastewater (Neyens & Baeyens, 2003). Therefore, presence of H_2O_2 due to the strong hydroxyl radical able to increase the adsorption's performance compared to the conventional adsorption process.

Chung and others (2017) stated that the presence of oxidants such as H_2O_2 , $S_2O_8^{2-}$ And KMnO₄ can increase the rate of caffeine adsorption in the reaction from water by using a facile modification of graphite sheet (Chung et al., 2017). The adsorptive ability of adsorbent with KMnO₄ is higher than H_2O_2 and $S_2O_8^{2-}$. Z.Zhang and others (2019) have stated that the dosage of H_2O_2 can increase the maximum adsorption capacity and adsorption efficiency of the process (Z. Zhang et al., 2019). The amount of H_2O_2 used in the reaction is significant because it produces the hydroxyl radical, a powerful radical for efficient oxidation. The dosage of H_2O_2 , on the other hand, is an essential parameter in COD removal because the right amount of H2O2 is needed to achieve higher COD removal. (H. Zhou, Kang, Zhou, Zhong, & Xing, 2018). In addition, oxidants also play an essential role in photocatalytic (Habibi & Shojaee, 2020) and Fenton oxidation (Bokare & Choi, 2014)

Abou-Elela and others (2014) revealed that Fenton oxidation is highly affected by the dosage of H_2O_2/COD ratio and Fe^{2+} concentration (Abou-Elela, Ali, & Ibrahim, 2014). The optimal H_2O_2 : COD ratio is 0.75, while the optimal H_2O_2/Fe^{2+} ratio is 50 to produce less sludge. Excessive H2O2 dosage, on the other hand, has an inhibitory action because

 H_2O_2 molecules absorb OH⁻ and generate other radicals such as HO²⁻, which has a lower oxidative strength than the hydroxyl radical (Collivignarelli, Pedrazzani, Sorlini, Abbà, & Bertanza, 2017; P, Kumar, Thakur, & Ghosh, 2019).

2.6.4 Effect of Contact Time

The contact time acts as an important parameter as it can alter the effects on adsorption process as well as the economic efficiency of the process. Besides, the chemical and physical structure such as surface area and binding constants of the adsorbent and the particle size of the adsorbate may differs the contact time (Soliman & Moustafa, 2020). Even though the contact time is depending on the type of wastewater, rate of agitation and other factors, but it still able to prove that adsorption process happen rapidly in the beginning of the experiment and remain constant once it achieved equilibrium. The adsorption process occurs rapidly at the beginning of the experiment as there are many unoccupied sites (Chingono, Sanganyado, Bere, & Yalala, 2018; Kushwaha, Srivastava, & Mall, 2010; Nandi et al., 2009). However, due to repulsive forces between the solute molecules in the solid and the bulk liquid phase, occupancy of the remaining vacant surface sites becomes difficult as contact time passes (Srivastava, Mall, & Mishra, 2005). Using commercial activated carbon and bagasse fly ash to treat dairy wastewater, Kushwaha and others (2010) confirmed rapid adsorption within 15 minutes (Kushwaha et al., 2010).

Buthiyappan and others (2019) studied the efficiency of iron oxides impregnated sugarcane bagasse adsorbent (ISCB) for the treatment of the dye water (Buthiyappan et al., 2019). The study concluded the rate of adsorption happened rapidly in the beginning as there were many unoccupied adsorption sites on the surface of ISCB. However, the adsorption was found to be decreased at the increase in the contact time. The repulsive

forces between the adsorbed dye molecules and the simulated dye solution caused a decrease in the adsorption performance (Chingono et al., 2018). In general, longer the contact time, higher the adsorption rate until it reaches equilibrium. And when it reaches equilibrium, the adsorption rate is equal to the desorption rate.

2.7 Adsorption Mechanism

Adsorption occurs via ion exchange, ion-pairing, electrostatic attraction, hydrophobic bonding, hydrogen bonding and dispersion (van der Waals) forces on the solid-liquid surfaces. The adsorption mechanism of a surfactant largely depends on the nature of the adsorbent and surfactant (Siyal, Shamsuddin, Low, & Rabat, 2020). Physical adsorption can be ascribed to the intermolecular gravitation, namely Van der Waals force or dispersion force. Because of the weak interaction, no chemical bonds involved and low adsorption heat, the solid adsorbents can be regenerated quickly and keep their original structure unchanged. At the same time, chemical adsorption refers to the chemical reaction between surface functional groups of adsorbent and adsorbate molecules (Zhu, Shen, & Luo, 2020). The main difference between physical adsorption and chemical adsorption is chemical adsorption usually involves one single surface layer, while physical adsorption involves multilayers, especially in high pressure (Le-Minh, Sivret, Shammay, & Stuetz, 2018). Besides, chemical adsorption presents more selectivity than physical adsorption because it only occurs between special groups and certain VOCs. The adsorption heat used for old and new bonds alternating during the chemical reaction is much higher, requiring high activation energy. So, the adsorption rate of chemisorption can be accelerated by high temperature, while physical adsorption is the opposite.

Furthermore, chemical adsorption is usually irreversible owing to the potent combination of chemical bonds, and the original forms of adsorbate may be changed during the desorption process (Zhu et al., 2020). On the other hand, physical adsorption is a reversible process, and adsorbents can be regenerated easily. It should be noted, physical adsorption and chemical adsorption mainly exist simultaneously in the practical adsorption process.

2.8 Adsorption Kinetic and Isotherm

Adsorption kinetics provide valuable insights into the adsorption mechanism and its ratelimiting steps. Kinetic isotherms are modelled by pseudo-zero order, pseudo-first-order, and pseudo-second-order (A. A. Mohammed & Kareem, 2019). Adsorption isothermal models are essential tools for studying adsorption behaviors and mechanisms as it used to reflect the interaction between adsorbents and adsorbates (W. Huang et al., 2018). Adsorption isotherms explained the amount of adsorbate adsorbed by unit mass of adsorbent from the liquid phase. It is essential to analyze adsorption equilibrium data for the design optimization of an adsorption system. Langmuir, Freundlich and Temkin model is most commonly used models of adsorption.

Langmuir isotherm is an ideal monolayer adsorption model. It reflects that the molecules adsorbed on the adsorbent surface can form a monolayer, and each molecule adsorbed on the surface has the same adsorption activation energy (Y. Zhou, Chen, Lu, Tang, & Lu, 2011). The model has the following equation (Langmuir, 1918):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{Eq. 2.1}$$

 q_e — equilibrium absorption capacity (mg/g) q_m —maximum adsorption capacity(mg/g) C_e — equilibrium concentration of adsorbate (mg/L)

 K_L — adsorption equilibrium constant (L/mg)

Freundlich isotherm is a model for multilayer adsorption. Generally, the Freundlich model is applied to describe the adsorption performance for highly interactive species or organic component on those materials with large specific surface area and developed pore structure such as activated carbon (Y. Zhou, Lu, Zhou, & Liu, 2019). The model was introduced by (Swearingen & Dickinson, 1931):

$$q_e = K_F C_e 1/n$$

(*Eq*. 2.2)

- q_e equilibrium absorption capacity (mg/g)
- C_e equilibrium concentration of adsorbate (mg/L)

n-adsorption constant represents the adsorption strength

 K_F —Adsorption capacity constant of adsorbent related to adsorption capacity (mmol/g)

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules decreases linearly with coverage due to adsorbent–adsorbate interactions. The adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The linearised Temkin isotherm is given by (Akpen, Aho, & Mamwan, 2018):

$$q_e = B_1 \ln c_e + B_1 \ln K_T \tag{Eq. 2.3}$$

 q_e — equilibrium absorption capacity (mg/g)

 C_e — equilibrium concentration of adsorbate (mg/L)

 B_1 —adsorption constant related to the heat of adsorption

 K_T —Adsorption capacity constant of adsorbent related to adsorption capacity (L/mg)

Hossain and others (2019) revealed that removing COD, BOD, and TSS from POME using FeSO₄.7H₂O followed the second-order kinetics modelling (Hossain et al., 2019). R. R. Mohammed and others (2014)has also proved that the adsorption process for treatment of POME followed the second-order kinetics modelling (R. R. Mohammed, Ketabchi, & McKay, 2014).

In the study of removal of Pb (II) and Zn (II) from aqueous solution by using green adsorbent, the R² values for pseudo-first-order model were less than that of the pseudosecond-order model for both ions signifying that the pseudo-second-order is better correlated than the pseudo-first-order model (Adebisi, Chowdhury, & Alaba, 2017). In terms of adsorption isotherm, the Langmuir model provides the best fit for Pb (II) adsorption and Zn (II). In the study of adsorption of polymers onto iron oxides (Veloso, Filippov, Filippova, Ouvrard, & Araujo, 2020), the equilibrium data were studied using Freundlich and Langmuir models, and it was found to fit the Freundlich one best. The values for Freundlich constants indicate that the mechanism that contributes most to the adsorption process was hydrogen bonding. However, the coexistence of more than one adsorption mechanism best explains the process itself and explains the differences found amongst theories over the years. In the recent study of adsorptive removal of phenol using faujasite-type Y zeolite, it has proved that Langmuir isotherm is found to be the best model fitted to the equilibrium data, and the results indicated that the adsorption kinetic data were fitted more closely to the Pseudo-second order (Ba Mohammed et al., 2019). In conclusion, the study of isotherm and kinetic is significant in adsorption as it can study the mechanism of adsorption in details.

2.9 Palm Oil Mill Effluent (POME)

Palm oil is Malaysia's largest industry, affecting the country's agriculture and economy. Currently, Malaysia accounts for 28% of world palm oil production and 33% of world exports. As one of the largest producers and exporters of palm oil and palm oil products, Malaysia plays a vital role in meeting the growing global need for sustainable oil palm products. Only in 2020 years, the total production of crude palm oil is 19,140,000 tonnes. Whereas in 2021, the total production of crude palm oil is expected to be 19,600,000 tonnes. Hence palm oil industry had become the major contributor to Malaysia's GDP as it had a high production rate (Wu, Mohammad, Jahim, & Anuar, 2010).

On the other hand, palm oil plantations and their related industries are mainly concerned with generating large amounts of waste such as trunks, empty fruit bunches, shells and fibers. As reported by Hamzah and others (2019), 62 % of palm oil mill effluent (POME), 20 % of empty fruit bunches (EFB), 13 % of mesocarp fiber (MF) and 5 % of palm kernel shell (PKS) have been generated from fresh fruit bunch (FFB) extraction (Hamzah, Tokimatsu, & Yoshikawa, 2019). Oil palm wastes contain biomass in lignocelluloses, thus providing potential in many applications by turning them into value-added products. Besides, palm oil is also one of the significant wastewater producers as it takes approximately 1500 liters of water to process 1000 kg of FFB.

There will be around 2.5 – 3.0 tonnes of POME discharge for every ton of crude palm oil produced during the extraction process. Most of the water used is released as a wastewater which will ended up as be palm oil mill effluent (POME) (R. R. Mohammed et al., 2014). POME is colloidal. It is a mixture of hydro cyclone wastewater, sterilizer condensate and separator sludge which is in a ratio of 1:9:15, respectively. On the other hand, POME characteristics strongly depend on different batches, days, factories, processing

technique, age or type of fruit, discharge limit, etc. The factors affect the characteristics of POME in term of pH, BOD, TSS, COD, Colour of POME. In addition, the quality and quantity of the discharged POME will also affect the biological treatment process of POME. The palm oil mill production rate has increased from about 10 million in 1960 to 72.27 million in 2020 to achieve the demand for crude palm oil internationally and locally. The large production will eventually generate a large amount of POME. Over the years, the amount of POME produced is expected to increase every year due to the demand needed.

2.10 POME Treatment Technologies

Among all the wastewater that generated, POME has been classified as the most difficult waste to handle due to large production, toxic organic pollutant that unable to treat efficiently using conventional treatment method (Z. S. Lee, Chin, Lim, Witoon, & Cheng, 2019). Treatment of POME can be classified into 2 main categories such as biological treatment, and physicochemical treatment (Holkar, Jadhav, Pinjari, Mahamuni, & Pandit, 2016).

Biological treatment is commonly used in most of the palm oil mill industry in the earlier phase as it acts as the best performance in treating POME (Choong, Chou, Norli, & Reviews, 2018; Yaser et al., 2009). Anaerobic treatment normally focusses on pretreatment of raw POME while aerobic treatment is conducted after anaerobic process. The ponding system as anaerobically digested POME from the ponds could be used to culture algae, and it is reliable and stable. However, ponding systems requires long retention time and large land areas, making them not suitable for factories near urban and developed regions (Chin, Lee, & Mohammad, 1996). Nahrul and others (2017) and Othman and others (2014) have reported that anaerobic treatment was found to be reduced the levels of COD to within 100 mg/L to 1725 mg/L, BOD (100 mg/L - 610 mg/L) and ammoniacal nitrogen within 100 mg/L to 200 mg/L after 45 – 60 days (Nahrul, Nor, Ropandi, & Astimar, 2017; Othman et al., 2014). Even though anaerobic treatment requires long retention time but it is able to remove more than 90% of BOD and COD from raw POME (Poh, Chong, & bioenergy, 2014; Shafie et al., 2016). Besides by using aerobic processes with a suitable level of dissolved oxygen, filamentous growth and sludge bulking in POME could be prevented, and if the oxygen input exceeds the requirement of the aerobic microorganisms, the system would be more efficient with shorter hydraulic retention time than anaerobic digestion. On the other hand, the aeration system in aerobic digestion is very energy-intensive, and POME is not nutritionally balanced for the aerobic growth of microorganisms (Wu et al., 2010). Abdullah and others (2004) have reported that about 90% of COD and BOD removal rate had achieved using aerobic treatment (A. Z. Abdullah, Ibrahim, & Ab. Kadir, 2012). In summary, even though biological treatment able to treat POME efficiently but it requires longer retention time and larger area is needed.

Chemical treatment consists of using different types of chemicals to aid and fasten the process. Where, Fenton oxidation is one of the Advanced oxidation processes (AOPs), has been extensively studied for various type of wastewater. Advanced oxidation processes (AOPs) are the only method which are capable of degrading hardly decomposable organic compounds and often applied as polishing technologies in wastewater treatment. Among all the AOPs such as radiation, photocatalysis, sonolysis, electrochemical oxidation technologies, Fenton-based reactions, and ozone-based processes, Fenton oxidation is considered the most effective in wastewater treatment especially for POME (D. Gamaralalage, Sawai, & Nunoura, 2019; J. L. Wang & Xu, 2012). As it requires less energy, does not need any special equipment and effective in

removal of many hazardous organic pollutants from wastewater. Saeed and others (2015) have reported that about 97% of color removal and 91% of COD removal on POME were achieved by using Fenton oxidation (Saeed, Azizli, Isa, & Bashir, 2015). Similar results was also obtained by Mustapha and others (2020) where 83% and 99% were obtained for COD and color removal respectively (Mustapha Mohammed Bello, Raman, & Asghar, 2020). In summary, Fenton oxidation is one of the effective and potential method for treatment of any wastewater as it overcome most of the disadvantage of biological treatments with a faster treatment and a less space needed.

adsorption, coagulation-flocculation Physicochemical treatment such as and photocatalytic are only capable in migrating but unable to decompose the organic pollutants and normally treat as tertiary treatment (Alhaji et al., 2018). Among all others treatment adsorption is one of the most environment friendly method to treat wastewater (Ahmed et al., 2015). Where the performance of adsorption strongly depends on the characteristic of adsorbent. Mohammed and Chong (2014) have reported that the used of modified banana peel as an adsorbent able to reduce colour, TSS, COD, and BOD up to 95% for POME (R. R. Mohammed & Chong, 2014). The beauty of coagulation & flocculation are they can destabilize POME suspension by adding chemical so that larger aggregates could be formed. Moreover, it does not require pH adjustment, high TSS removal, inexpensive and readily available for inorganic coagulants. However, an increase in operation temperature may reduce the efficiency of the coagulationflocculation process, and inorganic coagulants are enormously dependent on suitable pH adjustment (W. J. Ng et al., 1987). Hossain and others (2019) have conducted a jar test on POME where removal efficiency of 70% COD, 80% BOD, and 85% TSS were obtained (Hossain et al., 2019). Photocatalytic have the ability to mineralize organic compounds as well as destroy pathogenic microorganisms in wastewater (Zheng, Shen, Shi, Cheng, & Yuan, 2017). Many studies had been conducted where TiO_2 is used to degrade organic

pollutant in the wastewater due to its characteristic such as low toxicity, low cost, high activity, and high chemical stability (Alhaji et al., 2018; C. K. Cheng, Deraman, Ng, & Khan, 2016; K. H. Ng & Cheng, 2015). Ng and others (2015) have reported that about 78% of COD reduction was obtained from 168ppm of POME (K. H. Ng & Cheng, 2015).

In summary, every treatment has its own pros and cons. Hence selecting the suitable and effective treatment is the ultimate goal for each waste based on different aspects.

Biological Treatment	Chemical Treatment	Physicochemical Treatment
 Anaerobic Treatment 	 Fenton Oxidation 	Adsorption
 Aerobic Treatment 		 Coagulation-Flocculation
		Photocatalytic
		 Membrane Filtration
		 Ultrasonication

 Table 2. 3: POME Treatment Technologies

2.11 Design of Experiment

Design of Experiments (DOE) requires a minimal number of experiments to achieve a regression model by combining the individual effects of different variables and their interactions. In contrast with one-factor-at-time (OFAT), several significant factors can be changed and optimized simultaneously in the multivariate DOE (Jacyna, Kordalewska, & Markuszewski, 2019). Therefore, the main drawback of the OFAT such as time-consuming and not economically viable with no capability to detail the interaction between the studied variables can be overcome by DOE approach (Montgomery, 2017). Moreover, there are also others type of DOE such as full factorials, fractional factorials,

screening experiments, response surface methodology, evolutionary operations (EVOP) and mixture experiments.

Among other response surface methodology (RSM) is a valuable tool in designing the experiments and optimizing different environmental processes. RSM is a collection of mathematical and statistical methods helpful in designing the experiments, developing models by considering the interactions of parameters, and process optimization (Karimifard & Alavi Moghaddam, 2018). The main objective of RSM is to obtain the optimum operational conditions for the system or to acquire a region that satisfies the operating specifications (L. Zhang, Zeng, & Cheng, 2016). There are many classes of response surface designs that are occasionally useful in practice, such as full factorial design (FFD), central composite design (CCD), Box-Behnken design (BBD), and Doehlert design (DD) (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008).

Among these methods, CCD is the most frequently used design under RSM. It is appropriate for fitting second-order polynomial equations that have been often discussed to optimize several research problems (Asghar, Abdul Raman, & Daud, 2014). CCD provides equal information as the three-level FFD but with considerably fewer experimental runs. CCD builds on a factorial design; it just adds centre points and star (axial) points, effectively transforming your "cube" of inference into a fully rotatable, symmetric star. Ferreira and others have compared all the design strategies (2007) (Ferreira et al., 2007).

Throughout all the reported studies, CCD was used as the design experiment when there are more than four parameters in the study (Anfar et al., 2017; Bagheri, Ghaedi, Asfaram, Alipanahpour Dil, & Javadian, 2019; Dehghani et al., 2020). In comparison, BBD was

used when there are only three parameters in the study (Vinod Kumar Gupta et al., 2017; Y. He et al., 2020; Iqbal, Bakar, Toemen, Razak, & Azelee, 2019). BBD is good design for RSM as it permits estimation of the parameters of the quadratic model. Second, it is building of sequential designs. Third, detection of lack of fit of the model. Fourth, use of blocks in BBD. In conclusion, all the design strategy needs to be chosen wisely before experimenting.

2.12 Summary of Literature Review

The agricultural waste in the world has increased rapidly due to the growth of the country's agricultural industry, population, and social economy, which leads to serious environmental and health issues. Most of the agricultural wastes can be converted into green adsorbent due to their chemical properties, including the availability of functional groups such as hydroxyl, amino and carboxylic groups, which lead to the higher surface area, more active sites, and high adsorption efficiency. As one of the largest producers and exporters of palm oil and palm oil products, Malaysia plays a vital role in meeting the growing global need for sustainable oil palm products. On the dark side, large production will eventually generate a large amount of solid waste such as trunks, empty fruit bunches, shells, and fibres, leading to a solid waste management issue. Palm oil mill effluent (POME) has become the most considerable water pollution, leading to major environmental problems faced by Malaysia.

The Malaysian government has imposed stringent limits on the quality of the discharged wastewater because of the harmful impacts of wastewater on the environment and society. The conventional wastewater treatment processes for the palm oil industry are less efficient to satisfy the Department of Environment Malaysia (DOE). Therefore, considerable efforts are being made to find a practical, simple, stand-alone, small,

economically feasible and easy operation. Among the treatment techniques, the adsorption process can treat wastewater contaminated with high chemical oxygen demand (COD) and biological oxygen demand (BOD), oil and grease, suspended solids, ammonia-nitrogen, heavy metal concentration and high content of degradable organic matter.

The adsorption process is more effective than other wastewater treatment technologies in terms of cost, flexibility, simplicity of design, ease of operation, and insensitivity to toxic pollutants. However, the practical application of adsorption processes has drawbacks due to longer contact time and adsorbent costs. Therefore, there has been continuous research on exploring alternatives to develop biomass-based adsorbent from agriculture waste such as peanut shell, coconut shell, banana peel, palm kernel shell, garlic peel and rice husks for the removal of various heavy metal, anionic and cationic dyes, and persistent organic pollutants in the past years. Besides, the efficiency of raw biomass adsorbent can be improved through various methods such as chemical modification, physical modification, biological modification, mineral impregnation, and magnetic modifications. Based on the past studies, the adsorption performance of raw biomass adsorbent can also increase by combining or hybridizing with other powerful adsorbents, inorganic compounds, and organic compounds such as iron oxide, titanium dioxide, graphene oxide, magnesium oxide, zeolite, polymer, and sulfone.

Adsorption with oxidants resulted in a high oxidation rate, high adsorption potential, consistent reusability, and easy separation. The critical factors that affect the efficiency of the adsorption process with oxidants are the initial pH of the solution, the dosage of oxidants, dosage of adsorbent, contact time and temperature. Additionally, the literature

also confirms that minimal studies have been conducted on adsorption processes with oxidants using real wastewater, particularly POME wastewater.

Therefore, this study aimed to develop a high-performance hybrid magnetite biomassbased adsorbent from palm kernel shell (PKS) by incorporating with iron oxide and zeolite for POME wastewater treatment using adsorption with oxidants. The newly synthesized adsorbent's efficiency is evaluated in terms of stability, COD, and colour removals. The effects of various operating parameters such as initial pH of the POME wastewater, dosage of adsorbent, dosage of H_2O_2 and contact time on the degradation efficiency were analyzed. Each operating parameter was evaluated using Central Composite Design (CCD), a form of Response Surface Methodology (RSM).

CHAPTER 3: METHODOLOGY

3.1 Introduction

In this chapter, the materials and methods used to conduct the experiments and analyses are presented. The newly developed hybrid magnetite biomass-based adsorbent based on palm kernel shell and zeolite (Zeolite-Fe/PKSAC) will be characterized using SEM/EDX, FTIR, VSM, BET and XRD. Hence, the stability of the adsorbent will be examined by using adsorption experiment. Response surface methodology is used to design the experiments. Operating parameters such as initial pH, contact time, dosage of adsorbent and dosage of oxidants (H₂O₂) were used to determine the degradation efficiencies in terms of COD and colour removals. The following Figure 3.1 shows the overall methodology for this study.



Figure 3. 1: Flow diagram of overall methodology

All the chemicals were reagent grade and used without further purification. Ferrous sulfate (FeSO₄•7H₂O), ferric chloride (FeCl₃•6H₂O), sodium hydroxide (NaOH), hydrogen peroxide 33% (H₂O₂), sulfuric acid (H₂SO₄), zeolite and ethanol have been purchased from Sigma Aldrich (M) Sdn. Bhd. Activated carbon-based palm kernel shell (PKSAC) was purchased from Pacific Activated Carbon, Malaysia. Biologically treated POME has been collected from a local palm oil mill in Selangor Malaysia. Ultrapure water was used for all the experiments.

3.3 Description of the Procedures Including Safety Measures

3.3.1 Synthesis of Fe/PKSAC Composite

5 g of ground activated carbon, 3.66 g FeSO₄•7H₂O and 6.66 g FeCl₃•6H₂O were placed into a 500 mL beaker containing 100 mL of ultrapure water. The solution was stirred and heated to 65 °C for mixing propose. After 30 minutes of stirring, the solution was cooled down to 40 °C. Then the pH was adjusted to 10 - 11 to precipitate the iron hydroxides by using 5 M NaOH solution, and the solution was stirred for an hour. After that, the solution was left overnight and covered with cling film. The pipette was used to remove the supernatant, and then precipitates were washed with ultrapure water first then was rinsed with ethanol. After the ethanol drained, the precipitate was moved to the aluminum tray and dried at 80 °C for about 4 hours. Then, the precipitate was washed by using ultrapure water, and the magnetic rod was used to collect the activated carbon particles. The magnetically activated carbon particles dried at 80 °C overnight. After that, the dried Fe/PKSAC was stored in an airtight bottle.

3.3.2 Synthesis of Zeolite-Fe/PKSAC Composite

2.5 g of the zeolite and 5 g Fe/PKSAC (0.5:1) were placed into a 500 mL beaker containing 100 mL of ultrapure water and was stirred for 6 hours at 60 °C. Then the mixture was placed in an ultrasonic bath for 45 min, and the mixture was left at room temperature for 24 hours. The mixture was then washed and centrifuged to separate the adsorbent from the solution. Lastly, the synthesis adsorbent (Zeolite-Fe/PKSAC) was dried in the oven at 60°C overnight (T. Liu, Wang, Zhang, & Zhao, 2017).

3.3.3 Characterization of Adsorbents

The surface functional groups of the synthesized adsorbents were characterized using Fourier Transformation Infrared (FTIR) with a Perkin Elmer Spectrometer (Frontier) in the adsorption range of 500 – 4000 cm-1. The morphology and elemental composition of the adsorbents were examined with Scanning Emission Microscopy (SEM) and Energy Dispersive X-ray (EDX) spectroscopy using Thermo Fisher Scientific (Phenom ProX) from Netherlands. The changes in the morphology of the adsorbents were analyze using X-Ray Diffraction (XRD) analysis (Tedesco & Brunelli, 2017). Vibrating sample magnetometer (VSM) (LakeShore 340) was used to evaluate the magnetic properties of the adsorbents. The textural properties such as specific surface area and porosity of the adsorbents were analyzed using Brunauer Emmett Teller (BET), (Micrometrics ASAP 2020 (TRISTAR II 3020 Kr) analysis.

3.3.4 Adsorption Experiment Using Zeolite-Fe/PKSAC and Fe/PKSAC

The adsorbent capacity (Zeolite-Fe/PKSAC) was evaluated using adsorption processes with H₂O₂ to treat POME. The initial pH of the POME was adjusted to desire condition by using 0.5 M H₂SO₄ acid and 1 M NaOH alkaline. The desired amount of ZeoliteFe/PKSAC and H₂O₂ were added into the sample POME solution, and the sample solution was stirred continuously at a constant rate of 200 rpm. At the end of each experiment, the sample solution was obtained and filtered to remove the adsorbent. Thus, colour removal was measured immediately. Right after the colour removal reading was taken, the pH of the sample solution was adjusted to the alkaline base by using 1 M NaOH with the ratio of every 1ml of 200 mM of H₂O₂ solution with 10ml of 1M NaOH. Hence, the COD removal was measured. For the reusability study, the used adsorbent was washed with ultrapure water, followed by 0.1 M NaOH for 10 minutes. After that, the used adsorbent was washed with distilled water thrice. Lastly, the adsorbent was dried in an oven for 1.5 hours and stored for the next experiment. Yet, the performance of the Fe/PKSAC also evaluated through the same procedure as evaluating the performance of Zeolite-Fe/PKSAC. On the others hand, the whole set experiment was repeated with adsorption processes without H₂O₂. All the experiments were duplicated, and data were presented as averages with standard deviations.

3.4 Response Surface Methodology-Central Composite Design (RSM-CCD)

The adsorption experiment had been conducted using response surface methodology (RSM) with the aid of Design-Expert software. RSM is a multivariate statistical tool used for optimization of analytical methods. RSM method is one of the suitable methods for fitting a quadratic surface. Thus, it able to optimize the process parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. RSM also very useful for developing the empirical model building, improving, and optimizing processes parameter and it can also be used to find the interaction of several affecting factors as it is a collection of mathematical and statistical techniques. In general, RSM is a statistical method that uses quantitative data from the related experiment to determine regression model and to optimize a response (output
variable) which is influenced by several independent variables (input variables) (Behera, Meena, Chakraborty, & Meikap, 2018). In this study it was found that the colour and COD removal of POME strongly depends on four different parameters like pH, contact time, adsorbent dosage, and oxidants (H₂O₂) dosage. Different set of experiments were conducted to understand the interactive effects of each parameter on others as well as overall removal efficiency. Initially, there will be a total of 256 experiments need to be conducted with the combination of 4 parameters. Hence, it will involve a huge amount of chemicals used and yet lead to higher cost to the experiments if all the experiment is conducted. This will also create wastage of chemicals as the samples will be discarded after the experiments (Bagheri et al., 2019). Therefore, to minimize the waste of chemicals and conduct an optimal number of experiments, response surface methodology - central composite design (RSM-CCD) framework is used to design the experimental matrix based on 4 independent variables. A total of 100 experiments were conducted in this study.

3.5 Experimental Design, Data Analysis and Process Optimization

Design Expert Software Version 10 was used for statistical design of experiments. Response surface methodology central composite design (RSM-CCD) was applied in this study to optimize four independent variables: dosage of adsorbent, dosage of H₂O₂, contact time and pH value. Preliminary experiments were carried to determine the ranges for the operating parameters. The adsorption study conditions to identify the optimum operating conditions used including dosage of adsorbent 1 g/L – 5 g/L, dosage of H₂O₂ 40 mM – 200 mM, contact time 10 min to 60 min and pH value from 3 to 9. Analysis of variance (ANOVA) was used to evaluate the interaction between independent variables and the responses. The quality of the fit regression model was expressed by determination coefficient, R₂. In terms of statistical significance, Fishers F-test was used. It determined

whether the model was accepted or rejected based on the probability (p-value) with 95 % confidence level. Lastly, based on the predicted models the numerical optimizer was used to determine the optimum values for each operating parameter.

3.6 Analytical Methods

The COD and colour removal of POME were analyzed based on the experimental data that collected. UV Spectrophotometer was used to determine COD and colour removal according to American Public Health Association (APHA) standard method. The experiments were run in triplicates, and data was reported as mean and standard deviations (Ching, Yusoff, Aziz, & Umar, 2011; Kaur, Mor, & Ravindra, 2016). The colour was measured using Platinum-Cobalt (APHA/Hazen) Color Standards after filtration using a UV-Spectrophotometer (Spectroquant Pharo 300, Merck, Germany) in ADMI unit. APHA 5220B: Open Reflux Method in milligrams per litre (mg/L) unit was used for COD measurement. The formulas for removal percentage of COD and colour were shown in equation 3.1.

Removal in percentage(%) =
$$\frac{C_i - C_f}{C_i}$$
 (Eq. 3.1)

where C_i and C_f refer to the initial and final values of color or COD concentration, respectively. The Langmuir model was applied for determination of the maximum adsorptive capacities of the adsorbent (Desta, 2013; R. R. Mohammed et al., 2014). Synthesized hybrid magnetite biomass-based adsorbents were tested on real wastewater POME, and the experimental data was applied to pseudo-zero (Eq. 3.2), pseudo-first (Eq. 3.3) and pseudo-second kinetic models (Eq. 3.4) (A. A. Mohammed & Kareem, 2019).

$$Q_t = -K_1 t + Q_e \tag{Eq. 3.2}$$

$$\ln(Q_t) = -K_2 t + \ln(Q_e)$$
 (Eq. 3.3)

$$\frac{1}{Q_t} = K_3 t + \frac{1}{Q_e}$$
 (Eq. 3.4)

where Q_t is the amount of colour removed at time t, Q_e is the adsorptive capacity at the equilibrium time, whereas K_1 (M/s), K_2 (1/s) and K_3 (1/Ms) are the pseudo-zero, pseudo-first and second order constant rates, respectively (Ahsan et al., 2018).

3.7 Safety Precautions

The hazardous information of the chemicals used in this study was collected and provided in Table 3.1. Table 3.1 shows that most of the chemicals used in this study categorized as a dangerous and proper precaution were taken while handling them. Appropriate personal protective equipment (PPE) including chemical safety goggles, gloves, face mask, and lab coat were used while conducting experiments. The standard safety procedure of preparing the chemical solution was adhered in this work, which also includes the use of a fume cupboard. Additionally, waste generated, excess chemicals and unused collected real wastewaters are stored in a proper container prior to disposal.

No.	Chemical		Potential hazard		Preventive measures
1	Palm kernel shell	٠	May cause irritation to	•	Kept in air-tight container
	activated carbon		respiratory tract, skin,		and avoid from ignition
	(<250 nm)		and eye.		sources and combustible
		•	Prolonged exposure		materials.
			can cause mucous	•	Working area was well
			membranes irritation.		ventilated.
		•	Weakly explosive and	•	PPE was well-equipped
			may form combustible		during laboratory work.
			dust concentrations in		
			air.		

Table 3. 1: Safety data sheets of chemicals used in this study

No.	Chemical	Potential hazard	Preventive measures
2	Zeolite powder (<20 μm)	 May cause irritation to respiratory tract. Excessive exposure can cause carcinogenesis (a form of carcinogen). 	Kept in air-tight container and avoid from ignition sources and combustible materials. Working area was well ventilated. PPE was well-equipped during laboratory work.
3	Hydrogen peroxide (H ₂ O ₂)	 Corrosive to eyes, skin, and respiratory system. Causes severe skin burns and eye damage. Harmful if swallowed. Harmful if inhaled. May intensify fire. 	Steps involved H ₂ O ₂ was conducted in fume chamber. PPE was well-equipped during laboratory work.
4	Ferrous sulfate heptahydrate (FeSO4.7H2O)	 Causes severe • irritation to eyes, skin, gastrointestinal tract and respiratory tract. Harmful if swallowed. May cause central nervous system effects. 	PPE was well-equipped during laboratory work.
5	Iron (III) chloride hexahydrate (FeCl3·6H2O)	 Causes burns by all • exposure routes including eyes, skin, digestive tract, and respiratory tract. 	PPE was well-equipped during laboratory work.
6	Potassium permanganate (KMnO4)	 Acute toxicity to oral, dermal and inhalation. Causes skin corrosion and serious eye damage. 	PPE was well-equipped during laboratory work.

Table 3. 1: Continued

No.	Chemical	Potential hazard	Preventive measures
7	Sulfuric acid (H ₂ SO ₄)	 Causes respiratory • irritation. Causes severe eye damage and skin • burns. Potentially explosive at concentrated form. Causes irritation to nose and throat and cause difficulties 	Steps involved H ₂ O ₂ was conducted in fume chamber. PPE was well-equipped during laboratory work.
		breathing if inhaled.Can burn holes in the stomach if swallowed.	
8	Sodium hydroxide (NaOH)	 Causes irritation to eyes, skin, and mucous membrane. Causes severe skin burns and eye damage. May cause severe irritation to gastrointestinal tract if swallowed. 	Steps involved H ₂ O ₂ was conducted in fume chamber. PPE was well-equipped during laboratory work.
9	Ethanol (C ₂ H ₅ OH)	 Causes severe eye irritation. Causes moderate skin irritation. May cause gastrointestinal irritation. Inhalation of high concentrations may cause central nervous system effects. 	Steps involved H ₂ O ₂ was conducted in fume chamber. PPE was well-equipped during laboratory work.

Table 3. 1: Continued

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter discussed the result obtained in this study. The flow of the chapter follows the sequence of the objective. The first part of the chapter discusses the properties of the iron oxide-palm kernel shell activated carbon (Fe/PKSAC) and the zeolite iron oxide palm kernel shell activated carbon (Zeolite-Fe/PKSAC). The activated carbon has been characterized using FTIR, SEM-EDX, XRD, VSM and BET analyses. The second part of the chapter evaluated the adsorption properties of Fe/PKSAC and Zeolite-Fe/PKSAC activated carbon in removing POME with and without the aid of oxidant (H₂O₂). Lastly, the kinetics, isotherms, and mechanism of adsorptions have been discussed.

4.2 Characterization of Fe/PKSAC and Zeolite-Fe/PKSAC Adsorbents

4.2.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR analysis conducted has determined the existence of several functional groups in the activated carbon. The FTIR spectra for PKSAC, Fe/PKSAC and Zeolite-Fe/PKSAC before and after adsorption are presented in Figures 4.1 - 4.3. The functional groups such as hydroxyl (OH–), double-bonded (C=C), carbon-oxygen (C-O), and amine (NH2) were found in the activated carbon. Overall, the analysis shows that some peaks have remained, shifted, disappeared, and some new peaks appeared due to impregnation of material or adsorption.

Figures 4.1 - 4.2 (a) show the FTIR spectra for PKSAC and Fe/PKSAC, which have distinctive characteristic peaks and wavenumbers. The sharp peaks obtained at 3711 cm^{-1} and 3000 cm^{-1} for PKSAC and Fe/PKSAC could be suggesting the presence of hydroxyl

group stretching (O–H stretching). This finding revealed the existence of a lignocellulose structure of palm kernel shell.

The sharp bands of 2996 cm⁻¹ in PKSAC and Fe/PKSAC might be due to the asymmetric and symmetric C-H stretching (Mustapha Mohammed Bello et al., 2020; Saka, 2012). Besides, the medium peaks at a wavelength of 1580 cm⁻¹ might be due to the presence of C=C stretching. Moreover, C=O stretching was observed at 1280 cm⁻¹ (Misnon, Zain, Aziz, Vidyadharan, & Jose, 2015). The existence of C=O is probably indicating the presence of an amide group in the palm kernel shell. The sharp peak at 563 cm⁻¹ confirmed iron oxide's presence in PKSAC (D'Cruz, Madkour, Amin, & Al-Hetlani, 2020). The analysis shows that iron oxide has been successfully deposited to the PKSAC surface. A similar result reported by Misnon and others (2015) (Misnon et al., 2015). After treatment, the FTIR analysis of Fe/PKSAC has been recorded to verify any structural changes. As seen in Figure 4.2 (b), the majority of the peaks are maintained after adsorption, indicating the stability of the Fe/PKSAC. However, after the adsorption, a new prominent peak at 3220 cm⁻¹ was detected, most likely representing O-H's.



Figure 4. 1: FTIR spectrum of PKSAC



Figure 4. 2: FTIR spectrum of Fe/PKSAC (a) before and (b) after adsorption

Figure 4.3 presents the overlays of the FTIR identified for Zeolite-Fe/PKSAC before and after adsorption. The adsorption process led to very similar adsorption bands to the characteristics of the band occurring before treatment. This is confirming that adsorption does not affect the structure of Zeolite-Fe/PKSAC.

The broad peak at a wavelength of 3700–3400 cm⁻¹ elucidated the existence of hydroxyl groups stretching (Khanday, Marrakchi, et al., 2017). Besides, the appearance of two peaks at 1082 and 798 cm⁻¹ indicates the asymmetric and symmetric stretching vibrations of SiO₄ or AlO₄ structure of Zeolite, respectively (Khanday, Asif, et al., 2017; Khanday,

Marrakchi, et al., 2017). The bands at around 560 cm⁻¹ attributes to Fe–O bond stretching, and they confirm the existence of iron oxide in the zeolite-based activated carbon (D'Cruz et al., 2020). Moreover, epoxy C-O stretching's presence corresponds to the peak at 1220 cm⁻¹ (Khanday, Asif, et al., 2017).

In summary, the FTIR analysis proved the effective impregnation of iron oxide and Zeolite, indicating the successful development of Fe/PKSAC and Zeolite-Fe/PKSAC.



Figure 4. 3: FTIR spectrum of Zeolite-Fe/PKSAC (a) before (b) after adsorption

4.2.2 Scanning Emission Microscopy (SEM)

SEM micrographs of PKSAC, Fe/PKSAC and Zeolite-Fe/PKSAC are shown in Figure 4.4 (a), (b) and (c), respectively. The surface morphology of PKSAC showed low porosities, rough, irregular, and amorphous structure (Figure 4.4 (a)). Meanwhile, Fe/PKSAC (Figure 4.4 (b)) has exhibited a crystal surface with significant pores. The presence of white crystals and small agglomerated particles on the surface of PKSAC, which is not observed in PKSAC, may indicate iron oxide nanoparticles' presence (Ianoş et al., 2018; Y.-C. Lee et al., 2020). Thus, the impregnation of iron oxide has resulted in more pores.

However, the modification of PKSAC by zeolite and iron oxide resulted in a significant reduction in micro pore volume, loose texture and reduced crystal surface, as shown in Figure 4.4 (c). the accumulation of iron oxide and zeolite resulting in reductions of BET surface area, but it still exhibits great magnetic properties (T. Liu et al., 2017). However, a large pore diameter is observed in Zeolite-Fe/PKSAC for effective adsorption (Khanday, Marrakchi, et al., 2017). The conclusion drawn in this study is similar to what Jian and others (2018) and Gu and others observed (2019) (Gu et al., 2019; Jain et al., 2018).



Figure 4. 4: Morphology of (a) PKSAC (20um - 4000× magnification), (b) Fe/PKSAC

(10um - 8000× magnification) and (c) Zeolite-Fe/PKSAC (10um - 8000×

magnification)



Figure 4. 4: Continued

4.2.3 Energy Dispersive X-ray (EDX)

The chemical compositions of PKSAC, Fe/PKSAC and Zeolite-Fe/PKSAC determined using EDX is shown in Table 4.1. Raw PKSAC comprised 60.7 % of Carbon, 24.6 % of Oxygen. A high-carbon attributed to a significant-organic content in PKSAC. However, Fe/PKSAC consists of lesser Carbon (40.9 %) and higher Oxygen (49.9 %) than raw PKSAC. When the percentage of oxygen is reduced, fewer cation sites are available for adsorption (Dominguez et al., 2020). Thus, Fe/PKSAC tends to increase the oxygen concentration, indicating an increase in adsorption sites. The presence of Iron (Fe) (9.1 %) indicating the successful impregnation of iron nanoparticles on the surface of the PKSAC. The presence of iron in the adsorbent may cause an oxidation reaction in the experiment, increasing the Oxygen content.

On the other hand, Zeolite-Fe/PKSAC shows more carbon content and reduced amount of iron and oxygen content than Fe/PKSAC and PKSAC (61.4 % of Carbon, 34.8 % of Oxygen and 3.8 % of Iron). The high carbon (> 60.0 %) attributed to the high organic

content in PKSAC for significant AC yield than most other sources. Because Zeolite is a carbon material, the amount of carbon increases in Zeolite-Fe/PKSAC (Mustapha Mohammed Bello et al., 2020; Das & Mishra, 2020). Similar to the result reported by Das et al. (2020), as well as Amesh et al. (2020), indicates that Zeolite adds a significant increment to the Carbon content (Amesh, Suneesh, Robert Selvan, Venkatesan, & Chandra, 2020; Das & Mishra, 2020). EDX analysis also further justified that iron oxide and Zeolite have been successfully incorporated in the adsorbent through co-precipitation and ultrasonic mixing.

 Table 4. 1: Chemical composition of PKSAC, Fe/PKSAC and Zeolite-Fe/PKSAC

Material	C (%)	O (%)	Fe (%)	Ca (%)
PKSAC	60.7	24.6	-	14.6
Fe/PKSAC	40.9	49.9	9.1	-
Zeolite-Fe/PKSAC	61.4	34.8	3.8	-



Figure 4. 5: EDX Analysis of (a) PKSAC, (b) Fe/PKSAC and (c) Zeolite-Fe/PKSAC

4.2.4 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) analysis is conducted to determine the crystallographic structure of the adsorbent. The range of the proposed pattern is in the range of $2\theta = 10.0^{\circ}$ to 80.0°. Figure 4.6 shows the XRD patterns of both Fe/PKSAC and Zeolite-Fe/PKSAC using X-Ray Diffraction (XRD) analyses XRD patterns shown various peak shifts and changes in peak intensities with the addition of different elements. The major iron peaks present as dominant phases of α -Fe and γ -Fe are identified at angle 20: 30.2, 32.1, 35.5, 43.3, 53.5, 56.8, 62.7 and 73.9, respectively (An, Tahmasebi, Zhao, Matamba, & Yu, 2020). Both the XRD pattern of Fe/PKSAC and Zeolite-Fe/PKSAC are similar, indicating that both adsorbents have existed in crystalline form. However, the peak intensity of Zeolite-Fe/PKSAC is lower than Fe/PKSAC, which further proves that iron oxide lost during the ultrasonic mixing process of Zeolite-Fe/PKSAC. Also, the size of crystals also nano-sized, which is less than 5.0 nm. A similar result has been reported by Yang yu and others (2018) (Y. Yu, Yu, Shih, & Chen, 2018). This result further supports SEM/EDX analysis that the iron magnetic nanoparticles have been successfully incorporated into the raw PKSAC.



Figure 4. 6: The XRD spectra of (a) Fe/PKSAC and (b) Zeolite-Fe/PKSAC



Figure 4. 6: Continued

4.2.5 Vibrating sample magnetometer (VSM)

Vibrating sample magnetometer (VSM) analysis is used to evaluate the adsorbent's magnetic properties at room temperature. The magnetic hysteresis loop of both adsorbents is plotted between magnetization (emu/g) and magnetic field (G). The saturation magnetization value is around 16.6 emu/g, suggesting superparamagnetic properties, according to the Fe/PKSAC hysteresis loops. At the same time, the Zeolite-Fe/PKSAC has a saturation magnetization value of 10.6 emu/g. Compared to Fe/PKSAC, the magnetization value has slightly reduced, most probably due to the replacement of iron oxide by Zeolite particles. Tang and others (2019) also have reported that when titanium is introduced into the iron oxide adsorbent, the composite's magnetic properties have reduced significantly (Tang et al., 2019). It should be noted that Zeolite-Fe/PKSAC has meets the criteria of solid-liquid separation where it can be separated by an exterior magnetic field (S. Wang et al., 2019).

In summary, both adsorbent, Fe/PKSAC and Zeolite-Fe/PKSAC can be separated by using an external magnet. The result obtained in line with the studies of Javadian and

others (2020) and Jonidi Jafari and others (2017) (Javadian, Ruiz, Saleh, & Sastre, 2020; Jonidi Jafari et al., 2017).



Figure 4. 7: Magnetization curves of Fe/PKSAC and Zeolite-Fe/PKSAC

4.2.6 Brunauer Emmett Teller (BET)

 N_2 adsorption-desorption isotherms of Fe/PKSAC and Zeolite-Fe/PKSAC are shown in Figures 4.8 (a) and (b), respectively. According to IUPAC nomenclature, pores can be described based on average diameters as micropores (d < 20.0 Å), mesopores (20.0 < d < 500.0 Å), and macropores (d > 500.0 Å) (Das & Mishra, 2020). Both curves show in Figure 4.8 classified as type-IV isotherms, which reveal it belong to mesoporosity. At low pressure, both adsorbents were revealed to have a micro-porosity structure (Pillai, Dharaskar, Sinha, Sillanpää, & Khalid, 2020).

In summary, BET analysis shows that Fe/PKSAC and Zeolite-Fe/PKSAC are rich in both microporous and mesopores structures. However, based on the specific surface area,

micropore surface area, micropore volume and total pore volume of Fe/PKSAC is better than Zeolite-Fe/PKSAC (Table 4.2). Zeolite-Fe/PKSAC (573.3 m²/g and 0.319 cm³/g) shows about 10% reduction in surface area and total pore volume compared to Fe/PKSAC (618.6 m²/g and 0.358 cm³/g). The result justified the accumulation of Zeolite on the surface area Fe/PKSAC (Silva et al., 2017). Abdullah and others report a similar result (2020) and Antoniou and others (2014) (N. H. Abdullah, Shameli, Abdullah, & Abdullah, 2020; Antoniou et al., 2014).

 Table 4. 2: Comparison of BET surface area, micropore surface area, micropore volume and total pore volume of adsorbents

	Fe/PKSAC	Zeolite-Fe/PKSAC
BET surface area (m^2/g)	618.6	573.3
Micropore surface area (m ² /g)	458.0	418.6
Micropore volume (cm ³ /g)	0.183	0.167
Total pore volume (cm ³ /g)	0.358	0.319
Pore diameter (Å)	2.315	2.226





Fe/PKSAC



Figure 4. 8: Continued

4.2.7 Point of Zero Charge (pH_{PZC})

Figure 4.9 shows a plot of pH_{PZC} for both Fe/PKSAC and Zeolite-Fe/PKSAC adsorbents. It is known that the surface of adsorbent is neutral at pH = pHpzc, negatively charged at pH > pHpzc, and positively charged at pH < pHpzc (Baccar, Sarrà, Bouzid, Feki, & Blánquez, 2012). The pHpzc of both adsorbents are observed to be around 5.3. Both adsorbents are positively charge at acidic condition at pH < 5.3 while negatively charge at neutral or alkaline condition when pH > 5.3. Other studies also reported that adsorbent that developed by palm kernel shell, iron oxide, zeolite has a pHpzc between 4 to 6 (Anyika, Asri, Majid, Jaafar, & Yahya, 2017; Paul, Kasera, Kolar, & Hall, 2020; Shavandi et al., 2012; Watanabe & Seto, 1986). Moreover, at alkaline condition pH 12 the adsorbents are negatively charge hence it performs better with cationic pollutants or cationic dye and vice versa.



Figure 4. 9: pH_{PZC} plot of Fe/PKSAC and Zeolite-Fe/PKSAC

4.3 Adsorption Study using Fe/PKSAC and Zeolite-Fe/PKSAC

4.3.1 Experimental Results

Tables 4.3 - 4.4 shows the experimental design suggested by RSM- CCD and the result obtained for the adsorption using Fe/PKSAC and Zeolite-Fe/PKSAC. A total of 40 experiments have been conducted for each adsorbent. The effect of operating conditions, including adsorbent dosage (1 g/L - 5 g/L), contact time (10 min – 60 min) and initial pH of the POME (3 - 9) for colour removal and COD removal efficiency have been investigated.

				Colour	Removal
Dun	Inde	pendent V	Efficiency (%)		
Run	Adsorbent	pН	Contact		Zeolite-
	(g/L)	•	Time (min)	Fe/PKSAC	Fe/PKSAC
1	1.0	3.0	60.0	66.0	54.7
2	3.0	1.0	35.0	80.9	75.9
3	3.0	6.0	35.0	50.3	28.2
4	5.0	9.0	60.0	66.6	48.3
5	3.0	6.0	35.0	43.7	29.8
6	1.0	9.0	10.0	19.1	13.3
7	0.4	6.0	35.0	14.3	12.0
8	1.0	3.0	10.0	56.3	48.3
9	5.0	3.0	10.0	85.7	75.3
10	3.0	6.0	35.0	52.9	31.4
11	3.0	6.0	35.0	52.1	34.0
12	3.0	6.0	35.0	53.1	35.2
13	3.0	11.0	35.0	78.7	64.0
14	5.0	3.0	60.0	96.8	86.7
15	1.0	9.0	60.0	40.3	14.7
16	6.4	6.0	35.0	79.7	55.5
17	5.0	6.0	10.0	56.9	41.2
18	3.0	6.0	35.0	51.1	32.4
19	3.0	6.0	7.0	35.8	28.0
20	3.0	6.0	77.0	54.3	34.4

Table 4. 3: Experimental design suggested by RSM, and the result obtained on colour

removal efficiency

Table 4. 4: Experimental design suggested by RSM, and the result obtained on COD

removal	efficiency

				COD Remo	val Efficiency
Dun	Indep	endent V	ariables	(%)
Kun	Adsorbent	mII	Contact		Zeolite-
	(g/L)	рп	Time (min)	Fe/PKSAC	Fe/PKSAC
1	1.0	3.0	60.0	21.6	27.4
2	3.0	1.0	35.0	63.2	47.8
3	3.0	6.0	35.0	35.0	18.7
4	5.0	9.0	60.0	41.8	29.5
5	3.0	6.0	35.0	35.0	19.7
6	1.0	9.0	10.0	11.8	7.4
7	0.4	6.0	35.0	5.8	2.9
8	1.0	3.0	10.0	29.2	19.5

				COD Remo	val Efficiency
Dun	Indep	endent V	ariables	(*	%)
Kull	Adsorbent	nЦ	Contact		Zeolite-
	(g/L)	pm	Time (min)	Fe/PKSAC	Fe/PKSAC
9	5.0	3.0	10.0	60.5	48.2
10	3.0	6.0	35.0	36.1	17.6
11	3.0	6.0	35.0	35.3	18.7
12	3.0	6.0	35.0	35.0	18.7
13	3.0	11.0	35.0	44.5	34.5
14	5.0	3.0	60.0	71.6	57.9
15	1.0	9.0	60.0	2.9	15.5
16	6.4	6.0	35.0	51.3	29.7
17	5.0	9.0	10.0	37.6	23.7
18	3.0	6.0	35.0	33.7	18.7
19	3.0	6.0	7.0	26.1	11.3
20	3.0	6.0	77.0	36.3	19.0

Table 4.4: Continued

4.3.2 Statistical Analysis

4.3.2.1 Analysis of variance

Tables 4.5 - 4.6 present the results of ANOVA for Fe/PKSAC and Zeolite-Fe/PKSAC. The F-values obtained for colour removal using Fe/PKSAC, and Zeolite-Fe/PKSAC were 76.3 and 144.3. Simultaneously, the F-values for COD removal efficiency were 32.9 and 123.3 for Fe/PKSAC and Zeolite-Fe/PKSAC, respectively. The F-values shows that both models were significant at a 95 % confidence level. The result proved that Zeolite-Fe/PKSAC has a better F value compared to Fe/PKSAC. ANOVA shows that the reduced quadratic model is best-fitted for both Fe/PKSAC and Zeolite-Fe/PKSAC. The regression model equations of colour and COD removal using coded factors shown in Eq. 4.1 for Fe/PKSAC, Eq. 4.2 for Zeolite-Fe/PKSAC, Eq. 4.3 for Fe/PKSAC and Eq. 4.4 for Zeolite-Fe/PKSAC. The positive sign of the terms in the equation implies a synergistic effect, while the negative sign implies the antagonistic effect (Hameed, Tan, & Ahmad, 2008).

Fin	al equation in t	erms of coded factors for Color Removal Efficiency (%)
Eq. 4.1	Fe/PKSAC	$47.4 + 17.2*A - 13.0*B + 6.1*C + 15.9*B^{2}$
Eq. 4.2	Zeolite-	$30.8 + 14.2*A - 16.9*B + 2.7*C + 19.3*B^2$
	Fe//PKSAC	
Fin	al equation in t	erms of coded factors for COD Removal Efficiency (%)
Eq. 4.3	Fe//PKSAC	$35.6 + 16.3 * A - 10.7 * B + 1.2 * C + 4.0 * A * C - 3.7 * A^2 + 0.0 * 0.0 * A^2 + 0.0 *$
		7.9*B^2
Eq. 4.4	Zeolite-	$18.2 \pm 9.9 \text{``A} - 10.0 \text{``B} \pm 3.3 \text{``C} - 3.6 \text{``A} \text{``B} \pm 11.8 \text{``B} \text{``2}$
	Fe//PKSAC	

The p-values < 0.05 shows that dosage of adsorbent (A), pH (B), and contact time (C) were the significant model terms for both adsorbents for colour removal as well as for COD removal. The model R² value is close to 1, and the differences between adjusted and predicted R² < 0.5, indicating high accuracy of the model. The R² coefficient of Fe/PKSAC for colour and COD removal efficiency are 0.953 and 0.950, respectively. The R² coefficient of Zeolite-Fe/PKSAC were 0.975 and 0.983 for colour and COD removal efficiency, respectively. The result shows that the model does not justify only less than 2.5 % of the total variation, which reveal a high correlation between predicted and observed values of the response. The R² values of Zeolite-Fe/PKSAC are higher for both COD and colour removal, revealing the model's accuracy.

The adequate precision (Adeq. Precision) corresponds to the range of the predicted values to the average prediction error, and a greater than four ratios is preferred. Tables 4.5 - 4.6 shows that the colour removal and COD removal model for Fe/PKSAC and Zeolite-Fe/PKSAC have adequate precision of 31.6 and 40.5, 22.9 and 41.1, respectively. Zeolite-Fe/PKSAC shows greater Adeq. Precision compared to Fe/PKSAC further indicated that Zeolite-Fe/PKSAC model is better to navigate the design space than Fe/PKSAC. Figures 4.10 (a) and (b) and Figures 4.11 (a) and (b) show the graph of predicted versus actual Colour and COD removal efficiency. It can be seen that a straight line is obtained, further indicating the agreement between the predicted and the experimental response.

Source	Sum of	df	Mean	F-Value	p-value
	Squares		Square		
		Fe/PKS	SAC		
Model	8049.7	4.0	2012.4	76.3	< 0.0001
A-Dosage of					
Adsorbent	4019.3	1.0	4019.3	152.4	< 0.0001
B-pH	1934.2	1.0	1934.2	73.3	< 0.0001
C- Contact Time	502.2	1.0	502.2	19.0	0.0006
B^2	2476.7	1.0	2476.7	93.9	< 0.0001
Lack of Fit	333.9	10.0	33.4	2.7	0.1418
R-Squared			0.953		
Adj R-Squared			0.941		
Pred R-Squared			0.880		
Adeq Precision			31.6		
	Ze	olite-Fe/	PKSAC	U	
Model	8323.7	4.0	2080.9	144.3	< 0.0001
A-Dosage of					
Adsorbent	2746.1	1.0	2746.1	190.4	< 0.0001
B-pH	3235.4	1.0	3235.4	224.3	< 0.0001
C- Contact Time	100.6	1.0	100.6	7.0	0.0185
B^2	3625.7	1.0	3625.7	251.4	< 0.0001
Lack of Fit	182.5	10.0	18.2	2.7	0.1429
R-Squared			0.975		
Adj R-Squared			0.968		
Pred R-Squared			0.926		
Adeq Precision			40.5		

 Table 4. 5: ANOVA analysis for the CCD for colour removal efficiency



Figure 4. 10: Predicted versus Actual plot for Colour removal (a) Fe/PKSAC (b) Zeolite-Fe/PKSAC

Source	Sum of	df	Mean	F-Value	p-val
	Squares		Square		
		Fe/PK	SAC		
Model	5608.9	7.0	801.3	32.9	< 0.00
A-Dosage of					
Adsorbent	3629.3	1.0	3629.3	148.8	< 0.00
B-pH	1312.6	1.0	1312.6	53.8	< 0.00
C-Contact Time	18.6	1.0	18.6	0.8	0.399
AC	126.7	1.0	126.7	5.2	0.04
A^2	196.3	1.0	196.2	8.0	0.01
B^2	605.2	1.0	605.2	24.8	0.000
C^2	109.5	1.0	109.5	4.5	0.05
Lack of Fit	289.7	7.0	41.4	71.1	0.000
R-Squared			0.950		
Adj R-Squared			0.922		
Pred R-Squared			0.752		
Adeq Precision			22.9		
	Ze	eolite-Fe/	PKSAC		
Model	3588.4	6.0	598.1	123.3	< 0.00
A-Dosage of					
Adsorbent	1326.9	1.0	1326.9	273.6	< 0.00
B-pH	1129.6	1.0	1129.6	232.9	< 0.00
C- Contact Time	144.4	1.0	144.4	29.8	0.000
AB	104.8	1.0	104.8	21.6	0.000
B^2	1362.0	1.0	1362.0	280.8	< 0.00
C^2	19.9	1.0	19.9	4.1	0.063
Lack of Fit	60.8	8.0	7.6	17.1	0.003
R-Squared			0.983		
Adj R-Squared			0.975		
Pred R-Squared			0.950		
Adeq Precision			41.4		



Figure 4. 11: Predicted versus Actual plot for COD removal (a) Fe/PKSAC (b) Zeolite-

Fe/PKSAC

4.3.3 Optimization and Model Validation

Table 4.7 shows the predicted and the experimental results obtained for the selected optimum condition. The experimental value is close to the predicted values, with a deviation of less than 5.0 %. The model is considered reliable for this study. Table 4.7 shows that Fe/PKSAC achieved the highest colour removal of 93.2 % within 40 min contact time than Zeolite-Fe/PKSAC, which took 60 min to obtain 87.5 % of colour removal. On the other hand, Zeolite-Fe/PKSAC achieved 62.6 % of COD removal, which is slightly higher than Fe/PKSAC (58.1 %). COD is one of the essential parameters in wastewater treatment, normally does not meet the discharge requirement (Z. Zhou et al., 2019). The presence of Zeolite in Fe/PKSAC possibly enhanced the COD removal efficiency as Zeolite has excellent stability in acidic conditions, with larger surface area, high ion exchange capacity and selectivity, especially for cation and a rigid porous structure (Al-Jubouri & Holmes, 2020). Therefore, when Zeolite incorporates with Fe/PKSAC, it forms a greater capping adsorbent than Fe/PKSAC to separate cationic ions and heavy metals and anionic ions (T. Liu et al., 2017), which resulted in higher degradation efficiency. In summary, both Fe/PKSAC and Zeolite-Fe/PKSAC activated carbon shows more than 85.0 % and 55.0 % of colour removal and COD removal, respectively.

Adsorbents	Adsorbent Dosage	Contact Time	рН	Colour removal efficiency (%)		COD removal efficiency (%)	
	(g/L)	(min)		Pred.	Exp.	Pred.	Exp.
Fe/PKSAC	5.0	40.0	3.0	90.0	93.2	60.0	58.1
Zeolite- Fe/PKSAC	5.0	60.0	3.0	84.0	87.5	61.0	62.6

Table 4. 7: Predicted and Experimental Results of optimization conditions

* Pred.: Predicted, Exp.: Experimental

4.3.4 Effects of Operating Parameters

4.3.4.1 Initial pH

The pH of the solution is an important parameter as the change of pH value affects the adsorbent's active site and surface (Wan Ngah & Hanafiah, 2008). It should be noted that different adsorbent will behave differently towards the effect of pH (Ibrahim, Ang, & Wang, 2009). The effect of pH on the adsorption process was investigated by varying the solution pH between 3 to 9. Figures 4.12 - 4.13 show the effect of pH and dosage of adsorbent on the colour removal and COD removal for Fe/PKSAC and Zeolite-Fe/PKSAC.

As can be seen in Figures 4.12 - 4.13, when 5 g/L dosages of adsorbent are used and the pH increases from 3 to 9, the colour removal efficiency decreases from 90 % to 70 % for Fe/PKSAC and 80 % to 50 % for Zeolite-Fe/PKSAC, respectively. And when the lowest amount of adsorbent (1 g/L) is used, and the pH is changed from 3 to 9, the highest colour removal was achieved at pH 3, 65 % and 50 % for Fe/PKSAC and Zeolite-Fe/PKSAC, respectively. The result revealed that the highest colour removal achieved at maximum adsorbent of 5 g/L and most acidic conditions is pH 3. When the pH is increased from 3 to 9 using 5 g/L adsorbent within 60 minutes of contact time, COD removal decreases from 65 percent to 45 percent for Fe/PKSAC and 50 percent to 25 percent Zeolite-Fe/PKSAC. However, when 1 g/L of adsorbent dosage is used at alkaline condition (pH 9), Fe/PKSAC and Zeolite-Fe/PKSAC achieved less than 10 % COD removal within 60 min. It is proven that the solution's initial pH has a strong interaction with the dosage of adsorbent in this study. Both results revealed that the best removal rate on colour and COD for Fe/PKSAC and Zeolite-Fe/PKSAC achieved at the acidic condition compared to an alkaline condition.

The significant decreased in the colour and COD removal efficiency for both adsorbent is observed when the pH is increased from 3 to 9. The adsorbent's surface became more negatively charged and increased the repulsion between the adsorbate and magnetite nanoparticles adsorbent (Padmavathy et al., 2016). The functional groups of adsorbents will remain intact at acidic condition but deprotonate into anionic groups at alkaline condition (Y. W. Cheng et al., 2020). Moreover, the acidic condition will aggravate POME to break the oil particles and destabilization all the organic compound, heavy metal and suspended solid in the solution. Besides, many other studies have reported that the adsorption process's optimum pH is at the acidic range (pH 3 - 4) (Nandi et al., 2009; Sokker, El-Sawy, Hassan, & El-Anadouli, 2011). Al-Jubouri and Holmes (2020) also reported that Zeolite-Fe/PKSAC performs better in acidic condition than alkaline condition for colour and COD removal, respectively, due to the presence of Zeolite (Al-Jubouri & Holmes, 2020).

So, it's obvious that Fe/PKSAC and Zeolite-Fe/PKSAC acts as a cation adsorbent in this study, where the strong acidic condition will lead to a strong cationic charge on the surface of both adsorbents as well as on the magnetite particles (Iron Oxide) and Zeolite (Saifuddin & Dinara, 2011). Hence, both adsorbent Fe/PKSAC and Zeolite-Fe/PKSAC perform well in acidic condition for colour and COD removal efficiency.



Figure 4. 12: Contour (2D) plot for (a) Colour (b) COD removal efficiency of initial pH

and dosage of adsorbent for Fe/PKSAC (Contact time = 60 min)



Figure 4. 13: Contour (2D) plot for **(a)** Colour **(b)** COD removal efficiency of initial pH and dosage of adsorbent for Zeolite-Fe/PKSAC (Contact time = 60 min)

4.3.4.2 Adsorbent Dosage

The effect of adsorbent dosage on the colour removal and COD removal was studied by varying the adsorbent dosage between 1 g/L and 5 g/L. Figures 4.14 - 4.15 shows the effect of adsorbent dosage and contact time on the colour removal and COD removal of POME for Fe/PKSAC and Zeolite-Fe/PKSAC, respectively.

As can be seen in Figure 4.14 (a), when the adsorbent dosage is increased from 1 g/L to 5 g/L at the acidic condition of pH 3 and 60 min of contact time, the colour removal is increased from 65 % to 95 % for Fe/PKSAC and 55 % to 80 % for Zeolite-Fe/PKSAC, respectively. This result proved a strong interaction between adsorbent dosage and contact time in this study and further justify results obtained in ANOVA analysis where adsorbent dosage and contact time are the significant model term for Fe/PKSAC and Zeolite-Fe/PKSAC in colour removal. Whereas under similar conditions, COD removal efficiency increased from 35 % to 68 % for Fe/PKSAC and 28 % to 60 % for Zeolite-Fe/PKSAC, respectively, when the adsorbent dosage is increased from 1 g/L to 5 g/L.

The adsorption performance increase with the increase in adsorbent dosage as the number of the active site and binding site will correspond with the increase in dosage of adsorbent and increase removal efficiency (Shukla, Zhang, Dubey, Margrave, & Shukla, 2002). The above results had proven that the dosage of adsorbent play an important role in this study, where the increase in dosage of adsorbent is directly proportional to the colour and COD removal rate (M. Abdel-Aziz, 2018). The adsorption process is linearly correlated to the dosage of adsorbent as the adsorption efficiency will increase with the dosage of adsorbent until saturated (Mahato, Krithiga, & Mary Thangam, 2020). A similar result was reported by Mohammed and Chong (2014). They have stated that higher adsorbent dosage strongly influenced the adsorption as more adsorption sites are available for the adsorbent (R. R. Mohammed & Chong, 2014). Moreover, Amuda and others (2006) and Devi and others (2008) also has reported that when there is an increase in dosage of adsorbent, higher colour and COD removal rate can be achieved until it reaches equilibrium (Amuda & Ibrahim, 2006; Devi, Singh, & Kumar, 2008).

In summary, the dosage of adsorbent significantly affects both colour and COD removal rate and acts as one of the critical parameters in the adsorption process. However, the increase in dosage of adsorbent will greatly affect the cost for industrial application. Hence, an optimum dosage for both Fe/PKSAC and Zeolite-Fe/PKSAC needed to be obtained to achieve a cost-effective treatment method.



C: Contact Time

Figure 4. 14: Contour (2D) plot for (a) Colour (b) COD removal efficiency of adsorbent dosage and contact time for Fe/PKSAC (Initial pH = 3)



C: Contact Time

Figure 4.14: Continued





dosage and contact time for Zeolite-Fe/PKSAC (Initial pH = 3)



Figure 4.15: Continued

4.3.4.3 Contact Time

In this study, the contact time was varied from 10 min to 60 min to study the effects of contact time on the colour and COD removal efficiencies of real POME wastewater. Figures 4.16 - 4.17 show the interaction between the contact time and initial pH of the solution's solution on the colour and COD removal efficiency for Fe/PKSAC and Zeolite-Fe/PKSAC, respectively.

Under the optimum condition of 5 g/L dosages of adsorbent at acidic condition, the colour removal efficiency for Fe/PKSAC increased from 85 % to 95 %, and Zeolite-Fe/PKSAC increased from 70 % to 80 % when the contact time is increased from 10 min to 60 min. At alkaline condition, increasing the contact time from 10 min to 60 min also resulted in the increase of colour removal for Fe/PKSAC (60 % to 70 %) and Zeolite-Fe/PKSAC (44 % to 50 %). COD removal also shows increment for Fe/PKSAC (60 % to 70 %) and Zeolite-Fe/PKSAC (40 % to 50 %) when the time is increased from 10 min to 60 min at

the optimum condition of 5 g/L dosages of adsorbent and pH 3. This result shows a good interaction between contact time and the initial pH of the solution. Figures 4.16 - 4.17 also clearly show that adsorption happened rapidly within 10 min of contact time and increases slowly over time.

This phenomenon could be further explained as many unoccupied adsorption sites on the adsorbent surface during the initial stage. With the passage of contact time, the remaining vacant surface sites' occupancy became difficult due to repulsive forces between the solute molecules in the solid and the bulk liquid phase (Srivastava et al., 2005). Similar results were reported by Chingono and others (2018) and Teshale and others (2020), where the adsorption process occurs rapidly within 10 - 15 min (Chingono et al., 2018; Teshale, Karthikeyan, & Sahu, 2020). When the contact time increase beyond 30 min, the removal rate for colour and COD will increase slowly, but once the removal rate had reached its maximum, the increased in the removal rate is insignificant for both Fe/PKSAC and Zeolite-Fe/PKSAC adsorbents. Hence, it can be concluded that adsorption efficiency increases with time and reaches saturation when reached the maximum capability of the adsorbent (Ying, Raman, Bello, & Buthiyappan, 2020).

In summary, contact time is an essential parameter for both Fe/PKSAC and Zeolite-Fe/PKSAC adsorbents in colour and COD removal. It acts as a cost-saving factor in the real industrial application. As longer contact time will eventually increase the process's cost, it is important to ascertain the appropriate contact time to increase the treatment efficiency. In this study, 40 min and 60 min of contact time were optimized as the best contact time for Fe/PKSAC and Zeolite-Fe/PKSAC, respectively.


Figure 4. 16: Contour (2D) plot for (a) Colour (b) COD removal efficiency of contact time and pH for Fe/PKSAC (Adsorbent Dosage = 5 g/L)



Figure 4. 17: Contour (2D) plot for (a) Colour (b) COD removal efficiency of contact time and pH for Zeolite-Fe/PKSAC (Adsorbent Dosage = 5 g/L)

4.3.5 Reusability Study

An adsorbent's regeneration ability is one of the most important factors from both economic and environmental aspects. An adsorbent's ability to be used several times without losing its adsorbent capacity is an essential consideration in industrial application (Tri et al., 2020). Figure 4.18 and Table 4.8 show the result obtained for the reusability study for Fe/PKSAC and Zeolite-Fe/PKSAC over five consecutive cycles. As shown in Figure 4.18, after the 5th cycle, the colour removal efficiency for Fe/PKSAC shows a sharp decrease from 93.2 % to 76.0 %, whereas Zeolite-Fe/PKSAC shows a minimal reduction of 5.6 % from 87.5 % to 81.9 %. Zeolite-Fe/PKSAC can maintain most of its adsorbent capability compared to Fe/PKSAC, possibly due to the presence of Zeolite as it has a special characteristic such as high porosity, large surface area, high regeneration potential, strong acidic stability and etc (Khalil et al., 2020). This study's result is in line with the research conducted by Pillai and others (2020) (Pillai, Kakadiya, Timaniya, Dharaskar, & Sillanpaa, 2020). In summary, Zeolite-Fe/PKSAC is preferable compared to Fe/PKSAC due to its good stability and high reusability. As in industrial application, outstanding regeneration performance of Zeolite-Fe/PKSAC will eventually lead to lesser cost investment in actual application and lesser solid waste generated after wastewater treatment (H. Li et al., 2019). Hence, an adsorbent's regeneration properties are the most critical criteria and act as the first consideration in adsorption application.

	Fe/PKSAC	Zeolite-Fe/PKSAC
Regeneration 1st Cycle (%)	93.2	87.5
Regeneration 5th Cycle (%)	76.0	81.9
Total Amount % lost	17.2	5.6

 Table 4. 8: Reusability of Fe/PKSAC and Zeolite-Fe/PKSAC



Figure 4. 18: Reusability of Fe/PKSAC and Zeolite-Fe/PKSAC

4.3.6 Adsorption Capacity

The adsorption capacity of an adsorbent is one of the important parameters to analyze absorbent efficiency. Adsorption capacity studies the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent. The effect of adsorbent dosage and adsorption capacity at a time for both Fe/PKSAC and Zeolite-Fe/PKSAC summarised in Figure 4.19. The adsorption capacity decreases from 104 mg/g to 48.6 mg/g and 82 mg/g to 44.8 mg/g for Fe/PKSAC and Zeolite-Fe/PKSAC, respectively, when the dosage of adsorbent increases from 1 g/L to 5 g/L at the acidic condition and 60 min of contact time. Under optimized condition at pH 3 and 5 g/L dosage of adsorbent, Zeolite-Fe/PKSAC (44.2 mg/g within 40 min contact time), as can be seen in Table 4.9. It can be said that the presence of Zeolite greatly improved the adsorption capacity of hybrid Zeolite-Fe/PKSAC. The results also show that adsorbent dosage also has a significant effect on adsorption capacity. This phenomenon can be explained as at high dosage of adsorbent, overlapping and aggregation of the adsorbent occur which causes the reduction of adsorption capacity

of the adsorbent (Mengmeng Wang et al., 2015). A higher dosage of adsorbent may not increase the adsorbent performance as numbers of active sites exceeded the amount of pollutant in the solution where the efficiency of an adsorbent might not fully utilize (Altaf, Lin, Tadda, Zhu, & Liu, 2021).

Table 4. 9: Adsorption Capacity of Fe/PKSAC and Zeolite-Fe/PKSAC under optimize

conditions (pH = 3 and Adsorbent Dosage = 5 g/L)

	Adsorption Capacity (mg/g)
Fe/PKSAC	44.2
Zeolite-Fe/PKSAC	47.6



Figure 4. 19: Adsorption Capacity for Fe/PKSAC and Zeolite-Fe/PKSAC on the effect

of dosage of adsorbent

4.3.7 Comparison of Adsorption Study

Table 4.10 shows the comparison of adsorption efficiency of Fe/PKSAC and Zeolite-Fe/PKSAC. The results show that Fe/PKSAC has achieved higher colour removal of 93 % within 40 min. At the same time, Zeolite-Fe/PKSAC requires 60 min of contact time to

achieve 88 % of colour removal. On the other hand, Zeolite-Fe/PKSAC achieved 5 % higher COD removal (63 %) than Fe/PKSAC (58 %). Besides, Zeolite-Fe/PKSAC also retained its adsorbent capability over five cycles with a minimal decrease (5.6 %) than Fe/PKSAC (17.2 %.) rectify that Zeolite-Fe/PKSAC has a higher reusability capacity compared to Fe/PKSAC.

Besides, Zeolite-Fe/PKSAC (47.6 mg/g) also achieved higher adsorption capacity than Fe/PKSAC (44.2 mg/g). This may be due to the presence of aluminium, oxygen, and metals like titanium, Tin, Zinc, in Zeolite which permit the passage of molecules that below a certain size (Andraka et al., 2017; Montalvo et al., 2020). It also has excellent stability in acidic condition, high ion exchange capacity and selectivity, especially for cation (Al-Jubouri & Holmes, 2020). Therefore, when the Zeolite is incorporated with Fe/PKSAC, it forms a greater capping adsorbent (Zeolite-Fe/PKSAC) compared to Fe/PKSAC to separate cationic ions and heavy metals, as well as anionic ions (T. Liu et al., 2017). In the practical application, it contributes to lesser solid waste generation and cost-saving. Zeolite-Fe/PKSAC performed better than Fe/PKSAC in terms of stability as its ability to maintain its adsorption capacity over five cycles and a higher degradation rate based on the COD removal efficiency.

Adsorbent	рН	Dosage Adsorbent (g/L)	Ct (min)	CR (%)	COD Rem. (%)	Sludge	BET (m²/g)	SEM/ EDX (C %)
Fe/PKSAC	3.0	5.0	40.0	93.0	58.0	NO	618.6	34.0
Zeolite-	3.0	5.0	60.0	88.0	63.0	NO	573.3	42.9
Fe/KSAC								

Table 4. 10: Comparison of Fe/PKSAC and Zeolite-Fe/PKSAC

*CR: Colour Removal, Ct: Contact Time, COD Rem.: COD Removal

4.4 Peroxide Assisted Adsorption Process using Fe/PKSAC, and Zeolite-Fe/PKSAC Activated Carbon

4.4.1 Experimental Results

The results obtained for colour and COD removal using Fe/PKSAC and Zeolite-Fe/PKSAC with the addition of H_2O_2 shown in Tables 4.11 - 4.12, respectively. A total of 60 experiments were conducted to evaluate the performance of Fe/PKSAC, and Zeolite-Fe/PKSAC assisted H_2O_2 adsorption processes. The result shows that both adsorbents were able to remove more than 80 % of colour and 70 % of COD.

Table 4. 11: Experimental design suggested by RSM, and the result obtained on colour

removal	efficiency

					Colour l	Removal
		Indep	Efficiency (%)			
Run	Dosage of	Adsorbent	Contact Time	pН	Fe/PKSAC	Zeolite- Fe/PKSAC
	11202 (iiii))	(g/2)	()		$+ H_2O_2$	+ H ₂ O ₂
1	120.0	3.0	35.0	6.0	76.5	43.9
2	40.0	1.0	60.0	9.0	69.1	24.1
3	200.0	1.0	60.0	9.0	69.4	42.3
4	40.0	5.0	10.0	3.0	83.7	86.1
5	120.0	3.0	15.0	6.0	78.3	43.1
6	200.0	5.0	60.0	9.0	79.1	55.5
7	40.0	5.0	60.0	9.0	79.9	40.8
8	200.0	1.0	10.0	9.0	70.0	41.7
9	280.0	3.0	35.0	6.0	73.9	54.1
10	120.0	3.0	35.0	6.0	77.9	44.9
11	40.0	1.0	60.0	3.0	76.5	62.4
12	200.0	5.0	10.0	3.0	82.7	87.1
13	40.0	1.0	10.0	9.0	71.4	21.7
14	120.0	3.0	35.0	12.0	74.2	67.8
15	120.0	3.0	35.0	6.0	76.1	45.3
16	120.0	3.0	35.0	6.0	76.1	44.5
17	200.0	1.0	60.0	3.0	73.0	68.8
18	200.0	1.0	10.0	3.0	77.1	66.8
19	120.0	7.0	35.0	6.0	82.7	66.6
20	200.0	5.0	60.0	3.0	80.1	93.4

					Colour l	Removal
		Indep	endent Variables		Efficier	ıcy (%)
Run	Dosage of H2O2 (mM)	Adsorbent Contact Time (g/L) (min)		рН	Fe/PKSAC + H2O2	Zeolite- Fe/PKSAC + H ₂ O ₂
21	120.0	3.0	35.0	6.0	74.6	46.1
22	40.0	1.0	10.0	3.0	79.5	59.6
23	200.0	5.0	10.0	9.0	80.1	55.1
24	40.0	5.0	10.0	9.0	80.3	47.7
25	120.0	1.0	35.0	6.0	70.0	30.4
26	40.0	5.0	60.0	3.0	76.5	93.4
27	40.0	3.0	35.0	6.0	78.5	25.7
28	120.0	3.0	35.0	0.0	N/M	N/M
29	120.0	3.0	35.0	6.0	76.7	46.5
30	120.0	3.0	85.0	6.0	76.1	51.5

Table 4.11: Continued

** N/M: Not Measured

Table 4. 12: Experimental design suggested by RSM, and the result obtained on COD

		Indepe	ndent Variable	COD Removal Efficiency (%)		
Run	Dosage of H2O2 (mM)	Adsorbent (g/L)	Contact Time (min)	рН	Fe/PKSAC + H2O2	Zeolite- Fe/PKSAC + H ₂ O ₂
1	120.0	3.0	35.0	6.0	74.7	63.7
2	40.0	1.0	60.0	9.0	65.0	55.3
3	200.0	1.0	60.0	9.0	73.7	67.9
4	40.0	5.0	10.0	3.0	73.0	71.1
5	120.0	3.0	15.0	6.0	73.2	67.6
6	200.0	5.0	60.0	9.0	76.3	75.0
7	40.0	5.0	60.0	9.0	71.0	57.1
8	200.0	1.0	10.0	9.0	72.9	66.1
9	280.0	3.0	35.0	6.0	80.0	69.7
10	120.0	3.0	35.0	6.0	74.7	63.7
11	40.0	1.0	60.0	3.0	71.0	58.9
12	200.0	5.0	10.0	3.0	80.8	68.9
13	40.0	1.0	10.0	9.0	67.0	45.8
14	120.0	3.0	35.0	12.0	70.0	70.5
15	120.0	3.0	35.0	6.0	74.5	63.9
16	120.0	3.0	35.0	6.0	75.0	63.4
17	200.0	1.0	60.0	3.0	75.8	69.2

removal efficiency

					COD R	emoval
		Indepe	Efficiency (%)			
Run	Dosage of H2O2 (mM)	Adsorbent (g/L)	Contact Time (min)	рН	Fe/PKSAC + H2O2	Zeolite- Fe/PKSAC + H ₂ O ₂
18	200.0	1.0	10.0	3.0	77.6	69.7
19	120.0	7.0	35.0	6.0	75.5	72.4
20	200.0	5.0	60.0	3.0	79.7	75.5
21	120.0	3.0	35.0	6.0	74.7	63.7
22	40.0	1.0	10.0	3.0	71.0	58.4
23	200.0	5.0	10.0	9.0	75.3	70.8
24	40.0	5.0	10.0	9.0	69.0	57.9
25	120.0	1.0	35.0	6.0	73.4	65.3
26	40.0	5.0	60.0	3.0	75.0	71.8
27	40.0	3.0	35.0	6.0	67.9	59.7
28	120.0	3.0	35.0	0.0	N/M	N/M
29	120.0	3.0	35.0	6.0	74.7	63.7
30	120.0	3.0	85.0	6.0	74.7	69.2

Table 4.12: Continued

** N/M: Not Measured

4.4.2 Statistical Analysis

4.4.2.1 Analysis of variance

ANOVA analysis is summarised in Tables 4.13 - 4.14. The result shows that the reduced 2FI model and reduced quadratic model were fitted for Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂ for the colour removal efficiency. Whereas RSM-CCD suggested linear model and Reduced 2FI for Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂, respectively COD removal. The final equations of colour and COD removal in terms of coded factors were expressed by equation (4.5), equation (4.6), equation (4.7) and equation (4.8). For colour removal, the p-values < 0.05 for dosage of H₂O₂ (A), the dosage of adsorbent (B), pH (C), contact time (D), the dosage of adsorbent and pH (BC) and pH and contact time (CD) indicated that those parameters are significant. Besides, the dosage of H₂O₂ and adsorbent (AB), the dosage of H₂O₂ and pH (AC), and the second-order effect of pH (C²) were the significant additional term for Zeolite-Fe/PKSAC + H₂O₂ that

must include in the equation for colour removal. On the other hands, for COD removal, the dosage of H_2O_2 (A), the dosage of adsorbent (B) and pH (C) are significant for Fe/PKSAC + H_2O_2 , and dosage of H_2O_2 (A), the dosage of adsorbent (B), pH (C) and dosage of H_2O_2 and pH (AC) were significant for Zeolite-Fe/PKSAC + H_2O_2 . The contact time (D) is not significant for both adsorbent.

Fina	Final equation in terms of coded factors for Color Removal Efficiency (%)						
Eq. 4.5	Fe/PKSAC	76.7 - 0.6*A + 3.4*B - 1.7*C - 1.2*D + 0.5*A*B +					
		1.4*B*C + 0.8*C*D					
Eq. 4.6	Zeolite-Fe/	45.4 + 4.5*A + 10.6*B - 17.8*C + 1.3*D - 1.8*A*B +					
	PKSAC	2.9*A*C - 2.1*B*C - 1.4*C*D + 14.1*C^2					
Fin	al equation in ter	ms of coded factors for COD Removal Efficiency (%)					
Eq. 4.7	Fe/ PKSAC	73.8 + 3.1*A + 1.3*B - 2.1*C + 0.2*D					
Eq. 4.8	Zeolite-Fe/	65.5 + 4.5*A + 2.9*B - 1.9*C + 1.1*D + 2.6*A*C					
	PKSAC						

Statistical analysis for both adsorbents was presented in Tables 4.13 - 4.14. The F-values of 45.4 and 322.2 show that the colour removal model was significant at a 95% confidence level for Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂, respectively. While F-values for COD removal for Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂ were 77.9 and 12.5, respectively. Based on the results, Zeolite-Fe/PKSAC + H₂O₂ shows a better F value in the colour removal model but not in the COD removal model compared to Fe/PKSAC + H₂O₂. Overall, for both adsorbent, since the value of probability > F < 0.0001, there is only a 0.01 % chance that the F-value could achieve through the noise (Venkataramanan, Subramaniyan, Kumar, Jawahar, & Prabhu, 2020). The R² values were 0.938 and 0.928 for Fe/PKSAC + H₂O₂, colour and COD removal. At the same time, Zeolite-Fe/PKSAC + H₂O₂ has the R² of 0.994 and 0.731 for both colour and COD removal, respectively. The adjusted R² for each adsorbent is also in reasonable agreement with the predicted R². as shown in Tables 4.13 - 4.14 (Qu, Meng, You, Ye, & Du, 2017). The results show that Zeolite-Fe/PKSAC + H₂O₂ has a higher R² value for colour removal but a lower R² value

for COD removal than Fe/PKSAC + H_2O_2 . Hence, in terms of colour removal, Zeolite-Fe/PKSAC + H_2O_2 shows a good agreement with the experimental and predicted values compared to Fe/PKSAC + H_2O_2 . In contrast, Figure 4.20 (a) and (b) and Figure 4.21 (a) and (b) shows predicted versus actual graphs for Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 . A straight line was obtained, further indicating the good agreement between the predicted and the experimental responses.

Adequate precision compares the range of the predicted values at the design points to the average prediction error. Both the model for colour removal shows the adequate precision ratios of 24.6 (Fe/PKSAC + H₂O₂) and 62.8 (Zeolite-Fe/PKSAC + H₂O₂) as can be seen in Table 4.13. And adequate precision ratios for COD removal of Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂ were 29.8 and 12.9, respectively. In summary, both adsorbents had verified that the models obtained for colour and COD removal were sufficient to navigate the CCD model since the ratio are greater than 4.0.

Source	Sum of	df	Mean	F-Value	p-value
	Squares		Square		
	Fe	/PKSAC	+ H ₂ O ₂		
Model	425.8	7.0	60.8	45.4	< 0.0001
A-Dosage of H ₂ O ₂	8.8	1.0	8.8	6.5	0.0184
B-Dosage of		1.0			
Adsorbent	283.1		283.1	211.5	< 0.0001
C-pH	60.3	1.0	60.3	45.0	< 0.0001
D-Contact Time	27.2	1.0	27.2	20.3	0.0002
AB	4.7	1.0	4.7	3.5	0.0763
BC	32.1	1.0	32.1	24.0	< 0.0001
CD	10.0	1.0	10.0	7.4	0.0126
Lack of Fit	22.4	16.0	1.4	1.2	0.4462
R-Squared			0.938		
Adj R-Squared	0.917				
Pred R-Squared			0.871		
Adeq Precision			24.6		

 Table 4. 13: ANOVA analysis for the CCD for colour removal efficiency

Source	Sum of	df	Mean	F-Value	p-value
	Squares		Square		
	Zeolite	e-Fe/PKS	$SAC + H_2O_2$		
Model	10098.0	9.0	1122.0	322.2	< 0.0001
A-Dosage of H ₂ O ₂	481.9	1.0	481.9	138.4	< 0.0001
B-Dosage of	2676.5	1.0	2676.5	768.6	< 0.0001
Adsorbent					
С-рН	5557.0	1.0	5557.0	1595.9	< 0.0001
D- Contact Time	42.0	1.0	42.0	12.1	0.0025
AB	51.7	1.0	51.7	14.8	0.0011
AC	130.8	1.0	130.8	37.6	< 0.0001
BC	68.7	1.0	68.7	19.7	0.0003
CD	29.8	1.0	29.8	8.6	0.0086
C^2	3188.5	1.0	3188.5	915.7	< 0.0001
Lack of Fit	61.4	14.0	4.4	4.6	0.0511
R-Squared	0.993				
Adj R-Squared	0.990				
Pred R-Squared	0.980				
Adeq Precision			62.8		

Table 4.13: Continued



Figure 4. 20: Predicted versus Actual plot for Colour removal (a) Fe/PKSAC + H₂O₂ (b) Zeolite-Fe/PKSAC + H₂O₂



 Table 4. 14: ANOVA analysis for the CCD for COD removal efficiency

Source	Sum of	df	Mean	F-Value	p-value			
	Squares		Square					
	Fe/PKSAC + H2O2							
Model	354.5	4.0	88.6	77.9	< 0.0001			
A-Dosage of H ₂ O ₂	230.1	1.0	230.1	202.3	< 0.0001			
B-Dosage of								
Adsorbent	38.4	1.0	38.4	33.7	< 0.0001			
C-pH	85.4	1.0	85.4	75.1	< 0.0001			
D-Contact Time	0.5	1.0	0.5	0.5	0.5017			
Lack of Fit	27.2	19.0	1.4	50.9	0.0002			
R-Squared			0.928					
Adj R-Squared			0.916					
Pred R-Squared			0.892					
Adeq Precision			29.8					
	Zeolite	e-Fe/PKS	$SAC + H_2O_2$					
Model	896.4	5.0	179.3	12.5	< 0.0001			
A-Dosage of H ₂ O ₂	480.4	1.0	480.4	33.5	< 0.0001			
B-Dosage of								
Adsorbent	213.6	1.0	213.6	14.9	0.0008			
C-pH	69.4	1.0	69.4	4.8	0.0382			
D- Contact Time	27.7	1.0	27.7	1.9	0.1776			
AC	105.3	1.0	105.3	7.3	0.0125			
Lack of Fit	329.7	18.0	18.3	651.8	< 0.0001			
R-Squared	0.731							
Adj R-Squared	0.673							
Pred R-Squared			0.542					
Adeq Precision			12.9					



Figure 4. 21: Predicted versus Actual plot for COD removal (a) $Fe/PKSAC + H_2O_2$ (b) Zeolite-Fe/PKSAC + H_2O_2

4.4.3 Optimization and Model Validation

Table 4.15 shows the predicted and the experimental results obtained for selected optimum conditions. As shown in Table 4.15, Zeolite-Fe/PKSAC + H₂O₂ achieved 83.1 % colour removal and 67.2 % of COD removal using 4 g/L of adsorbent dosage and 67.7 mM of H₂O₂ within 30 min at acidic condition (pH 3). Fe/PKSAC + H₂O₂ uses higher adsorbent dosage (5 g/L) and H₂O₂ (84.0 mM) compared to Zeolite-Fe/PKSAC + H₂O₂ to achieve 86.8 % of colour removal and 63.6 % of COD removal. As compared to without H₂O₂ adsorption process, Zeolite-Fe/PKSAC+ H₂O₂ gives a better COD removal by using a lesser amount of adsorbent within 30 min of contact time. Thus, the result revealed that the presence of H₂O₂ enhanced the COD removal efficiency and shortened the contact time. H₂O₂ is a strong oxidizing agent that produces hydroxyl radicals when it reacts with iron oxide and can oxidize organic compounds in wastewater. As a result of the presence of hydroxyl radicals, Fe²⁺ and Fe³⁺, Fenton oxidation may occur concurrently with adsorption with the presence of H₂O₂. (Jang, Seo, & Jeong, 2018).

Adsorbents	Adsorbent	H_2O_2	Contact	pН	Col	our	CC	DD
	Dosage	Dosage	Time		Rem	oval	Rem	oval
					Effici	iency	Effici	ency
					(%	6)	(%	(0)
	(g/L)	(mM)	(min)		Pred.	Exp.	Pred.	Exp.
Fe/PKSAC	5.0	84.0	30.0	3.0	82.7	86.8	65.0	63.6
$+ H_2O_2$								
Zeolite-	4.0	67.7	30.0	3.0	81.0	83.1	70.0	67.2
Fe/PKSAC								
$+ H_2O_2$								

Table 4. 15: Predicted and Experimental Results of optimization conditions

* Pred.: Predicted, Exp.: Experimental

4.4.4 Effects of Operating Parameters

4.4.4.1 Initial pH

The pH effect was investigated by varying the solution pH between 3 to 9 for Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 . Figures 4.22 - 4.23 show the effect of pH and dosage of adsorbent on the colour and COD removal. As can be seen from Figure 4.22 (a) and Figure 4.23 (a) for color removal similar trend was observed for both adsorbents where Fe/PKSAC + H_2O_2 (> 80 %) and Zeolite-Fe/PKSAC + H_2O_2 (> 90 %). Both the adsorbent achieved the highest colour removal at acidic condition (pH 3) within 30 min of contact time using 5 g/L adsorbent dosage. However, when the pH value is increased from 3 to 9 at 1 g/L adsorbent dosage, the colour removal efficiency of Fe/PKSAC + H_2O_2 from especially at alkaline condition.

Similar results are also obtained for COD removal, where the highest removal rate is achieved at the acidic condition for both adsorbents. Fe/PKSAC + H₂O₂ shows COD removal decreased from 74 % to 78 % when pH decreases from 9 to 3 at 1 g/L adsorbent dosage. At the similar condition, Zeolite-Fe/PKSAC + H₂O₂ also shows 3 % reduction from 68 % to 65 %. Based on the Figures (4.22 (b)), Fe/PKSAC + H₂O₂ shows the highest COD removal at 80 %, while Zeolite-Fe/PKSAC + H₂O₂ shows the highest COD removal at 75 % at the acidic condition and contact time of 30 min contact time using 5 g/L of adsorbent dosage.

The results show that peroxide assisted adsorption favours acid condition as compared to alkaline. Probably due to at low pH, heavy metal and organic substance in POME will be destabilized. Thus, it enhances the adsorption process (Wahi, Chuah Abdullah, Nourouzi Mobarekeh, Ngaini, & Choong Shean Yaw, 2017). Besides, since both adsorbents have a

positive charge on their surface, it will form a mutual attraction with pollutant in the POME that has a negative charge at its surface. However, deprotonation will occur on the adsorbents at alkaline condition due to the formation of -OH groups and repulsion will happen and decrease in adsorption. Besides, due to the presence of H_2O_2 , there might be Fenton oxidation happen simultaneously together with adsorption as the hydroxyl radical in H_2O_2 will react with the iron in the adsorbents during the acidic condition (Mustapha Mohammed Bello et al., 2020; Du et al., 2020; Fenton, 1894). Many studies also have reported that Fenton oxidation performs better in acidic condition (Mustapha Mohammed Bello et al., 2020; Hansson, Kaczala, Marques, & Hogland, 2012; Neyens & Baeyens, 2003; H. Zhou et al., 2018). In summary, it can conclude that the best colour and COD removal rate was achieved at the acidic condition for both Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂ adsorbents respectively.



B: Dosage of Adsorbent

Figure 4. 22: Contour (2D) plot for **(a)** Colour **(b)** COD removal efficiency of pH and dosage of adsorbent for Fe/PKSAC + H₂O₂ (Contact time = 30 min, H₂O₂ Dosage =



Figure 4.22: Continued



Figure 4. 23: Contour (2D) plot for **(a)** Colour **(b)** COD removal efficiency of pH and dosage of adsorbent for Zeolite-Fe/PKSAC + H₂O₂ (Contact time = 30 min, H₂O₂

Dosage = 200mM)



B: Dosage of Adsorbent

Figure 4.23: Continued

4.4.4.2 Adsorbent Dosage

Figures 4.24 - 4.25 show the effect of the dosage of adsorbent and H_2O_2 dosage on the colour removal and COD removal for Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 , respectively. The colour removal efficiency of Fe/PKSAC + H_2O_2 increases from 78.5 % to 82 % and Zeolite-Fe/PKSAC + H_2O_2 from 65.5 % to 90 % when adsorbent dosage increases from 1 g/L to 5 g/L using 120 mM of H_2O_2 dosage, 30 min of contact time and pH 3. On the other hand, the COD removal also increased from 75 % to 77 % and 64 % to 69 % for Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 at similar operating conditions. It shows that the dosage of adsorbent is directly proportional to colour and COD removal efficiency.

The adsorbent dosage can affect the adsorption in terms of availability of the surface area (R. R. Mohammed & Chong, 2014). Hence, increases in dosage of adsorbent eventually lead to the increase in the number adsorption sites available to adsorb pollutants from POME. Besides, the presence of H_2O_2 in this study also greatly enhance the adsorption process. At lower adsorbent dosage, the colour and COD removal efficiency was low as there was insufficient adsorption sites available and lesser iron oxide to decompose H_2O_2 in the reaction. Hence, the optimum dosage of adsorbent needed to be obtained to achieve the best efficiency for colour and COD removal in this study. As a result, the optimum dose will make the adsorption process more cost-effective while maintaining removal performance.

In summary, Zeolite-Fe/PKSAC + H_2O_2 is preferable compared to Fe/PKSAC + H_2O_2 as it requires lesser adsorbent (4 g/L) to achieve the desired outcome of the effluent as compared to Fe/PKSAC + H_2O_2 (5 g/L) in this study.

4.4.4.3 Dosage of H₂O₂

Hydroxyl radical (OH·) is well-known as a highly reactive radical for degrading organic matter in POME (Bala, Lalung, & Ismail, 2015; Lazar, Varghese, & Nair, 2012). In the present study, the effect of H_2O_2 on the adsorption process for both adsorbents was investigated. As shown in Figures 4.24 - 4.25, H_2O_2 assisted adsorption significantly impacts colour and COD removal for both Fe/PKSAC and Zeolite-Fe/PKSAC.

The result revealed that under optimum condition (30 min contact time and pH 3) at 5 g/L dosages of adsorbent, Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 able to achieve 83 % and 90 % of colour removal with the minimal amount of H_2O_2 (40 mM). In contrast, when the dosage of H_2O_2 increase from 40 mM to 200mM at similar condition,

Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 , the COD removal increased from 74 % to 80 % and 66 % to 73 % for COD removal, respectively. However, when 1 g/L dosage of adsorbent and 200 mM of H_2O_2 were used, Fe/PKSAC + H_2O_2 shows 77 % of COD removal Zeolite-Fe/PKSAC + H_2O_2 only obtained 68 %. The results above show a strong interaction between H_2O_2 dosage and adsorbent dosage on colour and COD removal efficiency.

It is interesting to note that hydroxyl radical can greatly enhance the colour removal of POME. The result also revealed that the COD degradation rate increase with the dosage of H_2O_2 . The result obtained in this study also in line with the other published work on dye and others wastewater as well (Gül & Özcan-Yıldırım, 2009; Zuorro, Fidaleo, & Lavecchia, 2013). The phenomena could be due to hydroxyl radical's ability of aggressively oxidize the organic compounds in POME. Where, oxidation of an organic compound results an increase in the number of carbon-heteroatom bonds, and/or a decrease in the number of carbon-heteroatom bonds, and/or a decrease in the number of carbon-hydrogen bonds, which can be confirmed with FTIR analysis. However, excessive dosage of H_2O_2 will exert an inhibitory effect as H_2O_2 molecules will consume OH· and form other radicals such as HO2·, which slow down the adsorption process (P et al., 2019). Moreover, Fenton oxidation might happen simultaneously with the adsorption process as iron oxide in the adsorbent acts as an important factor to react with the hydroxyl radical produce by H_2O_2 (Disni Gamaralalage, Sawai, & Nunoura, 2018).

In summary, the dosage of H_2O_2 proven to increase the adsorption process rate (Chung et al., 2017; Huling et al., 2017). Yet, there will not be any sludge generated for this treatment as compared to homogeneous Fenton oxidation. Overall, the presence of H_2O_2 gives a new alternative for the adsorption process in the wastewater industry.



Figure 4. 24: Contour (2D) plot for (a) Colour (b) COD removal efficiency of adsorbent dosage and H_2O_2 dosage for Fe/PKSAC + H_2O_2 (Contact time = 30 min, Initial pH = 3)



Figure 4. 25: Contour (2D) plot for (a) Colour (b) COD removal efficiency of adsorbent dosage and H_2O_2 dosage for Zeolite-Fe/PKSAC + H_2O_2 (Contact time = 30 min, Initial

pH = 3)

4.4.4.4 Contact Time

Figures 4.26 - 4.27 show the effect of contact time and pH on colour and COD removal. Based on the Figure 4.26 (a), Fe/PKSAC + H₂O₂ shows that the highest colour removal of 82 % within 10 min at the acidic condition with 5 g/L of adsorbent dosage. However, when the contact time is increased to 60 min, the removal rate decreased from 82 % to 78 %. In contrast, Zeolite-Fe/PKSAC + H₂O₂ achieved colour removal of 83 % and remain constant when the contact time increase from 10 min to 60 min at acidic condition. On the other hand, Fe/PKSAC + H₂O₂ achieved the highest COD removal of 80 % and remain constant, while Zeolite-Fe/PKSAC + H₂O₂ shows minor increment from 69 % to 71 % when the contact time increased from 10 to 60 min at pH 3. This result showed a strong interaction between contact time and the initial pH of the solution.

According to Ahmad and others (2005), the adsorption process occurs rapidly within 10 - 30 min due to the higher availability of active sites (Ahmad, Sumathi, & Hameed, 2005; Hasan et al., 2016). When the removal rate reaches the saturation point, the removal rate will remain constant or decrease due to the repulsive forces between the molecules (Sokker et al., 2011). With the presence of H_2O_2 , the reaction achieves equilibrium much faster compared to the conventional adsorption process. It should be highlighted that the adsorption process's contact time can be shortened with peroxide assisted adsorption. Hydroxyl radical produced by H_2O_2 is highly reactive, which triggers the adsorption process to happen rapidly. In summary, this study has also proven that the presence of H_2O_2 can greatly improve the efficiency of adsorption while minimizing the contact time.



Figure 4. 26: Contour (2D) plot for (a) Colour (b) COD removal efficiency of contact time and pH for Fe/PKSAC + H_2O_2 (Adsorbent Dosage = 5 g/L, H_2O_2 Dosage = 200mM)



Figure 4. 27: Contour (2D) plot for (a) Colour (b) COD removal efficiency of contact time and pH for Zeolite-Fe/PKSAC + H_2O_2 (Adsorbent Dosage = 5 g/L, H_2O_2 Dosage =

4.4.5 Reusability Study

Figure 4.28 depicts the result of the reusability study using Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 over five consecutive cycles. Zeolite-Fe/PKSAC + H_2O_2 retained its adsorbent capability over five cycles with a minimal reduction of 2.9 % from 83.9 % to 81.0 %. However, Fe/PKSAC + H_2O_2 shows decrease of 6.6 % from 81.7 % to 80.5 %. The result shows that Zeolite can increase the adsorbent's stability, as reported in previously published articles (Khalil et al., 2020; Khanday, Asif, et al., 2017; Khanday, Marrakchi, et al., 2017; Min Wang et al., 2018). Compared with the previous experiment, both activated carbons that impregnated with Zeolite show the ability to be reused and maintain their adsorbent capacity over the 5th cycle. Hence in the industrial application, the ability to reuse and regeneration acts as an important criterion as it can greatly reduce the adsorption cost in wastewaters application (Pham, Lee, & Kim, 2016).

	H_2O_2	
	Fe/PKSAC + H ₂ O ₂	Zeolite-Fe/PKSAC + H ₂ O ₂
Regeneration 1st Cycle (%)	87.1	83.9
Regeneration 5th Cycle (%)	80.5	81.0
Total Amount % lost	6.6	2.9

Table 4. 16: Results of Reusability of Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC +



Figure 4. 28: Reusability of Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂

4.4.6 Adsorption Capacity

Figure 4.29 shows the results obtained for the adsorption capacity of $Fe/PKSAC + H_2O_2$ and Zeolite-Fe/PKSAC + H_2O_2 . The highest adsorption capacity of 228 mg/g and 258.4 mg/g were achieved using Fe/PKSAC+ H_2O_2 and Zeolite-Fe/PKSAC+ H_2O_2 . respectively, when 1 g/L adsorbent and 200mM of H₂O₂ were used at 30 min of contact time and acidic condition. However, when the adsorbent dosage increased to 5 g/L, the adsorbent capacity of both adsorbents decreases significantly (Figure 4.29). At the lower adsorbent dosage, the adsorbent's surface area can be fully occupied by the pollutants. In contrast, increases in the dosage might cause more surface area available, leading to decreases in adsorption capacity (J. Li, Liu, Huang, & Wang, 2016). Under optimized condition at pH 3 and within 30 min contact time, Zeolite-Fe/PKSAC+ H₂O₂ shows the highest adsorption capacity at 73.3 mg/g using 4 g/L adsorbent and 67.7 mM of H₂O₂ as compared to Fe/PKSAC+ H₂O₂ obtained 55.2 mg/g at 5 g/L adsorbent and 84.0 mM of H₂O₂, as shown in Table 4.17. Both studies also revealed that the presence of Zeolite greatly improves the adsorption capacity of the adsorbent. Moreover, Zeolite-Fe/PKSAC has proven to maximize its efficiency in the adsorption process with the presence of H₂O₂. The results obtained are in line with the study reported by A. Zhou and others (2018) (A. Zhou et al., 2018).

Table 4. 17: Adsorption Capacity of Fe/PKSAC+ H₂O₂ and Zeolite-Fe/PKSAC+ H₂O₂

under	optimize	conditions	(pH =	3 and	Contact	Time =	30 m	in)
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	Adsorption Capacity (mg/g)
$Fe/PKSAC + H_2O_2$	55.2
Zeolite-Fe/PKSAC + H_2O_2	73.3



Figure 4. 29: Adsorption Capacity for Fe/PKSAC + H_2O_2 and Zeolite-Fe/PKSAC + H_2O_2 on the effect of dosage of adsorbent

4.4.7 Comparison of Peroxide Assisted Adsorption Study

Table 4.18 shows the comparison of peroxide assisted adsorption process using Fe/PKSAC and Zeolite-Fe/PKSAC. As shown in Table 4.18, both Fe/PKSAC and Zeolite-Fe/PKSAC managed to achieve more than 80 % and 60 % of colour and COD removals, respectively. Zeolite-Fe/PKSAC uses a lesser amount of adsorbent and H₂O₂ (4 g/L; 67.7 mM) than Fe/PKSAC (5 g/L; 84.0 mM) to achieve more than 80 % of colour removal. Besides, Zeolite-Fe/PKSAC also retain its adsorbent capability over five cycles, with only 2.9 % loss compared to Fe/PKSAC, which losses about 6.6 % of adsorption performance. Besides, under the optimized conditions, Zeolite-Fe/PKSAC (73.3 mg/g) also shows 25 % higher adsorption capacity as compared to Fe/PKSAC (55.2 mg/g).

In summary, the minimal consumption of adsorbent and oxidants, shorter contact time and better reusability capacity revealed by the Zeolite-Fe/PKSAC, making it better adsorbent than Fe/PKSAC. Besides, the peroxide assisted H₂O₂ also increased the COD degradation and shortened the adsorption process's contact time. The integration of H_2O_2 with iron oxides can produce powerful reactive species such as OH· radical to attack and degrade the solution's recalcitrant compounds (Y. Wei et al., 2019). Furthermore, the formation of OH· radical greatly improves the contact time compared to the conventional adsorption process. In summary, many authors have also reported that the presence of H_2O_2 able to improve the adsorption process (Giamello, Calosso, Fubini, & Geobaldo, 1993; Kim, Bokare, Koo, & Choi, 2015; Lousada & Jonsson, 2010; Pettine, Campanella, & Millero, 1999)

Adsorbent	pН	Dosage	Dosage	Contact	Colour	COD
		Adsorbent	H ₂ O ₂	Time	Removal	Removal
		(g/L)	(mM)	(min)	(%)	(%)
$Fe/PKSAC + H_2O_2$	3.0	5.0	84.0	30.0	87.0	63.0
Zeolite-Fe/PKSAC	3.0	4.0	67.7	30.0	83.0	67.0
+ H ₂ O ₂						

Table 4. 18: Comparison of Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂

4.5 Adsorption Kinetics

The kinetic study of the activated carbon with and without the addition of H_2O_2 under the optimum condition has been summarised in Tables 4.19 - 4.20, respectively. Both adsorbents managed to achieve > 80 % of colour removal within 4 min for peroxide assisted adsorption; however, adsorbents have taken a minimum of 10 min to achieved > 80 % without adding H_2O_2 . These results have proven that adsorption happens rapidly at the beginning of the experiment, and the presence of H_2O_2 shorten about 2.5 times the contact time. J. Wang and others (2019) also have reported that the adsorption can occur at the beginning of contact time, due to the number of vacant sites available initially with weak resistance to mass transfer (J. Wang, Zhang, Kang, & Zhang, 2019). Besides, there will only be a slight increase of colour removal until it reached maximum as the

adsorbent's free surface decreased due to the increased coverage by the bound ions (Rafiq, Nazir, Durr e, Shah, & Ali, 2014). Therefore, both adsorbents' adsorption process can be divided into two processes – the fast adsorption stage and the slow adsorption stage.

The pseudo-zero order, pseudo-first order, and pseudo-second-order were fitted to the experimental data to identify the adsorption kinetics characteristics. The regression coefficients, R^{2,} expressed the consistency between experimental data and the model predicted values. The kinetics study results for both adsorbents with and without H₂O₂ have been shown in Figures 4.30 - 4.31. The adsorption kinetics curves show similar adsorption features for Fe/PKSAC and Zeolite-Fe/PKSAC with and without the addition of H₂O₂. The pseudo-second-order model fits the best for the adsorption processes on the Fe/PKSAC and Zeolite-Fe/PKSAC activated carbon. The regression coefficients, R² of more than 0.9400, suggested that the adsorption rate was proportional to the square of the pollutant concentration. The regression coefficients, R^2 of the pseudo-second-order reaction kinetics for adsorption process using Zeolite-Fe/PKSAC and Fe/PKSAC were 0.9496 and 0.9912 respectively, which are higher than pseudo-zero order (Zeolite-Fe/PKSAC, $R^2 = 0.8992$ and Fe/PKSAC, $R^2 = 0.9345$) and pseudo-first order (Zeolite-Fe/PKSAC, $R^2 = 0.9282$ and Fe/PKSAC, $R^2 = 0.9834$). Whereas Zeolite-Fe/PKSAC + H_2O_2 and Fe/PKSAC + H_2O_2 also obtained R^2 of 0.9331 and 0.9724 for the Pseudosecond order kinetic which is greater than Pseudo-zero order (Zeolite-Fe/PKSAC + H₂O₂, $R^2 = 0.9211$ and Fe/PKSAC + H₂O₂, $R^2 = 0.9412$) and Pseudo-first order (Zeolite-Fe/PKSAC + H₂O₂, $R^2 = 0.928$ and Fe/PKSAC + H₂O₂, $R^2 = 0.9632$) reaction kinetic. The pseudo-second-order model kinetic equation contains the two stages of the adsorption process-surface adsorption and internal diffusion which may be suitable for this adsorption process (Sadati Behbahani, Rostamizadeh, Yaftian, Zamani, & Ahmadi, 2014; Tissera, Wijesena, Yasasri, de Silva, & de Silva, 2020).

Time	Kinetic Study under Optimum	a Condition on colour removal (%)
(Min)	Fe/PKSAC	Zeolite-Fe/PKSAC
0	0.00	0.00
10	88.22	83.26
20	92.25	85.74
30	93.80	88.06
40	95.35	89.61
50	N/M	90.23
60	N/M	90.39

Condition on colour removal efficiency

**N/M: Not Measured



Figure 4. 30: (a) Pseudo-Zero-order, (b) Pseudo-First order and (c) Pseudo-Second

order reaction kinetic for the colour removal by adsorption process



Figure 4. 30: Continued

Table 4. 20: Kinetic Study	y of Fe/PKSAC + H ₂ C	O ₂ and Zeolite-Fe/Pl	$KSAC + H_2O_2$ under
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Time	Kinetic Study under Optimum Condition on colour removal (%)				
(Min)	Fe/PKSAC + H2O2	Zeolite-Fe/PKSAC + H ₂ O ₂			
0	0	0			
2	78.9	80.5			
4	82.6	80.6			
6	83.6	83.3			
8	84.9	83.7			
10	86.7	84.9			

Optimum Condition of	on colour removal	efficiency
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Figure 4. 31: Continued

4.6 Adsorption Isotherms

Adsorption isotherms show the relationship between adsorbate adsorbed onto the active site of adsorbent and the solution's concentration at equilibrium conditions (Hameed & El-Khaiary, 2008). In this study, the data were fitted to three different isotherm models,

including Langmuir, Freundlich and Temkin isotherms, as summarised in Tables 4.21 - 4.22. To determine the Langmuir isotherm, the values of C_e/q_e were plotted of against C_e as shown in Figure 4.32 (a) and Figure 4.33 (a). Furthermore, the values of $logq_e$ and $log c_e$ were plotted to evaluate the Freundlich isotherm parameters of 1/n and K_F as shown in Figure 4.32 (b) and Figure 4.33 (b). The isotherm curves, q_e against $ln c_e$ was plotted for Temkin isotherm were plotted and shown in Figure 4.32 (c) and Figure 4.33 (c).

Based on the result obtained, the R² value of the Langmuir isotherm model is larger than Freundlich and Temkin isotherm, suggesting that Langmuir isotherm fitted the best for the adsorption process with and without H₂O₂ for Fe/PKSAC and Zeolite-Fe/PKSAC. Langmuir isotherm shows monolayer adsorption for the activated carbon developed in this study (Akpen et al., 2018). Furthermore, it also indicates that the active sites were homogeneously distributed on the adsorbent's surface (R. R. J. I. Mohammed, 2013).

The separation factor (R_L) is one of the dimensionless parameters for Langmuir isotherm. The adsorption process might be linear if R_L =1, favourable if R_L within 0 to 1 or unfavourable if $R_L > 1$ (Khandaker, Toyohara, Saha, Awual, & Kuba, 2020). Otherwise, it is difficult for adsorption on an adsorbent to occur. Tables 4.21 - 4.22, the R_L values for the adsorption for Fe/PKSAC, Zeolite-Fe/PKSAC, Fe/PKSAC + H₂O₂ and Zeolite-Fe/PKSAC + H₂O₂ are within 0 to 1, indicating that the adsorption is a favourable process. The adsorption is a nearly irreversible process (Hall, Eagleton, Acrivos, & Vermeulen, 1966). Hence, the results justify that the Langmuir model can fit the adsorption process with and without H₂O₂ well. The maximum adsorption capacity obtained for Zeolite-Fe/PKSAC + H₂O₂ is larger than many other modified and unmodified adsorbents derived from natural zeolites and natural palm kernel shell (Alshameri et al., 2014; Moreno-Marenco, Giraldo, & Moreno-Piraján, 2020; Neolaka, Supriyanto, Darmokoesoemo, & Kusuma, 2018). It may because Zeolite, iron oxide, and H_2O_2 greatly improved the maximum adsorption capacity and the surface area of the adsorbent towards the adsorption process for POME.

In summary, the higher R^2 values proved the Langmuir model's validity well fitted for both Zeolite-Fe/PKSAC and Fe/PKSAC in the adsorption process with and without the addition of H₂O₂. The result obtained in this study were in line with many other studies which reported that Langmuir isotherm is more favourable for COD and Color removal for biomass adsorbent (Desta, 2013; Hameed & Ahmad, 2009; Hasan et al., 2016; R. R. Mohammed & Chong, 2014).

Isotherm	Parameters	Adsorbent			
		Fe/PKSAC	Zeolite-Fe/PKSAC		
Langmuir	Q_{max}	19.6	20.4		
	K _L	0.9	0.73		
	\mathbf{R}^2	0.9940	0.9916		
	R_L	0.01	0.01		
Freundlich	1/n	0.2	0.2		
	K_F	11.1	10.65		
	\mathbb{R}^2	0.9672	0.9720		
Temkin	<i>B</i> ₁	2.9	3.4		
	K_T	38.86	20.2		
	\mathbb{R}^2	0.9537	0.9590		

 Table 4. 21: Isotherm Constant Parameter and Correlation Coefficients Calculated for

 Adsorption Study


Figure 4. 32: Isotherm model of Fe/PKSAC and Zeolite-Fe/PKSAC (a) Langmuir (b)

Freundlich (c) Temkin for adsorption process

Table 4. 22: Isotherm Constant Parameter and Correlation Coefficients Calculated for

Isotherm	Parameters	Adsorbent					
		Fe/PKSAC + H ₂ O ₂	Zeolite-Fe/PKSAC+ H ₂ O ₂				
Langmuir	Q_{max}	19.2	24.1				
	K_L	1.2	0.36				
	\mathbb{R}^2	0.9987	0.9924				
	R_L	0.01	0.03				
Freundlich	1/n	0.2	0.3				
	K_F	11.8	10.4				
	\mathbb{R}^2	0.9508	0.9841				
Temkin	<i>B</i> ₁	2.7	4.4				
	K_T	69.6	7.1				
	\mathbb{R}^2	0.9709	0.9766				

Adsorption Study with H₂O₂





Langmuir (b) Freundlich (c) Temkin for adsorption process with H₂O₂



Figure 4. 33: Continued

4.7 Plausible Adsorption Mechanism

Figure 4.34 presents the plausible adsorption mechanisms for peroxide assisted adsorption for POME by considering initial solution pH, as well as FTIR analysis. Based on previously discussed FTIR analysis also clearly explains the deformation and stretching vibrations of the functional group after the adsorption of pollutants. Palm oil mill effluent (POME) with an acidic pH contains high chemical oxygen demand (COD) and biological oxygen demand (BOD), oil and grease, suspended solids, ammonia-nitrogen, heavy metal concentration and high content of degradable organic matter (A. Adeleke et al., 2019b; Khemkhao, Techkarnjanaruk, & Phalakornkule, 2015; Okwute & Nnennaya, 2007). The surface of modified PKSAC shows porous structures and a greater amount of carbon, oxygen and iron-containing functional groups. The adsorption mechanism is summarized in Figure 4.34. The most representative mechanism of pollutants adsorption onto adsorbent could be through hydrogen bonding, $n-\pi$ interactions and electrostatic interaction between the functional group of POME and the adsorbent's surface (Dinh et al., 2019; Luo, Bai, & Zhu, 2018). The possible bond

formation mechanism between organic matters and heavy metals and the functional group of the adsorbent has been shown in Figure 4.34 (c), (d) and (e).

At acidic condition (pH 3), both adsorbents show a weak electrostatic interaction with the pollutant (-NH₄+) in the aqueous solution. Moreover, if the pollutant remains in neutral form, it will lead to a low electrostatic interaction but may involve more hydrogen bonding or n- π interactions (K. Yang & Xing, 2010). The FTIR analysis shows that broad adsorption peaks at 3700-3400 cm⁻¹ indicate hydroxyl groups' presence (-OH). Hence, the adsorption of POME most probably assisted by hydrogen bonding to enhance the surface interactions between pollutant and adsorbent. Furthermore, the presence of amine functional groups that originated from the palm kernel shell may also contribute to hydrogen bonds (Weiben Yang, Zheng, Xue, & Lu, 2011). Additionally, the benzene group in the pollutant might be protonated during the acidic condition, which makes it as an π -electron acceptor where it might form $n-\pi$ interactions between adsorbents (Bedia, Peñas-Garzón, Gómez-Avilés, Rodriguez, & Belver, 2018). The proposed mechanism that reported in this study is in line with works reported by previous researchers, where adsorption mechanism could be through mainly two different interaction which including hydrogen bonding and n- π interactions (Allouss, Essamlali, Amadine, Chakir, & Zahouily, 2019; To, Hadi, Hui, Lin, & McKay, 2017; Tran, You, Nguyen, & Chao, 2017).

Besides, Figure 4.34 (a) and (b) show that physical adsorption and Fenton oxidation happen simultaneously in this study. The presents of iron oxide in the adsorbent will react with the oxidants (H₂O₂) and speed up the adsorption process to happened immediately (A. Adeleke et al., 2019a; Liang et al., 2020). Wei and others (2020) also reported that adsorption and oxidation could happen simultaneously with oxidants' presence (D. Wei et al., 2020).



Figure 4. 34: Proposed adsorption mechanisms of adsorption process with H₂O₂: (a)
Physical adsorption, (b) Fenton oxidation, (c) electrostatic interactions, (d) H-bonding interactions and (e) n-π interactions

4.8 Comparison of Adsorption Efficiency of Zeolite-Fe/PKSAC with and without the addition of H₂O₂

Table 4.23 summarized the adsorbent performance of Zeolite-Fe/PKSAC with and without the addition of H_2O_2 . The results show that the adsorption process without H_2O_2 requires 5 g/L of adsorbent and 60 min of contact time to achieve 87.5 % and 62.6 % of colour and COD removals, respectively. On the other hand, using only 4 g/L of adsorbent

and a shorter contact time of 30 min, peroxide assisted adsorption managed to achieve higher degradation efficiency of 67.2 % and slightly lower colour removal (83.1%) compared to the adsorption process without H₂O₂. However, it should be noted that peroxide assisted adsorption able to maintain its colour removal efficiency above 80 % by using a 20 % lower adsorbent dosage, 50 % lesser contact time. The radicals produced by H₂O₂ is highly reactive and able to oxidise pollutants while assisting the adsorption process in a short period. Also, the presence of H₂O₂ increased the degradation rate of COD removal. Besides, Fu and others (2016) have reported that H₂O₂ can destroy POME organic compounds into a harmless product such as CO₂ and H₂O (Fu, Juang, Huq, & Hsieh, 2016). Recently, many studies also have proven that the presence of H₂O₂ can greatly enhance the contact time of the adsorption process and the removal efficiency as well as improving the reusability of the adsorbent (Huang, Huang, Wang, & Zheng, 2018; Jyothi, Yesodharan, & Yesodharan, 2018; Zulfiqar, Sufian, Rabat, & Mansor, 2021).

Table 4. 23: Comparison of Zeolite-Fe/PKSAC on adsorption study with and without

Present of H2O2	рН	Dosage Adsorbent (g/L)	Dosage H2O2 (mM)	Contact Time (min)	Colour Removal (%)	COD Removal (%)
NO	3.0	5.0	-	60.0	87.5	62.6
YES	3.0	4.0	67.7	30.0	83.1	67.2

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4.9 Summary

Table 4.24 summarized the results obtained for Fe/PKSAC and Zeolite-Fe/PKSAC adsorbents with and without the addition of H_2O_2 . The adsorption performance of Zeolite-Fe/PKSAC + H_2O_2 is preferable compared to Fe/PKSAC, Zeolite-Fe/PKSAC and Fe/PKSAC + H_2O_2 as it uses lesser adsorbent (4 g/L) and requires shorter contact time

(30 min) to achieve the desired outcome. Zeolite-Fe/PKSAC + H_2O_2 also shows significant reusability ability up to the 5th cycle compared to others. Furthermore, the presence of H_2O_2 also reduced the contact time for the adsorption process by 50 %. Hence, the adsorption process with the addition of H_2O_2 by using Zeolite-Fe/PKSAC is proven to be the most effective adsorbent in terms of cost for POME treatment.

Adsorbent	pН	Ads.	$[H_2O_2]$	Ct	CR	COD	qe	TAL ^{5th}	С	Fe	Mag.	
		(g/L)	(mM)	(min)	(%)	Rem.	(mg/g)	(%)	(%)	(%)	(emu/g)	
						(%)						
Fe/PKSAC	3.0	5.0	-	40.0	93.0	58.0	44.0	17.2	40.9	9.1	16.6	
Zeolite-	3.0	5.0	-	60.0	88.0	63.0	48.0	5.6	61.4	3.8	10.6	
Fe/KSAC												
Fe/PKSAC	3.0	5.0	84.0	30.0	87.0	63.0	55.0	6.6	40.9	9.1	16.6	
$+ H_2O_2$												
Zeolite-	3.0	4.0	67.7	30.0	83.0	67.0	73.0	2.9	61.4	3.8	10.6	
Fe/PKSAC												
$+ H_2O_2$												

Table 4. 24: Comparison of Adsorption Processes

**Ads. : Adsorbent dosage, [H₂O₂]: Dosage of hydrogen peroxide (oxidant), C_t: Contact Time, CR: Colour Removal, COD Rem.: COD Removal, q_e: Adsorption Capacity, TAL^{5th}: Total Amount Lost after 5th Cycle, Mag.: saturation magnetization

CHAPTER 5: CONCLUSION

5.1 Conclusion

The aim of this study is to develop an abundantly available waste-based high-performance adsorbent for recalcitrant wastewater treatment for adsorption process. In this study, two types of biomass-based adsorbent (Fe/PKSAC and Zeolite-Fe/PKSAC) were developed by incorporating PKS with iron oxide and zeolite. The treatment efficiency of adsorbents through adsorption with and without the aid of peroxide (H₂O₂) were evaluated using a laboratory sized experimental setup for palm oil mill effluent (POME). Several parameters were used to evaluate the effectiveness of adsorbents through adsorption process, including COD removal, decolorization efficiency, and adsorption capacity. Effect of adsorption such as dosage of adsorbent, dosage of H₂O₂, pH condition and contact time were also evaluated in this study.

The RSM-CCD optimization tool was used successfully to determine the most significant operating parameters and optimum condition of adsorbent, oxidant (H₂O₂), pH and Contact time to increase the removal efficiencies, while reducing the operating cost directly. The FTIR, XRD, BET, VSM, SEM and EDX analyses of adsorbents were used to evaluate the characteristic of adsorbent such as surfaces area, chemical composition, magnetic properties, crystallinity, and stability. The main conclusion derived from the study was based on the defined objectives and related activities as follows:

Objective 1

 Hybrid magnetite biomass-based adsorbent based on palm kernel shell activated carbon /Iron oxide /Zeolite was synthesized using co-precipitation and ultrasonic mixing method.

- The Fourier Transform Infrared (FTIR) analysis revealed that both the adsorbents Fe/PKSAC and Zeolite-Fe/PKSAC contains OH, N–H, C=O and C= C, which are essential for removing pollutants in the wastewater.
- 3. After incorporating with iron oxide and zeolite, the iron and carbon content in both adsorbents had increased and were consistent with SEM analysis, where the presence of white crystal indicates the presence of iron oxide nanoparticles.
- 4. The Fe/PKSAC and Zeolite-Fe/PKSAC illustrated a high saturation magnetization and easily separated using an external magnet.

Objective 2

- Solution of pH was observed to be the most significant parameter affecting the performance of the adsorbent compared to adsorbent dosage, dosage of H₂O₂ and contact time in this study.
- Under optimized conditions, Fe/PKSAC and Zeolite-Fe/PKSAC achieved colour removal of 93.2 % and 87.5 % respectively and COD removal of 58.1 % and 62.6 % respectively.
- In term of reusability, Zeolite-Fe/PKSAC retained its adsorbent capability over five cycles as it showed a minimal decrease (5.6 %) compared to Fe/PKSAC (17.2 %).
- 4. On the other hand, adsorption with the present of H₂O₂, Zeolite-Fe/PKSAC+H₂O₂ achieved 83.1 % of colour removal and 67.2 % of COD removal. Fe/PKSAC+H₂O₂ was managed to achieve higher colour removal (86.8 %) and lower COD removal (65.6 %) compared to Zeolite-Fe/PKSAC+H₂O₂.
- 5. Zeolite-Fe/PKSAC+H₂O₂ used lesser adsorbent and H₂O₂ (4 g/L; 67.7 mM) compared to Fe/PKSAC+H₂O₂ (5 g/L; 84.0 mM). Moreover, Zeolite-

Fe/PKSAC+H₂O₂ was able to retain its adsorbent capability over five cycles, with only 2.9 % loss compared to Fe/PKSAC+H₂O₂ with 6.6 % loss.

- Moreover, Zeolite-Fe/PKSAC+H₂O₂ (73.3 mg/g) achieved the highest adsorption capacity as compared to Fe/PKSAC+H₂O₂ (55.2 mg/g), Zeolite-Fe/PKSAC (47.6 mg/g) and Fe/PKSAC (44.2 mg/g).
- In summary, even though adsorption was able to achieve 4.4 % higher colour removal rate compared to adsorption with H₂O₂, but its required higher adsorbent dosage, longer contact time.
- 8. Therefore, Zeolite-Fe/PKSAC was preferred over Fe/PKSAC due to better adsorption capability and higher stability.

Objective 3

- 1. Both adsorbents (Zeolite-Fe/PKSAC and Fe/PKSAC) were best fitted with Langmuir isotherm and the pseudo-second-order kinetic model, which it revealed the monolayer adsorption on a surface that was homogenous in adsorption affinity.
- 2. Besides, there might be physical adsorption and Fenton oxidation happen simultaneously in the process due to the present of iron oxide and H₂O₂. Hence, it would speed up the whole reaction of adsorption process.
- 3. Furthermore, the possible mechanism of pollutants adsorption on to adsorbents could be through electrostatic interaction, hydrogen bonding and $n \pi$ interactions between the functional group of POME and surface of adsorbents.

In summary, this study proven that palm kernel shell which was able to convert into a high-performance adsorbent for the adsorption of POME in tertiary treatment. Peroxide-

assisted adsorption could improve adsorption performance significantly while minimize adsorbent dosage and contact time. This study could provide a dual benefit to the palm oil industry, as its solid waste could be converted into a useful adsorbent thereby saving costs in wastewater treatment.

5.2 Application of this study

Adsorption process is widely used in industrial application specially for removing heavy metals, organic and inorganic pollutants from aqueous industrial sludge, surface waters, drinking water, groundwater, process water and wastewater. Hence, the PKS based adsorbent developed in this study has a huge potential to be used in any of the applications mentioned above. Besides, the adsorbent has a good ability towards colour removal, so it can be potentially used for dye removal. In advance, the present of H₂O₂ can greatly reduce the contact time in the adsorption process. Hence, adsorption with H₂O₂ will be strongly recommended for cottage industrial or developed countries that having space constraints. In summary, the adsorbent that developed can be use in any adsorption process application specially on wastewater treatment.

5.3 **Recommendations for Future Studies**

This research has shown that modified biomass-based adsorbent for oxidant assisted adsorption process have a potential to be used in treating POME wastewater. It is noted that there are few other aspects that not included in this study due the limitations of time and availability of equipment.

There are several areas of research that could give better perspectives in terms of possible applications. Some recommendations for further studies are presented below:

- The biomass-based adsorbent may possibly modify with others method such as biological modification, mineral impregnation, magnetic modifications or combining or hybridizing with other powerful adsorbents, inorganic compounds, and organic compounds such as iron oxide, titanium dioxide, graphene oxide, magnesium oxide, polymer and sulfone can be used to increase the capacity and efficiency of biomass-based adsorbent in treating industrial wastewaters. This could be a potential area of further study.
- Other response such as biological oxygen demand (BOD), oil and grease, suspended solids, ammonia-nitrogen, heavy metal concentration and high content of degradable organic matter need to be studied for industrial applications of modified biomass-based adsorbent.
- The data obtained in this study from these are not sufficient information for industrial scaled up. The column or pilot study should be used to simulate full scale applications.

5.4 Output of This Study

Two manuscripts have been published in ISI ranked journal from this work and one more technical paper is being drafted. The details are given in Appendix A and Appendix B.

5.5 Knowledge Contribution

The following are the knowledge contributions from this study:

- Established a new strategy in enhancing the adsorption performance of palm kernel shell based activated carbon for colour and COD removal by adding optimized level of H₂O₂.
- 2. Established the hybrid PKS synthesis procedure using ultrasonic mixing.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

No	Articles	Status
1	Kwong Chia Jun, Abdul Aziz Abdul Raman*, and Archina	Published
	Buthiyappan (2020) Treatment of Oil Refinery Effluent	
	Using Bio-adsorbent Developed from Activated Palm Kernel	
	Shell and Zeolite. RSC Advances 10 (40), 24079-24094 ISI-	
	indexed, Q1, IF=3.070	
2	Kwong Chia Jun, Archina Buthiyappan and Abdul Aziz	Published
	Abdul Raman* (2021) Application of Magnetic-Biomass	
	Derived Activated Carbon as an Adsorbent for The	
	Treatment of Recalcitrant Wastewater. Chemical Papers,	
	1336-9075. ISI-indexed, Q2, IF=1.68	
3.	Kwong Chia Jun, Abdul Aziz Abdul Raman*, and Archina	Being Drafted
	Buthiyappan (2021) Review on Possibility of Agriculture	
	Waste act as adsorbent for The Treatment of Industrial	
	Wastewater Through Adsorption with Oxidants. Expected to	
	submit by 1 st December 2021 in Chinese Journal of Chemical	
	Engineering. ISI-indexed, Q2, IF=1.911	

