LANTHANUM ORTHOFERRITE AS PHOTOCATALYST PREPARED USING SOL-GEL METHOD FOR OILY WASTEWATER TREATMENT

NUR AISYAH BINTI JAMALUDIN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

NOVEMBER 2020

DEDICATION

Dedicated to my beloved family.

I love you.

ACKNOWLEDGEMENT

In the name of Allah the Most Gracious and Most Merciful, praises be to Him and Salam to our Prophet Muhammad S.A.W for giving me the strength upon completing of this study. In preparing this thesis, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts in this research. In particular, I wish to express my sincere appreciation to my main thesis supervisor, Dr Farhana Aziz, for encouragement, guidance, critics, and to never giving up for me and also friendship. I am also very thankful to my co-supervisor, Dr Norhaniza Yusof and Dr Nor Akmal Fadil for their guidance, advices and motivation. Without their continued support and interest, this thesis would not have been the same as presented here. My fellow postgraduate students should also be recognised for their support. My sincere appreciation also extends to all my colleagues and others who have aided at various occasions. Their views and tips are useful indeed. In addition to that, I would also like to extend my gratitude to FCEE faculty staff for all their help and guidance throughout my master study. Unfortunately, it is not possible to list all of them in this limited space. I am also grateful to all my family members especially both my parents who has pushed me towards my decision in getting into postgraduate study and supported me in every decision I made. Thank you for all friends and colleague who always been there and understand me.

ABSTRACT

Lanthanum orthoferrite ($LaFeO_3$) is the perovskite type of photocatalyst that has potential to treat oily wastewater. Compared to better-known titanium dioxide (TiO_2), $LaFeO_3$ has been found to have a smaller band gap. The key purpose of this study was therefore to manipulate the physicochemical properties of $LaFeO_3$ in order to enhance the degradation of oily wastewater by calcination heat treatment. Synthesis of the photocatalyst via the sol-gel route produced positive result. The precursor and $LaFeO_3$ were characterized using X-ray diffraction for crystallinity test, thermogravimetric analysis and differential thermal analysis for thermal decomposition, ultraviolet- visible spectroscopy for optical properties, Fourier-transform infrared spectroscopy and Brunauer-Emmett-Teller, BET for surface area and field emission scanning electron microscope (FESEM) for surface morphology analysis. $LaFeO_3$ was calcined at different temperature ranging from 500-900°C in two hours. Using glucose as chelating agent, $LaFeO_3$ calcined at 600°C started to have a complete crystal structure. Sharper and stronger peak indicated greater crystallization with increasing calcination temperature, where crystallite sizes of 7.29 nm, 11.55 nm, 12.60 nm and 15.43 nm were obtained for samples calcined at 600 to 900°C. FESEM images revealed that samples calcined at 600°C appeared to be in porous and regular shape, forming a large network system with smaller particles size and higher surface area compared to samples calcined at higher temperature. The BET surface areas for the samples were 3.89 m^2/g, 15.68 m^2/g, 6.43 m^2/g, 4.63 m^2/g, and 2.40 m^2/g at the aforementioned calcination temperature intervals. The perovskite photocatalyst calcined at 600°C was thus chosen as the finest photocatalyst to undergo photocatalytic study. This $LaFeO_3$-600 had the most outstanding surface area (15.68 m^2/g) with the lowest band gap value (1.88 eV) and smallest crystal size (7.29nm) compared to the others. Photocatalytic activity was conducted for 180 minutes where the first 30 minutes were for adsorption and desorption. The effects of the initial concentrations under visible light irradiation have been studied for 150 minutes and the findings indicate that the degradation efficiency were 70 %, 80 % and 65 % for concentrations of 1000 ppm, 10000 ppm and 20000 ppm respectively. Less than 5% was removed under visible light irradiance (photolysis), showing the stability of the pollutant. In conclusion, the perovskite-based photocatalyst $LaFeO_3$ was successfully prepared via the sol-gel method, where $LaFeO_3$-600 demonstrated the highest efficiency in degrading synthetic oily wastewater by up to 80% in 180 minutes.

ABSTRAK

Lantanum ortoferit ($LaFeO_3$), adalah jenis fotomangkin perovskit yang berpotensi untuk merawat air kumbahan berminyak. Berbanding dengan titanium dioksida (TiO_2), yang lebih terkenal, $LaFeO_3$ telah diketahui mempunyai jurang jalur yang lebih kecil. Tujuan utama kajian ini adalah untuk memanipulasi sifat fizik-kimia $LaFeO_3$ untuk meningkatkan degradasi air sisa berminyak dengan rawatan haba kalsinasi. Hasil sintesis fotomangkin melalui kaedah sol-gel menghasilkan keputusan yang positif. Prapenanda dan $LaFeO_3$ dicirikan menggunakan pembelauan sinar-X untuk ujian pengkristalan, analisis termogravitimetrik dan analisis kebezaan terma untuk penguraian terma, spektroskopi ultraviolet dan cahaya kelihatan untuk sifat optik, spektroskopi transformasi inframerah Fourier dan Brunauer-Emmett-Teller, BET untuk luas permukaan, dan mikroskop elektron imbasan pancaran medan (FESEM) untuk analisis morfologi permukaan. $LaFeO_3$ dikalsin pada suhu berlainan antara 500°C hingga 900°C dalam masa dua jam. Menggunakan glukosa sebagai ejen pengkelat, $LaFeO_3$ yang di kalsinasi pada suhu 600°C mula membentuk struktur kristal yang lengkap. Puncak yang lebih tajam dan kuat menunjukkan penghabluran kristal yang lebih ketara dengan peningkatan suhu kalsinasi, di mana kristalit berukuran 7.29 nm, 11.55 nm, 12.60 nm, and 15.43 nm diperoleh untuk sampel dari 600°C hingga 900°C. Imej FESEM menunjukkan bahawa sampel yang dikalsinasi pada suhu 600°C kelihatan berliang dan bentuk biasa, membentuk sistem rangkaian besar dengan saiz partikel yang lebih kecil dan luas permukaan yang lebih luas berbanding sampel yang dikalsinasi pada suhu yang lebih tinggi. Luas permukaan BET untuk semua sampel ialah 3.89 m^2/g, 15.68 m^2/g, 6.43 m^2/g, 4.63 m^2/g, dan 2.40 m^2/g dengan selang peningkatan suhu kalsinasi yang telah dinyatakan diatas. Fotomangkin perovskit yang dikalsinasi pada suhu 600°C dipilih sebagai fotomangkin yang paling berpotensi untuk menjalani kajian fotobermangkin. $LaFeO_3$-600 ini mempunyai luas permukaan yang luar biasa (15.68 m^2/g) dengan nilai jurang jalur terendah (1.88 eV) dan saiz kristal yang kecil (23.82 nm) berbanding dengan yang lain. Aktiviti pemangkin foto dilakukan selama 180 minit dengan 30 minit yang pertama sebagai masa penjerapan dan penyerapan. Kesan kepekatan awal di bawah penyinaran cahaya boleh lihat telah dijalankan selama 150 minit dan penemuan menunjukkan bahawa kecekapan degradasi adalah 70%, 80% dan 65% masing-masing bagi kepekatan awal 1000ppm, 10000ppm, dan 20000ppm. Hanya kurang daripada 5% disingkirkan di bawah sinaran cahaya yang boleh dilihat (fotolisis), menunjukkan kestabilan bahan pencemar. Kesimpulannya, fotomangkin berasaskan perovskit $LaFeO_3$ telah berjaya disintesis melalui kaedah sol-gel, di mana $LaFeO_3$-600 menunjukkan kecekapan tertinggi dalam melakukan degradasi air kumbahan berminyak sintetik sehingga 80% dalam masa 180 minit.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AOPs	-	Advanced Oxidation Processes
BET	-	Brunauer, Emmet and Teller
BOD	-	Biochemical Oxygen Demand
COD	-	Chemical Oxygen Demand
DTA	-	Differential Thermal Analysis
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier-transform Infrared Spectroscopy
IUPAC	-	International Union of Pure and Applied Chemistry
JCPDS	-	Joint Committee on Powder Diffraction Standards
$LaFeO_3$	-	Lanthanum Orthoferrite
N_2	-	Nitrogen gas
TDS	-	Total Dissolved Solid
TiO_2	-	Titanium Dioxide
UV-Vis	-	Ultraviolet Visible Spectroscopy/Spectrometry
UV	-	Ultraviolet
XRD	-	Xray Powder Diffraction

LIST OF SYMBOLS

°C	-	Degree Celsius
λ	-	Lambda
Nm	-	Nanometer
cm^{-1}	-	Per centimeter
g	-	Gram
L	-	Liter
m	-	meter
h	-	Hour
a.u.	-	Absorbance unit
eV	-	Electron volt
%	-	Percentage
M	-	Molar
mL	-	Milliliter
Ppm	-	Parts per million
min	-	minutes

CHAPTER 1

INTRODUCTION

1.1 Research Background

Petrochemical industries, oil and petroleum industries, transportation have generated oily wastewater that can be harmful to the environment. If left untreated, oily wastewater, which is usually emulsified, can have a significant negative impact on facilities. Water is the main source of living; untreated wastewater could affect drinking water and endanger aquatic resources. Significant threats that can be identified include soil, human, air and water (Jamaly *et al.*, 2015) . China has decided to limit as much as 10g/mL the maximum allowable emissions of oily wastewater in the country showing that oily wastewater is at a hazardous level (Yu *et al.*, 2017).

In the oil and gas (O&G) industries, water will be produced in a high quantity and can be said to be the most productive in a day. O&G industries handle more water than oil on a daily basis (Adham *et al.*, 2018). Water used primarily to maintain the pressure of the reservoir and through floods of water, may increase the recovery of oil (Adham *et al.*, 2018). There are few technologies available to treat oily wastewater such as gravity seals, dewatering, flotation, coagulation and membrane separation technologies that are called traditional methods, although advanced oxidation processes (AOPs) and hybrid technologies are the new technologies. Conventional methods such as treatment of wastewater will not completely remove contaminants from water. Researchers therefore always find a new and alternative way to treat wastewater so that the contaminants can not only be transferred to another phase, but can be permanently eliminated. Figure 1.1 shows the photo-induced electron-hole pair formation mechanism in a semiconductor TiO_2 particle with the presence of a water pollutant (P).

Countless harmful mixtures of hydrocarbons, chemical components and heavy metals in oily wastewater. There is a typical limit for oil and fat discharges depending on the type of oil. For example, the discharge limits for mineral and synthetic oils are 10-15 mg/L while for those of vegetable and animal based from 100-150 mg/L (Purification *et al.*, 2011). Oily wastewater needs to be treated because it can affect drinking water and groundwater resources, endangering aquatic resources and human health, affecting crop production and destroy the natural landscape.

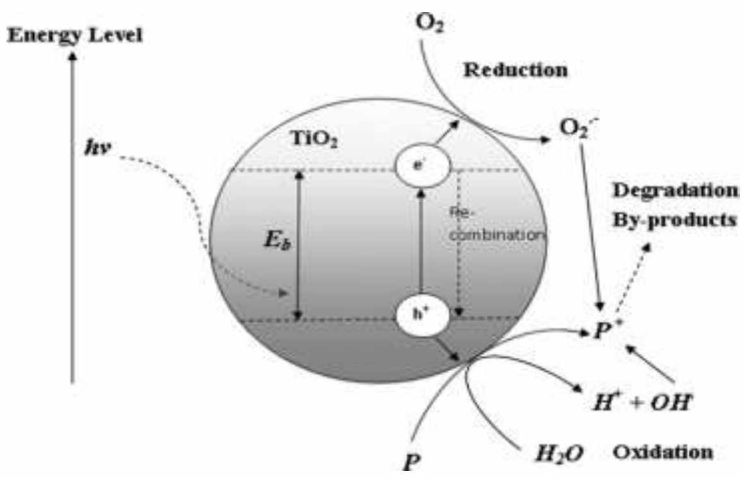

Figure 1.1 Reaction mechanisms of TiO_2 photocatalysis (Umar and Abdul, 2013).

Various kind of materials has been created and alter to get the best result in water treatment. Photocatalyst either heterogenous or homogenous being study to advance the treatment. Titanium Oxide (TiO_2) is the best and most common photocatalyst used to remove contaminants. This TiO_2 receives wide attention in the field of research due to its high catalytic activity, high stability and lower rate (Shao, 2013). Other than TiO_2, some other photocatalyst used are $LaNiO_3$ (Li *et al.*, 2010) Bi_2WO_6 (Shang *et al.*, 2008) and $BiFeO_3$ (Humayun *et al.*, 2016).

Photocatalyst nanoparticles can be synthesis by hydrothermal method, combustion method, sol-gel method, co-precipitation method, micro emulsion method, thermal decomposition method and sono-chemical method. The common and widely used method of synthesizing photocatalyst nanoparticles is through sol-gel method. The advantages of this method are controllable size, less complex, cost-effectiveness and low temperature growth. Textural and structural material properties have been shown to be strongly influenced by the parameters of synthesis and processing. Synthesis parameters, including precursor types, molar ratios between reactants, solvents, complexion agents, pH, temperature of synthesis and temperature of calcination.

Perovskite with typical ABO_3 formula such as $NaTaO_3$, $KTaO_3$, $LaFeO_3$ have a higher photocatalytic activity due to its narrow band gap, unique crystal structure and electronic properties. Citrical acid and glucose-based sol-gel methods were used in the previous study and were successfully synthesized by $LaFeO_3$. Based on previous studies, the temperature used for calcining while synthesizing was undeniably affected by the structure, particle size and properties of the final product, but rarely explored and reported. Advantages of the structure of perovskite:

(a) Their crystal structures generally provide an appropriate electronic structure that shifts the band gap energy to visible-light absorption.

(b) Their crystal structural arrangements allow lattice distortions, significantly affecting the separation of photogenerated charge carriers and avoiding ~~the~~ recombination processes.

Thus, the possibility of controlling the physicochemical properties of perovskite structures allows the relationship between structural properties and photo-catalytic activity to be unraveled, making this material a good alternative to TiO_2 photocatalyst.

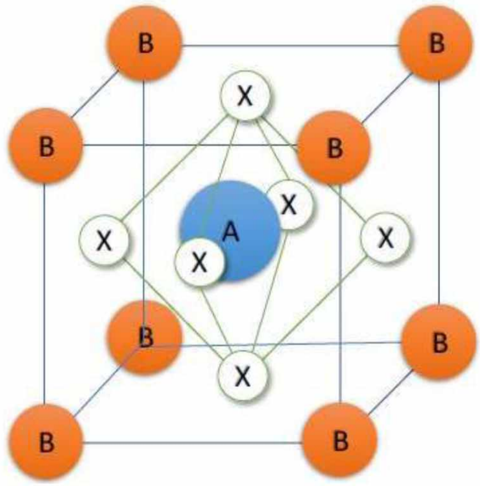

Figure 1.2 Structure of perovskite ABO_3 crystal (Yahya *et al.*, 2018)

In this study, lanthanum-based photocatalyst Lanthanum Orthoferrite ($LaFeO_3$) with narrow band gap was synthesized to replace TiO_2 as a photocatalyst to be activated using visible light. A study was conducted on the effect of the calcination temperature on the physicochemical properties and the photocatalytic degradation performance of the synthesized $LaFeO_3$.

Glucose is more favourable as a complexing agent because of its eco-friendly nature, low cost, ease of use and reproducibility. The use of glucose as a chelating agent often results in convenience that requires less energy to synthesize high-purity nanoparticles. The main role of glucose is to generate a highly viscous and stable mixture solution, which prohibited the aggregation of cations and favoured the formation of $LaFeO_3$ phase. The glucose structure is a ring with five hydroxyl groups and can form complexes with the La and Fe cations in the precursor solution, resulting in the simultaneous crystallisation of the La and Fe cations as the water evaporates. Calcination temperatures are also known to have an impact on physicochemical properties such as band gap, surface crystalline and morphological properties (Shen *et al.*, 2016).

1.2 Problem Statement

Titanium dioxide (TiO_2) is the most widely studied since it is non-toxic, chemically stable, commercially available and inexpensive. However, TiO_2 can only be activated with ultraviolet light (< 390 nm) as it cannot be activated by visible light due to the high band gap (3.2eV). The other barrier used by TiO_2 as a photocatalyst is the rapid recombination of the electron-hole pair. Due to this limitation, this method is still practically not in use in the large industry. The wide band gap of TiO_2 limits their absorption of light within the ultraviolet region. The semiconductor must have a small band gap in order to get as much sunlight as possible. The band gap is one of the main factors to be considered for photocatalytic activity. Generally, the acceptable value of band gap of most photocatalysts that can be activated by visible light irradiation are below 3.0 eV. In that case, current researchers preferred $LaFeO_3$ nanoparticles due to its narrow band gap.

$LaFeO_3$ is considered to be an effective visible-light driven photocatalyst for photocatalytic reactions due to its narrow band gap and optoelectronic properties. The UV source requires a large amount of electrical energy, which would result in high costs in practical applications. However, TiO_2 is not ideal for all purposes and is rather weak in processes associated with solar photocatalysis due to its wide band gap (3.0–3.2 eV), making it impractical to set up large technological processes based on TiO_2. Studies on the synthesization of $LaFeO_3$ and its purpose as a photocatalyst were rarely reported, the smallest band gap from pure $LaFeO_3$ was 2.07eV at 900°C via the auto-combustion route. In addition, research has also studied the impact of calcination temperature on the physiochemical properties of synthesised photocatalysts in ways of producing photocatalysts at lower cost and energy consumption.

1.3 Objective of Study

The main aim of this study is to develop a new photocatalyst based on perovskite with low band gap (< 2.2 eV) for the treatment of oily waste water. The study aim can be further elaborated as follows:

1. To examine the effects of calcination temperature on $LaFeO_3$ crystal formation.
2. To determine the physicochemical properties of $LaFeO_3$ through the route of the sol gel.
3. To identify the photocatalytic degradation performance of the synthesized $LaFeO_3$ for potential applications of oily wastewater treatment.

1.4 Scope of Study

In order to achieve the stated objectives, the following scopes have been drawn up:

1. Synthesizing the $LaFeO_3$ perovskite using the glucose sol-gel method as a complexing agent. The temperature of the calcination ranged from 500-900°C.

2. Characterization of the physicochemical properties of the synthesized $LaFeO_3$ in terms of thermal stability, morphological properties, surface areas, crystallinity, structural analysis and optical properties using Fourier Transform Infrared Spectra (FTIR), Thermogravimetric analysis (TGA), Field Emission Scanning Electron Microscope (FESEM), Brunauer–Emmett–Teller (BET) surface area, Xray powder diffraction (XRD) and UV-Vis spectrophotometer.

3. The optimal photocatalyst was selected by comparing the data collected. Optimal samples with a high surface area, a low band gap value and a small crystal size were selected.

4. Evaluating the photocatalytic activity of the selected $LaFeO_3$ photocatalyst in degrading oily synthetic wastewater by varying the operating parameters, including the irradiation time (0-180 min) and the initial concentration (1000,10000, 20000 ppm) under visible light irradiation. The catalytic load remains unchanged at 1.0 g/mL. The aliquot taken was characterized by the use of UV-Vis to determine degradation.

1.5 Significance of Study

Study on synthesizing $LaFeO_3$ via glucose sol gel route rarely reported, previous study found that the lowest calcination time for pure $LaFeO_3$ with orthorhombic structure was 500°C with a molar ratio between complexing agent and metal 3:10 and glucose as a complexing agent (Liu and Xu, 2011). No band gap value reported. A study conducted by Parida et al. 2010, using citric acid as a complexing agent, showed that a high surface area with a molar ratio of 3:5 with a band gap value of 2.1 eV can be achieved. Previous studies using citric acid as a complexing agent have shown that pure $LaFeO_3$ can only be achieved with a high calcination temperature > 550°C (Khalil *et al.*, 2016; Lebid and Omari, 2013; Qi *et al.*, 2003). Deep research on the synthesizing of visible-light driven photocatalysts, which can be produced at a minimum molar ratio between the complexing agent and the metal (3:5), has therefore been conducted starting at a minimum calcination temperature of 500-900°C. The crystallization of $LaFeO_3$ nanoparticles is known to have been favoured at high calcination temperature (Liu and Xu, 2011; Shen *et al.*, 2016). This $LaFeO_3$ is possible to create energy-saving and environment friendly technology to treat oily wastewater.

REFERENCES

Ab Halim, M. H., Nor Anuar, A., Abdul Jamal, N. S., Azmi, S. I., Ujang, Z., and Bob, M. M. (2016). Influence of high temperature on the performance of aerobic granular sludge in biological treatment of wastewater. *Journal of Environmental Management*.

Abazari, R., and Sanati, S. (2013). Perovskite LaFeO3 nanoparticles synthesized by the reverse microemulsion nanoreactors in the presence of aerosol-OT: Morphology, crystal structure, and their optical properties. *Superlattices and Microstructures, 64*, 148-157.

Adham, S., Hussain, A., Minier-matar, J., Janson, A., and Sharma, R. (2018). Membrane applications and opportunities for water management in the oil & gas industry. *Desalination*(September 2017), 0-1.

Ali, W., Ullah, H., Zada, A., Alamgir, M. K., Muhammad, W., Ahmad, M. J., et al. (2018). Effect of calcination temperature on the photoactivities of ZnO/SnO2 nanocomposites for the degradation of methyl orange. *Materials Chemistry and Physics, 213*, 259-266.

Alther, G. R. (2014). OILS FOUND IN WASTEWATER, What Are They?, How to Separate and Eliminate Them From Wastewater, A Layman's Guide to Emulsion Breaking. (248).

Aman, D., Zaki, T., Mikhail, S., and Selim, S. A. (2011). Synthesis of a perovskite LaNiO3 nanocatalyst at a low temperature using single reverse microemulsion. *Catalysis Today, 164*(1), 209-213.

Banerjee, S., Pillai, S. C., Falaras, P., O'Shea, K. E., Byrne, J. A., and Dionysiou, D. D. (2014). New Insights into the Mechanism of Visible Light Photocatalysis. *The journal of physical chemistry letters, 5*(15), 2543-2554.

Behzad, K., and Dorranian, D. (2016). Effect of calcination temperature on the size and optical properties of synthesized ZnO nanoparticles EFFECT OF CALCINATION TEMPERATURE ON THE SIZE AND OPTICAL. (March), 2-8.

Camel, V., and Bermond, A. (1998). The use of ozone and associated oxidation processes in drinking water treatment. *Water Research, 32*(11), 3208-3222.

Can, Z. S., and Gurol, M. D. (2001). Effect of bromide ions on formaldehyde formation during ozonation of drinking waters. *Water Science and Technology: Water Supply, 1*(4), 119-124.

Charles, A., and Cheng, C. K. (2019). Photocatalytic treatment of palm oil mill effluent by visible light-active calcium ferrite: Effects of catalyst preparation technique. *Journal of Environmental Management, 234*.

Chen, D., and Ye, J. (2007). SrSnO 3 Nanostructures: Synthesis, Characterization, and Photocatalytic Properties. *Chemistry of Materials, 19*(18), 4585-4591.

Cheryan, M., and Rajagopalan, N. (1998). Membrane processing of oily streams. Wastewater treatment and waste reduction. *Journal of Membrane Science, 151*(1), 13-28.

Cole, J. P., Federico, C. R., Lim, C. H., and Miyake, G. M. (2019). Photoinduced Organocatalyzed Atom Transfer Radical Polymerization Using Low ppm Catalyst Loading. *Macromolecules, 52*(2).

Dhinesh Kumar, R., and Jayavel, R. (2014). Facile hydrothermal synthesis and characterization of LaFeO3 nanospheres for visible light photocatalytic applications. *Journal of Materials Science: Materials in Electronics, 25*(9), 3953-3961.

Di Valentin, C., Pacchioni, G., and Selloni, A. (2004). Origin of the different photoactivity of N-doped anatase and rutile TiO2. *Physical Review B - Condensed Matter and Materials Physics, 70*(8), 1-4.

Dovletoglou, O., Philippopoulos, C., and Grigoropoulou, H. (2002). Coagulation for Treatment of Paint Industry Wastewater. *Journal of Environmental Science and Health, Part A, 37*(7), 1361-1377.

Duan, X., Sun, H., and Wang, S. (2018). Metal-Free Carbocatalysis in Advanced Oxidation Reactions. *Accounts of Chemical Research, 51*(3), 678-687.

Ela, S. I. A.-e., and Nawar, S. S. (1980). Treatment of Wastewater From an Oil and. *4*, 47-52.

Elleuch, R. S., Hammemi, I., Khannous, L., Nasri, M., and Gharsallah, N. (2013). Wastewater treatment of bottle oil washing water (BOWW) by hybrid coagulation–flocculation and biological process. *Desalination and Water Treatment, 52*(7-9), 1362-1369.

Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., and Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials, 170*(2-3), 530-551.

Fang, F., Han, H., Zhao, Q., Xu, C., and Zhang, L. (2013). Bioaugmentation of biological contact oxidation reactor (BCOR) with phenol-degrading bacteria for coal gasification wastewater (CGW) treatment. *Bioresource Technology, 150*, 314-320.

Farhadi, S., and Siadatnasab, F. (2011). Perovskite-type LaFeO3 nanoparticles prepared by thermal decomposition of the La[Fe(CN)6]??5H2O complex: A new reusable catalyst for rapid and efficient reduction of aromatic nitro compounds to arylamines with propan-2-ol under microwave irradiation. *Journal of Molecular Catalysis A: Chemical, 339*(1-2), 108-116.

Feng, J., Liu, T., Xu, Y., Zhao, J., and He, Y. (2011). Effects of PVA content on the synthesis of LaFeO3 via sol-gel route. *Ceramics International, 37*(4), 1203-1207.

Féris, L. A., and Rubio, J. (1999). Dissolved Air Flotation (DAF) performance at low saturation pressures. *Filtration and Separation, 36*(9), 61-65.

Fezzani, B., and Ben Cheikh, R. (2010). Two-phase anaerobic co-digestion of olive mill wastes in semi-continuous digesters at mesophilic temperature. *Bioresource Technology, 101*(6), 1628-1634.

Fujii, T., Matsusue, I., and Takada, J. (2012). Superparamagnetic Behaviour and Induced Ferrimagnetism of LaFeO3 Nanoparticles Prepared by a Hot-Soap Technique. *Advanced Aspects of spectroscopy*.

Fujishima, A., Rao, T. N., and Tryk, D. A. (2000). Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1*(1), 1-21.

Gálvez, E. D., Cruz, R., Robles, P. A., and Cisternas, L. A. (2014). Optimization of dewatering systems for mineral processing. *Minerals Engineering, 63*, 110-117.

Gao, X. F., Sun, W. T., Ai, G., and Peng, L. M. (2010). Photoelectric performance of TiO2 nanotube array photoelectrodes cosensitized with CdS/CdSe quantum dots. *Applied Physics Letters, 96*(15), 3-5.

Ge, C., Wang, L., Liu, G., and Wu, R. (2019). Effects of calcination temperature on the electromagnetic properties of carbon nanotubes/indium tin oxide composites. *Journal of Alloys and Compounds, 775*.

Giannakas, A. E., Ladavos, A. K., and Pomonis, P. J. (2004). Preparation, characterization and investigation of catalytic activity for NO + CO reaction of LaMnO3 and LaFeO3 perovskites prepared via microemulsion method. *Applied Catalysis B: Environmental, 49*(3), 147-148.

Gómez-Cuaspud, J. A., Vera-López, E., Carda-Castelló, J. B., and Barrachina-Albert, E. (2017). One-step hydrothermal synthesis of LaFeO3 perovskite for methane steam reforming. *Reaction Kinetics, Mechanisms and Catalysis, 120*(1), 167-179.

Gong, C., Zhang, Z., Lin, S., Wu, Z., Sun, L., Ye, C., et al. (2019). Electrochemical synthesis of perovskite LaFeO3 nanoparticle-modified TiO2 nanotube arrays for enhanced visible-light photocatalytic activity. *New Journal of Chemistry, 43*(42).

Gosavi, P. V., and Biniwale, R. B. (2010). Pure phase LaFeO3 perovskite with improved surface area synthesized using different routes and its characterization. *Materials Chemistry and Physics, 119*(1-2), 324-329.

Grabowska, E. (2016). Selected perovskite oxides: Characterization, preparation and photocatalytic properties-A review (Vol. 186, pp. 97-126).

Griffini, O., Bao, M. L., Barbieri, K., Burrini, D., Santianni, D., and Pantani, F. (1999). Formation and Removal of Biodegradable Ozonation By-Products during Ozonation-Biofiltration Treatment: Pilot-Scale Evaluation. *Ozone: Science & Engineering, 21*(1), 79-98.

Gupta, V. K., Pathania, D., Agarwal, S., and Singh, P. (2012). Adsorptional photocatalytic degradation of methylene blue onto pectin–CuS nanocomposite under solar light. *Journal of Hazardous Materials, 243*, 179-186.

Hanafy, M., and Nabih, H. I. (2007). Treatment of Oily Wastewater Using Dissolved Air Flotation Technique. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 29*(January), 143-159.

Hu, C.-C., and Teng, H. (2007). Influence of structural features on the photocatalytic activity of NaTaO3 powders from different synthesis methods. *Applied Catalysis A: General, 331*, 44-50.

Humayun, M., Zada, A., Li, Z., Xie, M., Zhang, X., Qu, Y., et al. (2016). Enhanced visible-light activities of porous BiFeO3 by coupling with nanocrystalline TiO2 and mechanism. *Applied Catalysis B: Environmental, 180*, 219-226.

Hunge, Y. M., Mahadik, M. A., Moholkar, A. V., and Bhosale, C. H. (2016). Photoelectrocatalytic degradation of oxalic acid using WO3 and stratified WO3/TiO2 photocatalysts under sunlight illumination. *Ultrasonics Sonochemistry*.

Ibhadon, A., and Fitzpatrick, P. (2013). Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts, 3*(1), 189-218.

Jafarinejad, S., and Jiang, S. C. (2019). Current technologies and future directions for treating petroleum refineries and petrochemical plants (PRPP) wastewaters. *Biochemical Pharmacology*, 103326-103326.

Jamaly, S., Giwa, A., and Hasan, S. W. (2015). Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities. *Journal of Environmental Sciences (China), 37*, 15-30.

Jeganathan, J. (2011). Examining options for treating oily wastewaters. *Environmental Science & Engineering Magazine*, 42-45.

Ji, K., Dai, H., Deng, J., Song, L., Xie, S., and Han, W. (2013). Glucose-assisted hydrothermal preparation and catalytic performance of porous LaFeO3 for toluene combustion. *Journal of Solid State Chemistry, 199*, 164-170.

Kako, T., Zou, Z., Katagiri, M., and Ye, J. (2007). Decomposition of Organic Compounds over NaBiO 3 under Visible Light Irradiation. *Chem. Mater.*(7), 198-202.

Kanhere, P., and Chen, Z. (2014). A review on visible light active perovskite-based photocatalysts (Vol. 19, pp. 19995-20022).

Kaombe, D. D., and Hägg, M.-B. (2014). Forward osmosis for the dewatering of pyrolysis oil aqueous phase. *Separation and Purification Technology, 138*, 92-97.

Karhu, M. (2015). *Treatment and Characterisation of Oily Wastewaters*.

Khalil, K. M. S., Elhamdy, W. A., Said, A. E.-A. A., and Elsamahy, A. A. (2016). Porous LaFeO3/Silica Nanocomposites via Sol-Gel Mixing Involving Citric Acid. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 506*, 840-848.

Kim, D. S., Han, S. J., and Kwak, S.-Y. (2007). Synthesis and photocatalytic activity of mesoporous TiO2 with the surface area, crystallite size, and pore size. *Journal of Colloid and Interface Science, 316*(1), 85-91.

Kiss, Z. L., Kocsis, L., Keszthelyi-Szabó, G., Hodúr, C., and László, Z. (2014). Treatment of oily wastewater by combining ozonation and microfiltration. *Desalination and Water Treatment*(June 2015), 1-8.

Komova, O. V., Simagina, V. I., Mukha, S. A., Netskina, O. V., Odegova, G. V., Bulavchenko, O. A., et al. (2016). A modified glycine–nitrate combustion method for one-step synthesis of LaFeO3. *Advanced Powder Technology, 27*, 496-503.

Konieczny, K., Bodzek, M., and Rajca, M. (2006). A coagulation–MF system for water treatment using ceramic membranes. *Desalination, 198*(1-3), 92-101.

Kozakova, Z., Pajurkova, J., Davidova, J., Halamova, I., and Krcma, F. (2014). Organic Dye Decomposition by DC Diaphragm Discharge : Comparison of UV , Electrolytic and Ozone Effect Organic Dye Decomposition by DC Diaphragm Discharge : Comparison of UV , Electrolytic and Ozone Effect. (December).

Kriipsalu, M., Marques, M., Nammari, D. R., and Hogland, W. (2007). Bio-treatment of oily sludge: The contribution of amendment material to the content of target contaminants, and the biodegradation dynamics. *Journal of Hazardous Materials, 148*(3), 616-622.

Kumada, N., Kinomura, N., and Sleight, A. W. (2000). Neutron powder diffraction refinement of ilmenite-type bismuth oxides: ABiO3 (A = Na, Ag). *Materials Research Bulletin, 35*(14), 2397-2402.

Kumar, M., Srikanth, S., Ravikumar, B., T.C.Alex, and Das, S. K. (2009). Synthesis of pure and Sr-doped LaGaO3, LaFeO3 and LaCoO3 and Sr,Mg-doped LaGaO3 for ITSOFC application using different wet chemical routes. *Materials Chemistry and Physics, 113*(2), 803-815.

Lai, G. S., Yusob, M. H. M., Lau, W. J., Gohari, R. J., Emadzadeh, D., Ismail, A. F., et al. (2017). Novel mixed matrix membranes incorporated with dual-nanofillers for enhanced oil-water separation. *Separation and Purification Technology, 178*, 113-121.

Lebid, M., and Omari, M. (2013). Synthesis and Electrochemical Properties of LaFeO3 Oxides Prepared Via Sol–Gel Method. *Arabian Journal for Science and Engineering, 39*(1), 147-152.

Leong, S., Razmjou, A., Wang, K., Hapgood, K., Zhang, X., and Wang, H. (2014). TiO2 based photocatalytic membranes: A review (Vol. 472, pp. 167-184).

Li, S., and Wang, X. (2015). Synthesis of different morphologies lanthanum ferrite (LaFeO3) fibers via electrospinning. *Optik, 126*(4), 408-410.

Li, X. b., Liu, J. t., Wang, Y. t., Wang, C. y., and Zhou, X. h. (2007). Separation of Oil from Wastewater by Column Flotation. *Journal of China University of Mining and Technology, 17*(4).

Li, Y., Yao, S., Wen, W., Xue, L., and Yan, Y. (2010). Sol–gel combustion synthesis and visible-light-driven photocatalytic property of perovskite LaNiO3. *Journal of Alloys and Compounds, 491*(1), 560-564.

Lin, C. H., Huang, C. W., Wang, P. H., Guo, T. F., and Wen, T. C. (2020). Sol–gel ZnO modified by organic dye molecules for efficient inverted polymer solar cells. *Journal of the Taiwan Institute of Chemical Engineers, 107*.

Liu, G. M., Wang, Y. J., Wang, D. S., and Liu, Q.-Y. (2013). Comparison of one-level microendoscopy laminoforaminotomy and cervical arthroplasty in cervical spondylotic radiculopathy: a minimum 2-year follow-up study. *Journal of Orthopaedic Surgery and Research, 8*(1), 48-48.

Liu, T., and Xu, Y. (2011). Synthesis of nanocrystalline LaFeO3 powders via glucose sol-gel route. *Materials Chemistry and Physics, 129*(3), 1047-1050.

Lu, J., Jiang, Y., Zhang, Y., Huang, J., and Xu, Z. (2015). Preparation of gas sensing CoTiO3 nanocrystallites using EDTA as the chelating agent in a sol–gel process. *Ceramics International, 41*(3), 3714-3721.

Lu, M., Zhang, Z., Yu, W., and Zhu, W. (2009). Biological treatment of oilfield-produced water: A field pilot study. *International Biodeterioration & Biodegradation, 63*(3), 316-321.

Ma, L., He, J., Wang, J., Zhou, Y., Zhao, Y., Li, Y., et al. (2019). Functionalized Superwettable Fabric with Switchable Wettability for Efficient Oily Wastewater Purification, in Situ Chemical Reaction System Separation, and Photocatalysis Degradation. *ACS Applied Materials and Interfaces, 11*(46).

Miranda-García, N., Suárez, S., Maldonado, M. I., Malato, S., and Sánchez, B. (2014). Regeneration approaches for TiO2 immobilized photocatalyst used in the elimination of emerging contaminants in water. *Catalysis Today, 230*, 27-34.

Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Ismail, A. F., Abd Mutalib, M., and Jamil, S. M. (2015a). Incorporation of N-doped TiO2 nanorods in regenerated cellulose thin films fabricated from recycled newspaper as a green portable photocatalyst. *Carbohydrate Polymers, 133*, 429-437.

Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Ismail, A. F., and Nor, N. A. M. (2015b). Photodegradation of phenol by N-Doped TiO2 anatase/rutile nanorods assembled microsphere under UV and visible light irradiation. *Materials Chemistry and Physics, 162*, 113-123.

Moslehyani, A., Ismail, A. F., Othman, M. H. D., and Matsuura, T. (2015). Design and performance study of hybrid photocatalytic reactor-PVDF/MWCNT nanocomposite membrane system for treatment of petroleum refinery wastewater. *Desalination, 363*, 99-111.

Mozia, S. (2010). Photocatalytic membrane reactors (PMRs) in water and wastewater treatment. A review. *Separation and Purification Technology, 73*(2), 71-91.

Nöh, H. (1988). Separators and Emulsion Separation Systems for Petroleum, Oil, and Lubricants BT - Pretreatment in Chemical Water and Wastewater Treatment: Proceedings of the 3rd Gothenburg Symposium 1988, 1.–3. Juni 1988, Gothenburg. In H. H. Hahn and R. Klute (Eds.), (pp. 217-225). Berlin: Springer Berlin Heidelberg.

Padaki, M., Surya Murali, R., Abdullah, M. S., Misdan, N., Moslehyani, A., Kassim, M. A., et al. (2015). Membrane technology enhancement in oil–water separation. A review. *Desalination, 357*, 197-207.

Parida, K. M., Reddy, K. H., Martha, S., Das, D. P., and Biswal, N. (2010). Fabrication of nanocrystalline LaFeO3: An efficient sol-gel auto-combustion assisted visible light responsive photocatalyst for water decomposition. *International Journal of Hydrogen Energy, 35*(22), 12161-12168.

Peng, L., Bao, M., Wang, Q., Wang, F., and Su, H. (2014). The anaerobic digestion of biologically and physicochemically pretreated oily wastewater. *Bioresource Technology, 151*, 236-243.

Phokha, S., Pinitsoontorn, S., Rujirawat, S., and Maensiri, S. (2015). Polymer pyrolysis synthesis and magnetic properties of LaFeO3 nanoparticles. *Physica B: Condensed Matter, 476*, 55-60.

Piticescu, R. M., Vilarnho, P., Popescu, L. M., and Piticescu, R. R. (2006, 2006). *Hydrothermal synthesis of perovskite based materials for microelectronic applications*.

Pondstabodee, S., Scamehorn, J. F., Chavedej, S., and Harwell, J. H. (1998). Cleanup of Olly Wastewater by Froth Flotation: Effect of Microemulsion Formation. *Separation Science and Technology, 33*(4), 591-609.

Purification, N. A. T. C. o. W., Management in Mediterranean, C., Coca-Prados, J., Gutiérrez-Cervelló, G., and SpringerLink. (2011). *Water Purification and Management*.

Qi, X., Zhou, J., Yue, Z., Gui, Z., and Li, L. (2003). A simple way to prepare nanosized LaFeO3 powders at room temperature.

Quan, X., Tan, H., Zhao, Q., and Sang, X. (2007). Preparation of lanthanum-doped TiO2 photocatalysts by coprecipitation. *Journal of Materials Science, 42*(15), 6287-6296.

Sadrzadeh, M., Gorouhi, E., and Mohammadi, T. (2008). Oily Wastewater Treatment Using Polytetrafluoroethylene (Ptfe) Hydrophobic Membranes. *Water-Observatory.Net*, 1-11.

Safa, M., Alemzadeh, I., and Vossoughi, M. (2014). Biodegradability of oily wastewater using rotating biological contactor combined with an external membrane. *Journal of Environmental Health Science and Engineering, 12*(1), 117-117.

Sahoo, L. K., Bandyopadhyay, S., and Banerjee, R. (2014). Water and energy assessment for dewatering in opencast mines. *Journal of Cleaner Production, 84*, 736-745.

Saleh, R., and Djaja, N. F. (2014). UV light photocatalytic degradation of organic dyes with Fe-doped ZnO nanoparticles. *Superlattices and Microstructures, 74*, 217-233.

Scholz, W., and Fuchs, W. (2000). Treatment of oil contaminated wastewater in a membrane bioreactor. *Water Research, 34*(14), 3621-3629.

Shabbir, G., Qureshi, A. H., and Saeed, K. (2006). Nano-crystalline LaFeO3 powders synthesized by the citrate–gel method.

Shang, M., Wang, W., Sun, S., Zhou, L., and Zhang, L. (2008). Bi 2 WO 6 Nanocrystals with High Photocatalytic Activities under Visible Light. *The Journal of Physical Chemistry C, 112*, 10407-10411.

Shen, H., Xue, T., Wang, Y., Cao, G., Lu, Y., and Fang, G. (2016). Photocatalytic property of perovskite LaFeO3 synthesized by sol-gel process and vacuum microwave calcination. *Materials Research Bulletin, 84*, 15-24.

Takei, T., Haramoto, R., Dong, Q., Kumada, N., Yonesaki, Y., Kinomura, N., et al. (2011). Photocatalytic activities of various pentavalent bismuthates under visible light irradiation. *Journal of Solid State Chemistry, 184*(8), 2017-2022.

Tanaka, H., and Misono, M. (2001). Advances in designing perovskite catalysts. *Current Opinion in Solid State and Materials Science, 5*(5), 381-387.

Tang, P., Chen, H., Cao, F., and Pan, G. (2011). Magnetically recoverable and visible-light-driven nanocrystalline YFeO3 photocatalysts. *Catalysis Science & Technology, 1*(7), 1145-1145.

Tang, P., Tong, Y., Chen, H., Cao, F., and Pan, G. (2013). Microwave-assisted synthesis of nanoparticulate perovskite LaFeO3 as a high active visible-light photocatalyst. *Current Applied Physics, 13*(2), 340-343.

Taskin, B., Gozen, A. G., and Duran, M. (2011). Selective quantification of viable Escherichia coli bacteria in biosolids by quantitative PCR with propidium monoazide modification. *Applied and Environmental Microbiology, 77*(13), 4329-4335.

Taylor, P., Hanafy, M., and Nabih, H. I. (2007). Energy Sources , Part A : Recovery , Utilization , and Environmental Effects Treatment of Oily Wastewater Using Dissolved Air Flotation Technique Treatment of Oily Wastewater Using Dissolved Air. (March 2013), 37-41.

Theingi, M., Tun, K. T., and Aung, N. N. (2019). Preparation, Characterization and Optical Property of LaFeO3 Nanoparticles via Sol-Gel Combustion Method. *SciMedicine Journal, 1*(3).

Thirumalairajan, S., Girija, K., Ganesh, I., Mangalaraj, D., Viswanathan, C., Balamurugan, A., et al. (2012). Controlled synthesis of perovskite LaFeO3 microsphere composed of nanoparticles via self-assembly process and their associated photocatalytic activity. *Chemical Engineering Journal, 209*, 420-428.

Thirumalairajan, S., Girija, K., Ganesh, V., Mangalaraj, D., Viswanathan, C., and Ponpandian, N. (2013a). Novel synthesis of LaFeO3 nanostructure dendrites: A systematic investigation of growth mechanism, properties, and biosensing for highly selective determination of neurotransmitter compounds. *Crystal Growth and Design, 13*(1), 291-302.

Thirumalairajan, S., Girija, K., Hebalkar, N. Y., Mangalaraj, D., Viswanathan, C., and Ponpandian, N. (2013b). Shape evolution of perovskite LaFeO3 nanostructures: a systematic investigation of growth mechanism, properties and morphology dependent photocatalytic activities. *RSC Advances, 3*(20), 7549-7561.

Umar, M., and Abdul, H. (2013). Photocatalytic Degradation of Organic Pollutants in Water. *Organic Pollutants - Monitoring, Risk and Treatment*.

Viet, P. V., Thi, C. M., and Hieu, L. V. (2016). The High Photocatalytic Activity of SnO2 Nanoparticles Synthesized by Hydrothermal Method. *Journal of Nanomaterials, 2016*.

Villagrán-Olivares, A. C., Gomez, M. F., Barroso, M. N., and Abello, M. C. (2020). Hydrogen production from ethanol: Synthesis of Ni catalysts assisted by chelating agents. *Molecular Catalysis, 481*.

Wu, L., Ge, G., and Wan, J. (2009). Biodegradation of oil wastewater by free and immobilized Yarrowia lipolytica W29. *Journal of Environmental Sciences, 21*(2), 237-242.

Wu, S. Y., Liu, X. Q., and Chen, X. M. (2010). Hydrothermal synthesis of NaNbO3 with low NaOH concentration. *Ceramics International, 36*(3), 871-877.

Xie, P., Zhang, L., Chen, J., Ding, J., Wan, Y., Wang, S., et al. (2019). Enhanced degradation of organic contaminants by zero-valent iron/sulfite process under simulated sunlight irradiation. *Water Research, 149*.

Yahya, N., Aziz, F., Jamaludin, N. A., Mutalib, M. A., Ismail, A. F., Salleh, W. N., et al. (2018). A review of integrated photocatalyst adsorbents for wastewater treatment. *Journal of Environmental Chemical Engineering, 6*(6).

Yan, S.-y., Xie, Y., Liu, T., and Yu, H.-t. (2010). Electronic structures and ferroelectric instabilities of cubic AVO(3) (A = Sr, Ba, and Pb) perovskites by first-principles calculations. *Journal of physics. Condensed matter : an Institute of Physics journal, 22*(12), 125501-125501.

Yang, G., Jiang, Z., Shi, H., Xiao, T., and Yan, Z. (2010). Preparation of highly visible-light active N-doped TiO2 photocatalyst. *Journal of Materials Chemistry, 20*(25), 5301-5301.

Yu, B., Leung, K. M., Guo, Q., Lau, W. M., and Yang, J. (2011). Synthesis of Ag-TiO2 composite nano thin film for antimicrobial application. *Nanotechnology, 22*, 115603-115603.

Yu, L., Han, M., and He, F. (2013). A review of treating oily wastewater. *Arabian Journal of Chemistry*.

Yu, L., Han, M., and He, F. (2017). A review of treating oily wastewater.

Zhang, T., Zhao, K., Yu, J., Jin, J., Qi, Y., Li, H., et al. (2013). Photocatalytic water splitting for hydrogen generation on cubic, orthorhombic, and tetragonal KNbO3 microcubes. *Nanoscale, 5*(18), 8375-8383.

Zhao, X., Wang, Y., Ye, Z., Borthwick, A. G. L., and Ni, J. (2006). Oil field wastewater treatment in Biological Aerated Filter by immobilized microorganisms. *Process Biochemistry, 41*(7), 1475-1483.

Zheng, W., Liu, R., Peng, D., and Meng, G. (2000). Hydrothermal synthesis of LaFeO 3 under carbonate-containing medium. (March), 20-23.