The use of bimetallic heterogeneous oxide catalysts for the Fenton reaction.



Dissertation submitted in fulfillment of the requirements for the Degree of **Magister Technologiae** in the Department of Chemistry, Faculty of Applied and Computer Sciences, Vaal University of Technology:

> By Io No

Mgedle Nande

Under the supervision of:

Supervisor: Dr. E. L. Viljoen

Co-supervisors: Prof. A. E. Ofomaja

&

Prof. M. Scurrell (UNISA)

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Declaration

I, Mgedle Nande, declare that this dissertation was composed by myself, that the work contained herein is my own. All sources of cited are indicated and acknowledged by means of comprehensive reference list. I further declare that this work has not been previously submitted for any degree or professional qualification or organisation outside Vaal University of Technology.

.....

(Candidate signature)

.....day of.....2019

Dedication

I dedicate this work to my Lord and saviour Jesus Christ, the late grandfather Ngqonyela Mgedle, the late grand Mother Nongezile Sityata, my papa Vukile Mgedle, my mother Nolufefe Mgedle and my aunt Lungiswa Mgedle.

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Research output

This work has been presented in six different conferences in South Africa:

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MGEDLE, N., VILJOEN, E., OFOMAJA, A. E. & SCURREL, M. The effect of Fe/Mn mass ratio on a bimetallic oxide heterogeneous catalyst supported on silica for the degradation of methylene blue. Vaal University of Technology 3nd interdisciplinary conference. 2018. 17 August, Vaal University of Technology Quest Conference Center, Vanderbijlpark, South Africa, *Oral presentation*.

MGEDLE, N., VILJOEN, E., OFOMAJA, A. E. & SCURREL, M. Preparation of bimetallic catalyst calcined by microwave and conventional methods (oven) for the Fenton reaction. South African Nanotechnology Initiative (SANI). 2018. 16 November, Vaal University of Technology Quest Conference Center, Vanderbijlpark, South Africa, *Oral presentation*. Received second best presenter award.

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Abstract

Water contaminated with non-biodegradable organics is becoming increasing problematic as it has a hazardous effect on human health and the aquatic environment. Therefore, the removal of organic contaminants is of importance and an active heterogeneous Fenton catalyst is thus required. The literature indicates that a bimetallic oxide Fenton catalyst is more active than an iron oxide catalyst. This study focused on increasing the activity of iron-based Fenton catalysts with the addition of transition metals such as manganese, cobalt and copper and optimizing the preparation method.

In this study, bimetallic oxide (Fe-Cu, Fe-Mn, Fe-Co) and monometallic oxide (Fe, Cu, Mn,Co) catalysts supported on silica SiO₂ where prepared by incipient wetness impregnation. The total metal oxide contents were kept constant. The catalysts where calcined in two different ways, in a conventional oven and in a microwave. These catalysts were characterized with XRD, XPS and CV and were tested for the degradation of methylene blue dye at 27°C.

The catalysts calcined in a microwave oven had a higher catalytic activity than those prepared in a conventional oven. The bimetallic oxide catalysts outperformed the monometallic oxide catalysts in the degradation of methylene blue. The Fe₂MnO_x prepared by microwave energy were the most active catalyst yielding the highest percentage of degradation of methylene blue dye (89.6%) after 60 minutes.

The relative amounts of manganese and iron oxide were varied while keeping the total metal content in the catalyst the same. The optimum ratio of Fe to Mn was 1:7.5 since it yielded the most active catalyst. A 96.6 % removal of methylene blue was achieved after 1 hour of degradation.

Lastly this ratio 1Fe:7.5Mn was prepared by varying different microwave power (600, 700 and 800 W) and irradiation time (10, 20 and 30 min). The optimum microwave power and irradiation time was 800W and 10 min with the methylene blue percentage removal of 96.6 % after 1 hour of degradation.

Thesis outline

This thesis is divided into 8 chapters

Chapter 1: Introduction (background), aim and objectives.

Chapter 2: Literature review.

Chapter 3: Chemicals and methodology.

Chapter 4: Results, discussion and conclusions for the preparation of monometallic oxide heterogeneous oxide catalyst and Fe-M (M is Mn, Cu and Co) bimetallic oxide heterogeneous catalyst calcined by microwave and conventional methods (oven) for the Fenton reaction.

Chapter 5: Results, discussion and conclusions for the different Fe/Mn mass ratios.

Chapter 6: Results, discussion and conclusions for optimizing the microwave calcination method.

Chapter 7: Overall conclusions.

Chapter 8: References.

Appendix A: Catalyst preparation.

Appendix B: Dilution factor, % removal, integrated-first order and integrated-second order reaction.

Appendix C: XRD crystallite size was calculated with Scherrer equation.

Appendix D: Redox potentials for half reaction for the metal ions and for the radicals.

List of abbreviations and acronyms

- AOP's Advanced Oxidation Processes
- AAS Atomic Absorption Spectroscopy
- Conv Conventional oven
- CV- Cyclic Voltammetry
- Epa Anodic Peak Potential
- Epc Cathodic Peak Potential
- Ipc Current at the Cathode
- Ipa-Current at the Anode
- MB Methylene Blue
- MW Microwave
- ORP Oxidation Reduction Potential
- TOC- Total Organic Compounds
- WHO- World Health Organisation
- XPS-X-ray photoelectron spectroscopy
- XRD- X-ray powder diffraction

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Chapter 1: Introduction

1.1. Background

Water pollution is increasingly becoming a problem due to industrialization. The main water pollutants are inorganic and organic in nature. These pollutants consist of industrial chemicals, pesticides, dyes, pharmaceuticals and personal care products (Brillas et al., 2009). This study focussed on the organic pollutant, methylene blue dye that is resistant to biodegradation due to its aromatic structure. In the past, several methods such as the advanced oxidation processes (AOPs), biological treatment and physical adsorption processes have been developed for the removal of such pollutants from wastewater (Rad et al., 2015). Often these organic pollutants (dyes) are recalcitrant and therefore resist biological treatment and the physical adsorption process (Elwakeel et al., 2017). AOP's have been widely applied as a promising alternative to conventional technologies, such as activated carbon adsorption and incineration (Fida et al., 2017). AOPs are distinguished by the production of powerful, highly reactive species and non-selective oxidants that can operate at near ambient temperatures and pressure. These oxidants include hydroxyl radicals (·OH) as a major oxidizing agent (Munoz et al., 2015) and (·HO₂) as a minor oxidizing agent (Masomboom et al., 2010) may be able to completely degrade organic pollutants (dyes) into less harmful compound such as CO₂ and H₂O. The most commonly utilized AOPs include: photo degradation, heterogeneous photo catalytic oxidation, photo degradation by simulated sunlight, simulated UV, gold nanoparticles or rutile titanium (IV) oxide, plasmon photo catalyst, treatment with ozone, peroxide/UV systems, Fenton and photo-Fenton reaction (EIShafei et al., 2017).

The Fenton reaction was selected as the AOP for this study. The major setback of a heterogeneous catalyst is due to its lower catalytic activity compared to the homogeneous Fenton reaction (Costa *et al.*, 2006). In the literature it has been reported that the activity of a heterogeneous catalyst could be improved by many methods such as support

modification, promoting the catalyst by incorporating Fe with other transition metals and improving the preparation methods. This study investigated two methods that could be utilized in order to increase the catalytic activity of a heterogeneous catalyst: (i) the choice of calcination during the catalyst's preparation (Rad *et al.*, 2015) and (ii) the use of a bimetallic system (Wang *et al.*, 2016).

Problem statement

Water contaminated with organics that resist biodegradation is becoming increasingly problematic as it has hazardous effects on human health and aquatic environments. Therefore, the removal of such organic contaminants is of importance. In the past the use of a single iron oxide catalyst has been used. However, these iron oxide (monometallic) catalysts suffer from a low catalytic activity. Therefore, an active heterogeneous Fenton catalyst is required to increase the activity of iron oxide-based Fenton catalysts.

Hypothesis

Based on literature it can be hypothesised that the bimetallic catalyst calcined in the microwave will yield a more active catalyst than monometallic catalysts and catalysts prepared using a conventional oven.

Aim

The aim was to increase the Fenton activity of an iron oxide-based Fenton catalyst using bimetallic oxide catalysts and optimizing the calcination procedure during the catalyst preparation.

Objectives

To prepare mono metallic oxide and bimetallic heterogeneous oxide catalysts

- To prepare mono metallic oxide heterogeneous catalysts composed of Fe, Co, Cu and Mn and bimetallic heterogeneous oxide catalysts Fe:M (where M can be Co, Cu and Mn) supported on silica, calcined by the microwave and conventional method (oven).
- To characterize the catalysts with XRD, Cyclic Voltammetry and XPS.
- To determine the effect of monometallic and bimetallic heterogeneous catalysts on the activity during the Fenton reaction.
- To determine the amount of leaching during the degradation of methylene blue dye.
- To determine the amount of hydroxyl radicals formed during degradation studies.
- To measure the dominating redox reaction with Oxidation Reduction Potential.
- To study the influence of temperature on the activation.

To select the best bimetallic oxide heterogeneous catalyst and vary the Fe to M content.

- To characterize catalysts with XRD and CV.
- To determine the effect of Fe to Mn ratio of a bimetallic oxide heterogeneous catalyst on the activity during the Fenton reaction.
- To determine the amount of leaching during the degradation of methylene blue dye.
- To determine the amount of hydroxyl radicals formed during degradation studies.
- To measure the dominating redox reaction with Oxidation Reduction Potential.

To prepare the best bimetallic oxide ratio at different microwave power and time.

- To characterize catalysts with XRD.
- To determine the effect of microwave power and time on the activity during the Fenton reaction.

Chapter 2: Literature review

2.1 Water pollution

Water pollution remains a serious problem due to the large amounts of toxic contaminants that are detected in surface waters including rivers, drinking water and ground water (Arora *et al.*, 2019). These pollutants consist of industrial chemicals, pesticides, dyes, pharmaceuticals and personal care products (Brillas *et al.*, 2009). The removal of such contaminants from surface and ground water is of importance since they have hazardous effects on human health and the aquatic environment (Arora *et al.*, 2019).

2.2 Methylene as a model organic pollutant

In this study methylene will be used as model component to simulate polluted water. Methylene blue is a cationic dye (see Figure 2. 1). It is a typical heterocyclic aromatic compound and thus recalcitrant to oxidation (Kermaionoryani *et al.*, 2016).



Figure 2. 1: Methylene blue structure (Hegyesi et al., 2017).

A possible degradation pathway of methylene blue is shown in Figure 2. 2 (Wang et al., 2014). Ideally the methylene blue needs to be fully mineralized to carbon dioxide and water since the intermediates like phenol is also harmful to the environment. The following Figure was adapted from Ammar *et al.* (2001) and Liotta *et al.* (2009).



(a) Detected by GC/MS (extraction of ions)(b) detected by LC/MS



Figure 2. 2: Degradation pathway of methylene blue (Ammar *et al.*, 2001; Liotta *et al.*, 2009).

2.3 The Fenton reaction

In this study the Fenton oxidation reaction was used to degrade the organic pollutant, methylene blue, in water. The Fenton reaction involves the activation of H_2O_2 by iron ions to form active oxygen species that oxidize organic or in organic species (Bello *et al.*, 2019). In this process both iron ions (Fe²⁺ and Fe³⁺) are simultaneously present regardless of the starting material. The mechanisms for the Fenton reaction are represented in Equation (2.1) to (2.11). Equation (2.1) is the core equation for the Fenton process and during this reaction ferrous ion initiates and catalyses the oxidation Fe²⁺ to Fe³⁺ to decompose hydrogen peroxide to hydroxyl radicals.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- k \approx 70 M^{-1} s^{-1}$$
 (2.1)

Equation (2.2) is the regeneration reaction of ferrous ion. In this reaction ferric ion reacts with excess H_2O_2 to form ferrous ion and this reaction is known as a Fenton-like reaction. This reaction generally occurs at a slower rate compared to the Fenton reaction (Equation (2.1) (Neyens *et al.*, 2003). Hydroperoxyl radicals are also produced during the Fenton-like reaction and these radicals can also attack organic contaminants. However, they are less reactive compared to hydroxyl radicals.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H + OH^+ k \approx 0.002 - 0.01 M^{-1} s^{-1}$$
 (2.2)

The following reactions are involved during the Fenton reation. However, Equation (2.2) to Equation (2.5) are considered as limiting reactions due to the consumption of hydrogen peroxide and the regeneration of ferrous ions from ferric ions Equation (2.2). Equation (2.3) and (2.4) shows the consumption of hydroxyl radicals and hydroperoxyl radicals by the Fenton reagent are therefore unwanted reactions that decrease the oxidizing power of the Fenton system.

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH \sim k \approx 3.2 \times 10^8 M^{-1} s^{-1}$$
 (2.3)

$$Fe^{2+} + O_2H \to Fe^{3+} + HO_2^-$$
 (2.4)

$$Fe^{3+} + O_2H \rightarrow Fe^{2+} + H^+ + O_2 \quad k \approx 1.2 \times 10^{-6} M^{-1} s^{-1}$$
 (2.5)

It has been reported that other reactions such as radical-radical and hydrogen peroxideradical reaction occur during the Fenton process as shown in Equation 2.6-2.9. However, these reactions can be referred to as radical scavengers.

$$^{\circ}OH + ^{\circ}OH \rightarrow H_2O_2 \ k \approx 6.0 \ M^{-1} \ s^{-1} \ (6.0 \ x \ 10^{-1})$$
 (2.6)

$$^{\bullet}OH + H_2O_2 \rightarrow ^{\bullet}O_2H + H_2O \tag{2.7}$$

$$O_2H + O_2H \rightarrow H_2O_2 + O_2$$
(2.8)

$$O_2H + OH \rightarrow H_2O + O_2 \tag{2.9}$$

Eq (2.10) has been reported to be very slow compared to other reactions of $^{\circ}O_{2}H$ and therefor can be neglected.

$$O_2H + H_2O_2 \rightarrow OH + H_2O + O_2 \quad k \approx 3 \text{ M}^{-1} \text{ s}^{-1}$$
 (2.10)

Eq (2.11) leads to the unnecessary utilization of the oxidant and therefore increases the cost of the Fenton system (Neyens *et al.*, 2003; Fotecha-camara *et al.*, 2016).

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{2.11}$$

Fenton and Fenton-like processes (Fe²⁺/Fe³⁺/H₂O₂) were found to be the most efficient advanced oxidation processes for the removal of recalcitrant organic pollutants from wastewater due to the low cost of iron and hydrogen peroxide reagents, simplicity (Esteves *et al.*, 2015), good organic abatement (Rossi *et al.*, 2014), high removal

efficiency within a short period of time and ability to complete the destruction of contaminants into harmless and environmentally friendlier compounds such as carbon dioxide and water. However, there are basically two kinds of Fenton processes namely, classic homogeneous and heterogeneous Fenton's processes.

The homogeneous Fenton oxidation is one of the most promising and widely used AOPs; however, this process requires stoichiometric amounts of Fe²⁺ and large amounts of acid, usually sulphuric acid since it is more efficient at lower pH values (pH 3) (Costa *et al.*, 2006). The major setback of using the homogeneous Fenton process is that at higher pH (around 5-8) the iron catalyst loses its catalytic activity (Lam and Hu. 2013) and the spent acid (added to wastewater before treatment) and base (added to wastewater after treatment) increases the cost of the wastewater treatment. The homogeneous Fenton reaction also results in sludge formation and requires a separation step for the removal of the treatment (Wang *et al.*, 2014). However, a heterogeneous catalyst seems to overcome the shortcomings of a homogeneous catalyst.

The main advantage of a heterogeneous Fenton-like process is not only the easy separation of catalyst from the reaction but also the ability to oxidise the acidic, basic and neutral pollutants discharged to the environment and efficiently degrade the organic pollutants into CO₂ and H₂O (Karthikeyan *et al.*, 2016). The use of iron oxides is an advantage as it reacts at neutral pH with no sludge formation and can be recovered easily (Pouran *et al.*, 2015). However, the solid iron oxide used presented a weak catalytic activity. This lower catalytic activity is attributed to the slow regeneration rate of the Fenton reagent (Fe²⁺) as shown in Equation (2.2). Furthermore, the Fe content leaches from catalyst into the solution and is difficult to separate from the treated water. This weakens the catalytic activity in the long term (Pouran *et al.*, 2015). The development of a catalyst with a high catalytic activity, good stability, and recyclability is thus of considerable interest.

Catalyst composition and preparation methods

In this study a bimetallic system supported on silica was used to increase the catalytic activity of a heterogonous catalyst in a Fenton-like reaction. Different metals such as Co,

Cu, and Mn will be incorporated with iron with the aim of increasing the catalytic activity of a Fenton reaction. Therein different calcination methods were employed as they also play a role on the activity of a Fenton reaction.

2.4 The choice of a calcination method during the preparation of the catalyst

It has been reported that the particle size, particle size distribution, crystalline phase, surface area, dispersion and shape of the particles play an important role in the catalytic activity of a heterogeneous Fenton-like reaction (Wu *et al.*, 2014, Compas *et al.*, 2015, Gao *et al.*, 2019). Tremendous efforts are being made toward controlling these properties.

Compas *et al.* (2015) reported that the heterogeneous catalyst properties depend on the preparation method. For example, Rad *et al.* (2015) prepared cobalt ferrite nanoparticles using both conventional and microwave heating methods. They reported that the nanoparticles calcined by microwave were more uniform and smaller (16.7 nm) than those calcined by conventional methods (25.4 nm). This phenomenon was attributed to heat gradient during the synthesis of the nanoparticles via the microwave that may affect the homogeneity compared to conventional synthesis. Furthermore, the rapid annealing using microwave heating resulted in the retention of the morphology, size and shape of the particles during the densification of the particles, which in turn results in the smaller size of the nanoparticles with a sharp diameter distribution compared with conventional method.

Similarly, Reubroycharoen *et al.* (2007) observed that nanoparticles prepared by microwave showed smaller particle size compared to those catalysts prepared by conventional heating. This was attributed to the agglomeration of the cobalt particles during conventional heating which is due to an outward liquid flow from the inside to the outside of the support and the concentration gradient of metal oxide on the surface of the support. This could lead to an accumulation of metal oxide on the outer region of the support. However, the agglomerated cobalt lowered the dispersion of cobalt and increase the average particle size of the supported cobalt crystallites. Furthermore, the rapid drying of the microwave reduced the time for the catalyst preparation. Moreover, the microwave calcination method resulted in the homogeneous dispersion of the cobalt on the surface

of the silica support. These results indicated that the short comings of the conventional calcination methods might be minimized using the microwave.

Furthermore, Reubroycharoen *et al.* (2007) investigated the effect of optimizing microwave irradiation time at 700 W microwave power on the catalytic activity of Co catalyst. They observed that as the microwave irradiation time was increased from 0, 5, 10 and 14 minutes there was an increase in the Fischer-Tropsch catalytic activity. Further increase on the irradiation time to 45 minutes led to no significant change on the catalytic activity in the Fischer-Tropsch reaction. The optimum irradiation time was determined to be 14 minutes.

A comprehensive study comparing activated carbon prepared by conventional and microwave heating has been done by Huang *et al.* (2011). This study reported that the main advantage of microwave heating is the treatment time that can be greatly reduced and which causes a reduction in the energy consumption and hence reduces the cost of the preparation. Moreover, the lotus stalks activated carbon prepared by microwave methods at 700 W for 15 minutes has a higher surface area and a higher total volume than that obtained by the conventional method. However, the activated carbon prepared by conventional heating acted as a better adsorbent for the removal of oxyltetracycline (OTC) from aqueous solution. This fact was attributed to surface characteristics of the two carbons.

The microwave power and irradiation time play a major role on the uniform dispersion of the particles, particle size and shape. Mousavi *et al.* (2015) studied the effect of different microwave power and irradiation time on the properties of zinc chromite nanostructures. Firstly, they kept the microwave power constant at 600 W. They observed that as they increased the irradiation time from 4 to 6 minutes, uniform particles and separated particles were formed due to sufficient time for the reaction. They also reported that further increase of irradiation time to 8 minutes led to an agglomeration of the particles. This was attributed to an increase in the kinetic energy of the prepared particles as this would increase the collision of the particles leading to agglomeration.

Parida & Parija. (2006) observed similar observations on their preparation of ZnO particles by varying the microwave calcination irradiation time. The photo catalytic

degradation percentage increased from 60 to 88% as the calcination irradiation time during the catalyst preparation was increased from 5 to 15 minutes. This was attributed to the small particle size and the lager surface area of the catalyst prepared using 15 minutes of calcination. However, a further increase in the calcination irradiation time during preparation led to a decrease in the percentage removal of the pollutant and thus a decrease in the catalytic activity. This was attributed to the sintering process as the irradiation time as increased.

Mousavi *et al.* (2015) also studied the effect of different microwave power (600 750 and 900 W) at 6 min on the properties of zinc chromite nanostructures. They observed that a further increase in the microwave power leads to larger particle sizes in the catalysts which is due to the agglomeration of the particles at higher microwave power. The optimum microwave power was 600 W 6 minutes.

Based on the literature reviewed above, it has been observed that all the studies showed different optimal irradiation time and power. This might be due to the different methods and reactions employed in these studies. The metal loading, metal precursor and the supporting material may also cause variation in the optimum microwave parameters. The calcination method needs to be optimized for a particular catalyst and reaction.

2.5 Bi-metallic oxide Fenton catalysts

The main limitation of the heterogeneous Fenton process is due to the lower rate of reduction of Fe³⁺ to Fe²⁺ and this reduces the overall rate of the •OH production (as shown in the reaction (i) and (ii)) which in turn lowers the catalytic activity of a Fenton system (Esteves *et al.*, 2015). Recently bimetallic systems seems to overcome the drawbacks faced by monometallic heterogeneous Fenton catalyst oxide (Han *et al.*, 2011). A bimetallic system oxide heterogeneous catalyst is the incorporation of Fe with other transition metal such as Cu, Mn, Cr, Co etc. (Pouran *et al.*, 2015). Bimetallic oxide catalysts exhibit synergetic properties and Wang *et al.* (2014) attributed this phenomenon to the two pairs of redox metals incorporated together. Other properties that a bimetallic catalysts exhibit includes the metal dispersion and interfacial structure which in turn enhance the degeneration rate of contaminants (Luo *et al.*, 2015). Figure 2. presents the

incorporation of Fe²⁺ and Cu⁺ which increases the production of the hydroxyl radical, by assisting each other with the regeneration of the active species.

The main advantage of a bimetallic system is that the transition metals that are incorporated with Fe can also act as Fenton-like catalysts. Transition metal ions like Cu⁺, Co²⁺ and Mn²⁺ ions can generate radicals according to Equations (2.12) (Wang *et al.*, 2014), (2.14) (Hu *et al*, 2017) and (2.16) (Costa *et al.*, 2006) and a reduction mechanism similar to that of Fe³⁺ has been reported for Cu²⁺ as shown in the equations below.

 $\begin{array}{l} Cu^{+} + H_{2}O_{2} \rightarrow Cu^{2+} + HO^{\cdot} + OH^{-} \dots \dots (2.12) \\ Cu^{2+} + H_{2}O_{2} \rightarrow Cu^{+} + HOO^{\cdot} + H^{+} \dots (2.13) \\ Co^{2+} + H_{2}O_{2} \rightarrow Co^{3+} + HO^{\cdot} + OH^{-} \dots (2.14) \\ Co^{3+} + H_{2}O_{2} \rightarrow Co^{2+} + HO_{2^{\cdot}} + H^{+} \dots (2.15) \\ Mn^{2+} + H_{2}O_{2} \rightarrow Mn^{3+} + HO. + OH^{-} \dots (2.16) \\ Mn^{3+} + H_{2}O_{2} \rightarrow Mn^{2+} + HOO^{\cdot} + H^{+} \dots (2.17) \end{array}$

Therefore, the outstanding catalytic activity of a bimetallic catalyst may be generally attributed to synergetic effects in relation to defect creation, novel active sites and facile redox interplay between iron and other metal (copper, cobalt, manganese, etc.) couples (see Figure 2.3) (Han *et al.*, 2011). Moreover, the addition of certain metals to the catalyst may stabilize the activity for the oxidation of organic pollutants in comparison with monometallic catalysts (Zhang *et al.*, 2014).



Figure 2. 3: Proposed synergistic effect of bimetallic metal oxides with redox interplay between the iron and additional metal such as Cu, Co and Mn (Magalhaes *et al.*, 2007).

The proposed equations for the interaction between couples (Mn-Fe and Co-Fe) of a bimetallic oxide catalyst are represented below (Wang *et al.*, 2015; Wang *et al.*, 2016).

$$Fe^{2+} + Co^{3+} \rightarrow Fe^{3+} + Co^{2+}$$
 (2.18)

$$Fe^{2+} + Mn^{3+} \rightarrow Fe^{3+} + Mn^{2+}$$
 (2.19)

Other transition metal oxides are also known to be active oxidation catalysts and could be more active than iron oxide. For example, copper oxide and cobalt oxide supported on activated carbon are more active than iron oxide supported on activated carbon (Huang *et al.*, 2015). On the other hand, manganese oxide supported on activated carbon was found to have a lower oxidation activity (Huang *et al.*, 2015). During testing it is important to keep the metal content (sum of transition metals) constant to ensure that the increase in activity due to the addition of a second metal oxide is not just due to an increase in the catalyst metal oxide content. Furthermore, an increase in activity may also just be due to the replacement of the iron oxide by a more active transition state metal like copper and cobalt. If a synergistic effect is achieved, the combined activity will be greater than the sum of the individual metal oxide's contributions as found by Wang *et al.* (2016) and shown in Figure 2.4.



Figure 2. 4: Synergism between copper oxide and iron oxide. Figure constructed from data of Wang *et al.* (2016).

Examples of mixed oxides used as oxidation catalysts will now be briefly discussed to demonstrate the advantages of using bi-metallic oxide catalysts.

Magalhaes *et al.* (2007 showed that the introduction of Cr-containing magnetite's Fe_{3-x}Cr_xO₄ showed a significant increase in the activity for degradation of a dye. The higher activity was attributed to more efficient regeneration of active Fenton species Fe²⁺ by a coupling of the redox pairs Fe^{3+/}Fe²⁺ and Cr^{3+/}Cr²⁺. On the other hand, they further explained Fe_{3-x}Cr_xO₄ does not directly promote the Fenton reaction in a direct mode but instead is involved in the H₂O₂ decomposition. XPS also showed that whenever Cr²⁺ is formed during the Fenton reaction it is rapidly converted back to Cr³⁺, Cr⁴⁺ and Cr⁶⁺.

The incorporation of copper into the structure of akageneite [iron oxide hydroxide or chloride mineral with formula $Fe^{3+}O(OH,CI)$] increased the catalytic activity of the catalyst since higher methylene blue discoloration and removal of organic carbon was observed dos Santos *et al.* (2016). They explained that the copper reduced by hydrogen peroxide can act as an electron donor reducing the ferric to ferrous ions that are more active in the Fenton reaction. Furthermore, copper, when Cu⁺ is formed, can promote the formation of hydroxyl radicals (highly oxidant species) in the Cupro-Fenton reaction.

Esteves *et al.* (2015) used c a cobalt-iron oxide bimetallic catalyst in their study. They prepared $Fe_3-xCo_xO_4$ nanoparticles that reacted with the peroxide to produce highly reactive and non-selective hydroxyl radicals capable of oxidizing any organic matter present in an aqueous solution. They found that the use of $Fe_3-xCo_xO_4/H_2O_2$ is very effective for the oxidation of organic matter. They also reported that it is easy to recover and reuse the catalyst for several reaction cycles without losing its catalytic activity and since it has magnetic properties one can just apply an external magnet for separating the catalyst from the water.

Iron-copper bimetallic nanoparticles embedded within ordered mesoporous carbon composite catalyst (CuFe-MC), were synthesized by Luo *et al.* (2015) for the heterogeneous Fenton-like process. A high mineralization efficiency was observed for phenol, benzoic acid, bisphenol-A, 2,4,6,-trichlorophenol, imidacloprid, ketoprofen, methylene blue and methyl orange when CuFe-MC was utilized. CuFe-MC has higher catalytic efficiency than homogeneous Fenton reagent (Fe²⁺) for the removal of total

organic carbon (TOC) of contaminants under the same reaction conditions. In this work CuFe-MC's high efficiency (94%) for the removal of TOC of imidacloprid (100 mgL⁻¹) was achieved in 12 hours, while only 38% was achieved by the homogeneous (Fe²⁺) Fenton catalyst. This remarkable performance of the heterogeneous Fenton-like catalyst was attributed to (i) the larger surface area, which plays a major role in the adsorption of organic contaminants and the mesostructure that favours rapid diffusion of reactants and products, (ii) the synergetic effect of iron and copper favours the redox cycles of Fe³⁺/Fe²⁺, Cu²⁺/Cu^{+,} enhancing the catalytic activity of the composite catalyst, (iii) the mesoporous carbon used as a supporting material can also activate the peroxide to form hydroxyl radicals. Furthermore, the bimetallic (CuFe-silica) catalysts were more active than the monometallic (Fe-silica) catalysts (Wang *et al.*, 2015).

Cu-Fe/SBA-15 (SBA-15 silica support) appeared to be an excellent bimetallic Fenton-like catalyst outperforming monometallic catalysts (Cu/SBA-15 Fe/SBA-15), as observed by Karthikeyan *et al.* (2016). They synthesized Cu-Fe bimetallic Fenton-like heterogeneous catalysts supported on mesoporous silica 15 (SBA-15) that was used to degrade N, N-diethyl-p-phenyl diamine (DPD) in water. Oxidative degradation of DPD at 100 M/L occurred over Cu-Fe/SBA-15 with 83% degradation within 120 min and the initial rate of degradation was first order in DPD for concentrations ranging from 100-500 mg/L. They also tested a physical mixture of monometallic catalysts (Cu/SBA-15 Fe/SBA-15) and found that the copper and iron need to be in direct contact (together on the same support) to achieve the synergistic effect.

Costa *et al.* (2003) studied the decomposition of peroxide in the presence of the pure spinel Co_3O_4 and a solution of $CoCl_2$ and compared it to that of cobalt substituted magnetite. They discovered that the cobalt substituted magnetite was much more active (with a zero order reaction rate constant (k) of 0.230 mmol min⁻¹) than the pure iron oxide, even though Co_3O_4 showed a slightly higher catalytic activity of (k = 0.044 mmol min⁻¹) compared to that of Fe₃O₄ (with k = 0.006 mmol min⁻¹).

Costa *et al.* (2006) studied the addition of nickel oxide, manganese oxide and cobalt oxide to magnetite on the oxidation rate of methylene blue. The addition of nickel oxide to the magnetite did not increase the catalytic activity as was in the case with the addition of

manganese oxide and cobalt oxide. The results showed only about 10% of colour removal after 50 min when the bimetallic Ni-Fe oxide catalyst was used in comparison to full decolorization after 10 minutes when either a Co-Fe oxide or Mn-Fe oxide catalyst was used. This low activity was attributed to the fact that nickel is only stable as Ni²⁺ species and other oxidation states like Ni³⁺ are not stable. As Ni²⁺ only replaces mainly Fe²⁺ in the magnetite structure the reaction is inhibited since Fe²⁺ is responsible for the initiation step.

Tang *et al.* (2018) reported on the synthesis of magnetic separable MnO_2/Fe_3O_4 supported on silica nanofibers for the degradation of Acid red 73. They observed that MnO_2/Fe_3O_4 nanofibers showed the highest catalytic activity for the removal of Acid red 73 than MnO_2 , Fe_3O_4 and $MnO_2+Fe_3O_4$. This high activity was attributed to the enhanced redox interplay between Fe(III)/Fe(II) (0.77 V) and Mn(IV)/Mn(III) (0.15 V). This study further reported that Mn(III) assisted the reduction of Fe(III) to Fe(II), since the potential of Mn(IV)/Mn(III) was lower than that of Fe(III)/Fe(II). The reaction mechanism is shown in Appendix D.

In contrast to the study conducted by Nawaz *et al.* (2016), this study reported a different potential value of Mn(IV)/Mn(III) that was (0.95 V) higher than that of Fe(III)/Fe(II) (0.77 V) indicating that the reduction of Mn(IV) by Fe(II) was dynamically favourable. The reaction mechanism is shown in Appendix D.

In the literature of a bimetallic system it was observed that the total percentage removal and the rate of the reaction was different for all the bimetallic catalysts used (Costa *et al.*, 2003; Pouran *et al.*, 2015; Wang *et al.*, 2016). This might be due to several reasons, namely, the method of preparation of the catalyst, supporting material, concentration of the pollutant, the nature of the pollutant used, pH used during the experimental and preparation method and the AOP's method used. Wang *et al.* (2016) indicated that the total metal content present in the catalyst might also affect the catalytic activity of the Fenton reaction. Lastly, the Fe/M ratio might also have an impact on the activity of a bimetallic catalysts under the same conditions and compare their activity.

Herein we report on the preparation of a 10% metal content monometallic (Fe, Mn, Co and Cu) and bimetallic (FeCo, FeCu and FeMn) catalyst supported on silica via the

incipient wetness impregnation method. The bimetallic catalysts were prepared by replacing a third of the Fe with a different metal, M (M= Mn, Co and Cu). The catalysts were calcined either by microwave power or conventional oven. The activity of these catalysts was tested during the degradation of MB.

Chapter 3: Methodology

In this chapter, various chemicals and materials utilized during this study are listed. Experimental methods for the catalyst preparation, characterization techniques and Fenton reaction (degradation of MB) are discussed. Other methods that were used during this study are also discussed. These methods include those for the leaching test, hydroxyl radical determination, Oxidation Reduction Potentials (ORP) and mass loss studies. The analytical instruments used in during this study and their methods are also discussed in this chapter. These instruments include the UV-vis, AAS and photoluminescence spectrophotometers.

3.1 Materials

Davisil Grade 643 Silica, 99 % with a pore volume of 1.15 cm³/g was purchased from Sigma-Aldrich and was used as supporting material for the heterogeneous oxide catalysts. Iron(III) nitrate nonahydrate (98 % Fe(NO₃)₃.9H₂O), copper(II) nitrate trihydrate (99 % Cu(NO₃)₂.3H₂O), manganese (II) nitrate tetrahydrate (97 % Mn(NO₃)₂.4H₂O), terephthalic acid (98%) and Methylene blue dye (97 % C₁₆H₁₈ClN₃S) were sourced from Sigma-Aldrich. Cobalt (II) nitrate hexahydrate (99% Co(NO₃)₂.6H₂O) and oxalic acid anhydrous (99% C₂H₂O₄) were obtained from Fluka. Hydrogen peroxide (in water, 30 % was purchased from Labo-Chem).

3.2 Catalyst preparation

In this part catalyst preparation will be discussed, Section 3.2.1 will deal with the preparation of different catalysts, namely Fe, Mn, Cu, Co, 2Fe1Mn, 2Fe1Cu and 2Fe1Co supported on silica and calcined by the conventional oven method (Conv) and microwave irradiation power (MW). The bimetallic catalyst with highest catalytic activity for the

degradation of methylene blue was selected to optimize the relative mass ratios of the two metals in the catalyst keeping the total metal content constant as explained in Section 3.2.1.3. The 2Fe1Mn catalyst showed the highest catalytic activity for MB dye degradation. Lastly, the ratio with highest catalytic activity was selected and prepared by varying the microwave power and time, details are in Section 3.2.1.4. In this case, 0,35Fe2,65Mn catalyst showed the highest activity during the Fenton reaction and was used to optimize the microwave calcination method. Figure 3. 1 shows the summarized catalyst preparation order. Catalyst preparation calculations are shown in Appendix A.





3.2.1 Preparation of heterogeneous oxide catalysts using different metals

During this study, a 5 g catalyst containing 10% of metal (Fe, Co, Cu and Mn) content was prepared using the incipient wetness impregnation method.

3.2.1.1 Preparation of monometallic oxide heterogeneous catalysts

During this study, monometallic oxide heterogeneous catalysts were prepared by dissolving iron (III) nitrate nonahydrate in a 250 mL beaker containing approximately 5 mL of deionized water as shown in Table 3. 1. Weighed mass of silica was added into the same beaker (Table 3. 1 illustrates the actual mass weighed). The volume of water used to dissolve the added corresponds to the pore volume of the silica support. The semi-dry mixture was then divided into two, one half was calcined by the conventional oven at 250 °C for 2 hours (the conventional oven took approximately 5 min to reach 250°C. Therefore, the mixture was in the oven for 2 H 5 min) The other half was calcined by microwave irradiation power at 800 W for 10 min. The same procedure was repeated for the Co Cu and Mn monometallic oxide catalysts.

3.2.1.2 Preparation of a bimetallic oxide heterogeneous oxide catalyst

During this study a bimetallic oxide catalyst was prepared by replacing a third of the iron in Fe₃O₄ with another metal, M (where M can be Co or Cu or Mn) to produce MFe₂O₄. These three bimetallic oxide catalysts were characterized and tested in methylene blue degradation.

In this study different masses, (see Table 3. 2) for the actual mass weighed) of iron (III) nitrate nonahydrate, copper (II) nitrate hexahydrate, manganese (II) nitrate hexahydrate and cobalt (III) nitrate hexahydrate were weighed and mixed into different 250 mL beakers with 5 mL of deionized water. About 4.3 g (see Table 3. 2) of silica support was weighed and added to the metal nitrate solution and stirred with a glass stirring rod. After mixing the catalysts were calcined by the oven at 250°C for 2 hrs. The same procedure for catalyst preparation was repeated for microwave calcination at 800 W for 10 minutes.
Table 3. 1: The mass of iron (III) nitrate nonahydrate, copper (II) nitrate trihydrate and manganese (II) nitrate tetrahydrate during the monometallic oxide heterogeneous catalyst preparation.

Catalyst name	Mass of Nitrate(s)	Mass silica (g)		
	(g)			
Fe	3.6250	4.2943		
Со	2.4709	4.3741		
Cu	1.9026	4.3001		
Mn	2.2803	4.3107		

Table 3. 2: The mass of iron (III) nitrate nonahydrate, copper (II) nitrate trihydrate and manganese (II) nitrate tetrahydrate during the preparation of a bi-metallic oxide heterogeneous catalyst.

Catalyst	Mass of nitrate(s)	Mass silica (g)	
	(g)		
FeCo	Fe: 2.4114	4.2815	
	Co: 0.8759		
FeCu	Fe: 2.4108	4.2903	
	Cu: 0.7246		
FeMn	Fe: 2.4091	4.3004	
	0.7541		

3.2.1.3 Preparation of Fe/Mn heterogeneous oxide catalyst by varying the mass ratios

The 2Fe1Mn bimetallic catalyst showed a higher percentage removal of methylene blue compared to other bimetallic oxide catalysts. Therefore Fe: Mn mass ratios were varied as shown in Table 3. 3. The total metal content in the catalyst was kept constant at 10%. The same procedure described in Section 3.2.1.2 was followed; however, the microwave calcination method was utilized at this stage since it yielded a more active catalyst.

Table 3. 3: The mass of iron(III) nitrate nonahydrate and manganese (II) nitrate tetrahydrate during the preparation of a bi-metallic oxide heterogeneous catalyst by varying the mass ratio of Fe:Mn metals.

Catalyst	Mass of	Mass of	Mass of
	Fe(NO3)3.9H2O	Mn(NO3)2.4H2O	Silica (g)
	(g)	(g)	
Fe	3.6250	0.0000	4.2943
2Fe1Mn	2.4091	0.7541	4.3004
1,5Fe1,5Mn	1.1808	1.1203	4.3007
1Fe2Mn	1.2103	1.5013	4.3011
0,5Fe2,5Mn	0.6030	1.8714	4.3069
0,425Fe2,575Mn	0.5128	1.9306	4.3100
0,35Fe2,65Mn	0.4201	1.9905	4.9603
0,25Fe2,75Mn	0.3012	2.0661	4.3090
Mn	0.0000	2.2803	4.3107

3.2.1.4 Preparation of 0,35Fe2,65Mn at different microwave power and time

In this section, the mass ratio (0,35Fe2,65Mn) oxide catalyst that showed the highest catalytic activity was used to optimize the microwave calcination method by varying

microwave power and time during the calcination step. The preparation method described in Section 3.2.1.1 was used. See Table 3.4 for a summary of the variation of parameters. This was done to determine the influence of microwave irradiation power and time on the catalytic activity of the heterogeneous oxide catalyst during the Fenton like reaction.

600 W	700 W	800 W
10 min	10 min	10 min
20 min	20 min	20 min
30 min	30 min	30 min

Table 3. 4: Different microwave power and time

3.2 Characterization of the catalysts

3.2.1 XRD

XRD analyses were done using the Shimadzu-XRD 700, X-Ray Diffractometer with Cu Ka radiation ($\lambda = 1.154056$ Å). A scan speed of 1 °/ minute, current 30 mA and voltage of 40 kV were used. The FWHM (Full-Width Half-Maximum) was determined by fitting a Gaussian peak using the Fityk program. The FWHM was used to calculate the average crystallite size using the Scherrer equation D=K λ / β cos θ (see appendix C). A value of 0.9 was used for the Scherrer constant K, 1.154056 Å for wavelength (λ), β is the line width FWHM as 20, θ is the Bragg angle, and D is the crystallite size.

3.2.2 X-ray photoluminescence (XPS)

X-ray photoelectron spectroscopy analysis was carried out on PHI 5000 scanning ESCA microprobe with a 100 μ m diameter monochromatic Al K α x-ray beam (hv = 1486.6 eV) generated by a 25 W, 15 kV electron beam to analyze different binding energy peaks. The pass energy set to 11 eV gave an analyzer resolution ≤ 0.5 eV. Multipack version 9

software was utilized to analyse the spectra to identify the chemical compounds and their electronic states using Gaussian–Lorentz fits.

3.2.3 Cyclic voltammetry (CV)

CV were carried out in a three-way electrode system using a Biologic SP 240 potentiostat workstation. The working, reference and counter electrode were glassy carbon electrodes, Ag/AgCl (in saturated KCl) and platinum wire, respectively. The glassy carbon electrode (GCE) was thoroughly cleaned with 0.3- and 1-micron alumina powder to eliminate impurities. The catalyst material (4 mg) was dispersed into 1 mL Dimethylformamide (DMF) solution using ultra sonification for 15 minutes to obtain a homogenous solution. DMF was used due to its larger molecule volume than water and DMF is more inert. A 20 μ L sample of the catalyst dispersion was drop cast on the clean GCE. The EIS experiments was carried out between frequency ranges of 100 KHz to 40 mHz with perturbation amplitude of 5 mV in 5 mM ferrocyanide containing 0.1 M KCl solution. Appendix D shows redox half reactions for the various metal ions.

3.3 Fenton reaction

The methylene blue degradation was performed by measuring 70 mL of distilled water which was poured into a 250 mL beaker covered with foil to prevent photo degradation. The beaker was placed on a magnetic stirrer hot plate, a stirrer bar was immersed inside the beaker, and the temperature was set at 27 °C at a stirring rate of 500 rpm. A volume of 10 mL from a 1000 ppm stock solution of methylene blue was also added to the same beaker. When the temperature of the solution reached 27°C, 0.05 g of catalyst was weighed and added to the beaker. The solution was stirred for 60 min at 500 rpm to allow absorption to take place with the temperature maintained at 27°C (the temperature sensor was immersed inside the solution). After 60 min, 20 mL of H₂O₂ was added to the beaker to initiate the Fenton reaction and degradation took place for 60 min.

A volume of 1 mL was sampled from the solution at predetermined time intervals [0 min (time of H₂O₂ addition), 2.5, 5, 7, 9, 11, 13, 15, 17.5, 20, 30 and 60 min] and poured into 100 mL volumetric flask. A 1 mL of isopropanol was added to that 100 mL volumetric flask (to quench the reaction). The 100 mL volumetric flask was made to the mark with deionized water and the solution was transferred to centrifuge tubes and centrifuged at 3500 rpm for 3 min to remove the catalyst from the solution. The concentration of the methylene blue was then measured by UV-vis spectroscopy. The dilution factor and percentage of degradation was calculated (see Appendix B). Pseudo first order and second order kinetics were fitted (see Appendix B).

3.4 UV-Vis spectroscopy

The concentration of methylene blue oxidation was measured with T80+ UV–VIS Spectrophotometer supplied by PG instruments, available with a variable spectral bandwidth of 0.5, 1, 2, 5 nm. This instrument uses a tungsten and deuterium lamp and samples were placed in a cuvette (quartz cell size 10 × 10 mm from PG instruments limited) and placed inside the instrument for quantitative analysis. The MB standard of 0.1, 0.2, 0.3, 0.4, 0.4, 0.5 0.6, 0.7, 0.8, 0.9 and 1 ppm were prepared and used to calibrate the UV-vis spectrometer.

3.5 Quantification of Fe, Co, Cu and Mn (Leaching test) using AAS

The concentrations of Fe, Co, Cu and Mn leached during degradation were determined by atomic absorption spectroscopy (AAS) (AA-7000 SHIMADZU). Hollow cathode lamps (HCL) of Fe (with a wavelength of 248.3 nm and a spectral width slit of 0.2 nm), Co (with a wavelength of 240.7 nm and a spectral width slit of 0.2 nm), Cu (with a wavelength of 324.8 nm and a spectral width slit of 0.5 nm) and Mn (with a wavelength of 279.5 nm and a spectral width slit of 0.2 nm) were used during the analysis. Acetylene gas was used as a purge gas throughout the analysis. The sample was carried out by acetylene and air followed by subsequent atomization in the flame.

3.5.1 Leaching test after the Fenton reaction

After the degradation of methylene blue dye as explained in Section 3.4, the solution was filtered with 0.45 μ m filter and the filtered solution was analyzed with AAS for determination of leached metal concentrations during degradation.

3.5.2 Leaching test under the same conditions

The degradation of methylene blue results in the formation of acids, like oxalic acid, as intermediates. The catalyst with the highest activity may yield the highest concentration of acids which is expected to result in the highest amount of leaching. The amount of leaching may thus be dependent on the activity of the catalyst. It is thus important to determine the concentration of leached metal ions under the same conditions to determine the catalyst stability independent of the catalyst activity. This was done by dispersing 0.02 g of each catalyst into a 10 mL of 0.2 molL⁻¹ of oxalic acid for 1 hour for catalysis at a stirring rate of 500 rpm. The resulting solution was filtered with a 0.45 μ m filter and measured with AAS.

3.6 Oxidation Reduction Potential (ORP)

Oxidation Reduction Potential meter HI2002 edge[®] with 5.5-inch LCD display, which uses an ORP/temperature digital electrode HI136180 that can measure a temperature range of -5 to 100 $^{\circ}$ C and a potential of +/- 2000 mV, was used to measure the tendency of the solution to release or accept the electrons. The degradation method was performed with the method described in Section 3.4. The ORP probe was then immersed into the solution (containing methylene blue dye, deionized water, hydrogen peroxide and the catalyst) to measure the tendency of a substance to oxidize or reduce. The potential (mV) was recorded at different time intervals [0 min (time of H_2O_2 addition), 2.5, 5, 7, 9, 11, 13, 15, 17.5, 20, 30 and 60 min].

3.7 Mass loss studies

Mass loss studies were performed to investigate the tendency of hydrogen peroxide to decompose to oxygen as shown in Equation 2.11. This is an unwanted reaction as it consumes the amount of H_2O_2 present in the reaction.

During these experiments, 20 mL of H₂O₂ was placed into a 250 mL beaker with a magnetic stirrer. The beaker was then weighed using a weighing balance supplied by RADWAG[®], model (AS 220/c/2) and the mass was recorded. A catalyst of approximately 0.005 g was weighed using the same weighing balance and was added into the same beaker. The beaker was then weighed again and thereafter placed into a magnetic stirrer supplied by Radley's innovation for chemistry (with a Pt1000 temperature sensor, Pt1000 Medium and Pt1000 safety circuit), the temperature was set at 27°C and the stirring rate was set to 500 rpm. The beaker with the solution was then weighed at different time intervals of 0, 2.5, 5, 7, 9, 11, 13, 15, 17.5, 20, 30 and 60 min.

3.8 Hydroxyl radical determination

The Fenton reaction is one of the reactions that are based on the oxidation of hydrogen peroxide to generate hydroxyl radicals which in turn degrade the dyes (methylene blue dye in this study) (Gao *et al.*, 2019). The catalyst that shows higher activity for the formation of these radicals is expected to have higher catalytic activity for the degradation of MB. Therefore, it is important to determine the formation of these radicals. In this study

terephthalic acid (TA) was used to determine the generation of hydroxyl radicals. TA readily reacts with \cdot OH to produce 2-hydroxyterephthlic acid (TAOH) which emits fluorescence around 424 nm on the excitation at 359 nm. This method was adopted from Wang *et al.* (2017) with some modifications. The difference between this method and that of Wang *et al.* (2017) is the addition of 20 mL H₂O₂ since this study was based on Fenton reaction and not photocatalysis.

A mass of 0.05 g catalyst was weighed and dispersed in an 80 mL of TA (5×10^{-4} molL⁻¹) aqueous solution with NaOH (2×10^{-3} molL⁻¹) and 20 mL 30% H₂O₂. The reaction was allowed to take place at a temperature of 27^oC and was stirred at 500 rpm. The samples were taken at different time intervals of 0 (before the addition catalyst), 0 (after the catalyst was added), 5, 10, 20 and 30 and analysed with a photoluminescence spectrophotometer

The emission of the nanoparticles was determined using the Jasco spectrofluorometer FP-8600 equipped with XE lamp, 150 W, with bandwidth excitation slit 5 nm and the emission ranging from 200-1010 nm. Fluorescent materials absorb UV light which is then emitted to longer (frequency visible) wavelength. The instrument consists of a UV source, a monochromator for selection of the desired wavelength for irradiation, a sample holder, a second monochromator is used to select the desired wavelength of detection and a phototube amplifier-output assembly. The fluorometer irradiates and then records the intensity of the light emitted by the sample on a plate. The wavelength of the excitation for all the particles was at 359 nm. The emitted intensity gives an indication of the amount of radical formation.

Chapter 4: The effect of the catalysts' composition and calcination method.

This chapter deals with the preparation of monometallic and bimetallic oxide heterogeneous catalysts calcined by conventional methods (oven) and microwave irradiation power for the degradation of methylene blue dye.

4.1 Preparation of monometallic oxide heterogeneous oxide catalyst and Fe-M (M is Mn, Cu and Co) bimetallic oxide heterogeneous catalyst calcined by microwave and conventional methods (oven) for the Fenton reaction.

4.1.1 Characterization of heterogeneous oxide catalyst with XRD

XRD was used to (i) determine the phase and the type of the oxide formed, (ii) identify the shifting of peaks between monometallic and bimetallic oxide catalysts to see if there was a change in the Fe structure when incorporated with other transition metals, and (iii) to also determine the crystalline size of the catalysts.

4.1.1.1 Identification of the phase

Figure 4. 1(a) and (b) shows the XRD analysis of Fe, FeCo, FeCu and FeMn catalyst calcined by conventional (Conv) and microwave irradiation power (MW), respectively. The results showed the existence of a single crystallographic phase corresponding to hematite Fe₂O₃, which was identified by its reflections in the XRD pattern (card number: 00-033-0664). Figure 4. 12(a) the XRD also indicated the formation of cobalt oxide (Co₃O₄) that corresponded to XRD pattern (card number: 00-042-1467). The presence of a single crystallographic phase corresponding to tenorite (CuO) with XRD pattern (card number: 00-048-1548) was observed in Figure 4. 12 (b).

The manganese catalyst showed the presence of pyrolusite also known as manganese black MnO_2 , which corresponded to the diffraction peaks of MnO_2 with card number 00-024-0735 as shown in Figure 4. 12(c). The XRD pattern in Figure 4.1 could be assigned to Fe₂O₃ (00-033-0664), as all the Fe, FeMn, FeCo and FeCu catalysts shared a single-

phase structure. No peaks for Mn, Co and Cu were observed in a bimetallic catalyst. This could be due to the high dispersion of these metal ions in the Fe₂O₃ lattice (Wang *et al.*, 2016). This may also be attributed to low metal loading of these transition metals to the Fe structure and too small metal particles deposited on silica (Wang *et al.*, 2015).

4.1.1.2 Identification of peaks shifts

There was no significant shifting in the diffraction peaks observed when the iron is incorporated with other transition metals (Co, Cu and Mn). This may indicate that a mixed spinel did not form. Only the iron oxide diffraction peaks were observed for the bimetallic catalysts which may be attributed to the low metal loading of the other transition metals to the Fe structure and too small metal particles deposited on silica (Luo *et al.*, 2015).

4.1.1.3 Determination of the crystallite size

The crystallite size of the catalyst might be influenced by the calcination method. Catalysts calcined by the microwave irradiation power (MW) showed smaller crystallite sizes compared to those calcined by a conventional oven method (Conv) except for copper oxide catalyst as shown in Table 4. 1. Similar results were observed by Rad *et al.* (2015). The conventional method heats from the outside of the catalyst particle to the inside due to heat transfer limitations. This leads to an outward liquid flow from the inside of the particle to the outside, which leads to agglomeration of the metal oxide on the outside of the particle (Reubroycharoen *et al.*, 2007), lowering metal dispersion and increasing the metal oxide particle size. Microwave heating has the advantage of rapid homogenous drying leading to uniform particle size distribution and physically strong pellets (Reubroycharoen *et al.*, 2007). The MW outperforms conventional oven heating in terms of thermal gradient and heating flow. The heating of MW irradiation decreases gradually from the centre of the material to the surface due to higher temperatures in the interior than at the surface leading to uniform metal distribution on the support (Reubroychaoen *et al.*, 2007; Rad *et al.*, 2015).



Figure 4. 1: XRD diffraction pattern of Fe, FeCu, FeCo and FeMn heterogeneous oxide catalysts calcined by (a) conventional oven (Conv) and (b) microwave irradiation power (MW).



Figure 4. 2: XRD diffraction pattern of monometallic and bimetallic oxide heterogeneous catalyst calcined by microwave power (MW) and conventional oven (Conv) for (a) Co and FeCo (b) Cu and FeCu, and (c) Mn and FeMn.

Table 4. 1: XRD crystallite size of Fe, FeMn, Mn, FeCo, Co, FeCu, Cu oxide heterogeneous catalyst calcined by conventional methods (oven) and microwave irradiation power.

	Crystalline size (nm), oxides and the peak angle			
	(degree)			
Catalyst name	Conventional oven (Conv)	Microwave (MW)		
Fe	12.1 (Fe ₂ O ₃ peak at 35.47)	10.6 (Fe ₂ O ₃ peak at 33.45)		
FeMn	6.7 (Fe ₂ O ₃ peak at 36.12)	4.4 (Fe ₂ O ₃ peak at 36.24)		
Mn	5.8 (MnO ₂ peak at 37.32)	5.1 (MnO ₂ peak at 37.18)		
FeCo	8.2 (Fe ₂ O ₃ peak at 33.52)	6.8 (Fe ₂ O ₃ peak at 37.50)		
Со	5.6 (Co ₃ O ₄ peak at 37.20)	5.0 (Co ₃ O ₄ peak at 36.96)		
FeCu	7.1 (Fe ₂ O ₃ peak at 33.10)	6.6 (Fe ₂ O ₃ peak at 32.75)		
Cu	6.8 (CuO peak at 37.01)	13.5 (CuO peak at 36.28)		

4.1.2 X-ray photoluminescence (XPS)

XPS analyses were also done for the catalyst calcined by microwave heating to see if peak shifts have occurred in the bimetallic oxide catalysts to indicate if a mixed oxide formed rather than two separate metal oxides. The peak positions for the Fe2p are shown in Table 4.2 and Figure 4.3 and no significant peak shifts were observed. XPS analyses were also done to determine the oxidation state of the iron to determine whether Fe₂O₃ or Fe₃O₄ was formed. Fe₂O₃ is expected since the catalysts were prepared with Fe³⁺ ions, calcined in air and small crystallites are expected to fully oxidize to Fe₂O₃ (Carvalho *et*

al., 2013). However, from the area ratios obtained from the XPS peak deconvolution (see Figure 4.2 and Table 4.2) it may indicate that Fe_3O_4 has formed. The catalyst is not magnetic which rather supports the formation of hematite (Fe_2O_3).

Table 4. 2: XPS values obtained by peak deconvolution of (a) Fe (b) FeCu (c) FeCo and (d) FeMn

Catalysts	Fe ²⁺ /Fe ³⁺	Fe ²⁺ peak position (eV)	Fe ³⁺ peak position
	Area ratio		(eV)
Fe	0,5	707,8	709,5
FeCu	1,1	708,1	710,3
FeCo	1,5	708,2	710,0
FeMn	1,0	708,1	709,9



Figure 4. 3: The XPS deconvoluted spectra of Fe2p in the following catalysts (a) Fe (b) FeCo (c) FeCu and (d) FeMn.

4.1.3 Cyclic voltammetry

The electrochemical behaviour of the catalysts was studied with CV. These analyses were conducted to see if the reduction/oxidation eV shifts have occurred in the bimetallic oxide catalysts to indicate if the metals are in proximity and can influence each other's' redox behaviours. During the Fenton reaction, the reduction of the metal oxides is much slower than the oxidation of the metal oxide. Therefore, a higher reduction potential (less negative) may indicate that the metal oxide will reduce easier and could be more active for the Fenton reaction. As expected the electrode without catalyst (bare) gave the lowest reduction peak currents compared to the electrodes with the catalysts (Figure 4.4). However, the metal supported catalysts produced peaks at different reduction potentials with the FeMn catalyst showing the highest potential peak of -0.21 (V). A decrease in the potential of FeCu, FeCo and Fe electrode was obtained at -0.19, -0.24 and -0.18 (V) in the CV curve, respectively. The difference in the potential values of these catalysts may be attributed to the slow or fast electron transfer rate and the activity of different catalysts (Ren *et al.*, 2015).

On the other hand, the FeMn catalyst showed the highest intensity current peak compared to the other catalysts indicating more active sites on the surface of the catalysts The trend was found to be in the following order FeCo<Fe<FeCu<FeMn. According to Ren *et al.* (2015) the difference in the activity of these catalysts depend on the chemical activity and the capacity of the transitive metal ions in the process of the reduction and oxidation. Wang *et al.* (2016) attributed this difference to the electrochemically accessible sites on the surface of the catalysts.

In addition, the ratio of anodic current to the cathodic current (Ia/Ic) for FeMn catalyst equals 1.00 (mA) indicating that the electron transfer for this catalyst was chemically reversible. This suggests that the electron that was donated by the electrode upon reduction was recovered during the oxidation process which in turn maintains the Fenton process during the degradation of MB representing a continuous oxidation-reduction process of the metal ions (Elgrishi *et al.*, 2017). The chemically reversibility trend was found to be in the following order FeCo<Fe<FeCu <FeMn (Table 4.3). If the extent of

oxidation-reduction process is not reversible it may lead to the deactivation of the catalyst during the Fenton reaction.

The peak to peak potential separation ($E_{pc}-E_{pa}$) depends on the relative rates of oxidationreduction as well as the number of electrons transferred. Equation 4.1 indicates that a value of 57 eV is expected for an electrochemical reversible single electron transfer and a value smaller than 57 eV for multiple electron transfers.

$$E_{pa} - E_{pc} = \frac{56.6 \text{ mV}}{n}$$
 (4.1)

One could speculate that a single electron transfer took place since the peak to peak potential separation is larger the 57 mV (Elgrishi *et al.*, 2017). The electron transfer for all the catalysts was electrochemically irreversible since the peak to peak separation is larger than 57 mV (Elgrishi *et al.*, 2017) as presented in Table 4.3.

The Fe and FeCo catalysts showed a less favourable slower electron transfer compared to FeMn and FeCu, respectively. The smaller peak separation for the FeMn and FeCu catalysts in comparison to the other catalysts may indicate that the continuous oxidationreduction process of the metal oxides that takes place during the Fenton reaction may be faster for the FeMn and FeCu catalysts and this may possibly lead to an increase the catalytic activity.

Catalyst	la	lc(mA)	la/lc	Ера	Ерс	Epc -	Emid(Epa+Epc)/2
	(mA)			(mV)	(mV)	Ера	(mV)
						(mV)	
Fe	0.034	-0.041	0.829	-36.90	-227.00	190.10	131.5
FeCo	0.032	-0.040	0.800	-46.60	-243.40	196.80	145.0
FeCu	0.043	-0.047	0.915	-98.00	-185.40	87.40	141.7
FeMn	0.05	-0.05	1.000	-117.60	-207.30	90.30	162.45

Table 4. 3: CV potential for different catalysts



Figure 4. 4: Cyclic Voltammograms of Fe, FeCu, FeMn and FeCo.

4.1.4 Oxidation Reduction potential (ORP)

The ORP is measured in volts (V) or millivolts (mV). The positive results indicate oxidizing agents (hydrogen peroxide, and radicals, which is stronger oxidizing agent than hydrogen peroxide, like hydroxide radicals and superoxide radicals) and the negative reading indicate reducing agents (which is not expected to be present during the Fenton reaction). He *et al.* (2009) showed that ORP can be used to monitor the Fenton reaction. They found that almost all the H_2O_2 was consumed when the ORP reached a maximum. This would be the point in the reaction were the Fenton reaction has converted the hydrogen peroxide to the stronger oxidizing radicals like hydroxide radicals. Thereafter the ORP decreases to a minimum (from 427 to 355 mV), indicating the completion of the Fenton reaction the relative oxidizing environments created by the different catalysts.

4.1.4.1 Repeatability of ORP

ORP repeatability studies were performed using the 2Fe1Mn oxide catalyst in five different runs. Each run was started with the new catalyst that was not reused. Figure 4.5 shows that a similar trend was observed among the ORP repeatability experiments. An average potential of 376 mV after 60 min with a standard deviation of 13.5 was obtained. No strong decrease in the ORP values were observed as also shown by He *et al.* (2009) which indicates that the Fenton reaction was not completed, meaning that there are still radicals like hydroxyl radicals present that can oxidize the pollutants.



Figure 4. 5: The repeatability of the 2FeMn heterogeneous oxide catalyst

4.1.4.2 Determination of the tendency of metal ions to reduce or oxidize

The ORP values of the different are shown in Figure 4.5 and the ORP values were between 320 and 466 mV. This is higher than the values reported by He *et al.* (2009). The difference between the FeCo and FeCu catalyst is 9 mV after 60 min which is smaller than 27 eV (2x standard deviation to account for 95% of the data) for the repeatability ORP measurements which may indicate that the FeCu and FeCo have similar ORP

values. The difference between the FeMn and FeCu is 38 eV after 60 min and the difference between the Fe and FeCu is 121 eV after 60 min which is larger than 27 eV which may indicate that these catalysts have different ORP values.

The ORP results showed that with Fe, FeCo and FeCu catalysts there was a slight decrease on the ORP values (between 2.5 and 60 min). However, this was different in the case of FeMn catalyst as this catalyst exhibited a slight increase in the ORP between 2.5 and 60 min. According to Kim *et al.* (2004) the increase in the ORP potential indicates the existence of the Fenton reagents that increase the radical formation in the reaction. No strong decrease in the ORP values were detected as observed by He *et al.* (2009) which indicates that the oxidization of the pollutants can still occur.



Figure 4. 6: The ORP results of different catalysts

4.1.5 Decomposition of hydrogen peroxide to oxygen (Mass loss)

Mass loss studies were performed to investigate the tendency of hydrogen peroxide to decompose to oxygen as shown in the Equation 4.1. This is an unwanted side reaction as it consumes the amount of H_2O_2 present in the reaction.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4.1}$$

4.1.5.1 Mass loss statistics

The mass loss repeatability studies were performed using the 2Fe1Mn bimetallic catalyst. Five experimental runs were performed and each run was started with a new catalyst. The catalyst was not reused. The results are shown in Figure 4.7. The average final mass was 22.69 g with a standard deviation of 0.20 g were obtained after 60 min. In Figure 4.8 the first order kinetic model is plotted and the average rate constant of 6.14×10^{-4} min⁻¹ with a standard deviation of 1.95×10^{-4} min⁻¹ was obtained.



Figure 4. 7: The repeatability results of 2Fe1Mn catalyst for mass loss studies.



Figure 4. 8: The repeatability results of 2Fe1Mn catalyst for first-order reaction kinetics.

4.1.5.2 Decomposition of hydrogen peroxide to oxygen (mass loss)

In Figure 4.9 the mass loss due to the formation of oxygen during the decomposition of H_2O_2 in the presence of Fe, Co, Cu and Mn monometallic oxide heterogeneous catalyst was measured.

The difference between the Fe and Co catalysts is 0.4 g after 60 min which is equal to 2σ of the repeatability test (0.4 g) which may indicate that the Fe and Co have similar mass loss values. The difference between the Fe and Cu is 0.7 g and the difference between the Fe and Mn is 2.16 g after 60 min which is larger than 2σ of the repeatability test (0.4 g) and this may indicate that these catalysts have different mass loss values. The Mn catalyst showed the highest activity for decomposition of hydrogen peroxide compared to all the other monometallic catalysts meaning that more H₂O₂ decomposed to O₂. The mass loss trend was found to be in the following order from Mn > Cu > Co \cong Fe.

The decomposition of H₂O₂ in the presence of Fe monometallic oxide catalyst, FeCo, FeCu and FeMn bimetallic oxide catalyst was also investigated as shown in Figure 4.10.

The difference between the Fe, FeCu and FeCo catalyst is 0.4 g after 60 min which may indicate that the Fe, FeCu and FeCo have similar mass loss values. The difference between the Fe and FeMn is 0.7 g after 60 min and may indicate that the FeMn catalysts have a larger mass loss value than the Fe catalyst. The mass loss trend was observed to be in the following order Fe≈FeCu≈FeCo<FeMn.check the sign?? The FeMn catalysts showed the highest mass loss due to H₂O₂ decomposition compared to other catalysts.



Figure 4. 9: The mass loss due to H_2O_2 decomposition studies when using monometallic oxide heterogeneous catalysts.



Figure 4. 10: The mass loss due to H_2O_2 decomposition studies when using bimetallic oxide heterogeneous catalyst.

4.1.6 Leaching

The leaching of metal ions from the heterogeneous oxide catalyst is an important problem for the Fenton process since it results in pollution, deactivation of the catalyst and promotes the homogeneous Fenton reaction due to the metal ions in the solution (Fontecha-Cámara *et al.*, 2016). The leaching of a heterogeneous catalyst can be attributed to different factors. During the degradation of the dyes, the formation of aromatic compounds and their oxidized by-products to form soluble complexes has also been reported to take place see Figure 2.2 in chapter 2.

The formation of these intermediates and metal complexes may depend on the activity of the catalyst being utilized. In other words, the catalyst with the highest activity may yield the highest concentration of intermediates like acids which can act as ligands to form metal complexes which are expected to result in the highest amount of leaching compared to the catalyst with lower catalytic activity. Therefore, it is important to test the leaching of metal ions under the same condition to elucidate if the leaching of the catalyst

was due to the formation of metal complexes or the instability of the catalyst (Ammar *et al.*, 2001).

The catalyst testing under the same conditions was performed using oxalic acid as described in Chapter 3.5 since different catalytic activities may result in different amounts of leaching. Oxalic acid is one of the intermediates formed during the degradation of MB. Pariente *et al.* (2015) and Rey et al. (2009) observed a significant decrease on the concentration of iron leaching as the concentration of oxalic acid was decreased. This phenomenon might be due to chelation (Liotta *et al.*, 2009). Hence leaching experiments under the same conditions were performed using oxalic acid. Oxalic acid is a bidentate ligand and therefore it bonds to the metal ion with two bonds forming a ring and allows the metal ions to bond with it more strongly. This might lead to more leaching of metal ions from the support and hence in this study oxalic acid was used to test the catalyst leaching under the same conditions.

4.1.6.1 Leaching repeatability of 2Fe1Mn during degradation

The repeatability study was performed using a 2Fe1Mn bimetallic catalyst (see Figure 4.11 (a)). Five replicates were performed, and each run was started with a new catalyst. After 60 min of adsorption and 60 minutes of Fenton reaction, the average Fe ion concentration leached was found to be 1.75 ppm with a standard deviation of 0.54 ppm and the average Mn ion concentration was 17.62 ppm with a standard deviation of 4.39 ppm after 60 min.

The amount leached in oxalic acid after 60 min was also determined and the results are shown in Figure 4.11(b). The average Fe ions leached was 120.79 ppm with a standard deviation of 20.80 ppm and the average Mn ions leached was 66.06 ppm with a standard deviation of 11.21 ppm.

Table 4. 4: WHO limit concentrations of metal ions this Table was adapted from (WHO, 1996, 2002, 2011; Chenniah et al. 2014).

Metal	WHO limit concentration (ppm)
Fe	0.3
Со	0.05
Cu	1.3
Mn	0.05



Figure 4. 11: Repeatability concentration of (a) The Fe ions in 2Fe1Mn in oxalic acid (b) The Fe ions in 2Fe1Mn during degradation.



Figure 4. 12: Repeatability concentration of Mn ions in 2Fe1Mn during the degradation and the dispersion of catalysts in oxalic acid.

4.1.6.2 Leaching of different catalysts

4.1.6.2.1 Leaching of Fe ions

The leaching of Fe ions during the degradation of MB and when the different catalysts were dispersed in oxalic acid are shown in Figure 4.13(a) and Figure 4.13(b), respectively. The statistical analysis of the leached metal ions was determined to verify if different amounts of the catalyst leached out. The difference between the leaching concentrations was calculated and compared to the 2σ of the repeatability test to account for the 95% confidence interval of the data. The results showed that the difference between the concentration of Fe ions in Fe & FeCo, Fe & FeMn and FeMn & FeCo catalysts was 0.81, 1.06 and 0.25 ppm, respectively after 60 min adsorption and 60 min catalysis, which is smaller than 2σ (1.08 ppm). This may indicate that the Fe & FeCo, Fe & FeMn and FeCo & FeCo catalysts have similar leached concentration values. The difference between the Fe and FeCu is 1.29 ppm after 60 min adsorption and 60 min catalysis which is larger than 1.08 ppm which may indicate that the FeCu catalysts leached the differently. The leaching trend was found to be in the following order Fe&FeCo≈Fe&FeMn≈FeCo&FeCu<Fe&FeCu. The Fe ions leached in the catalysts Fe, FeCo and FeMn were above the World Health Organization (WHO) limit see Table 4.4 but on the other hand, iron ions leached in FeCu heterogeneous oxide catalyst were below the WHO limit.

The Fe, FeCo, FeMn and FeCu catalysts were the dispersed in oxalic acid to determine leaching Fe ions under the same conditions see Figure 4.13(b). The difference between Fe and FeMn catalyst is 20.07 ppm which is less than 41.60 ppm for the 2σ. This indicated that these catalysts have similar leaching amounts. The difference between Fe & FeCo and Fe & FeCu is 111.30 and 67.14 ppm, respectively. The leached concentration between these catalysts is above the 2σ and this indicates that this catalyst have different leaching concentrations. The trend for the Fe ions leached under the same conditions is in the following order FeCo<FeCu<Fe≈FeMn. The trend of Fe ions leached during the degradation of MB and Fe ions when the catalyst is dispersed in oxalic acid are different. The difference between these trends might be due to the difference on the catalytic

activities of these catalyst. The catalysts that show higher catalytic activity might leach more than those with lower catalytic activity due to the intermediates that are produced during degradation. (See degradation pathways in Figure 2.2). Whereas when the catalysts are dispersed in oxalic acid different catalyst are exposed to the same conditions.

4.1.6.2.2 Leaching of other metal ions

Non-iron metal ion concentrations leached during the degradation of MB were also determined and the results are shown in Figure 4.14. The 2σ for other metal ions is 8.78 ppm. The Co (2.10 ppm) and Cu (0.36 ppm) ions in FeCo and FeCu catalysts leached the same since their concentration difference was 1.74 ppm which is below the 2σ . The difference between Mn ion leached from Mn and FeMn catalyst is 2.18 ppm which is below the 2 σ this indicated these two catalysts have similar leaching amounts. The Cu ions in Cu and FeCu and catalyst and the Co ions in Co and FeCo catalyst were above the 2σ indicating that these catalysts behaved differently. The trend for other metal ion leaching amounts was found to be increasing in the following order FeCu≈FeCo<Cu<FeMn≈Mn<Co. The leached metal ions for these catalysts were above the WHO limit, except for Cu ions in FeCu catalyst the WHO limit concentrations are represented in Table 4. 4.

Figure 4.14 shows the results of Fe, Co, Mn, Cu, FeCo, FeMn and FeCu catalysts when dispersed in oxalic acid. The repeatability results showed that the 2σ for other metal ions dispersed in oxalic acid is 22.42 ppm. The difference between the Mn ion from Mn and FeMn catalyst is 10.82 ppm indicating that Mn, FeCo and FeMn catalyst leached the same. The difference between Mn ions and Cu ions when using Mn and FeCu catalysts respectively is 30.38 ppm indicating that Mn, FeCu, Co and Cu catalysts behave differently. The trend for the leached metal ions was found to be in the following order Mn≈FeCo≈FeMn<FeCu<Co,Cu.



Figure 4. 13: The leaching metal ions (a) during degradation of MB for Fe metal ions (b) catalyst dispersed in oxalic for Fe ions.



Figure 4. 14: Leached metal ions during degradation and catalyst dispersed in oxalic acid for Co, Cu and Mn metal ions.

4.1.7 Radical determination

A series of radical detection experiments were conducted to identify the catalyst that produced more of hydroxyl radicals (active species) for the Fenton reaction and the degradation process (Upreti *et al.*, 2016). A higher florescence intensity relates to a higher

radical concentration. In Figures 4.15 and 4.16, radical experiments results suggested that FeCo catalyst showed the highest radical formation followed by FeCu, Fe and FeMn, respectively. In the catalyst FeCo and Fe, these radicals decreased after 20 min this phenomenon was attributed to the radical scavenging. A decrease in the radical production may lead to the lower degradation rate of MB. This was not observed in the case of the FeCu and FeMn catalysts while the radicals were increasing with time. Hence these catalysts showed higher catalytic activity.



Figure 4. 15: Radical determination of (a) Fe, (b) FeCo, (c) FeCu and (d) FeMn catalysts.



Figure 4. 16: Determination of radicals with different catalysts at different time (min) intervals.

4.1.8 Fenton and Fenton-like reaction

The degradation of methylene blue dye was performed as explained in Section 3.3 in Chapter 3 to test the catalytic activity of the heterogeneous oxide catalyst during the Fenton reaction. The first sample was taken few seconds after the addition of H_2O_2 and hence the initial percentage removal of MB for different catalysts start at different times.

4.1.8.1 Repeatability of the Fenton reaction

Repeatability studies (see Figure 4.17) were performed using the 2Fe1Mn bimetallic oxide catalyst. Each replicate was started with a new catalyst. The percentage removal is shown in Figure 4.17(a). Note that the percentage removal does not start at zero and this is due to the 60 min adsorption that took place before catalysis, as described in Chapter 3.3. An average percentage removal of 89.6% after 60 min with a standard deviation of 1.95 $\times 10^{-4}$ ppm⁻¹.min⁻¹ was obtained. The average R² for the pseudo-first

order kinetic model is 0.9550 and the average R² for the pseudo-second order is 0.9537. Therefore, the pseudo-first-order kinetic model fits better since the R² value is close to 1.0000. However, the results from Table 4.5 show that most reactions followed pseudo-second order and hence the pseudo-second order kinetic model was use for further studies.

In Figure 4.17(b) the pseudo-second order kinetic model is plotted and an average rate constant of 1.16 $\times 10^{-4}$ ppm⁻¹min⁻¹ with a standard deviation of 1.95 $\times 10^{-4}$ ppm⁻¹min⁻¹ was obtained.



Figure 4. 17: The repeatability of 2Fe1Mn bimetallic oxide heterogeneous catalyst (a) total percentage removal and (b) Second-order reaction kinetics.

4.1.8.2 Comparison of monometallic catalyst calcined by a conventional oven method and microwave.

The catalyst were calcined using conventional oven method (Conv) and the microwave (MW). Figures 4.19 and 4.20, and Table 4. 5 shows the influence of a calcination method on the total percentage removal during the Fenton reaction. The Co MW, Fe MW and Fe catalysts have similar k values since the difference between (0.00 ppm⁻¹.min⁻¹) and the k values of these catalysts is less than 2σ of the repeatability study (3.9 x10⁻⁴ ppm⁻¹.min⁻¹). On the other hand, the statistical difference between the Cu MW & Co Conv, Cu & Co MW and Mn MW is $3.95 \times 10^{-3} \text{ ppm}^{-1}$.min⁻¹, which is larger than 2σ and this may indicate that these catalysts have different catalytic activities. The degradation results showed that

Mn monometallic catalyst calcined by the microwave oven showed the highest degradation of the methylene blue dye compared to other monometallic catalysts.

4.1.8.3 Comparison of bimetallic catalyst calcined by conventional oven method and microwave.

The bimetallic oxide heterogeneous catalyst calcined by conventional oven (Conv) showed lower catalytic activity for the degradation of methylene blue compared to those calcined by the microwave (MW). The results are shown in Table 4. 5, 4.21 and 4.22. This was confirmed by the statistical analysis of these catalysts. The difference between the Fe conv and FeCo conv catalyst is $3.0 \times 10^{-4} \text{ ppm}^{-1}$.min⁻¹ after 60 min adsorption and 60 min catalysis which is smaller than $3.9 \times 10^{-4} \text{ ppm}^{-1}$.min⁻¹ (2σ of the repeatability study) this indicated that Fe conv and FeCo conv catalyst have similar catalytic activity. The difference between the Fe Conv & FeCu conv and Fe Conv & FeMn MW is larger than the 2σ indicating that the catalytic activity of these catalysts is different.

4.1.8.4 Comparison of monometallic and bimetallic catalyst calcined by microwave.

The monometallic and bimetallic oxide heterogeneous catalysts calcined by microwave irradiation power (MW) were compared. The bimetallic catalyst outperformed the Fe monometallic oxide catalyst as shown in Figure 4.23. The k values were extracted from Figure 4.13(d). The difference between the Fe & FeCo, Fe & FeCu and Fe & FeMn catalysts is 1.64×10^{-2} , 5.16×10^{-2} and 7.68×10^{-2} ppm⁻¹.min⁻¹ is larger than 3.9×10^{-4} ppm⁻¹.min⁻¹ (2 σ) which may indicate that the Fe, FeCu, FeCo and FeMn have different catalytic activity values. However, from Figure 4.13(d) it can be observed that the FeMn catalyst showed the highest activity for the degradation of MB compared to other bimetallic catalysts.

The degradation of MB dye follows both the pseudo-first-order and pseudo-second-order kinetics depending on the catalyst utilized in that experiment, as shown in Table 4. 5. Most of the data fitted pseudo second order better than pseudo first order based on the

higher R^2 values. The k values for the catalysts calcined by the microwave power was observed to be higher than the catalysts calcined by the conventional oven (Figure 12 and Table 4. 5).



Figure 4. 18: The pseudo-second order rate constant for the degradation of MB dye of the catalyst calcined by conventional heating and microwave irradiation.



Figure 4. 19: Comparison of monometallic oxide heterogeneous catalyst calcined by both conventional oven and microwave irradiation power on the oxidation of MB.



Figure 4. 20: Pseudo-second order of monometallic oxide heterogeneous catalyst calcined by conventional oven and microwave irradiation power.



Figure 4. 21: Comparison of Fe oxide monometallic catalyst and bimetallic oxide heterogeneous catalyst calcined by conventional oven and microwave on the oxidation of MB.


Figure 4. 22: Pseudo-second-order Fe oxide monometallic catalyst and bimetallic oxide heterogeneous catalyst calcined by conventional oven and microwave.



Figure 4. 23: Comparison between Fe monometallic with bimetallic catalysts calcined by MW.

Table 4. 5: R² of the pseudo first order and second order reaction kinetics and their k values and the percentage removal after Fenton reaction.

Conventional						Microwave				
Cataly st	Rate constant for a first order (min ⁻¹)	R ² for first order	Rate constant for second order (ppm ⁻ ¹ .min ⁻¹)	R ² for second order	Total % removal	Rate constant for a first order (min ⁻¹)	R ² for first order	Rate constant for second order (ppm ⁻ ¹ .min ⁻¹)	R ² for second order	Total % removal
Fe	2.9×10 ⁻³	0.8309	5.0×10 ⁻⁵	0.8325	48.40	4.0×10 ⁻³	0.9387	7.0×10 ⁻⁵	0.9531	47.50
Mn	3.5×10 ⁻²	0.8584	3.3×10 ⁻³	0.9426	73.00	2.2×10 ⁻²	0.9409	1.1×10 ⁻³	0.9896	89.05
Со	3.3×10⁻⁴	0.9169	5.0×10 ⁻⁵	0.9218	38.30	3.4×10⁻³	0.8032	6.0×10 ⁻⁵	0.8253	47.10
Cu	8.9×10 ⁻³	0.9691	2.0×10 ⁻⁴	0.9871	54.95	2.3×10 ⁻³	0.9360	3.0×10 ⁻⁵	0.9463	31.08
FeMn	2.4×10 ⁻²	0.9902	7.0×10 ⁻⁴	0.9596	81.80	2.7×10 ⁻²	0.9968	1.3×10 ⁻³	0.9389	89.60
FeCo	3.5×10 ⁻³	0.9209	6.0×10 ⁻⁵	0.9377	48.90	1.3×10 ⁻²	0.9279	3.0×10 ⁻³	0.8994	72.00
FeCu	3.5×10⁻³	0.7177	6.0×10 ⁻⁵	0.8749	66.50	1.9×10 ⁻²	0.9641	8.0×10 ⁻³	0.9883	85.90

4.1.9 Activation energy

Activation energy studies were conducted to determine the effect of temperature on the discoloration of MB. The study was also done to determine whether the FeMn bimetallic catalyst lowered the activation energy during the degradation of MB. The results obtained at three different temperatures (27, 40 and 50°C) using Fe and FeMn catalysts as shown in Figure 4.14. The results showed that an increase in temperature results in an increase in the total percentage removal of MB see Figure 4.24(a) for Fe catalyst and Figure 4.25(a) for FeMn catalyst. Li et al. (2016) observed a similar trend and attributed it to the dependency of the kinetic constants with the reaction temperature (Arrhenius law). Furthermore, the Arrhenius plot (lnk vs.1/T) shown in Figure 4.24 and Figure 4.24(b)) and FeMn (Figure 4.25(b)) catalysts was calculated to be 53.58 and 42.95 kJ·mol⁻¹, respectively. These results suggest that the oxidation of MB in an aqueous solution by this oxidation process requires a lower activation energy, which will lead to a higher rate constant (Arrhenius equation) and thus a higher rate for the Fenton reaction is expected.



Figure 4. 24: The plot of Fe catalyst for (a) Total percentage removal and (b) lnk vs. 1/T.



Figure 4. 25: The plot of FeMn catalyst for (a) Total percentage removal and (b) lnk vs. 1/T.

4.1.10 Discussion on the correlation between the crystallite size, ORP, H₂O₂ decomposition, radical formation and the rate constant.

The effect of the calcination method on the catalyst activity is shown in Figure 4.26. The catalyst calcined in the microwave had smaller particle sizes than the catalyst prepared using conventional calcination (see Figure 4.1). The crystallite size of a catalyst is expected to play a major role in the catalytic activity of a catalyst. Wan *et al.* (2016) studied the effect of size on catalytic activity and observed that the increase in the particle size of the nanoparticles led to a lower catalytic activity. The catalysts with the same chemical compositions but different crystallite sizes showed that there is an increase in the rate constant with a decrease in the crystallite size (see Figure 4.26). The catalysts, FeMn conv, FeCu MW and FeCo MW, have similar crystallite sizes but very different rate constants. This thus shows that not only the size but also the chemical composition has an influence on the rate constant.



Figure 4. 26: Crystallite size and k values of bimetallic and Fe monometallic catalyst. Blue legends: microwave calcination; orange legends: conventional calcination.

Fontecha-Cámara et al. (2016) reported that the leached metal ions during the Fenton reaction can act as homogeneous Fenton catalysts and therefore enhance the oxidation of methylene blue. The measured MB degradation or mineralization is thus catalysed by both Fenton mechanisms, heterogeneous and homogeneous. An increase in the amount of metal ions that leached is expected to increase the total rate of reaction. Figure 4.13 and Figure 4.14 presents the total metal ions concentration that leached. The results show that the FeMn bimetallic catalyst leaches the most compared to other bimetallic catalysts. Both Fe and Mn metal ions leach the most. On the other hand, the FeMn catalyst showed a higher percentage removal of up to 89.6% for the MB degradation. However, in this study it was realized in Figure 4.27 that the Co catalyst leached more compared to FeMn and yet the Co catalyst exhibited lower catalytic activity. Similarly, the Cu catalyst leached more compared to FeCo and FeCu and yet showed lower activity for the removal of MB. This indicates that the amount of leached metal ions did not play a major role during the Fenton reaction. No clear trend was observed in Figure 4.27(a) showing that the amount of leached metal ions does not explain the differences in the catalytic activities. This suggests that the higher catalytic activity of FeMn catalyst might not only be due to the leaching of this catalyst. However, when the leaching of metal ions was tested under the same conditions there was no linear relationship between the leached metal ion and the rate constant. This indicates that the leaching of metal ions was not the only effect that contributed to the catalytic activity of FeMn. The higher leaching of FeMn catalyst might be due to its smaller metal oxide particle size in comparison to the other catalysts. According to Rey et al. (2009), the smaller metal oxide particles leaches more than larger particles. The FeMn has the smallest nanoparticles as determined from XRD and it may explain why this catalyst leached the most.



Figure 4. 27: Leaching concentration during the (a) Fenton reaction vs the rate constant (b) when the catalysts were dispersed in oxalic acid vs the rate constant.

The ORP results showed that Fe, FeCo and FeCu catalysts exhibits a decrease in the ORP potential values. However, in Figure 4.28 it was observed that there was no linear relationship between the reaction constant and ORP potentials (mV). Although FeCu and FeCo showed the highest ORP with similar potential values there is a significant difference in rate constant of these catalysts. On the other hand, the FeMn catalyst showed a lower ORP potential and high catalytic activity. Lastly the Fe catalyst showed the lowest ORP potential and this catalyst exhibits the lowest catalytic activity.



Figure 4. 28: Correlation of the average ORP values with the rate constant of the Fenton reaction.

A higher radical concentration may be expected to lead to a higher rate of degradation of the methylene blue by the Fenton reaction. The radical determination experiments showed higher hydroxyl radical generation with the FeCo, Fe and FeCu catalysts than the FeMn catalyst but the FeMn catalyst had the higher Fenton rate of reaction. No correlation was found between the amount of radical formation and the rate constant as shown in Figure 4.29. The amount of radical formation does not explain the high activity of the MnFe catalyst. According to Ren *et al.* (2015) the more surface hydroxyl radical sites occupy in the binding surface of the catalysts the easier is the oxidation reaction to occur. Therefore, the highest activity of the FeMn catalyst might be due to the formation of radicals on the surface of the catalysts (Ren *et al.*, 2015) and not in the solution. This corresponds to the CV results since FeMn catalysts exhibit the highest current during oxidation and reduction indicating that this catalysts has more active sites on the surface and should be more capable of generating more radicals on the surface compared to the other catalysts. The lower activity of the catalysts of FeCo might be due to the generation of radicals in the reaction solution and not on the catalysts surface.



Figure 4. 29: Correlation of the radical determination intensity (at 20 min and non-identical λ) and with the rate constant of the Fenton reaction.

The decomposition of hydrogen peroxide to oxygen and water is an unwanted side reaction since the oxygen is a weaker oxidizing agent than hydroxyl radicals. A higher amount of this unwanted side reaction may lead to lower Fenton activity. No indirect correlation between the rate constant and the percentage decomposition were observed as shown in Figure 4.30. The FeMn catalyst showed the higher percentage decomposition of hydrogen peroxide to water and oxygen and the highest activity for the degradation of methylene blue compared to Fe, Co, Cu, FeCo and FeCu. Therefore the amount of decomposition of hydrogen peroxide to water and oxygen did not significantly negatively influenced the rate of the Fenton reaction. The FeMn catalyst showed the highest decomposition of H_2O_2 to O_2 relative to the other catalysts might be the reason for the FeMn to have the lowest radical generation intensity as well as the lower ORP potential values.



Figure 4. 30: Mass loss vs the rate of the reaction.

In addition, the redox pair potentials of Mn^{3+}/Mn^{2+} (1.51 V) (Costa *et al.*, 2006), Fe³⁺/Fe²⁺ (0.77 V), Co³⁺/Co²⁺ (1.81 V) (Garrido-Ramírez al., 2016) and Cu²⁺/Cu⁺ (0.17 V) (Wang *et al.*, 2016) of the monometallic catalyst suggests the rate at which these transition metals will be reduced or oxidized. The smaller the standard potential of the redox pairs the more they will oxidize and the slower the rate of the reaction since the active species will be generated at slower rate. Co has higher standard potential compared to Mn, and yet exhibited lower catalytic activity. The higher activity of manganese monometallic catalyst compared to that of cobalt monometallic catalyst was attributed to the smaller crystallite size as shown by XRD (Wan *et al.*, 2016). The XRD also showed the existence of Mn⁴⁺. (Tang *et al.*, 2019). Mn^{4+}/Mn^{3+} (0.15 V) oxidation states are unstable and therefore Mn⁴⁺ and Mn³⁺ will be reduced to the Mn²⁺ which is the most stable oxidation state of Mn.

Lastly, the presence of Co, Cu and Mn in the magnetite structure enhanced the oxidation of methylene blue. Similar results were observed in previous reports. Wang *et al.* (2015) attributed this to the synergistic effect of two metals in close contact. The half reaction in Appendix D shows that Cu⁺ can assist the reduction of Fe³⁺ to Fe² since this reaction is

thermodynamically favourable due to the potential difference of 0.6 v between Fe³⁺/Fe²⁺ (0.77 V) and Cu²⁺/Cu⁺ (0.17 V) and therefore the electron transfer is enhanced in FeCu by the redox pairs of Fe³⁺/Fe²⁺ and Cu²⁺/Cu⁺ (Wang et al. 2016; Garrido-Ramírez al., 2016). The opposite argument was used for cobalt and manganese than copper. In the case of cobalt and manganese the iron reduces the cobalt and manganese. The reduction of Co³⁺ or Mn²⁺, respectively by Fe²⁺ would be thermodynamically favourable due to the potential difference of 1.04 V between Fe^{3+}/Fe^{2+} (0.77 V) and Co^{3+}/Co^{2+} (1.81), and 0.73 V between Fe³⁺/Fe²⁺ (0.77 V) and Mn³⁺/Mn²⁺ (1.51 V). Therefore the electron transfer is enhanced in the case of FeCo and FeMn by the redox cycles of Fe³⁺/Fe²⁺ & Co³⁺/Co²⁺ and Fe³⁺/Fe² & Mn³⁺/Mn²⁺, respectively (Costa et al., 2006). However, in the case of Mn⁴⁺/Mn³⁺ and Fe³⁺/Fe²⁺ it is still not clear which metal ion assists the reduction of another metal ion as this depends on the standard reduction potential utilized. The explanations of Tang et al. (2019) and Nawaz et al. (2016) for the enhanced catalytic activity of the bimetallic catalyst contradict each other. Tang et al. (2019) reported that the standard reduction potential for Mn⁴⁺/Mn³⁺ is 0.15 V and the standard reduction potential for Fe³⁺/Fe²⁺ is 0.77 V these potentials indicate that the Mn³⁺ will donate electrons to Fe³⁺ and therefore Fe³⁺ will be reduced to Fe²⁺ due to the gain of electrons and Mn³⁺ will be oxidized to Mn⁴⁺ due to the loss of electrons. In contrast, Nawaz et al. (2016) reported that the standard reduction potential for Mn⁴⁺/Mn³⁺ is 0.95 V which is lower than that of Fe^{3+}/Fe^{2+} (0.77 V). Therefore in this case Fe^{2+} will assist in the reduction of Mn⁴⁺ to Mn³⁺. Various redox reaction equations are listed on the Appendix D showing that there are multiple ways in which the metal ions can be oxidised and reduced during the Fenton reaction.

In a bimetallic system there are two metal ions responsible for the activation of H_2O_2 to produce $\cdot OH$. However, these two metals also assist the reduction-oxidation cycle of each other to regenerate the Fenton reagent and therefore the rate at which hydroxyl radicals are produced is enhanced thus increasing the oxidation rate of MB. This enhanced reduction oxidation cycle is supported by the cyclic voltammetry results which showed a smaller peak to peak potential separation.

4.1.11. Conclusions

Monometallic (Fe, Co, Cu and Mn) and bimetallic (FeCu, FeMn and FeCo) heterogeneous catalysts supported on silica were prepared using the incipient wetness impregnation method. These catalysts were calcined either by conventional oven or microwave. The catalysts were used as Fenton-like catalysts on the oxidation of MB in water. Monometallic catalyst calcined by the conventional oven exhibited lower catalytic activity wherein catalyst calcined by microwave exhibited higher catalytic activity during the oxidation of MB (except for Cu catalyst). The Mn catalyst showed the highest catalytic activity for the monometallic catalysts for the degradation of MB. The bimetallic catalyst calcined by the conventional oven exhibited of MB compared to the bimetallic catalyst calcined by the conventional oven.

The higher Fenton activity was attributed to the smaller crystallite size of the catalyst calcined by the MW in comparison to the conventional oven which resulted in the larger active surface area of the catalysts. The monometallic catalysts calcined by MW had lower catalytic activities compared to the bimetallic catalysts calcined by the MW. The crystallite size as well as the chemical composition plays a role in the Fenton activity. The effect of the chemical composition could be attributed to the existence of a synergetic effect exhibited by the two metals in the bimetallic catalyst. No peak shifts in the XRD, and no binding energy changes in the XPS results were observed comparing the monometallic with the bimetallic catalysts which may indicate that mixed metal oxide crystals consisting both metals may not have formed.

The cyclovoltammetry results showed shifts in the reduction potentials, different peak to peak potential separations and different currents for the different catalysts which indicate that these catalysts exhibit different electrochemical properties. The FeMn catalyst showed the highest Fenton activity compared to all the catalysts. This catalyst produced fewer radicals, had a lower ORP and showed higher decomposition of H_2O_2 to O_2 compared to other catalysts and therefore a higher radical formation was not the reason for the higher activity of the FeMn catalysts.

The FeMn catalyst had the highest amount of leaching, smallest metal oxide particle size, a small peak to peak potential separation and the highest current in cyclic voltammogram in comparison to the other catalysts, and a lower activation energy in comparison to iron which may explain the higher activity of the catalyst.

Chapter 5: The effect of the Fe/Mn mass ratio on the catalytic activity of a Fenton reaction.

This section deals with the preparation of the FeMn catalyst by varying different mass ratios of Fe and Mn transition metals by keeping the total metal content constant. The following are the ratios that were studied: Fe, 2Fe1Mn, 1.5Fe1.5Mn, 1Fe2Mn, 0.5Fe2.5Mn, 0.35Fe2.65Mn, 0.25Fe2.75Mn and Mn. These catalysts will be calcined by microwave irradiation power.

5.1 Characterization

5.1.1 Catalyst characterization using XRD.

All the samples in Figure 5.1 displayed a broad peak at 23.2° and this peak was the indication of the presence of silica on the catalyst. A similar peak was also observed by Santos *et al.* (2016).The XRD results of the iron Fe oxide monometallic catalyst showed the existence of a single crystallographic phase corresponding to Hematite (Fe₂O₃) which was identified by the reflection in the XRD pattern with card number 00-033-0664.

The manganese monometallic oxide heterogeneous catalyst was also analysed and showed a single crystallographic phase corresponding to Akhtenskite (MnO_2), which corresponded to the diffraction peaks of MnO_2 with card number 00-024-0735 (see Figure 5.1.).

Figure 5.2 showed that as the percentage of manganese in different Fe-Mn catalysts increases, there was no significant peak shift observed. Since the peaks for iron oxide and manganese oxide are close to each other in the region 35-37° and the peaks are broad due to the smaller particle sizes, the peaks at a different position (between the iron oxide and manganese oxide peaks) observed for the 2Fe1Mn and 1.5Fe1.5Fe catalysts are more likely to be the combination of two peaks than shifts due to the formation of a mixed oxide. This is supported by the similar peak positions for the 1Fe2Mn, 0.5Fe2.5Mn,

0.35Fe2.65Mn and 0.25Fe2.75Mn catalysts as shown in Figure 5.2. Similar results were observed by Wang *et al.*, (2016). The sizes of the catalysts were also calculated (Table 5.1) and no trend was observed when varying different mass ratios of Fe-Mn.



Figure 5. 1: The XRD diffraction pattern for Fe, Fe-Mn at different mass ratios and Mn catalysts supported on silica.



Figure 5. 2: The manganese metal content and the peak positions.

Table 5. 1:	: Crystallite	sizes of	the prepare	d catalysts.
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Catalyst	Manganese content (%)	Sizes (nm)
Fe	0	10.6
2Fe1Mn	33	4.4
1,5Fe1,5Mn	50	6.7
1Fe2Mn	66	6.7
0,5Fe2,5Mn	83	6.8
0,35Fe2,65Mn	88	9.9
0,25Fe2,75Mn	92	10.2
Mn	100	5.0

5.1.2 Electrochemical characterization of Fe, Mn and 0.35Fe2.65Mn catalysts

During the Fenton reaction, the reduction of the metal oxides is considered the rate limiting step. Therefore, a higher reduction potential (less negative) may indicate that the metal oxide will reduce easier. The 0.35Fe2.65Mn catalyst was chosen to be studied its electrochemical properties since it showed the highest catalytic activity. However, Fe and Mn catalysts were chosen since they are present in 0.35Fe2.65Mn catalyst. The metal supported catalysts gave peaks at different potentials with the 0.35Fe2.65Mn catalyst showing the highest reduction potential peak (Epc) of -0.17 (V). A decrease in the potential of the Mn and Fe electrode was obtained at -0.20 and -0.18 (V) in the CV curve, respectively. The difference in the potential values of these catalysts may be attributed to the low or fast electron transfer rate and the activity of different catalysts (Ren *et al.*, 2015). The cell potential (Emid) of the 0.35Fe2.65Mn catalyst is also slightly lower than the Mn and Fe catalyst.

The 0.35Fe2.65Mn catalyst showed the highest intensity current peak compared to the other catalysts (Table 5.2) which may indicate more active sites on the surface of the catalysts. The trend was found to be in the following order Mn<Fe<0.35FeMn. According to Ren *et al.*, (2015) the difference in the activity of these catalysts depend on the chemical activity and the capacity of the transitive metal ions in the process of the reduction and oxidation. Wang *et al.* (2016) attributed this difference to the electrochemically accessible sites on the surface of the catalysts.

The electron transfer kinetics determines if a reaction is electrochemical reversible (Elgrishi *et al.*, 2017). For an electrochemical reversible reaction, the ratio of the current anode (Ia) to current cathode (Ic) must be equal to 1.00 (Elgrishi *et al.*, 2017). The electron transfer for all the catalysts was chemically irreversible since the ratio is less than 1 as presented in Table 5.2. The reversibility trend was in the following order Mn<Fe<0.35Fe2.65Mn. In addition, the electron transfer for all the catalysts was electrochemically irreversible since the peak to peak separation is larger than 57 mV as presented in Table 5.2 indicating that the rate of oxidation-reduction is slow.

The smaller peak separation for the 0.35Fe2.65Mn catalyst in comparison to the other catalysts may indicate the continuous oxidation-reduction process that happens during the Fenton reaction may be faster for the 0.35Fe2.65Mn catalyst leading to a more active catalyst.

Catalyst	la	lc	la/lc	Ера	Ерс	Epc -	Emid(Epa+
	(mA)	(mA)	(mA)	(mV)	(mV)	Epa (mV)	Epc)/2
							mV)
Fe	0.034	0.041	0.829	-36.90	-227.00	190.10	-131.95
0.35Fe2.65Mn	0.043	0.049	0.878	-85.00	-173.34	88.34	129.17
Mn	0.028	0.035	0.800	-56.00	-202.70	146.70	129.35

Table 5. 2: CV potentials for different catalysts



Figure 5. 3: Cyclic voltammograms of Fe, 0.35Fe2.65Mn and Mn catalysts.

5.2 ORP results

5.2.1 Repeatability using the 0.35Fe2.65Mn catalyst

These experiments were carried out by immersing the ORP probe into the Fenton system. Repeatability of the ORP was carried out with the catalysts 0.35Fe2.65Mn and the results are shown in Figure 5.4. The average potential for the five experiments was calculated to be 241.46 mV with a standard deviation of 1.98 mV (2 standard deviation of 3.96).



Figure 5. 4: The ORP repeatability using 0.35Fe2.65Mn catalyst.

5.2.2. The measurement of ORP using different catalyst.

The results from Figure 5.5 suggested the 0.5Fe2.5Mn and 0.25Fe2.75Mn catalysts have the same oxidation reduction potential since they exhibit a difference that is less than the 1.98 (2 standard deviation). However, all the other catalysts have different oxidation reduction potentials as they exhibit a larger difference than 2-standard deviation.

From Figure 5.5 the ORP results show that with Mn, 0.5F02.5eMn, 0.35Fe2.65Mn and 0.25Fe0.75Mn catalysts there was a decrease on the ORP values (between 0 and 30

min) after this interval there was no further decrease. However, this was different in the case of 2Fe1Mn catalyst as this catalyst exhibited a slight increase in the ORP between 2.5 and 60 min. According to Kim *et al.* (2004) the increase in the ORP potential indicate the existence of the Fenton reagents that increase the radical formation in the reaction. Lastly, the 1.5Fe1.5Mn and 1Fe2Mn catalysts showed a decrease in the ORP potentials between 0 and 20 min. However, after 20 min there was an increase in the ORP potentials (20 to 30 min) after there was no further increase or decrease in the potential. A sharp decrease indicated the completion of the Fenton reagent but this was not observed in Figure 5.5 (He *et al.*, 2009).



Figure 5. 5: The ORP measurements for the results.

5.3 Radical determination

The radical determination results in Figures 5.6 and 5.7 shows that 0.35Fe2.65Mn catalyst generated more radicals compared to the Mn catalyst. The produced radicals by both reactions increased with time. In contrast, the Fe catalyst produced the highest

radical concentration compared to Mn and 0.35Fe2.65Mn catalyst; however, the concentration of radicals decreased with time.



Figure 5. 6: Radical determination of (a) 0.35Fe2.65Mn and (b) Mn catalyst.



Figure 5. 7: Radical determination of Fe, 0.35Fe2.65Mn and Mn catalyst.

5.4 Decomposition of hydrogen peroxide to oxygen (Mass loss) 5.4.1 Mass loss repeatability using 0.35Fe2.65Mn catalyst

The mass loss repeatability studies were performed using the 2Fe1Mn bimetallic catalyst. Five experimental replicates were performed and each run was started with a new catalyst. The results are shown in Figure 5.8. The average final mass was 18.70 g with a standard deviation (σ) of 1.00 g obtained after 60 min. The 2 σ was calculated to be equal to 2.00g.



Figure 5. 8: Decomposition of H₂O₂ to O₂ using 0.35Fe2.65Mn mass ratio.

5.4.2 Mass loss with different catalysts

From Figure 5.9 the results show that the statistical difference between Fe and 0.5Fe2.5Mn catalysts is 1.90 g which is smaller than the 2.00 g (2σ). This suggests that all catalysts found between these two catalysts decomposes H₂O₂ to O₂ in a similar manner. However, the above-mentioned catalysts decomposed H₂O₂ to O₂ differently compared to the Mn catalysts, since the difference between these catalysts was above the 2 σ . These results also show that 1.5Fe1.5Mn and 0.35Fe2.65Mn catalysts showed

similar H_2O_2 decomposition mass values (statistical difference is 1.65 g). On the other hand, these catalysts showed a different H_2O_2 decomposition compared to 0.25Fe2.75Mn catalyst with a statistical difference of 2.65 g. The observed trend for these experiments was such that when the Mn mass ratio is increased in a bimetallic catalyst there was an increase in the decomposition of H_2O_2 to O_2 .



Figure 5. 9: Decomposition of H₂O₂ to oxygen using different mass ratio catalysts.

5.5 Leaching

5.5.1 Repeatability

Repeatability studies (see Figures 5.10, 5.11 and 5.13) were performed using the 0,35Fe2,65Mn bimetallic oxide catalyst. Each run was started with a new catalyst. The average concentration and the standard deviation were calculated and presented in Table 5.3.



Figure 5. 10: Leaching repeatability of (a) Leaching of the catalysts Fe ion using oxalic acid.



Figure 5. 11: The leaching of catalysts for Fe during the degradation of methylene blue.



Figure 5. 12: The leaching of the catalyst for Mn during the degradation and using oxalic acid.

Experiment and metal ion	Mean	σ	2σ
Fe oxalic acid	92.64	0.22	0.44
Fe degradation	0.72	1.06	2.12
Mn oxalic acid	61.60	1.48	2.96
Mn degradation	48.89	2.20	4.40

5.5.2 Leaching test from different mass ratios

5.5.2.1 Fe leaching metal ions

Leaching of Fe ions from the catalysts prepared by varying different mass ratios of Fe and Mn during the Fenton reaction was determined. The results are presented in Figure 5.13. The results obtained from these experiments exhibit a statically difference of 1.44 ppm which is less than 2σ . Statistically this implies that these catalysts showed similar Fe ion leaching concentrations. The leaching test was also done under the same conditions (catalysts dispersed in oxalic acid). The results from Figure 5.14 shows that these catalysts have different leaching concentrations since the statistical difference between Fe and 2Fe1Mn is larger (20.07 ppm) than 2σ as shown in Table 5.2. The trend to in found be the following order was 2Fe1Mn>Fe>0.5Fe2.5Mn>1.5Fe1.5Mn>1Fe2Mn>0.35Fe2.65Mn>0.25Fe2.75Mn.

The leached Fe ion concentrations compares well to the limits set by the World Health Organisation (WHO) where the Fe limit is 0.3 ppm (see Table 4.3), and the results were all above the limit.

5.5.2.2 Leaching of Mn ions

Leaching of Mn metal ions during degradation were also determined (Figure 5.15). The statistical difference between Mn, 2Fe1Mn, 0.5Fe2.5Mn, 0.35Fe2.75Mn and 0.25Fe2.75Mn is less than 2σ (4.40 ppm). This suggested that the above-mentioned catalyst have similar leached concentrations. However, the difference between Mn, 1.5Fe1.5Mn, 1Fe2Mn0.5Fe2.5Mn is larger than 2σ and this implies that these catalysts have different leached concentrations. The trend measured to be in the following:

Mn=2Fe1Mn<1Fe2Mn<1.5Fe1.5Mn<0.5Fe2.5Mn=0.25Fe2.75Mn=0.35Fe2.65Mn.

When the catalysts were dispersed in oxalic acid (Figure 5.15), the results showed that 0.5Fe2.5Mn, 0.35Fe2.65Mn, and 0.25Fe2.75Mn have similar leached Mn concentrations when compared to 2σ . On the other hand, Mn, 2Fe1mn, 1.5fe1.5Mn 1Fe2Mn and

0.5Fe2.5Mn catalysts showed different Mn leaching concentrations. The leaching trend was observed to be in the following order:

Mn<2Fe1Mn<1.5Fe1.5Mn<0.25Fe2.75Mn=0.5Fe2.5Mn=0.35Fe2.65Mn.

The leached Mn ions after degradation and after being dispersed in oxalic acid were above the WHO limit as presented in Table 4.4.



Figure 5. 13: Leaching concentrations of Fe ions during the degradation of methylene blue.



Figure 5. 14: Leaching concentrations of Fe ions using oxalic acid.



Figure 5. 15: Leaching concentrations of Mn ions when using oxalic acid and during the degradation.

5.6 Degradation of MB

5.6.1 Degradation repeatability using 0,35Fe2,65Mn.

Repeatability results in

Figure 4. 17 were performed using the 0,35Fe2,65Mn bimetallic oxide catalyst. Each replicate was started with a new catalyst. The percentage removal of methylene blue is shown in Figure 5.16. Note that the percentage removal does not start at zero and this is due to 60 min adsorption that took place before catalysis, as described in Chapter 3.4. An average percentage removal of 94.6% after 60 min with a standard deviation of 5.83 $\times 10^{-3}$ min⁻¹ was obtained. The R² for the pseudo-first order is close to one compared to the R² for the pseudo-second order. Therefore, the pseudo-first order kinetic model is more favourable. In Figure 5.17, the pseudo-first-order kinetic model is plotted and an average rate constant of 4.30 $\times 10^{-2}$ min⁻¹ with a standard deviation of 5.83 $\times 10^{-3}$ min⁻¹ was obtained.



Figure 5. 16: Degradation repeatability experiments for the total percentage removal of MB using the 0.35Fe2.65Mn catalyst.



Figure 5. 17: Pseudo-first-order reaction kinetics for the repeatability experiments.

5.6.2 Degradation of methylene blue with different catalyst ratios

The degradation of methylene blue was done in order to determine the catalytic activity of the catalysts prepared by varying different mass ratios. The results are displayed in Figures 5.18 and 5.19. Mn and 2Fe1Mn catalysts have similar catalytic activities since the difference between these catalysts is 0 which is less than 0.011 (2 standard deviation). The difference between Fe, Mn, 0.25Fe2.75Mn, 0.35Fe2.65Mn, 1Fe2Mn and 05Fe2.5Mn catalysts is larger than 2 standard deviations and this implies that these catalysts have different catalytic activities.



Figure 5. 18: The percentage removal for the degradation of methylene blue using the different catalysts of different ratios of each metal supported on silica in the presence of H_2O_2 .



Figure 5. 19: Pseudo first order reaction kinetics.

The degradation of methylene blue followed the first order reaction as seen in Table 5 where the R² for the first order is close to 1 whereas the R² for the second order is lower than 1. The reaction rates of each catalyst were also calculated as presented on Table 5.4 which shows that the reaction rates of Fe and Mn catalysts are very low while the bimetallic catalyst displayed higher reaction rates. This is also due to the effect of the synergy of the two incorporated catalysts which lead to catalytic activities higher than what was expected due to the combined effect of the metal oxides. This phenomenon can be observed in Figure 5.20, where the Fe and Mn monometallic catalysts display lower catalytic activities compared to the bimetallic catalysts. It can also be observed that the increase in the manganese metal content increased the catalytic activity of the bimetallic catalysts.

Catalyst	k (min ⁻¹)	R ² for first	k (ppm ⁻¹ min ⁻	R ² for second
		order reaction	²)	order reaction
Fe	4 x10 ⁻³	0,9385	7 x10 ⁻⁵	0,9531
2Fe1Mn	2.7 x10 ⁻²	0,9968	1.3 x10 ⁻³	0,9390
1.5Fe1.5Mn	4.3 x10 ⁻²	0,9929	5.1 x10 ⁻³	0,8403
1Fe2Mn	4.8 x10 ⁻²	0,9973	5.1 x10 ⁻³	0,8732
0,5Fe2,5Mn	5.6 x10 ⁻²	0,9759	6.2 x10 ⁻³	0,8625
0,35Fe2,65Mn	6.0 x10 ⁻²	0,9770	4.5 x10 ⁻³	0,9150
0,25Fe2,75Mn	5.8 x10 ⁻²	0,9941	3.9 x10 ⁻³	0,9437
Mn	3.5 x10 ⁻²	0,9409	1.1 x10 ⁻³	0,9896

Table 5. 4: The reaction rates and R^2 of each catalyst.



Figure 5. 20: The effect of increasing the fraction of Mn and decreasing that of Fe on the bimetallic catalyst.

5.7 Discussion on the correlation between the crystallite size, ORP, H₂O₂ decomposition, radical formation and the rate constant.

Previous studies reported that the particle size of the catalyst plays an important role on the catalytic activity of a Fenton reaction (Chen et al., 2017; Wan et al., 2016). Chen et al. (2017) reported that magnetic nanoparticles with a smaller particle size showed higher catalytic activity on the removal of Rhodamine B than the other. In this study, it was observed that there was no linear trend between the particle size and the rate constant and this may be explained by the different chemical compositions of the catalysts. In Figure 5.21 it was observed that the 2Fe1Mn catalyst showed the smallest crystallite size and yet exhibited lower catalytic activity compared to the 0.35Fe2.65mn catalyst with a larger particle size. This indicates that in this study it was not only the particle size that influenced the rate of the reaction but that the chemical composition plays an important role. Wang et al. (2016) investigated the effect of Fe/Cu mass ratio on the catalytic activity of a Fenton degradation of a dye. From their results they observed that the catalytic activity of a Fenton reaction depends highly upon the Fe/Cu ratio. They further observed that the optimum Fe/Cu mass ratio was 2Fe6Cu. Similarly, in Figure 5.13 it was observed that increasing the Mn fraction and decreasing the Fe fraction increased the Fenton activity. Wang et al. (2016) attributed this phenomenon to the synergistic effect of a bimetallic catalyst.



Figure 5. 21: Crystallite size and k values of different Fe:Mn bimetallic catalyst at mass ratios.

There was no linear correlation observed from Figure 5.22 on the radical generation and the rate constant. Since Fe catalysts showed the highest radical formation and lower rate constant compared to 0.35Fe2.65Mn that showed the lower radical formation and a high catalytic activity.



Figure 5. 22: Correlation of the radical determination intensity (at 20 min and at a wavelength of 409.87 nm) and with the rate constant of the Fenton reaction.

The other effect that might increase the catalytic activity of a Fenton reaction is the leaching of the metal ions in the solution (Pariente *et al.*, 2015; Pariente *et al.*, 2015). Fontecha-Cámara *et al.* (2016) reported that the leaching of metal ion io the solution can act as a homogeneous catalyst. The catalytic activity of a Fenton reaction might be enhanced since it is catalysed by two reaction mechanisms (heterogeneous and homogeneous). Herein it was observed in Figure 5.23 that there was a linear correlation between the rate constant and the leaching of metal ions during the degradation of MB. However, when the leaching of metal ions was tested under the same conditions (same oxalic acid concentration) there was no linear relationship between the leached metal ion and the rate constant. This may indicate that the higher activity of the catalysts, causing higher concentrations of acids for the degraded MB (see degradation pathway of MB in Section 2.2) resulted in the higher amounts of leaching. One may speculate that it was thus not the higher amounts of leaching that resulted in the higher catalytic activity due to the contribution of homogenous catalysis.



Figure 5. 23: Leaching concentration during the (a) Fenton reaction vs the rate constant (b) when the catalysts were dispersed in oxalic acid vs the rate constant.

The decomposition of H_2O_2 to O_2 and water is unwanted since it may lead to the lower catalytic activity of the Fenton reaction if the concentration of hydrogen peroxide is significantly decreased due to the unwanted side reaction. However, the mass loss experiments do not explain the highest catalytic activity of 0.25Fe2.65Mn ratio. This catalyst exhibits a high mass loss percentage and highest rate constant than the other catalysts (Fe, 2Fe1Mn, mn, 1.5Fe1.5Mn, 1Fe2Mn and 0.5Fe2.5Mn). Therefore, in this case the unwanted side reaction did not affect the rate constant for the Fenton reaction, and one may thus deduce that the concentration of the H₂O₂ was not significantly affected due to the decomposition of H₂O₂ to O₂ and H₂O. The correlation observed in Figure 5.24 may be explained by the fact that the same catalytic sites responsible for the Fenton reaction.


Figure 5. 24: Correlation between the mass loss and the rate of the reaction.

In Figure 5.25 it was observed that there was no linear relationship between the reaction constant and ORP potentials (mV). Since Fe and 1Fe2Mn showed the highest ORP with similar potential values and yet there is a significant difference in rate constant of these catalysts. On the other hand, 0.35Fe2.65Mn catalyst showed a lower similar ORP potential and high catalytic activity this corresponds to the results obtained by He *et al.* (2009). Lastly the Mn catalyst showed the lowest ORP potential and this catalyst exhibits the lowest catalytic activity.



Figure 5. 25: Correlation of the average ORP values with the rate constant of the Fenton reaction.

5.8 Conclusions

The results showed that the crystallite size of the catalyst did not play a major role on the catalytic activity when the Fe/Mn mass ratios were varied and that the chemical composition of the catalyst caused the differences in the catalytic activity. A synergistic effect between the Mn and Fe was observed since the bimetallic catalysts had an activity higher than the combined effect of the individual metal oxides. The synergistic effect may have been due to enhanced oxidation-reduction behaviour of the bimetallic catalysts during the Fenton reaction as indicated by the cyclovoltammetry results. The current was higher which indicated more catalytic active sites. The reduction potential was higher (less negative) for the bimetallic catalyst and the peak separation was smaller which may indicate an enhanced oxidation-reduction cycle which may explain the higher catalytic activity. Homogenous catalysts that leached more and had a higher catalytic activity. However, based on the leaching tests at similar oxalic acid concentration it was argued that the higher activity of the catalyst leads to higher concentrations of acid intermediates from the MB degradation causing an increase in leaching.

The ORP potential and radical formation did not show a linear correlation with the rate constant, since 0.35Fe2.35Mn catalyst showed the lowest ORP potential and exhibited a higher catalytic activity than the Fe catalyst. Lastly the 0.35Fe2.35Mn catalyst showed lower radicals produced compared to the Fe catalyst. Therefore, the ORP and radical formation do not explain the differences between the catalysts.

Chapter 6: The effect of microwave irradiation time and power.

The size of the metal oxide particles supported on silica depends on the irradiation time and microwave power (Reubroycharoen *et al.*, 2007). In this section the effect of irradiation time and the microwave power on the preparation 0.35Fe2.65Mn and their effect on the catalytic activity during the Fenton reaction was studied.

6.1 XRD

The microwave calcination irradiation times of 10, 20 and 30 minutes were tested for three power settings of 600, 700 and 800 W.

The peaks in the XRD patters in Figure 6.1 could be assigned to MnO₂ (00-024-0735). Very small broad peaks for MnO₂ were observed and the calculated sizes are shown in Table 6.1. No diffraction peaks for iron oxide was observed. This may be attributed to the low iron oxide loading and small iron oxide particles (Wang *et al.*, 2015).

Figure 6.2 and Table 6.1 shows that a microwave power of 600W yields the smallest manganese oxide nanoparticles for most of the catalysts. There is an increase in the manganese oxide particle size with an increase in the radiation time for the 700W and 800 W microwave power settings as seen in Figure 6.2 and Table 6.1. However, when the lowest microwave power of 600 W was used, the increase in radiation time did not have a significant effect on the particle size of the catalyst.

These observations may be explained by an increase in the kinetic energy when the temperature and collision between the manganese oxide particles led to agglomeration and sintering of the particles (Parida and Parija., 2006; Mousavi *et al.*, 2015).



Figure 6. 1: The XRD diffraction pattern for catalysts prepared using different microwave calcination procedures.

Catalyst	10 min	20 min	30 min
600 W	11.03	12.97	12.17
700 W	15.25	18.21	21.07
800W	10.23	13.53	18.65

Table 6. 1: XRD crystallite size (nm) calculated at 37°C.



Figure 6. 2: The effect of the microwave time and power during calcination.

6.2 Fenton reaction

The results for the catalytic activity during the degradation of MB are displayed in Figure 6.3. The percentage removal of MB after 1 hour was about 93.3% for all the catalysts as shown in Figure 6.3. However, the rate at which these reactions took place was different (Figure 6.4). The data for most of these experiments fit the pseudo first order better than pseudo second order based on the higher R² values as shown in Figure 6.4 and Table 6.2. Most of the catalysts calcined at 600 W were more active catalyst than the catalysts calcined at higher microwave powers. This can be explained by the catalyst calcined at 600W having the smallest crystallite sizes (see Figure 6.2). Figure 6.5 shows that the catalytic activity of a Fenton reaction decreases with increasing calcination time (min). A similar trend was observed by Reubroycharoen *et al.* (2007). These observations were attributed to an increase in the crystallite size of the particles as the irradiation time was increased. In Figure 6.6 the effect of the microwave time and power during calcination are combined and it shows that there is an inverse correlation between the size and the activity of the catalysts with the same chemical composition.



Figure 6. 3: The degradation of MB total percentage removal.



Figure 6. 4: Pseudo first order reaction kinetics.



Figure 6. 5: Rate constant of different catalysts at different time intervals.



Figure 6. 6: Effect of crystallite size on the rate constant (activity) of the catalysts.

Catalyst	Rate constant	R ²	Rate constant	R ²
power and	first order	first order	second order	second order
time	(min ⁻¹)		(ppm.min ⁻²)	
600W 10 min	4.9 x10 ⁻²	0.9516	5.2 x10 ⁻³	0.9388
600W 20 min	4.2 x10 ⁻²	0.9730	3.1 x10 ⁻³	0.9250
600W 30 min	4.1 x10 ⁻²	0.9701	2.7 x10 ⁻³	0.9532
700W 10 min	4.0 x10 ⁻²	0.9725	2.6 x10 ⁻³	0.9336
700W 20 min	3.8 x10 ⁻²	0.9572	2.1 x10 ⁻³	0.9376
700W 30 min	3.5 x10 ⁻²	0.9870	2.1 x10 ⁻³	0.9276
800W 10 min	5.0 x10 ⁻²	0.9879	1.1 x10 ⁻²	0.8910
800W 20 min	3.9 x10 ⁻²	0.8647	3.0 x10 ⁻³	0.9115
800W 30 min	3.6 x10 ⁻²	0.9278	2.2 x10 ⁻³	0.9913

Table 6. 2: R² of the pseudo first order and second order reaction kinetics and their k values (min⁻¹).

6.3 Conclusions

Most of the catalyst calcined at 600 W yielded more active catalysts than those calcined at higher microwave powers. This may be explained by the smaller metal oxide particles than formed at lower microwave power. An increase in the calcination time at 700W and 800W increased the metal oxide particle size and decreased the activity of the catalyst. An increase in calcination time at 600W did not affect the catalyst significantly. There is an inverse correlation between the metal oxide size and the activity of the catalysts with the same chemical composition.

Chapter 7: Conclusions and Recommendations

7.1 Conclusions

The manganese oxide catalyst was more active than the iron-, cobalt- and copper oxide monometallic catalysts and the FeMn oxide catalysts were more active than the FeCo, FeCu oxide bimetallic catalysts. The iron manganese ratio was optimised and the 0.35Fe2.65Mn was most active of all the catalysts.

The microwave calcination yielded catalysts with smaller crystallite sizes in comparison to conventional oven calcination. Keeping the chemical composition of the catalysts constant, the microwave calcined catalysts were more active than the catalysts calcined in a conventional oven and it can be explained by the smaller metal oxides that formed using microwave calcination. The microwave time and power were optimised keeping the chemical composition of the catalyst the same. An increase in the microwave calcination time and power resulted in an increase in the particle size and a decrease in the catalytic activity. However, when catalysts with different chemical compositions were compared, i.e. different metal oxides, different bimetallic combinations and different iron/manganese ratios, it was observed that the crystallite size was not the only factor that influenced the rate constant when the chemical composition varied. This indicates that the catalytic activity of a Fenton reaction was influenced by both crystallite size and the chemical composition.

ORP, amount of radical formation, metal ion leaching and mass loss due to the unwanted decomposition of hydrogen peroxide to oxygen did not explain the differences in the catalytic activities of the various bimetallic catalysts. The cyclic voltammetry results showed that the FeMn bimetallic catalyst had the highest current with a small difference between the peak potentials which may indicate more active sites and that the oxidation-reduction cycle of the metal ions is more facile for the FeMn bimetallic catalyst in comparison to the other catalysts. The cyclic voltammetry results may thus explain the higher activity of the FeMn catalyst. The addition of manganese to the iron catalyst,

decreased the activation energy of the Fenton reaction, which explains the increase the rate of reaction for the iron manganese bimetallic catalysts in comparison to the monometallic iron oxide catalyst.

7.2 Recommendations

The following recommendations are proposed for future studies. The preparation of a FeMn bimetallic catalyst using a single step method so as to improve the metal support interaction is recommended. Botas *et al.* (2010) reported on the preparation of Fe₂O₃/SiO₂ catalysts via a single step method using co-condensation of silica (TEOS) with the iron precursor as well as a two-step method where iron chloride was impregnated on a prepared silica support. Botas *et al.* (2010) reported that the catalyst prepared by a single step method showed a lower metal leaching concentration than the catalyst prepared using impregnation. Furthermore, the preparation of the support material from bio-waste instead of using commercial support is been recommended to lower the cost of these catalysts.

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Appendix A

Catalyst preparation

Aim is to prepare a 5g catalyst that contains 10% metal content:

mass of Fe =
$$\frac{10\%}{100\%}$$
 X 5g

= 0.5g mass of Fe

Calculate mol of Fe:

$$n = \frac{m}{Mm}$$

$$n = \frac{0.5g}{55.845 \text{ g/mol}}$$

= 0.008953 mol Fe

Convert mole of Fe to mole of Fe_2O_3 using the mol ratio:

1 mol of Fe:2 mol of Fe in Fe_2O_3 therefore:

mole of Fe₂O₃ =
$$\frac{\text{mole Fe}}{2}$$

= $\frac{0.008953 \text{ mol}}{2}$
= 0.004477 mole Fe₂O₃

Calculate the mass of Fe₂O₃:

 $m = n \ge Mm$

= 0.004477 mol x 159.687

 $= 0.714867 \text{ g of } \text{Fe}_2 \text{O}_3$

Calculate the mass of silica:

 $m = total mass of catalyst - mass Fe_2O_3$

= 5g - 0.714867g

= 4.28513g

Calculate mass of iron (III) nitrate nonahydrate using the mole ratio:

1 mole of Fe : 1 mole of Fe in $Fe(NO_3) \cdot 9H_2O$:

 $m=n \mathrel{x} Mm$

m = 0.008953 x403.999g/mol

m = 3.6171g

Calculate volume of H₂Oto be added:

Pore o silica = $1.15 \text{ cm}^3\text{g}^{-1}$

V = pore x m of silica

 $= 1.15 \text{ cm}^3/\text{g} \text{ x} 4.2851 \text{g}$

4.93 cm3

Appendix B Degradation of MB

Dilution factor is given as:

 $C1 \ge V1 = C2 \ge V2$

(0.104 mg / L)(0.1 L) = C2 (0.001 L)

 $C2 = \frac{0.0104 \text{ mg}}{0.001 \text{L}}$

C2 = 10.04 mg/L

The percentage removal is given as:

% removal =
$$\frac{(\text{Co}-\text{Ce})}{\text{Co}}$$
 X 100%
= $\frac{(100 \text{ mg/L} - 10.4 \text{ mg/L})}{100 \text{ mg/L}}$ X 100%
= 89.60 %

Reaction kinetics

Integrated rate laws (McMurry et al., 2015)

If the concentration of a reactant remains constant because it is in great excess with respect to the other reactant, its concentration can be included in the rate constant to simplify the rate equation, obtaining pseudo-first-order or pseudo second order rate equation. For example, during the Fenton reaction $[H_2O_2] + [MB] \rightarrow [H_2O] + [CO_2]$ the rate for this reaction is given by: rate=k[MB]^x[H₂O₂]^y. The H₂O₂ has a high concentration compared to MB such that its consumption is insignificant. Therefore, it can be assumed that the concentration of the H₂O₂ remains constant throughout the reaction. The rate of can be assumed to be rate=k_{abs} [MB]^x. The order of the reaction can be determined by performing some experiments (McMurry *et al.*, 2015).

Pseudo-first-order:

Pseudo – first – order = Ln[MB]

$$\frac{-d[MB]}{dt} = k[MB]$$

$$\int \frac{d[MB]}{[A]} = \int -kdt$$

$$\int \frac{1}{[MB} \cdot d[MB] = -k \int dt$$

$$\int_{0}^{t} \ln[MB]_{t} - \ln[MB]_{0} = -k(t - o)$$

$$\ln[MB]_{t} - \ln[MB]_{0} = -kt$$

$$\ln[MB]_{t} = -kt + \ln[MB]_{0}$$
Therefore Y = mx + c
Pseudo-second-order:
Pseudo-second – order = $\frac{1}{MB}$
Rate = k[MB]²

$$\frac{-d[MB]}{dt} = k[MB]^{2}$$

$$\int \frac{d[MB]}{[MB]^{2}} = \int -k \cdot dt$$

$$\int \frac{1}{[MB]^{2}} \cdot d[MB] = -k \int dt$$

$$\int_{0}^{t} \frac{-1}{[MB]} = -k \int_{0}^{t} t$$

$$\frac{-1}{[MB]_t} - \left(-\frac{1}{[MB]_0} = -k(t-o)\right)$$
$$\frac{1}{[MB]_t} - \frac{1}{[MB]_0} = kt$$
$$\frac{1}{[MB]_t} = kt + \frac{1}{[MB]_0}$$
$$y = mx + c$$

Therefore m = k

Appendix C

XRD crystallite size was calculated with Scherrer equation:

$$D = \frac{k \cdot \lambda}{\beta \cos \theta}$$

= $\frac{(0.9 \text{ nm})(0.015418 \text{ nm})}{(0.013673 \text{ rad})(\cos\left(\frac{0.583818 \text{ rad}}{2}\right))}$

= 10.60 nm

Where, D = Average Crystallite size, β = Line broadening in radians, θ = Bragg angle, λ = X-Ray wavelength

Appendix D

Redox potentials for half reaction for the metal ions were obtain from Markmary *et al.* (2015) and for the radicals were obtained from Armstrong *et al.* (2013).

For Fe metal ion

Fe ³⁺ +	$e^{-} \rightarrow Fe^{2+}$	+0.77 V
-	$(Fe^{2+} \rightarrow Fe^{3+} + e^{-}$	+0.77 V)
	$O_2 + e^- \rightarrow O_2^{}$	0.18 V
	$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{-}$	0.95 V
-	$(Fe^{2+} \rightarrow Fe^{3+} + e^{-}$	+0.77 V)
	$\underline{O_2 + H^+ + e^- \rightarrow HO_2}$	+010 V
	$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + HO_2$	0.67 V
-	$(Fe^{2+} \rightarrow Fe^{3+} + e^{-}$	+0.77 V)
	$\underline{HO_{2'}} + \underline{e_{+}} + \underline{H^{+}} \rightarrow \underline{H_{2}O_{2}}.$	+1.46 V
	$Fe^{2+} + HO_{2} + H^+ \rightarrow Fe^{3+} + H_2O_2$	+0.69 V
-	$(Fe^{2+} \rightarrow Fe^{3+} + e^{-}$	+0.77 V)
	$H_2O_2 + e^- + H^+ \rightarrow HO + H_2O$	+0.80 V
	$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^{-} + H_2O_{$	+0.03 V
-	$(Fe^{2+} \rightarrow Fe^{3+} + e^{-}$	+0.77 V)
	$HO^{\cdot} + e^{-} + H^{+} \rightarrow H_{2}O_{-}$	+2.73 V

 $Fe^{2+} + HO^{\cdot} + H^+ \rightarrow Fe^{3+} + H_2O....+1.96 V$

For Co metal ion

 $Co^{3+} + e^- \rightarrow Co^{2+}$+1.81 V

- $(Co^{2+} \rightarrow Co^{3+} + e^{-}....+1.81 \text{ V})$ $O_2 + e^{-} \rightarrow O_2^{-}....-0.18 \text{ V}$ $Co^{2+} + O_2 \rightarrow Co^{3+} + O_2^{-}...-1.99 \text{ V}$
- $(Co^{2+} \rightarrow Co^{3+} + e^{-} +1.81 \text{ V})$ $O_2 + H^+ + e^{-} \rightarrow HO_2$+010 V $Co^{2+} + O_2 + H^+ \rightarrow Co^{3+} + HO_2$-1.71 V
- $\begin{array}{l} & (\text{Co}^{2+} \rightarrow \text{Co}^{3+} + \text{e}^{-}....+1.81 \text{ V}) \\ \\ & \underline{\text{H}_2\text{O}_2 + \text{e}^{-} + \text{H}^{+} \rightarrow \text{HO}^{\cdot} + \text{H}_2\text{O}}....+0.80 \text{ V} \\ \\ & \text{Co}^{2+} + \text{H}_2\text{O}_2 + \text{H}^{+} \rightarrow \text{Co}^{3+} + \text{HO}^{\cdot} + \text{H}_2\text{O}....-1.01 \text{ V} \end{array}$
- $(Co^{2+} \rightarrow Co^{3+} + e^{-}...+1.81 \text{ V})$ <u>HO' + e' + H' \rightarrow H₂O....+2.73 V Co²⁺ + HO' + H' \rightarrow Co³⁺ + H₂O....+0.92 V</u>

For Cu metal ion

$Cu^+ + e^- \rightarrow Cu^{2+}$	+0.16 V
- $(Cu^{2+} + e^{-} \rightarrow Cu^{+} \dots$	+0.16 V)
$\underline{O_2} + e^- \rightarrow O_2^-$	0.18 V
$Cu^{2+} + O_2 \rightarrow Cu^+ + O_2^{-}$	0.34 V

10 V
06 V
16 V)
<u>46 V</u>
.30 V
16 V)
.80 V
.64 V
16 V)
.73 V
.57 V
.51 V
1.51 V)
).18 V
<u>).18 V</u> 1.69 V
) <u>.18 V</u> 1.69 V
) <u>.18 V</u> 1.69 V 1.51 V)
) <u>.18 V</u> 1.69 V 1.51 V) <u>010 V</u>
) <u>.18 V</u> 1.69 V 1.51 V) <u>010 V</u> .41 V
). <u>18 V</u> 1.69 V 1.51 V) <u>010 V</u> .41 V 1.51 V)
) <u>.18 V</u> 1.69 V 1.51 V) <u>010 V</u> .41 V 1.51 V) <u>1.46 V</u>

-	$(Mn^{2+} \rightarrow Mn^{3+} + e^{-}$	+1.51 V)
	$\underline{H_2O_2} + \underline{e}^{-}_{-} + \underline{H}^+ \longrightarrow \underline{HO} + \underline{H_2O}.$	+0.80 V
	$Mn^{2+} + H_2O_2 + H^+ \rightarrow Mn^{3+} + HO^{\cdot} + H_2O_{$	0.71 V

- $(Mn^{2+} \rightarrow Mn^{3+} + e^{-}$	+1.51 V)
$\underline{HO^{\cdot} + e^{-} + H^{+}} \rightarrow \underline{H_2O}$	+2.73 V
$Mn^{2+} + HO^{\cdot} + H^+ \rightarrow Mn^{3+} + H_2O$	+1.22 V

Bimetallic catalyst

	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77 V
-	$(Cu^+ \rightarrow Cu^{2+} + e^-)$	+0.16 V)
	$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+}$	+0.61 V

-	$(Fe^{2+}+e^{-}\toFe^{3+}$		+0.77 V)	
	$\underline{Co^{3+} + e^{-} \rightarrow Co^{2+}}$		<u>+1.81 V</u>	
	$Fe^{2+} + Co^{3+} \rightarrow Fe^{3+} + Co^{2+}$		+1.04 V	

- $(Fe^{2+} + e^{-} \rightarrow Fe^{3+}....+0.77 \text{ V})$ <u>Mn³⁺ +e⁻ \rightarrow Mn²⁺....+1.51 V</u>

$Fe^{2+} + Mn^{3+} \rightarrow$	Fe ³⁺ +Mn ²⁺	+0.73 V
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(Tang et al., 2018)

- $(Mn^{3+} \rightarrow Mn^{4+} + e^{-}...+0.15 \text{ V})$ Mn³⁺ + Fe³⁺ \rightarrow Mn⁴⁺ + Fe²⁺....+0.62 V (Nowaz et al., 2016)

-	$(Fe^{2+} + e^{-} \rightarrow Fe^{3+}$	+0.77 V)
	Mn^{4+} +e- → Mn^{3+}	+0.95 V
	$Mn^{4+} + Fe^{2+} \rightarrow Mn^{3+} + Fe^{3+}$	+0.18 V

Discrepancy in literature

Nowaz *et al.* (2016) reported that the reduction of Mn^{4+} by Fe^{2+} is thermodynamically favourable since the standard potential of Mn^{4+}/Mn^{3+} is 0.95 V larger than that of Fe^{3+}/Fe^{2+} (0.77 V). However, this was in contrast with the study presented by Tang *et al.* (2018) where the reduction of Fe^{3+} by Mn^{3+} was thermodynamically favourable since the standard redox potential of Fe^{3+}/Fe^{2+} (0.77 V) is larger than that of Mn^{4+}/Mn^{3+} (0.15 V). Therefore, it is not yet clear as to which metal ion assist the reduction of the other as these two studies reported different Mn^{4+}/Mn^{3+} potential values.