CHEMICAL ENGINEERING TRANSACTIONS

VOL. 81, 2020

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Qiuwang Wang, Min Zeng, Panos Seferlis, Ting Ma, Jiří J. Klemeš

ISBN 978-88-95608-79-2; **ISSN** 2283-9216

DOI: 10.3303/CET2081062

Catalytic Wet Peroxide Oxidation of Methyl Orange using Naturally-Occurring South African Ilmenite as a Catalyst

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The introduction of large quantities of organic contaminants into effluents from industrial and agricultural processes has lead to the increasing demand for water reuse. The viability of using naturally-occurring South African ilmenite as a catalyst in the catalytic wet peroxide oxidation (CWPO) process, using methyl orange (MO) as a model compound, was investigated. Intial operating conditions ([MO] = 10 $mg \cdot L^{-1}$, [H_2O_2] = 2.5 mM, ilmenite = 1,000 $mg \cdot L^{-1}$, pH = 3.0, temperature = ±20 °C) lead to a complete decolourisation of methyl orange following 90 min of reaction time. Further research investigated the influence of pH and irradiation on the degradation of methyl orange. A pH of 2.5 was found to lead to the fastest degradation rate, this is because at pH values lower than 2.5 an •OH radical scavenging effect occurs and at pH levels above 2.5 dissolved Fe can precipitate. The degradation rate was found to be further enhanced in the presence of irradiation with complete decolourisation of methyl orange occurring after 75 min after reaction time in the presence of UVA and visible light and after 60 min reaction time in the presence of UVB irradiation. This can be attributed to the photo-reductive dissolution of Fe on the ilmenite surface. These results showed that ilmenite could be used as an efficient, cost-effective catalyst for the degradation of aromatic compounds, such as methyl orange, in the CWPO process. The rate of degradation could be further increased with a decrease to a pH of 2.5 in the presence of UVB irradiation.

1. Introduction

Industrial and agricultural processes introduce large quantities of organic contaminants into natural water systems that cause a variety of ecological and health problems. This coupled with an increasing population has created a demand for clean, good quality water. One way of meeting this demand is through water reuse.

Conventional biological wastewater processes are widely used treatment for contaminants in wastewater however, these processes are incapable of degrading priority and some emerging pollutants. Advanced Oxidation Processes (AOPs) are a group of technologies that emerged as a solution (Ameta and Ameta, 2018). The principle behind AOPs is the generation of free radicals that participate in redox chemical reactions to degrade organic compounds. The Fenton Reagent and the Catalytic Wet Peroxide Oxidation (CWPO) are AOPs which makes use of iron salts or solids as catalysts in the presence of hydrogen peroxide to generate hydroxyl radicals. Although effective, these processes are expensive and labour-intensive. Therefore, research into viable, efficient and affordable catalysts is of pertinence.

Recent studies have investigated the use of naturally occurring minerals as efficient catalysts for AOPs. Naturally-occurring minerals are cost-effective and environmentally non-toxic and thus would be ideal for the treatment of wastewater (Munoz et al., 2017). Ilmenite ($FeTiO_3$) is a mineral with the potential as a catalyst in AOPs due to the presence of iron. Iron is an element that can easily accept or donate electrons making it ideal for the redox-based reactions in AOPs. A study conducted by García-Muñoz et al. (2016) it was shown that naturally occurring ilmenite could be used as a catalyst in the CWPO for the degradation of phenol. The authors further found that the degradation rate of phenol could be increased in the presence of broad-spectrum irradiation (λ = 300 nm – 800 nm). A later study conducted by García-Muñoz et al. (2017) showed how this method using ilmenite as a catalyst could also efficiently degrade more complex compounds such as sulfonamides found in hospital wastewater.

Paper Received: 20/04/2020; Revised: 13/05/2020; Accepted: 15/05/2020
Please cite this article as: Butt A.L., Tichapondwa S.M., 2020, Catalytic Wet Peroxide Oxidation of Methyl Orange using Naturally-Occurring South African Ilmenite as a Catalyst, Chemical Engineering Transactions, 81, 367-372 DOI:10.3303/CET2081062

The above studies show that naturally-occurring ilmenite can be an efficient catalyst for AOPs however to fully understand the mechanism at work further research is needed to determine the influence of the operating conditions on the system and the reaction pathways that occur. Furthermore, only a few studies have been conducted using ilmenite in the CWPO process, due to this, the effectivity of this method has only been studied on a small range of pollutants. This study makes use of methyl orange, an azo dye, as the target pollutant to widen the scope of the application of this process. Azo dyes are known to be resistant to degradation through biological wastewater treatment and thus make a model compound for this study. Apart from this, the study makes use of naturally-occurring South African ilmenite as a catalyst. When working with naturally-occurring minerals, the composition and mineralogy are expected to differ across regions where the mineral was sourced. Previous studies such as the one conducted by García-Muñoz et al. (2016) made use of purified ilmenite that was found consist of 75 % $FeTiO_3$ and 25 % TiO_2. These values are vastly different from other similar studies such as the one conducted by Pataquiva-Mateus et al. (2017) where they used Columbian sourced ilmenite that contained ranges of TiO_2 between 35 % and 47 %, as well as some other impurities such as quartz (SiO_2) and hematite (Fe_2O_3). To fully understand the catalytic activity of naturally-occurring ilmenite it is important to have a wide range of research conducted on different sources of ilmenite.

Firstly this study aimed to determine the viability of naturally-occurring South African ilmenite as a catalyst in the CWPO process using methyl orange as a target pollutant. Secondly, this study aimed to gain a better understanding of the mechanisms of reaction by investigating the influence of pH and irradiation on the system.

2. Methods and Materials

2.1 Materials

Pre-milled ilmenite (<54 μm) was supplied by AMIS Matrix Reference Materials (Product code: AMIS 0454). Methyl Orange (85 %), Sulphuric acid (98 %) and H_2O_2 (30 %) were purchased from Sigma Aldrich.

2.2 Catalyst characterisation

The mineral phases of the ilmenite were determined through X-Ray Diffraction (XRD) using a PANalytical X'Pert Pro powder diffractometer in θ-θ configuration with an X'Celerator detector and variable divergence with Fe filtered Co-Kα radiation (λ = 1.789 Å) fixed slits. Mineral phases were determined using X'Pert Highscore plus software by selecting the best-fitting pattern from the ICSD database. The relative phase weight percentage was estimated using the Rietveld method. Diffractograms were generated according to mineral phase d-spacing using mineral data obtained from the American Mineralogist Crystal Structure Database (AMCSD). Elemental composition was determined through X-Ray Fluorescence (XRF) using the Thermo Fisher ARL Perform'X Sequential XRF instrument with Uniquant software.

2.3 CWPO Process

All CWPO experiments were performed in an enclosed chamber lined with reflective material. A 400 mL solution of 10 $mg{\cdot}L^{-1}$ methyl orange with a pH of 3.0 (adjusted with H_2SO_4) was placed in the dark on a magnetic stirrer. Ilmenite equivalent to a 1,000 $mg{\cdot}L^{-1}$ loading was added to this solution and left to equilibrate for 30 min. Thereafter the reaction was activated through the addition of 2.5 mM H_2O_2. Samples were taken at 15 min intervals for 2h upon the addition of the catalyst and analysed using a WPA-Lightwave II spectrophotometer at a wavelength of 503 nm to determine degradation. Control experiments were also conducted in the absence of ilmenite and H_2O_2.

2.4 Influence of pH and irradiation

Experiments were conducted in a factorial design to determine the influence of pH and irradiation of the system. Previous studies have shown that in Fenton-like AOPs, particularly those using iron-based catalysts, work most effectively at low pH values, this is because iron-bearing minerals are sparsely soluble at pH values above 3 (Cornell and Schwertmann, 2003).

Table 1: The model and peak wavelengths of the different lamps used for irradiation studies

Lamp	Model	Peak Wavelength(s)
UVA	Philips TL-K 40W/10R Actinic BL Reflector	365 nm
UVB	Exo Terra Reptile UVB 200 18W, 60 cm	310 – 350 nm
Visible	Philips Master Super 80 TL-D 18W/865	440, 560, 640 nm

Studies have also shown that the presence of irradiation can increase degradation rates when using an iron-based catalyst in AOPs (Zazo et al., 2016). The effect of pH and irradiation was assessed by employing a factorial design using three different pH levels (2.0, 2.5, 3.0) and four different irradiation types (UVA, UVB, Visible and dark). These experiments made use of the same operating conditions as the above experiments whereby only pH adjustments and the presence of different irradiation wavelengths were added. Table 1 shows the model and wavelength corresponding to the different lamps used.

3. Results and Discussion

3.1 Catalyst Characterisation

The results of the XRD analysis are displayed as a diffractogram in Figure 1 with relative weight percentages given in Table 2.

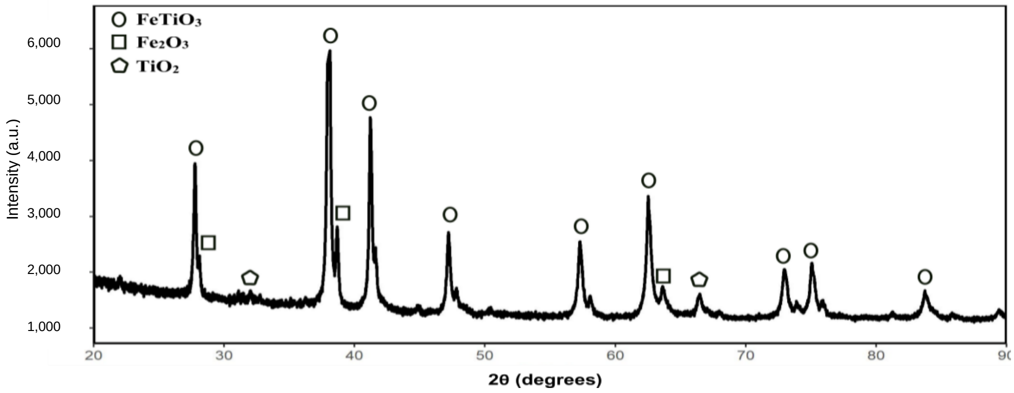

Figure 1: The mineral phases of the ilmenite catalyst as detected through XRD

The peaks corresponding to ilmenite were the most frequent and pronounced, indicating that the catalyst is predominantly made up of ilmenite. Peaks corresponding to hematite and rutile were also visible thus confirming their presence in the sample.

Table 2: The percentage composition of the mineral phases in the ilmenite sample as determined by XRD

Mineral Phase	Weight (wt.%)
Ilmenite ($FeTiO_3$)	83.53
Hematite (Fe_2O_3)	14.99
Rutile (TiO_2)	1.2
Quartz (SiO_2)	0.28

The results of the XRD analysis show that the dominant mineral phase of the catalyst is ilmenite followed by hematite. Hematite (Fe_2O_3) is a common iron oxide found in soils, it comprises of iron in the form of Fe(III) and can behave as an effective catalyst in AOPs under the correct conditions, contributing to the catalytic properties of the raw ilmenite sample (Munoz et al., 2017). The sample contained a low percentage of rutile and quartz and thus they will have a negligible contribution to the catalytic activity of the catalyst.

Table 3 shows the elemental composition in percentages of the catalyst sample as determined through XRF analysis.

Table 3: The elemental composition (%) of the ilmenite catalysed determined through XRF

Element	Weight (wt.%)
Iron (Fe)	34.60
Titanium (Ti)	32.30
Oxygen (O)	28.73
Silicon (Si)	1.34

Table 3 shows that iron and titanium comprise the largest weight percentages of the ilmenite sample. This is due to the majority of the sample being made up of the ilmenite mineral phase as was seen through XRD analysis. These results are similar to the expected theoretical weight percentages of pure ilmenite which are

36.8 % Fe, 31.6 % Ti and 31.6 % O, the differences can be attributed to the presence of hematite in the sample (Klein and Dutrow, 2007). Iron has the highest weight percentage which can be attributed to by the presence of hematite in the sample.

3.2 Degradation Studies

Figure 2 shows the degradation of methyl orange under various operating parameters including the control experiments with the absence of H_2O_2, ilmenite.

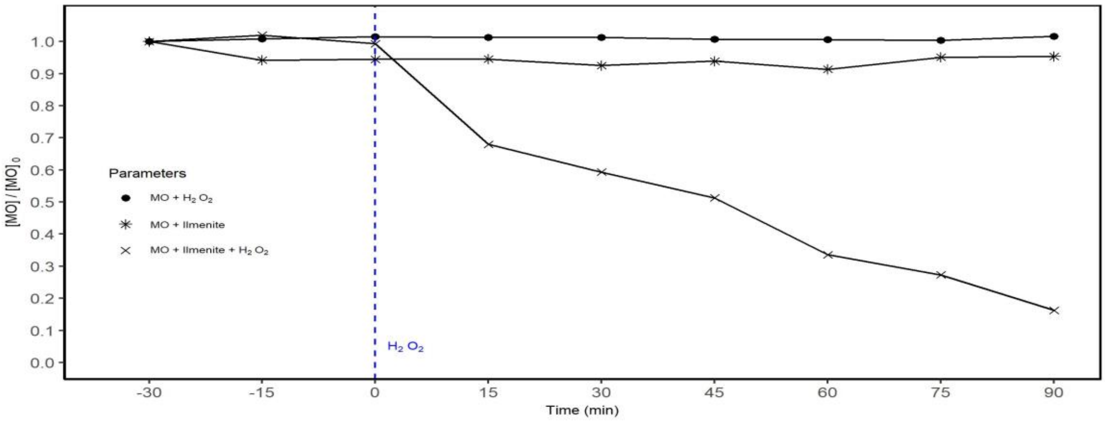

Figure 2: The degradation of methyl orange using ilmenite as a catalyst in the CWPO process. Operating conditions: [MO] = 10 mg·L^{-1}, [H_2O_2] = 2.5 mM, ilmenite = 1,000 mg·L^{-1}, pH = 3.0, temperature = ±20°C

As can be seen in Figure 2, the degradation of methyl orange was only observed in the presence of ilmenite and H_2O_2. This suggests that the degradation mechanism relies on an interaction between the ilmenite and the H_2O_2 for the generation of free radicals. The proposed reaction mechanism follows that similar to the Fenton reagent, the low pH creates an environment whereby the Fe on the ilmenite surface undergoes reduction generating Fe^{2+} in solution, Eq(1).

$$FeTiO_{3(s)} + 2H^{+}{}_{(aq)} \rightarrow FeTiO_{3(s)} + Fe^{2+}{}_{(aq)} \qquad (1)$$

Thereafter the dissolved Fe ions react with H_2O_2 to produce Fe^{3+}, OH^- and a •OH radical, Eq(2).

$$Fe^{2+}{}_{(aq)} + H_2O_{2(aq)} \rightarrow Fe^{3+}{}_{(aq)} + \bullet OH_{(aq)} + OH^{-}{}_{(aq)} \qquad (2)$$

The generated •OH radical reacts with the methyl orange compound, breaking down the azo dye bonds, producing short-chain organic acids, Eq(3).

$$C_{14}H_{14}N_3NaS_{(aq)} + \bullet OH_{\ (aq)} \rightarrow (Short\ Chain\ Organic\ Acids) \qquad (3)$$

The generated Fe^{3+} is reduced by the OH^- to generate more Fe^{2+} and another •OH radical, Eq(4).

$$Fe^{3+}{}_{(aq)} + OH^{-}{}_{(aq)} \rightarrow Fe^{2+}{}_{(aq)} + \bullet OH_{(aq)} \qquad (4)$$

The proposed reaction mechanism continues until the depletion of H_2O_2 in the system.

The presence of irradiation increased the rate of degradation at all pH levels. A study conducted by Walte and Morel (1984) showed that iron oxides can be solubilized through photodissociation that occurs on the iron oxide surface. Walte and Morel (1984) proposed the following reaction mechanism (Eq(5)):

$$FeOH^{2+} \overset{hv}{\rightarrow} + Fe^{2+}{}_{(aq)} + \bullet OH \qquad (5)$$

In the presence of irradiation, the rate of iron leaching into solution is increased through this proposed photoreduction and thus the rate of radical formation is increased.

The fastest degradation rate was observed in the presence of UVB irradiation at all pH levels. This is supported by current literature that shows the presence of irradiation can increase rates of degradation (García-Muñoz et al., 2016). A study conducted by Eskandarian et al. (2016) on the degradation of pharmaceuticals using TiO_2 examined the effect of different wavelengths on degradation efficiency. The study found that as irradiation wavelength increased degradation rates decreased. This could be the primary reason that UVB irradiation was found to lead to a faster degradation rate as compared to the UVA and Visible light wavelengths.

3.3 Effect of pH and irradiation

Figure 3 displays the rate of degradation of methyl orange at different pH values under various irradiation types.

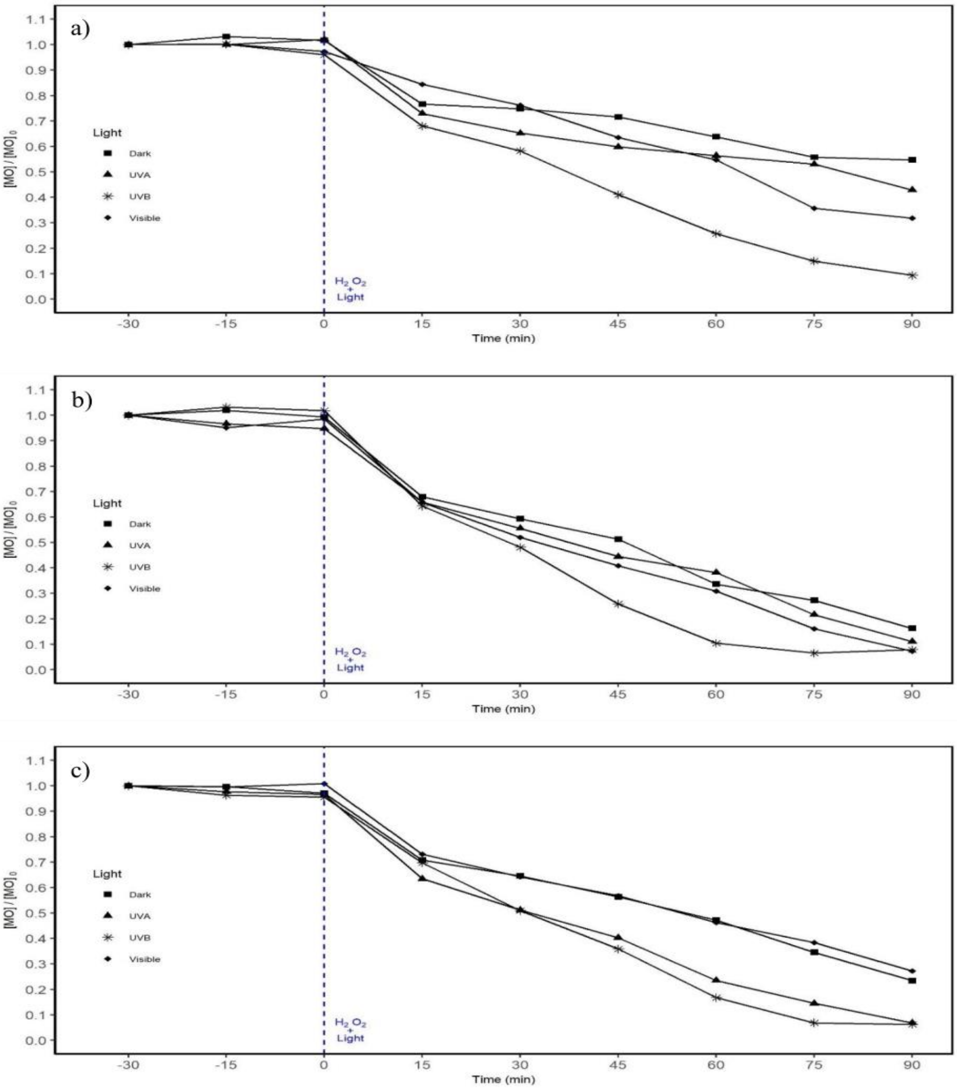

Figure 3: The degradation of methyl orange using ilmenite as a catalyst at different pH levels in the presence of various irradiation types. a) pH 2.0, b) pH 2.5, c) pH 3.0 Operating conditions: [MO] = 10 mg·L^{-1}, [H_2O_2] = 2.5 mM, ilmenite = 1,000 mg·L^{-1}, temperature = ±20 °C

A pH value of 2.5 was found to be optimal under the influence of UVB irradiation. This is explained through the behaviour of Fe and H_2O_2 at different pH values. At pH values above 3.0, the reduced iron re-oxidises and precipitates, decreasing the generation of •OH, whilst a pH value below 2.5 increases the scavenging effect of •OH by excess generated H^+ (Wang et al., 2016).

4. Conclusions

Naturally-occurring South African ilmenite has shown to be an effective catalyst for the degradation of methyl orange in the CWPO process. In the absence of irradiation at a pH of 3.0 complete decolourisation of methyl orange was achieved after 90 min of reaction. Degradation was only observed in the presence of H_2O_2 and ilmenite. The overall reaction relied on the presence of Fe^{2+} in solution which was provided soil due to reductive dissolution or iron at a low pH. Further studies on the effect of pH and irradiation showed that a pH of 2.5 was optimal in the presence of UVB irradiation. Under these conditions, complete decolourisation of methyl orange was achieved after 60 min of reaction. These results show that ilmenite can be used as a cost-effective catalyst in the CWPO process for the degradation of aromatic compounds in wastewater. This study further showed that using ilmenite in the CWPO process could effectively degrade the azo dye, methyl orange. Azo dyes are resistant to degradation through biological wastewater treatments, thus this process provides an effective alternative treatment for such pollutants especially in the context of textile wastewater effluents.

Further research is being conducted to determine the full extent of mineralisation of methyl orange in solution, as well as to determine the optimal levels of catalyst loading and H_2O_2 dosage to further increase the rate of degradation.

Acknowledgements

This work is based on the research supported in part by the National Research Foundation of South Africa (Grant Number: 117905).

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