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Synthesis of Iron-doped Titania Photocatalyst by Sol-gel Method and Its Application in Degradation of Dyes

Nur Afiqah Othman and Nursyafreena Attan*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
**Corresponding Author: nursyafreena@kimia.fs.utm.my*

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GRAPHICAL ABSTRACT

TiO_2 in white powder form Fe/TiO_2 in yellowish brown powder form

ABSTRACT

Amounts of dyes produced from industry has contribute to poor quality of water, thus destroying the ecosystem. In this study, TiO_2 and Fe/TiO_2 photocatalyst were prepared from sol-gel method that was calcined at 500°C for 2 hours. The prepared photocatalyst were characterized by Fourier Transform Infra-red Spectrophotometer (FTIR), thermogravimetry analyzer (TGA) and X-ray diffraction analyzer (XRD). FTIR spectral data exhibited the presence of functional groups of Ti-O-Ti vibrations at below 800 cm^{-1}. TGA result reveals that there was no mass loss after 500°C indicating the calcination temperature is optimal for achieve highly crystalline of TiO_2. XRD of synthesised photocatalyst showed the presence of anatase phases. The synthesised TiO_2 and Fe/TiO_2 were successfully used as photocatalyst for the degradation of methylene blue (MB) and methyl orange (MO) under irradiation of UV light, analyzed using UV-Visible spectrophotometer. The photocatalytic degradation using TiO_2 and Fe/TiO_2 photocatalyst for MB giving an efficiency of 20.6% and 53.2%, respectively while the degradation of MO recorded were 33.9% and 46.6% respectively. Both reactions followed the pseudo-first order reaction with rate constant of 0.0018 min^{-1} and 0.0065 min^{-1} for degradation of MB using TiO_2 and Fe/TiO_2 while rate constant for degradation of MO were 0.0034 min^{-1} and 0.0052 min^{-1}, respectively. Results show that Fe/TiO_2 displays higher photocatalytic activity than TiO_2 for both degradation of MB and MO dyes.

Keywords: Titanium dioxide, metal dopants, photocatalytic degradation, methylene blue, methyl orange

1. INTRODUCTION

The contamination of water from industrial will lead to water pollution which contains harmful toxic chemical such as dyes. The presence of chemical in water might reach the food chain through plants and aquatic animals hence cause diseases. The use of photocatalysis as wastewater treatment has managed to solve this problem due to its ability to degrade pollutant with stability, lack of toxicity and strong photoactivity. Photocatalytic reactions is known as one of an efficient method due to its excellent ability for decomposition of organic contamination in water [1].

Titanium dioxide is one of the photocatalyst materials that able to degrade the organic and inorganic pollutants. It is used as photocatalyst materials for solving environmental problems especially in the purification of wastewater as it is generally chemically and biologically inert, photoactive, and inexpensive [2]. Titanium dioxide has three crystal structure of brookite, rutile and anatase. Brookite is the least studied among these crystals due to difficulties to produce it as a pure phase. Rutile is the thermodynamically stable under most of the temperature and pressure conditions but anatase is stable when the particle size is small [3].

The process of photodegradation of pollutants by TiO_2 start by absorption of light radiation equal or higher than its band gap value which is 3.2 eV [4]. Absorption of light with energy equal or higher than the band gap of semiconductor is needed to initiate the photocatalytic reaction. Band gap is the energy difference between the valence band and conduction band. This phenomenon will lead to the excitation of the electrons from valence band to conduction band. Hence, the charge carriers, energy-rich electrons and holes are generated. In photocatalysis, the charge carriers transfer to the surface and initiate the photocatalytic reactions where superoxides and hydroxide radicals (•OH) are generated by the reaction of electrons at conduction band and valence band with oxygen and water molecules respectively [5].

The synthesis method of material can significantly influence the characteristic of the material. Sol-gel technique is widely used method to produce inorganic powders and coatings. In the sol-gel process, starting compounds called precursors consist of metal which surrounded by inorganic or organic ligands. Different starting materials can influence the morphology of the TiO_2 produced where a small crystallite size, high percentage of the anatase phase and high specific surface area of TiO_2 will increase the photocatalytic degradation efficiency [6].

TiO_2 is an ideal photocatalyst but there are some problems that might occur during photocatalyst reactions. Due to the high of electron/hole recombination rate, it results into lower photocatalytic activity since the electrons and holes do not have enough time to migrate to the surface and initiate the photocatalytic reactions [7]. It has been reported that introducing metals as the dopants into the crystal lattice of titania can trap both electrons and holes temporarily and hence reduce the electron/hole recombination and cause an increase in the photocatalytic activity [8]. Fe^{3+} ion has a very similar ionic radius to Ti^{4+} and can substitute for Ti^{4+} in the crystal lattice of TiO_2. Fe^{3+} reduces the electron/hole recombination rate significantly since it can trap both electrons and holes.

Many researchers have confirmed that the calcination process is crucial in the formation of doped TiO_2 and that the properties of photocatalyst such as surface area and crystallinity of doped TiO_2 are strongly dependent on the calcination temperature. However, with further increase in the calcination temperature, the surface area of TiO_2 started to decrease as well as the transformation of anatase to rutile phase, and thus, the photocatalytic activity of TiO_2 decreased [9].

Due to the high benefit and high significant application of TiO_2 and Fe/TiO_2, this study is carried out with photocatalysis degradation of methylene blue and methyl orange dyes.

2. EXPERIMENTAL

TiO_2 and Fe/TiO_2 were synthesized by using sol-gel method. TTIP was chosen as precursor, mixed with ethanol, acetic acid and distilled water to form TiO_2 white solution. For Fe/TiO_2 solution, $Fe(NO_3)_3.H_2O$ was diluted in 50 mL of distilled water before added into the white solution. The solution then was cooled and gelled for 22 hours in room temperature before it was dried in vacuum oven at 110°C for 23 hours. Finally, the TiO_2 and Fe/TiO_2 were calcined at 500°C for 2 hours in furnace, produced white and yellowish-brown powder, respectively. The characterization of TiO_2 and Fe/TiO_2 photocatalyst were carried out via FTIR, TGA and XRD analysis. The photocatalytic degradation for both TiO_2 and Fe/TiO_2 photocatalyst were tested on the degradation of cationic methylene blue (MB) and anionic methyl orange (MO) dyes solution. The photocatalysis then was performed under UV lamp and measured by UV-Visible spectrophotometer.

3. RESULTS AND DISCUSSION

In this study, the synthesised TiO_2 and Fe/TiO_2 both calcined at 500°C were characterised using Fourier Transform Infra-red Spectroscopy (FTIR), thermogravimetry analysis (TGA) and X-ray diffraction (XRD). The photocatalytic activity was measured by UV-Vis spectrophotometer.

3.1. Fourier Transform Infra-red Spectroscopy (FTIR)

The infrared spectra of both TiO_2 and Fe/TiO_2 photocatalyst were analysed by FTIR in the range of 4000 – 400 cm^{-1} as shown in Figure 1. The broad band around 3300 cm^{-1} corresponds to the stretching vibration of OH groups while the band at 1100 cm^{-1} corresponds to the OH bending in adsorbed water. These results ensure the presence of hydroxyl group in the structure of TiO_2 and Fe/TiO_2 samples. The adsorbed water and hydroxyl group are important to the photocatalytic reactions since they react with photo-excited holes on the catalyst surface to produce hydroxyl radicals. Band around 1620 cm^{-1} indicate the formation of C=C while band below 800 cm^{-1} is attributed to the Ti-O-Ti stretching vibrations [10].

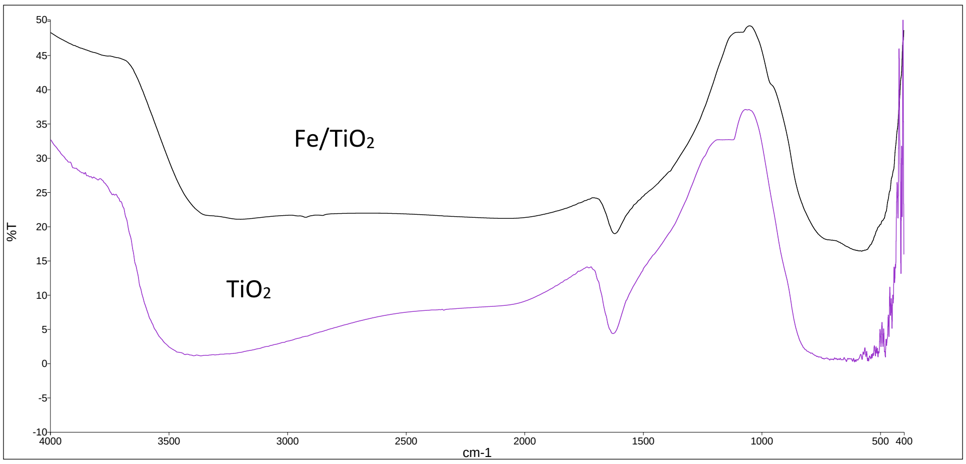

Figure 1. FTIR spectra of TiO_2 and Fe/TiO_2

3.2. Thermogravimetry analysis (TGA)

Table 1 shows the thermogravitmetry analysis (TGA) for TiO_2 and Fe/TiO_2 powder. The TGA curve reveals that there are two main stages of mass loss. The first mass loss was at temperature range 25°C to 100°C, corresponding to the loss of alcohol, adsorbed water and moisture on the surface of the material while mass loss around temperature 250°C to 480°C attributed to loss of organic matter remaining in the material.

Table 1. Percentage mass loss for TiO_2 and Fe/TiO_2 in TGA

Temperature, °C	Sample	Percentage mass loss, %
25 - 100	TiO_2	3.38
	Fe/TiO_2	3.17
250 - 480	TiO_2	2.39
	Fe/TiO_2	2.61

It can be seen in the addition of Fe content in TiO_2 will lead to slightly increment of the mass loss due to Fe doping causes the increases of absorption/adsorption of moisture by TiO_2 powders [11]. Result state there was no mass loss after 500°C which indicate the calcination temperature is optimal for achieve highly crystalline of TiO_2 and Fe/TiO_2.

3.3. X-ray diffraction (XRD)

XRD was used to identify the phase structure and crystallite size of the particles. Figure 2 shows the XRD patterns of TiO_2 and Fe/TiO_2 calcined at 500°C. The peak at 25.22 2θ degrees indicate to the main anatase peak (101). XRD analysis was carried out to determine the crystal size and the phases in the TiO_2 and Fe/TiO_2. All the samples were calcined at 500°C for 2 hours before analyzed. Eventually, their crystal structures in the TiO_2 and Fe/TiO_2 were examined. The results showed that in spite of the iron impurities within the TiO_2 structure, the structure remains unchanged, signifying that the iron impurity does not influence the TiO_2.

Figure 2 reveals the XRD spectra of the TiO_2 and Fe/TiO_2. As shown in the figure, the major peaks of the anatase phase at a 2θ angle emerge at 25.22, 37.92, 47.94, 53.91, 54.89, 62.66, 69.21 and 75.02 which indicate to the crystal planes of (101), (004), (200), (105), (211), (204), (220) and (125), respectively according to JCPDS files for TiO_2 anatase (JCPDS card no. 21-1272). This suggests that anatase phase exist in TiO_2 and Fe/TiO_2. However, the peaks emerge at 2θ angles of 20.70 corresponds to (121) crystal planes suggest that the brookite phase occurs in the TiO_2 and Fe/TiO_2 sample as reported in JCPDS file for TiO_2 brookite (JCPDS card no. 29-1360) [12]. Both sample of TiO_2 and Fe/TiO_2 show the same crystal phase as ionic radius of Fe^{3+} and Ti^{4+} are very close to each other, thus Fe^{3+} ions can easily replace the Ti^{4+} ions in the TiO_2 crystal structure, resulting the same structure of both TiO_2 and Fe/TiO_2.

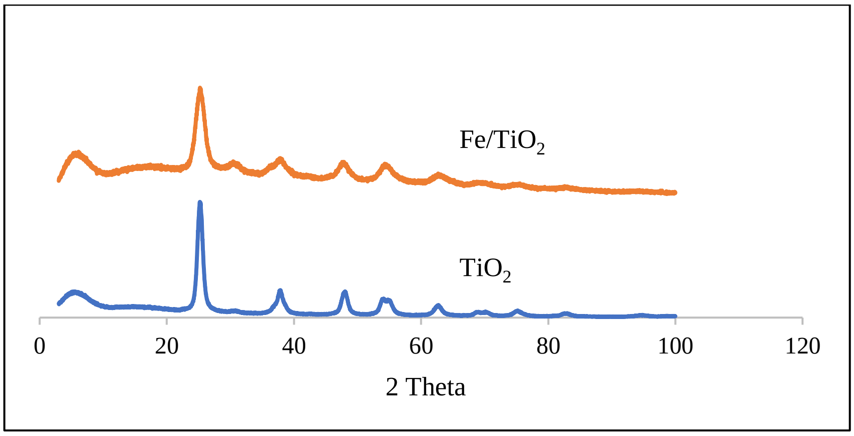

Figure 2. XRD pattern for TiO_2 and Fe/TiO_2

In order to calculate the particle size for TiO_2 and Fe/TiO_2 samples, Debye Scherrer formula in Equation (1) was used

$$D = \frac{0.89\lambda}{\beta \cos\theta} \tag{1}$$

where D is the crystalline size, λ is the wavelength of the XRD used (0.15418 nm), θ is the Bragg diffraction angle, and β is the full width at half its maximum intensity (FWHM) of diffraction pattern. The calculated crystallite size from the prominent (101) plane is found to be 8.36 nm and 5.39 nm for TiO_2 and Fe/TiO_2, respectively. The size for Fe/TiO_2 is smaller than TiO_2 because ionic radius of Fe^{3+} ion is smaller than Ti^{4+} ion, hence the presence of Fe^{3+} ions into TiO_2 cause the particle size decreases [11].

3.4. Photocatalytic degradation of dyes

The catalytic activity of TiO_2 and Fe/TiO_2 were evaluated in the degradation of 20 ppm for both MB and MO under UV light condition. The dyes solution was degraded in the presence of photocatalyst at different time interval. The photocatalytic activity is generally evaluated in term of percentage degradation of the pollutant's aqueous solution during photodegradation reaction under UV light by using the Equation (2) where A_o indicate initial absorption while A_t is absorption at t minute [12].

$$\%\ Degradation = \frac{A_0 - A_t}{A_0}\ x\ 100 \tag{2}$$

Figure 3 and 4 show the percentage of degradation for photocatalysis degradation of methylene blue and methyl orange with the presence of TiO_2 only. Result show there were 20.6% and 33.9% for percentage degradation of MB and MO respectively. This indicate TiO_2 photocatalyst help the degradation process in both cationic methylene blue and anionic methyl orange dyes.

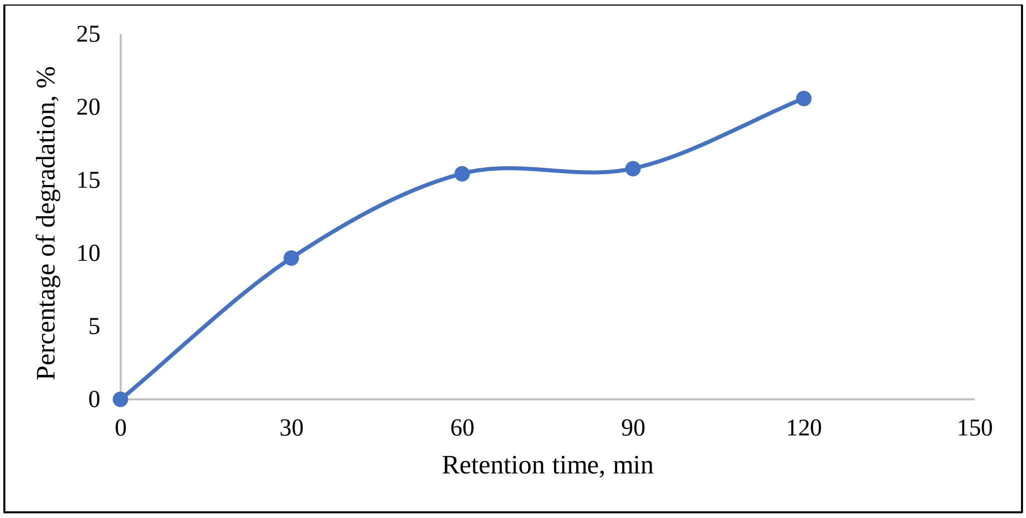

Figure 3. Percentage degradation of methylene blue with presence of TiO_2

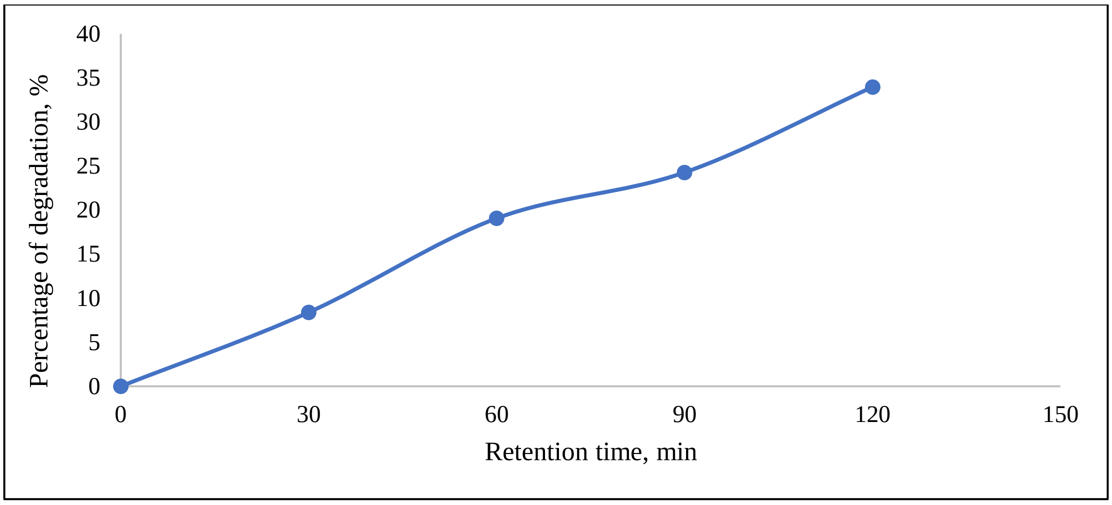

Figure 4. Percentage degradation of methyl orange with presence of TiO_2

The photocatalytic degradation of MB and MO then were repeated by using Fe/TiO_2. Figure 5 and 6 reveal the percentage of degradation for MB and MO with the presence of Fe/TiO_2.

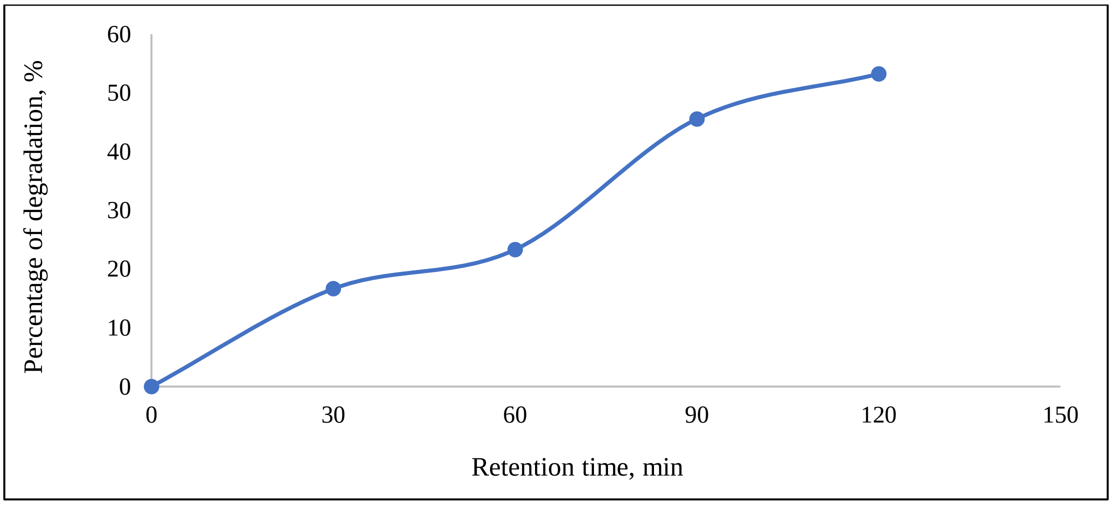

Figure 5. Percentage degradation of methylene blue with presence of Fe/TiO_2

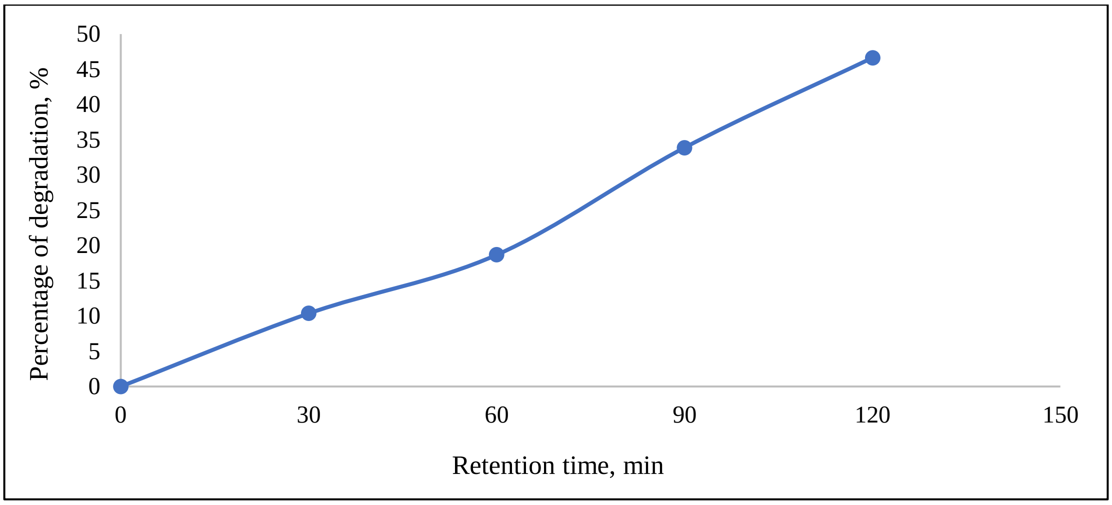

Figure 6 Percentage degradation of methyl orange with presence of Fe/TiO_2

From the result, it can be observed that there were 53.2% and 46.6% percentage of degradation in MB and MO solution respectively by using Fe/TiO_2 photocatalyst. Compare with photodegradation with the presence of TiO_2 only, it can be seen there were increment of percentage in degradation. This prove that Fe/TiO_2 also able to degrade cationic methylene blue and anionic methyl orange dyes better than TiO_2 only.

3.5. Kinetic Studies

Afterwards, kinetic reaction of photodegradation can be carried out using the pseudo-first order kinetic where the rate of reaction only depends on the concentration of dyes which are cationic methylene blue and anionic methyl orange. Concentration of photocatalyst, TiO_2 and Fe/TiO_2 are small than concentration of methylene blue and methyl orange during the reaction which leads to the concentration of photocatalyst effectively remained unchanged. This is because of their consumption is very small which change in concentration has become neglected. Hence, the reaction rate can be determined by series of Equation (3) as shown below [13]:

$$\ln[A]_t = -kt + \ln[A]_0 \tag{3}$$

In this study, the reaction order of degradation of methylene blue and methyl orange were approximated as pseudo-first order kinetic reaction. Based on the equation above, ln (A_t/A_o) against time was plotted to obtain the value of reaction rate constant from the slope of the linear line in graph.

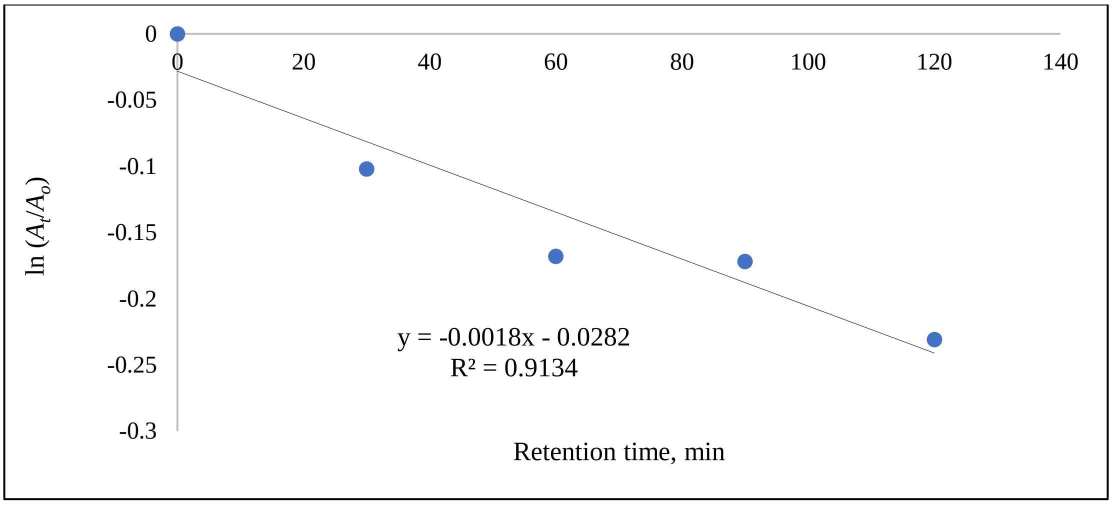

Figure 7. Plot of ln (A_t/A_o) against time for degradation of MB in the presence of TiO_2

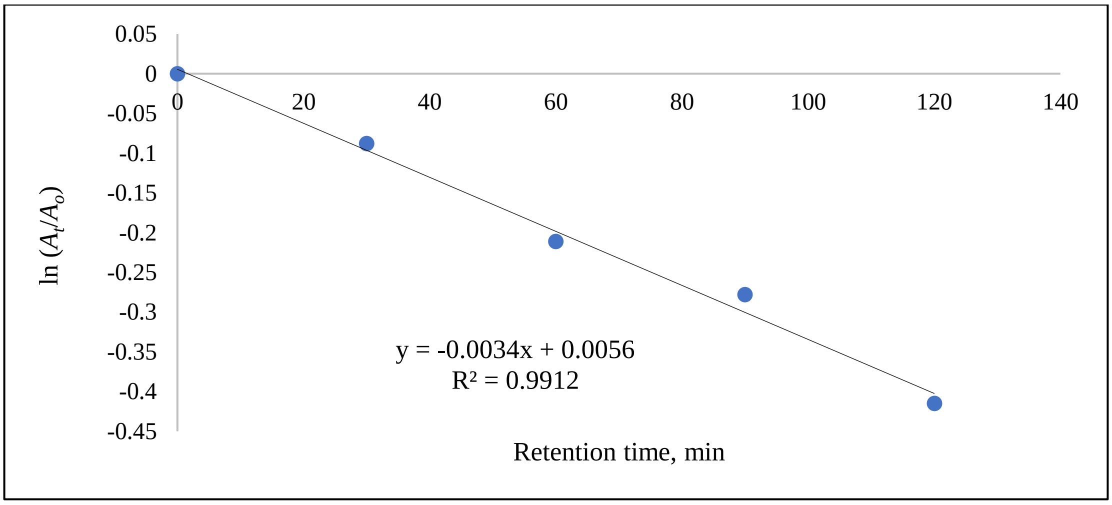

Figure 8. Plot of ln (A_t/A_o) against time for degradation of MO in the presence of TiO_2

Figure 7 and 8 show the graph of ln (A_t/A_o) against time for degradation of MB and MO under UV light in the presence of TiO_2. Based on the graph, rate constant obtained by using TiO_2 as photocatalyst for degradation of MB and MO were 0.0018 min^{-1} and 0.0034 min^{-1}, respectively.

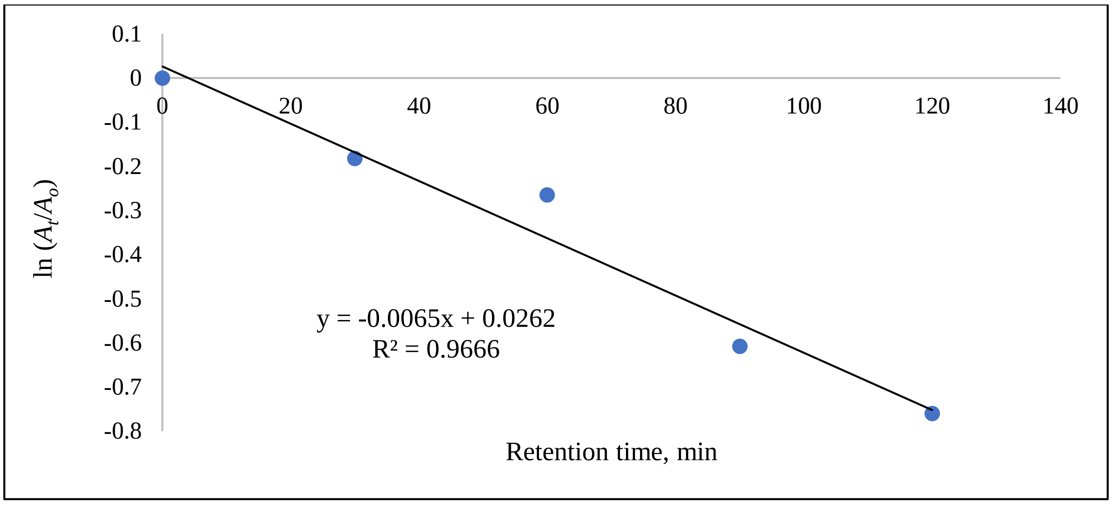

Figure 9. Plot of ln (A_t/A_o) against time for degradation of MB in the presence of Fe/TiO_2

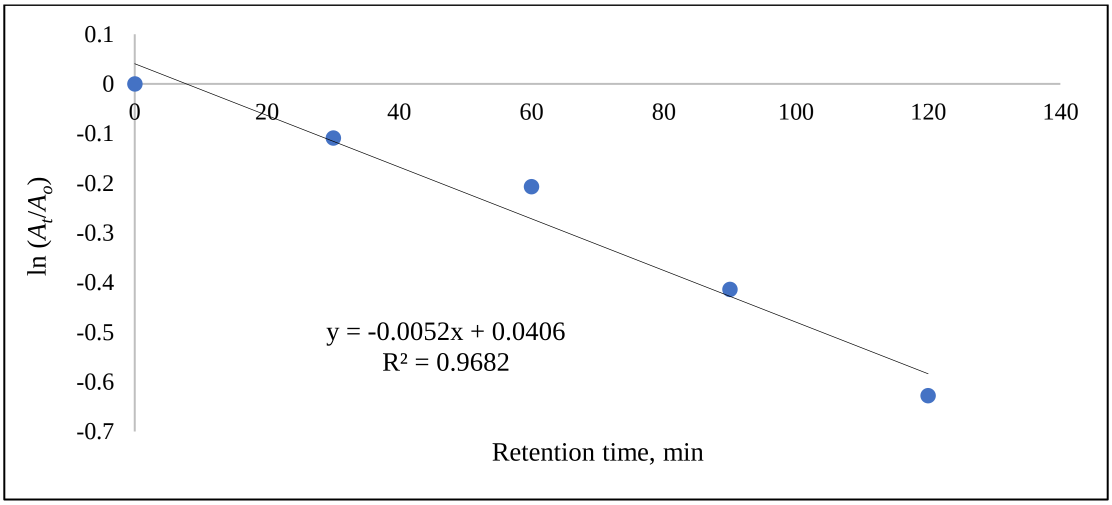

Figure 10. Plot of ln (A_t/A_o) against time for degradation of MO in the presence of Fe/TiO_2

The degradation of MB and MO were continued with the presence of Fe/TiO_2 photocatalyst. Figure 9 and 10 show the rate constant of the Fe/TiO_2 in the MB and MO were 0.0065 min^{-1} and 0.0052 min^{-1}, respectively. Based on the linear correlation between graph ln (A_t/A_o) againts time, it prove that both photocatalytic degradation of TiO_2 and Fe/TiO_2 in cationic methylene blue and anionic methyl orange follow pseudo-first order kinetic reaction.

4. CONCLUSION

Photocatalyst titanium dioxide, TiO_2 and iron doped titanium dioxide, Fe/TiO_2 were successfully synthesised via sol-gel method with calcination at 500 °C. Based on the characterization result by FTIR, TGA and XRD studies, it have proven that the presence of iron in titanium dioxide does exist and despite of the iron impurities within the TiO_2 structure, the anatase phase of structure remains unchanged. From the result of photocatalysis, it can be seen that percentage degradation of TiO_2 in methylene blue and methyl orange dyes obtained were 20.6% and 33.9% respectively. Meanwhile, percentage degradation with the presence of Fe/TiO_2 in menthylene blue and methyl orange were 53.2% and 46.6% respectively. This indicate the presence of Fe/TiO_2 improve the degradation of both cationic methylene blue and anionic methyl orange dyes by lowering the recombination rate of TiO_2. From kinetic studies, both TiO_2 and Fe/TiO_2 photocatalyst followed a pseudo-first order reaction. TiO_2 photocatalyst gave rate constant 0.0018 min^{-1} and 0.0034 min^{-1} for degradation of MB and MO respectively. In the same time, rate constant obtained for Fe/TiO_2 photocatalyst in degradation of MB and

MO were 0.0065 min^{-1} and 0.0052 min^{-1} respectively. Results show Fe/TiO_2 displays higher photocatalytic activity than TiO_2 for both degradation of cationic methylene blue and anionic methyl orange dyes.

REFERENCES

[1] Gaya, Umar Ibrahim, and Abdul Halim Abdullah., Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 9 (2008) 1-12.

[2] Mahlambi, M. M., C. J., Ngila, B. B., and Mamba. Recent developments in environmental photocatalytic degradation of organic pollutants: the case of titanium dioxide nanoparticles—a review. *Journal of Nanomaterials.* 5 (2015) 4-5.

[3] Mo, S. D., and W. Y. Ching, Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. *Physical Review B.* 51 (2005) 13-23.

[4] Huang, Fei, A. Y., and Hui, Z., Influences of doping on photocatalytic properties of TiO_2 photocatalyst. *Semiconductor Photocatalysis-Materials, Mechanisms and Applications.* 16 (2016) 50-53.

[5] Lee, Sung H., Photocatalytic nanocomposites based on TiO_2 and carbon nanotubes. *Chemical Society Reviews*. 41 (2004) 3-6.

[6] Tan, Y. N., C. L. W., and Rahman M., An Overview on the Photocatalytic Activity of Nano-Doped-TiO_2 in the Degradation of Organic Pollutants. *ISRN Materials Science.* 24 (2011) 6-7.

[7] Jafari, Tahereh., Photocatalytic water splitting-the untamed dream: a review of recent advances. *Molecules.* 21 (2016) 90 -93.

[8] Camarillo, Rinchend, Improving the photo-reduction of CO_2 to fuels with catalysts synthesized under high pressure: Cu/TiO_2. *Journal of Chemical Technology & Biotechnology*. 93 (2018) 1237-1248.

[9] Dam, Tapabrata, S. S. Jena, and Dillip K. P., Equilibrium state of anatase to rutile transformation for nano-structured Titanium Dioxide powder using polymer template method. *IOP Conference Series: Materials Science and Engineering*. 115 (2016) 42-45.

[10] Mahalingam, Tinchalan., Structural, optical, morphological and thermal properties of TiO_2–Al and TiO_2– Al_2O_3 composite powders by ball milling. *Physics Letters A*. 21 (2017) 1815-1819.

[11] Ganesh, I., Kumar, P. P., Gupta, A. K., Sekhar, P. S., Radha, K., Padmanabham, G., & Sundararajan, G. Preparation and characterization of Fe-doped TiO2 powders for solar light response and photocatalytic applications. *Process. Appl. Ceram,* 6(1) (2012) 21-36.

[12] Zhang, H., & Banfield, J. F. Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO2. *The Journal of Physical Chemistry B*, 104(15) (2000) 3481-3487.

[13] Van Driel, B. A., Kooyman, P. J., Van den Berg, K. J., Schmidt-Ott, A., & Dik, J., A quick assessment of the photocatalytic activity of TiO2 pigment. *Microchemical Journal*. 126 (2016) 168-170.