

## PREPARATION OF Al/Al<sub>2</sub>O<sub>3</sub> AND Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> PHOTOCATALYSTS FOR METHYL TERT-BUTYL ETHER DEGRADATION IN AQUEOUS PHASE UNDER UV LIGHT IRRADIATION

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### Abstract

Pollution of surface and groundwater by methyl tert-butyl ether (MTBE) is a serious world concern with respect to environment and human health. Human contact with MTBE has caused various ill-health problems such as fever, dizziness, cough, muscular aches, and irritation to the skin and eyes. Therefore, steps should be taken to reduce or totally eliminate the presence of such compounds in water. In this study, two types of photocatalysts, Al/Al<sub>2</sub>O<sub>3</sub> and Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> were tested in batch reactor system for the removal of MTBE in aqueous phase assisted by UV irradiation. The photocatalysts were prepared by anodic oxidation of Al plate in 0.4 M NaOH electrolyte solution. TiO<sub>2</sub> was deposited onto the surface of Al/Al<sub>2</sub>O<sub>3</sub> plate by electrolysis in an electrolyte solution containing a mixture of ammonium titanyl oxalate monohydrate, (NH<sub>4</sub>)<sub>2</sub>[TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>].H<sub>2</sub>O and hydrated oxalic acid, (COOH)<sub>2</sub>.2H<sub>2</sub>O. The results indicate that the percentage of MTBE degradation using Al/Al<sub>2</sub>O<sub>3</sub>/UV and Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/UV systems reached 89.35 % and 95.27 %, respectively. The effects of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and initial pH of MTBE aqueous phase were also studied using Al/Al<sub>2</sub>O<sub>3</sub> photocatalyst. In both systems, MTBE degradation decreased to 82.57 % in the presence of H<sub>2</sub>O<sub>2</sub>. While the optimum pH was found to be the original pH of the sample solution (pH 7.75). This study demonstrated that Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/UV system exhibited enhanced photoactivity, promoted better charge separation for degradation of organic pollutant in aqueous phase.

**Keyword:** Al/Al<sub>2</sub>O<sub>3</sub>, Electrodeposition, MTBE, Photocatalysis, TiO<sub>2</sub>

### Introduction

The replacement of gasoline additive (tetraethyl lead) by methyl *tert*-butyl ether (MTBE) since the 1970s provides a significant improvement in air quality due to less carbon monoxide being produced. Moreover, this type of additive was more preferred than alcohols as they are less difficult to handle (Pal et al., 2018). Unfortunately, this enhancement also leads to a negative impact to the environment, as it was detected frequently in groundwater as a results of its high water solubility (Tawabini & Makkawi, 2017). Although there are various existing water treatment approaches, photocatalytic process has been established to be one of the promising alternatives to combat this problem (Syazwani et al., 2018). The materials are normally used in powder form during photocatalytic water treatment. However, this type of materials is not efficient due to several drawbacks such as difficult and costly recovery process and accumulation of the photocatalyst contributes to a decrease in performance (Hir et al., 2017). Nonetheless, these problems might be well-resolved by immobilizing the photocatalytic materials on a support.

Aluminium (Al) is considered as good support since it is relatively light and cheap. When electrochemically oxidized, the aluminium oxide ( $\text{Al}_2\text{O}_3$ ) will be formed on the surface of Al plate, further protect from corrosion. Previous studies demonstrated that the use of Al plate as a support contributed to more stability when expose under UV irradiation, where the plate was not degraded by the presence of reactive radical species (e.g., hydroxyl radicals) throughout the process and was chosen as the suitable material for support in photocatalytic water treatment (Ali et al., 2010). Meanwhile, titanium dioxide ( $\text{TiO}_2$ ) was already established and extensively used for photocatalytic processes due to its large band gap energy (3.0 ~ 3.2 eV), chemically stable, low cost, and non-toxic (Bagheri et al., 2015). Aluminium coated with  $\text{Al}_2\text{O}_3$  could be beneficial for the deposition of  $\text{TiO}_2$  since  $\text{Al}_2\text{O}_3$  has pores and could act as carrier for  $\text{TiO}_2$ .

Therefore, the aim of the present work was to develop Al/ $\text{Al}_2\text{O}_3$  and Al/ $\text{Al}_2\text{O}_3$ / $\text{TiO}_2$  hybrid photocatalysts via electrodeposition technique and to examine their performance against MTBE degradation. Emphasis was placed on several operational parameters which include concentration of NaOH as electrolyte, initial pH, and oxidizing agent ( $\text{H}_2\text{O}_2$ ). It was hypothesized that the deposition of both aluminium oxide and titanium dioxide on the surface of the Al plate simultaneously improved its physicochemical properties to produce more radicals through heterojunction for the abatement of MTBE in aqueous phase.

## Materials and Methods

### Electrodeposition of Aluminium to form Aluminium Oxide

This experiment was conducted in two steps. The first step involved surface pre-treatment of the aluminium (Al) plates. The Al plate (6 cm × 5 cm × 0.1 cm) with a purity of 99.999% was rubbed with sandpaper to remove the natural oxide film, washed with distilled water and dried at room temperature. Then, the Al plate was etched by dipping in 2.0 M of NaOH solution for 3 min followed by washing with distilled water. Later, the Al plate was immersed in 3.0 M of  $\text{HNO}_3$  solution for another 3 min, washed with distilled water and dried at room temperature. In the second step, anodic oxidation of Al plate to form aluminium oxide ( $\text{Al}_2\text{O}_3$ ) surface was carried out by connecting the Al plate to the positive terminal (anode) and graphite plate (6 cm × 5 cm × 0.2 cm) to the negative terminal (cathode) of the power supply. A direct current (DC) voltage of 12 V was applied to the system while distance of both terminals was kept maintained at 5 cm and temperature of  $30 \pm 5^\circ\text{C}$  for 20 min. Then, the electrolysis was repeated for various concentrations of NaOH solution (0.1 to 0.4 M).

### Electrodeposition of $\text{TiO}_2$ onto Aluminium Oxide Substrate

The prepared electrolyte was a mixture solution containing ammonium titanyl oxalate monohydrate,  $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  ( $1.0 \times 10^{-2}$  M) and hydrated oxalic acid,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  ( $2.5 \times 10^{-3}$  M). The pH of the solution was adjusted to pH 4 using ammonium hydroxide,  $\text{NH}_4\text{OH}$  added drop-wisely. Then, Al/ $\text{Al}_2\text{O}_3$  plate was set as cathode while graphite plate as anode electrodes. The DC voltage (12 V) was applied to the system while distance of both terminals was kept maintained at 5 cm for another 20 min.

### Preparation of MTBE sample solution

The MTBE sample solution (4000 ppm) was prepared by pipetting 1352  $\mu\text{L}$  of MTBE (density,  $\rho$ : 0.740 g/mL) in 250 mL volumetric flask followed by adding the distilled water to the mark.

### Photodegradation of MTBE by using Al/ $\text{Al}_2\text{O}_3$ and Al/ $\text{Al}_2\text{O}_3$ / $\text{TiO}_2$ photocatalysts

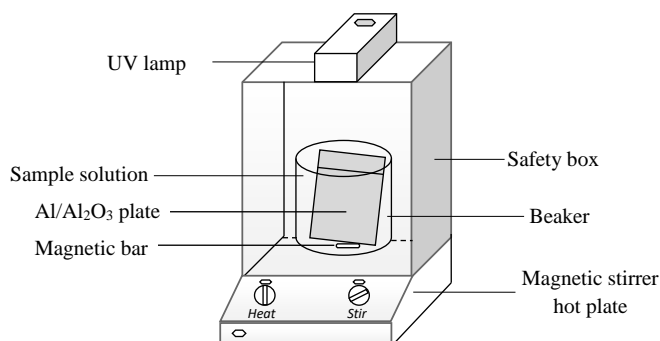
The prepared MTBE sample solution (150 mL) was put into a beaker and continuously stirred

for 30 min to form a homogeneous solution. Next, Al/Al<sub>2</sub>O<sub>3</sub> plate was dipped into the solution and UV lamp (6 W,  $\lambda = 365$  nm) was used as the energy source in this research. The beaker was sealed with parafilm to avoid evaporation. The solution containing MTBE was stirred in dark conditions for 30 min to achieve adsorption-desorption equilibrium and then irradiated with by a UV lamp for the next 3 hours. Sample of about ~5 mL was taken out at 30, 60, 90, 120, 150, 180, and 210 min time interval. Then, the absorbance of the sample was measured using UV-vis Spectrophotometer at  $\lambda_{\text{max}} = 195$  nm and the percentage of degradation was determined using formula in Equation (1).

$$\text{Percentage of degradation} = \frac{(A_0 - A_t)}{A_0} \times 100\% \quad (1)$$

Where  $A_0$  is the absorbance of MTBE before irradiation and  $A_t$  is the absorbance of MTBE at time “t”.

The experiment was repeated using Al/Al<sub>2</sub>O<sub>3</sub> plates that were prepared with various concentrations of electrolyte (0.2, 0.3 and 0.4 M NaOH) for comparison purpose and to determine the best concentration of electrolyte in the preparation these photocatalysts. All the procedures involve were then repeated using Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> photocatalysts. The degradation of MTBE was conducted in a 250 mL photoreactor, as shown in **Figure 1**.

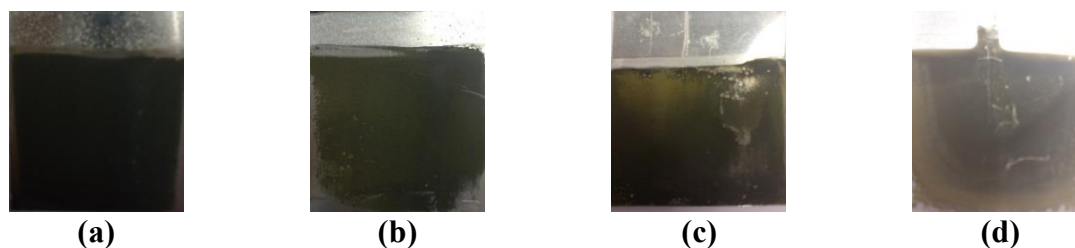


**Figure 1** Illustration of the photocatalytic reactor setup.

## Results and Discussion

### Preparation of Al/Al<sub>2</sub>O<sub>3</sub> photocatalyst

Prior to the anodization process, the surface pre-treatment of aluminium plate was required as to eliminate the natural oxide film exist on the plate. **Figure 2** shows four plates prepared at different concentrations of NaOH.



**Figure 2** Al/Al<sub>2</sub>O<sub>3</sub> plate prepared in four different concentrations of NaOH electrolyte: (a) 0.1 M, (b) 0.2 M, (c) 0.3 M, and (d) 0.4 M

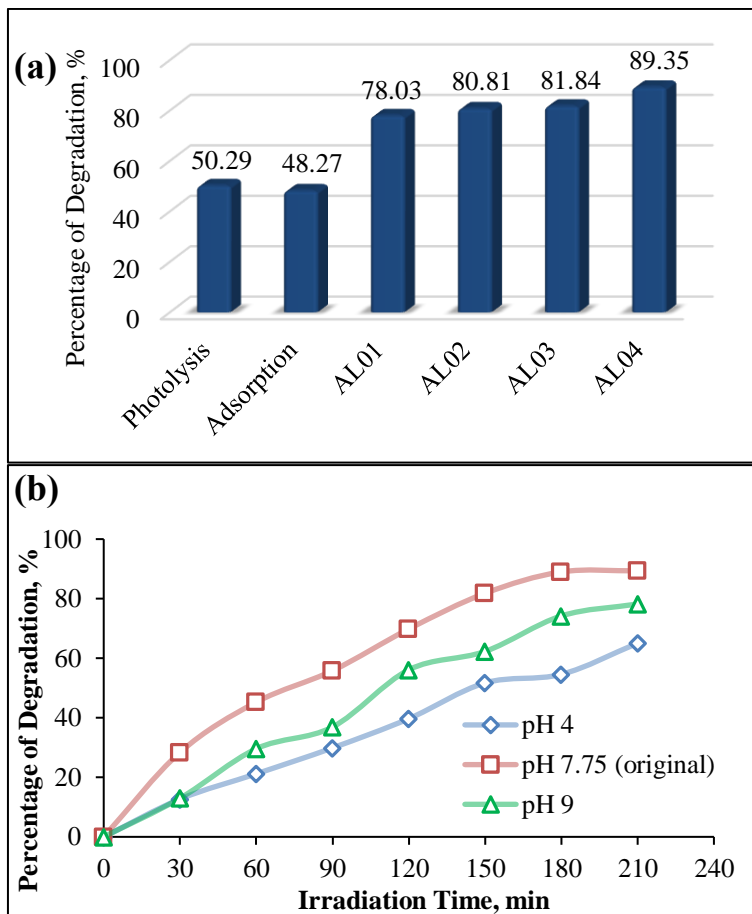
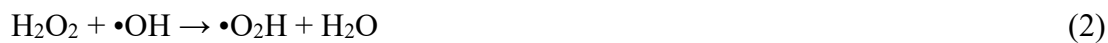
### Photocatalytic activity of the Al/Al<sub>2</sub>O<sub>3</sub> and Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> photocatalysts

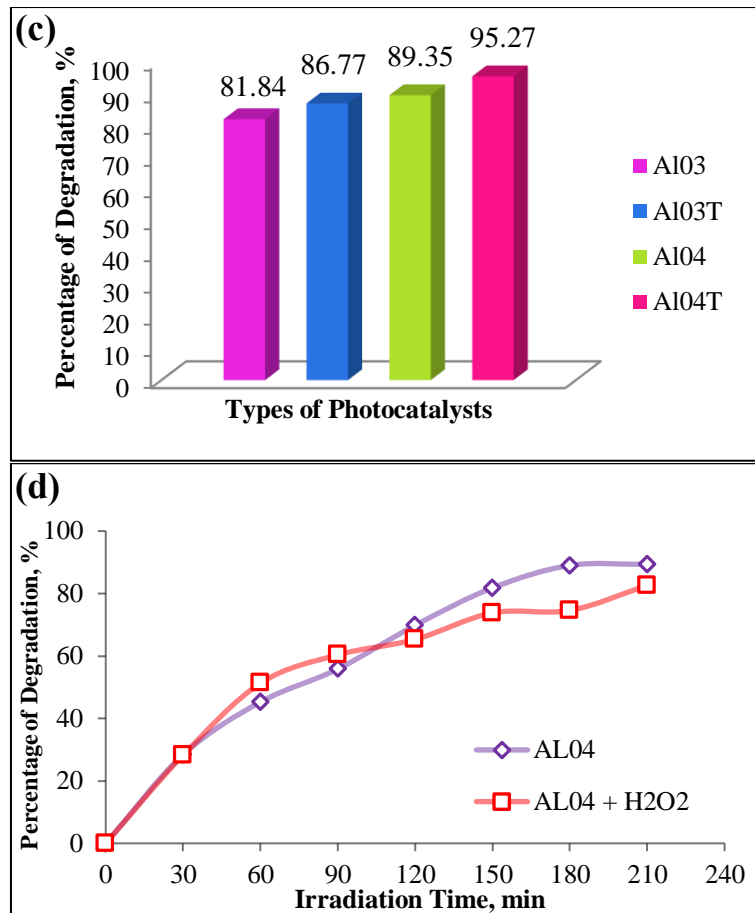
At the initial step, the photocatalytic degradation of MTBE was conducted with Al/Al<sub>2</sub>O<sub>3</sub> photocatalyst prepared using various NaOH concentrations (0.1 to 0.4 M) as the electrolyte in the anodic oxidation of Al<sub>2</sub>O<sub>3</sub> photocatalysts. The photoactivity of the prepared photocatalysts in the degradation of MTBE is displayed in **Figure 3**. The results indicate that the degradation percentage of MTBE were proportional to the concentration of NaOH electrolyte solution in the preparation of Al<sub>2</sub>O<sub>3</sub> photocatalysts. Thus, NaOH with concentration of 0.4 M was the best concentration for the preparation of Al/Al<sub>2</sub>O<sub>3</sub> plate. At this concentration, it is believed that there is formation of extra pores on the surface of the photocatalyst and these pores acted as a channel for the adsorption of MTBE from the outer surface to the interior surface of the photocatalyst (Mohamed et al., 2016). Thus, the degradation efficiency of the photocatalyst was higher with percentage obtained was 89.35%. Meanwhile, the photolysis of MTBE in the absence of Al/Al<sub>2</sub>O<sub>3</sub> photocatalyst shows lower degradation percentage of 50.29% and the percentage of MTBE adsorption was 48.27% within 210 min of reaction time (**Figure 3a**).

The difference in pH values could also influence the degradation percentage of MTBE sample in the aqueous phase. The results show that in the acidic solution (pH 4.0) gave only 65.05% of the MTBE degradation which was lower than that of pH 9.0 (78.21%). In the neutral or acidic aqueous phase, MTBE sample hydrolyzed slowly, with hydrolysis being more rapid in the alkaline condition. MTBE was protonated to bring the positive charge (electropositive) on the surface of Al/Al<sub>2</sub>O<sub>3</sub> (Safari et al., 2013). Moreover, the positively charged photocatalyst has higher adsorption towards the negatively charged MTBE due to the attraction force, which favors the interaction of holes ( $h_{vb}^+$ ) or hydroxyl radicals ( $\bullet\text{OH}$ ) with the MTBE molecules. At more alkaline pH level, the Al<sub>2</sub>O<sub>3</sub> surface becomes negatively charged by adsorbed OH<sup>-</sup> and adsorption of MTBE is not favorable (**Figure 3b**). The optimum condition of initial pH in the photodegradation of MTBE was determined at pH 7.75 (89.35%) which was the original pH of the sample solution. In the meantime, the degradation of MTBE using Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (ALT03 and ALT04) was always higher than that of Al/Al<sub>2</sub>O<sub>3</sub> (AL03 and AL04) photocatalysts. AL04 prepared in the best condition of the electrolyte concentration, NaOH shows higher photodegradation efficiency compared with AL03 photocatalyst. As expected, the immobilization of TiO<sub>2</sub> onto Al/Al<sub>2</sub>O<sub>3</sub> surface photocatalyst enhanced the degradation efficiency as compared to Al/Al<sub>2</sub>O<sub>3</sub> alone with the percentage obtained was 95.27%. This result is ~9% higher than ALT03 that was used for MTBE degradation under the same conditions (Figure 3c). These findings can be further explained based on **Figure 4**, whereby coupled photocatalysts not only enhances its photocatalytic activity but also suppress the recombination of  $h_{vb}^+$  and  $e_{cb}^-$  through heterojunction by facilitating the charge carrier transfer. The excellent charge carrier migration becomes a vital aspect for enhanced photocatalytic performance (Hir et al., 2018).

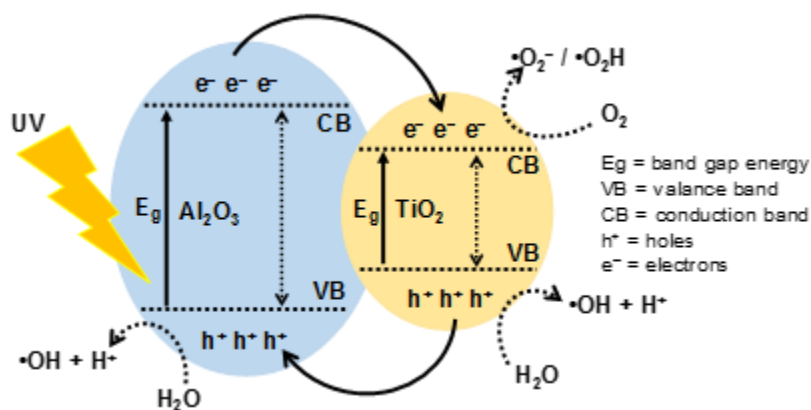
Whilst, the effect of H<sub>2</sub>O<sub>2</sub> on photodegradation of MTBE was investigated by the addition of H<sub>2</sub>O<sub>2</sub> (3 ppm) in Al/Al<sub>2</sub>O<sub>3</sub>/UV system. Initially, the degradation of MTBE in the presence of H<sub>2</sub>O<sub>2</sub> reached 60%, a little bit higher than that of pristine MTBE solution, for the first 60 min of reaction. When prolonging the reaction times up to 210 min, the degradation percentage of MTBE solution containing H<sub>2</sub>O<sub>2</sub> only reached at 82.57%, which was slightly lower than the degradation percentage of MTBE solution alone (89.35%). It is believed the lower degradation percentage was due to the occurrence of excess H<sub>2</sub>O<sub>2</sub> scavenge the valuable  $\bullet\text{OH}$  that are generated by either the photooxidation of OH<sup>-</sup> by  $h_{vb}^+$  or direct photolysis of H<sub>2</sub>O<sub>2</sub> and produce a much weaker peroxy radicals ( $\bullet\text{O}_2\text{H}$ ). Moreover, the excess H<sub>2</sub>O<sub>2</sub> can react with  $h_{vb}^+$  on the catalyst surface, thus inhibits the photocatalytic degradation process of MTBE (Figure 3d). This scenario has been explained by Pouloupoulos et al., (2019) whereby H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> bonds

can be broken by UV irradiation leading to the formation of •OH radicals. Excessive amount of H<sub>2</sub>O<sub>2</sub> would become a significant competitor for •OH, hence the reduced oxidative destruction of MTBE. This is expressed in Equation (2).





**Figure 3** (a) Percentage of degradation, photolysis and adsorption of Al/Al<sub>2</sub>O<sub>3</sub> prepared with various concentrations of NaOH electrolyte (0.1–0.4 M), (b) Effect of initial pH by using AL04, (c) Comparison between Al/Al<sub>2</sub>O<sub>3</sub> and Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> prepared with two concentrations of NaOH electrolyte (0.3 and 0.4 M), (d) Effect of H<sub>2</sub>O<sub>2</sub> on the degradation of MTBE in aqueous phase by using AL04



**Figure 4** Schematic diagram illustrating the separation and transfer of photogenerated electron-hole pairs in Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/UV system

### Conclusion

Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> photocatalyst found to be the most effective catalyst where they exhibited higher photocatalytic activity on the MTBE degradation compared with Al/Al<sub>2</sub>O<sub>3</sub> when exposed under UV irradiation. The percentage degradation of MTBE by using ALT04 photocatalyst was 95.27% and yet, 89.35% of MTBE degradation was obtained for AL04 photocatalyst. Aluminium coated Al<sub>2</sub>O<sub>3</sub> was useful as a substrate for the TiO<sub>2</sub> because the Al<sub>2</sub>O<sub>3</sub> has pores and acted as a carrier for the photocatalyst. Meanwhile, the Al/Al<sub>2</sub>O<sub>3</sub> photocatalyst gave higher degradation percentage at pH 7.75, which was the original pH of the MTBE aqueous phase. However, in the presence of excess H<sub>2</sub>O<sub>2</sub> as the oxidizing agent, the percentage of degradation was significantly reduced to 82.57% due to presence of excessive amount of •OH radicals in the working solution which are competing against each other.

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### Conflict of interests

The authors declare that there are no conflicts of interest associated with this publication, and there has been no significant financial support for this work that could have influenced its outcome.

### References

- Ali, R., Abu Bakar, W. A. W., & Teck, L. K. (2010). Zn/ZnO/TiO<sub>2</sub> and Al/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Photocatalysts for the Degradation of Cypermethrin. *Modern Applied Science*, 4(1), 59–67.
- Bagheri, S., Hir, Z. A. M., Yousefi, A. T., & Hamid, S. B. A. (2015). Progress on mesoporous titanium dioxide: Synthesis, modification and applications. *Microporous and Mesoporous Materials*, 218(2015), 206–222.
- Hir, Z. A. M., Abdullah, A. H., Zainal, Z., & Lim, H. N. (2017). Photoactive Hybrid Film Photocatalyst of Polyethersulfone-ZnO for the Degradation of Methyl Orange Dye: Kinetic Study and Operational Parameters. *Catalysts*, 7(11), 1–16.
- Hir, Z. A. M., Abdullah, A. H., Zainal, Z., & Lim, H. N. (2018). Visible light-active hybrid film photocatalyst of polyethersulfone-reduced TiO<sub>2</sub>: photocatalytic response and radical trapping investigation. *Journal of Materials Science*, 53(18), 13264–13279.
- Mohamed, M. A., W. Salleh, W. N., Jaafar, J., Ismail, A. F., Mutalib, M. A., Sani, N. A. A., ... Ong, C. S. (2016). Physicochemical characteristic of regenerated cellulose/N-doped TiO<sub>2</sub> nanocomposite membrane fabricated from recycled newspaper with photocatalytic activity under UV and visible light irradiation. *Chemical Engineering Journal*, 284, 202–215.
- Pal, D. B., Lavania, R., Srivastava, P., Singh, P., Srivastava, K. R., Madhav, S., & Mishra, P. K. (2018). Photo-catalytic degradation of methyl tertiary butyl ether from wastewater using CuO/CeO<sub>2</sub> composite nanofiber catalyst. *Journal of Environmental Chemical Engineering*, 6(2), 2577–2587.
- Pouloupoulos, S. G., Yerkinova, A., Ulykbanova, G., & Inglezakis, V. J. (2019). Photocatalytic treatment of organic pollutants in a synthetic wastewater using UV light and combinations of TiO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and Fe(III). *PLoS ONE*, 14(5), 1–20.

Safari, M., Nikazar, M., & Dadvar, M. (2013). Photocatalytic degradation of methyl tert-butyl ether (MTBE) by Fe-TiO<sub>2</sub> nanoparticles. *Journal of Industrial and Engineering Chemistry*, 19(5), 1697–1702.

Syazwani, O. N., Mohd Hir, Z. A., Mukhair, H., Mastuli, M. S., & Abdullah, A. H. (2018). Designing visible-light-driven photocatalyst of Ag<sub>3</sub>PO<sub>4</sub>/CeO<sub>2</sub> for enhanced photocatalytic activity under low light irradiation. *Journal of Materials Science: Materials in Electronics*, 30(1), 415–423.

Tawabini, B., & Makkawi, M. (2017). Remediation of MTBE-contaminated groundwater by integrated circulation wells and advanced oxidation technologies. *Water Science & Technology: Water Supply*, 18(2), 399–407.