

The Surface Distribution and Recyclability Study on Photodegradation Methylene Blue dye of Immobilized TiO₂ under Surfactant Effect

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ABSTRACT

Immobilised titanium dioxide (TiO₂) was prepared using commercially available carbon-doped TiO₂ from Kronos VLP 7000 (Kronos). TiO₂ was immobilised using a low amount of polyvinyl alcohol (PVA) as a polymer binder with various surfactants onto a glass plate as a support material using the double-sided adhesive tape (DSAT) technique. The photocatalytic activity of the immobilised TiO₂ was evaluated by photocatalytic degradation of methylene blue (MB) dye. The prepared immobilised TiO₂ without surfactant showed a poor coating with an uneven surface layer. In contrast, a significant surface improvement was observed by adding surfactant due to the dispersion of the PVA binder. The immobilised TiO₂ with cetyltrimethylammonium bromide (CTAB) has shown better coating distribution and high adhesiveness compared with other surfactants. The XRD spectrum showed no phase transformation from anatase to rutile on immobilised TiO₂ and TiO₂-CTAB with an identical peak spectrum for both samples. PVA was represented by C-C, C-O, and O-H bonding peaks. In contrast, CTAB represented C-C bond stretching vibration, C-H bond stretching vibration, and C-N bond stretching functional vibration groups in immobilised TiO₂-CTAB detected by FTIR analysis. The immobilised TiO₂-CTAB shows good reusability and adhesiveness. It shows slightly lower photocatalytic activity with suspension mode TiO₂ for the first three cycles. However, higher photoactivity was observed beyond the third cycle, nearly three times faster than TiO₂ in suspension mode for the 8th-10th cycles. This might be due to the synergistic effect of CTAB that plays a role as surface distribution and pore-forming agent, making the increment of TiO₂ surface active site to the reactant volume ratio.

Keywords: *Surface Morphology, Kronos, DSAT, Immobilized Kronos-CTAB, Reusability*

INTRODUCTION

Heterogeneous photocatalysts have emerged as the primary focus of researchers conducting dye degradation. This photocatalyst also has high stability for degrading organic pollutants. Photocatalysis is a technique that uses UV radiation to decompose organic dyes into water and carbon dioxide via photocatalysts or semiconductors. TiO_2 , ZnO , Fe_2O_3 , CdS , ZnS , and V_2O_5 are examples of photocatalysts that have been used in photocatalysis techniques. Photocatalyst has environmental benefits such as saving water, energy, chemicals, and other cleaning materials [1]. These photocatalysts are used in either slurry or immobilised form in the photocatalysis process.

Photocatalysis in a slurry system with suspended nanoparticles is the most common type of system that has been used. The significant advantage of the slurry system is the high volume of the specific surface area of photocatalyst nanoparticles in contact with the substrate in the suspension [2]. However, in practical use, immobilised reactor systems are preferred. This immobilised system allows photocatalysis to operate continuously without filtration, and the catalytic support can be recycled. However, the immobilised photocatalyst has some limitations, including a low surface coating intact with the support material and poor surface smoothness, leading to lower efficiency and cosmetic flaws [2, 3]. Many researchers have immobilised TiO_2 on silicate support materials such as MCM-41, immobilised TiO_2 on Na-HZSM-5 as a composite, and tin and titanium are incorporated into the rice husk silica nanocomposites. Recently, the immobilised system of TiO_2 has been designed with a new approach of binder known as Double Sided Adhesive Tape (DSAT) [4]. However, this immobilised TiO_2 photocatalyst still has limitations, including poor distribution surface on the support material due to high energy. It tends to agglomerate TiO_2 particles between each other, causing a low surface intact on the support material [5, 6].

A surfactant can be employed as a dispersion to overcome agglomeration and poor surface distribution on the immobilised TiO_2 . The surfactant's molecular structure and amphiphilic properties can block the high-density aggregation of nanoparticle photocatalysts and act as a stabiliser and a dispersant [7]. Thus, the surface of the immobilised TiO_2 can be enhanced to be well distributed with a high surface intact on the support material. Hence, the catalytic activity of immobilised TiO_2 is retained. Therefore, in the present work, the enhancement of surface distribution on immobilised TiO_2 was conducted in the early-stage preparation of the coating solution using different types of surfactants. These surfactants, including sodium benzoate, polyethylene glycol (PEG) and cetyltrimethylammonium bromide (CTAB), were used in this experiment in order to find the optimum surfactant for enhancing the surface coating of the immobilised TiO_2 .

EXPERIMENTAL

Preparation of Immobilized TiO_2

Immobilised TiO_2 was prepared using commercially available carbon-doped TiO_2 (Kronos VLP 7000). The formulation of the photocatalyst was prepared by homogenising 1.57 g carbon-doped TiO_2 in 40 mL distilled

water with both 8 ml of PVA and CTAB, respectively, under continuous stirring for 24 h. Next, the prepared formulation was coated onto a glass plate which was previously stacked with double-sided adhesive tape (DSAT) with dimension 5 cm (height) x 7 cm (length) by using a brush coating technique [4-6]. The mass loading of the coated photocatalyst was standardised at 0.050 ± 0.003 g. The immobilised TiO₂ photocatalysts were cleaned in aerated condition with light irradiation for one hour using distilled water before photocatalytic activity. A similar procedure was repeated by replacing CTAB with PEG and sodium benzoate to study the TiO₂ immobilisation effect on different surfactants.

Characterization Studied

The surface of the immobilised TiO₂ at various surfactants was observed using an Olympus stereomicroscope (model SZ2-LGB). Fourier Transform Infrared Spectroscopy (FTIR), brand Perkin Elmer FTIR spectrometer 1650 within range wavenumber from 4000 cm⁻¹ to 400 cm⁻¹ was used to determine the compound present in the samples. The X-ray diffractometer (XRD) (PANalytical X'Pert Pro PW3060/20 from Jerman) was used to determine both immobilised samples' crystallinity and phase transformation in 2θ ranges of 20 to 90.

Photocatalytic Activity of Immobilized TiO₂

The photocatalytic activity study of immobilised TiO₂ samples with various surfactant effects was conducted in glass cells 150 x 100 x 80 mm (L x W x H). The immobilised photocatalytic activity of the immobilised photocatalyst was carried out using 15 mL of 12 mg L⁻¹ MB poured into the glass cell. The immobilised photocatalyst was then immersed into a glass cell containing MB and was irradiated with a 55-W fluorescent lamp with 450 W m⁻² of light intensity, as illustrated in Figure 1. An aquarium pump model NS 750 was used as an aeration source of oxygen. 3 mL of aliquot was taken from the glass cell at a specific interval, and measure the absorbance was using UV-spectrophotometer (HACH DR 1900) [4-6]. The photodegradation rate was determined by following Langmuir Hinshelwood kinetic model using a pseudo-first-order rate constant to identify the photocatalytic efficiency of prepared then immobilised TiO₂. The same procedure was repeated for the TiO₂ in suspension mode as a comparison study.

$$r = dC / dt = k' KC / 1 + KC \quad \text{Equation 1}$$

$$r = k' KC = kC \quad \text{Equation 2}$$

$$\ln C_0/C = kt \quad \text{Equation 3}$$

Equation 1 describes the Langmuir Hinshelwood Kinetic model where r is a rate constant, C is the substrate concentration (mg L⁻¹) at a given time (t, second), K is Langmuir Hinshelwood adsorption equilibrium constant (mg L⁻¹) and k' is the surface reaction rate (mg L⁻¹ min⁻¹). At a high diluted solution ($M < 10^{-3}$, $C < 108$ mg L⁻¹), the term KC is negligible concerning time t, the above equation 1 will be simplified as an apparent or pseudo-first-order equation shown in equation 2: Where the k represent the first-order rate constant of the reaction (min⁻¹) C₀ is the initial concentration of the dye (mg L⁻¹), and the t is the irradiation time (min) by plotting ln (C₀/C) versus t of the equation 3 yield a straight line whose slope

is k . the rate constant, k was discovered for each photocatalyst sample and used to measure the photocatalytic activity of the sample.

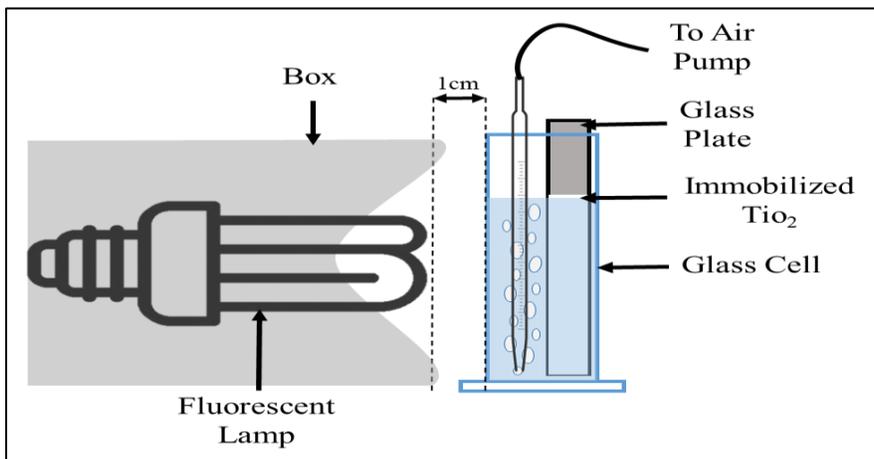


Figure 1: Schematic diagram of the experimental photocatalytic activity configuration

Reusability Study of Immobilized TiO₂

The optimum surfactant effect of immobilised TiO₂ underwent the reusability study by repeating the photocatalytic activity procedure using the same immobilised sample for ten cycles. The immobilised TiO₂ sample was air-dried to remove excessive water and continued washing using distilled water for an hour before the next cycle until ten reusability experiment studies were completed.

RESULTS AND DISCUSSION

Stereomicroscope

The immobilised TiO₂ was prepared using different surfactants to enhance the surface distribution of the immobilised catalyst. Three types of different ionic surfactants were used in the preparation of immobilised TiO₂, which are cetyltrimethylammonium bromide (CTAB), polyethylene glycol (PEG) and sodium benzoate (SB), which are cationic, anionic and non-ionic respectively [8-10]. Three different formulations using different surfactants were coated onto a glass plate via the DSAT method and marked as TiO₂-CTAB, TiO₂-PEG, and TiO₂-SB.

Figure 2 shows the stereomicroscope images of the immobilised TiO_2 coating surface with and without surfactants. All TiO_2 immobilised coating samples have shown the TiO_2 intact to the support glass plate. An immobilised TiO_2 coating sample (without surfactant) has shown a poorer coating ability where TiO_2 was not coated entirely onto the glass cell with a rough surface coating due to the agglomeration of PVA. The immobilised TiO_2 with additional surfactants has shown a better coating effect where the smooth immobilised TiO_2 surface was observed. It shows that the presence of surfactant prevents the PVA agglomeration [11-13].

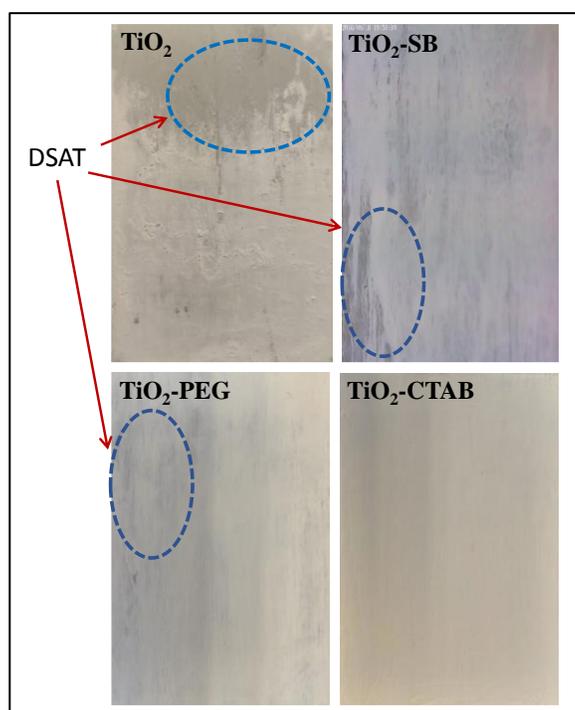


Figure 2: Stereomicroscope images of immobilised TiO_2 surface coating with and without surfactant effect

Immobilised TiO_2 -CTAB coating has an even-surface coating compared to immobilised TiO_2 -PEG and TiO_2 -SB coating plates. Immobilised TiO_2 -PEG coating plate has easily leached out from the plate, causing the solution to become cloudy. In contrast, the TiO_2 -SB coating plate has difficulty remaining attached to the DSAT binder during the coating process. Thus, the immobilised TiO_2 , TiO_2 -PEG and TiO_2 -SB plates cannot perform photocatalytic activity as immobilised mode catalysts since the catalyst does not attach to the coating plate. Immobilised TiO_2 -CTAB coating plate has shown better adhesiveness coating where it does not leach out when in contact with dyes before or after photocatalytic activity. This is due to the CTAB molecules that can be retained as a double layer on the catalyst's surface and act as protecting agents [14].

Characterisation Study

The XRD pattern of relative intensity versus 2θ for immobilised TiO_2 and immobilised TiO_2 -CTAB is shown in Figure 3. Based on the XRD pattern, no phase transformation is observed from anatase to rutile for immobilised TiO_2 -CTAB since the preparation of immobilised TiO_2 -CTAB does not involve high temperature. Moreover, there are no crystallinity changes based on the prepared immobilised TiO_2 -CTAB particles.

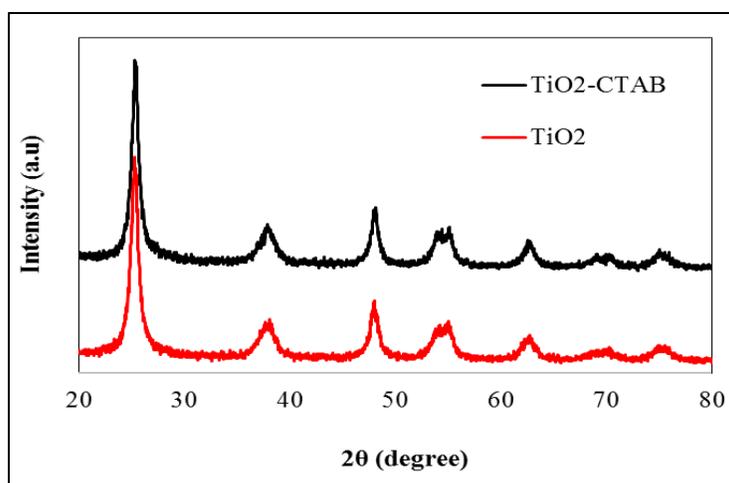


Figure 3: XRD pattern of immobilised TiO_2 and TiO_2 -CTAB

Figure 4 a) shows that the FTIR spectrum begins with PVA, CTAB, immobilised TiO_2 and immobilised TiO_2 -CTAB. The spectra reveal a broad peak in the region of 3600 to 2600 cm^{-1} on both immobilised TiO_2 and immobilised TiO_2 -CTAB, as can be seen in Figure 4 b), indicating the characteristic of O-H stretching mode of interacting hydroxyl groups and the symmetric asymmetric O-H stretching mode of molecular water of Ti^{4+} [15]. The peaks at 719 , 1426 , and 1633 cm^{-1} in immobilised TiO_2 -CTAB indicated the presence of C-C stretching bond vibration, C-H bond bending of C-H₂ and C=O of carbonyl stretch of PVA, respectively.

However, the peaks representing O-H stretching and C-O stretching do not appear in immobilised TiO_2 -CTAB due to the low percentage of PVA in the sample [16]. At the same time, regions 1500 and 2856 - 2918 cm^{-1} indicated the presence of C-C bond stretching vibration and C-H scissoring vibration of the $\text{CH}_3\text{-N}^+$ in CTAB, respectively, in the immobilised TiO_2 -CTAB sample [17-18]. C-N stretching vibration band at peak 966.1 cm^{-1} is shifted to 956 cm^{-1} in the immobilised TiO_2 representing the functional group of CTAB was observed in immobilised TiO_2 -CTAB as shown in Figure 3 b) [18].

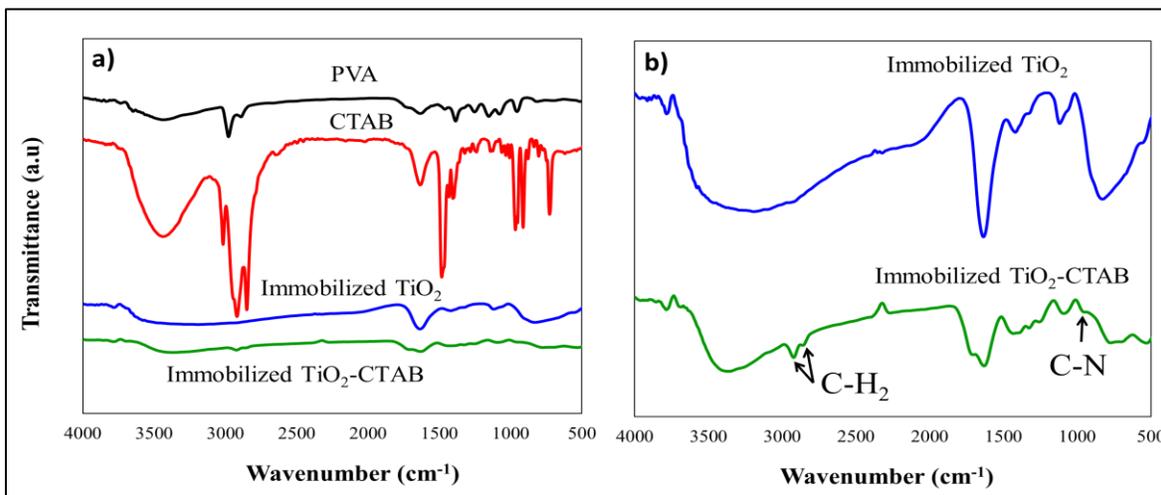


Figure 4: FTIR spectra of a) PVA, CTAB, immobilised TiO_2 and TiO_2 -CTAB and b) enlargement scale for immobilised TiO_2 and TiO_2 -CTAB

Photocatalytic Activity and Reusability Study of Immobilized Photocatalyst

In Figure 5 c), the photocatalytic activity study was conducted for ten cycles to examine the reusability of immobilised TiO_2 -CTAB under the photocatalysis process. The graph shows that the reusability trend of immobilised TiO_2 -CTAB increases significantly from the first to the eighth cycle. It was observed that the immobilised TiO_2 -CTAB surface has slight changes due to the removal of the binder or polymer that was previously added to the solution. It was observed that the highest photocatalytic activity occurred at the eighth cycle of immobilised TiO_2 -CTAB, and it was a 24 and 42 % increment in comparison with the suspension modes of TiO_2 and P25, respectively.

The highest photocatalytic degradation rate of the eighth cycle immobilised TiO_2 -CTAB is believed to come from several factors; i) increasing the TiO_2 surface-active site from the PVA removal upon cycle. ii) synergistic effect of the CTAB enhances surface distribution as protecting and pore-forming agent of TiO_2 [14,19,20]. We also believe that CTAB functional group (C-C) may be transformed into (C=C) as it can act as a sensitizer [21].

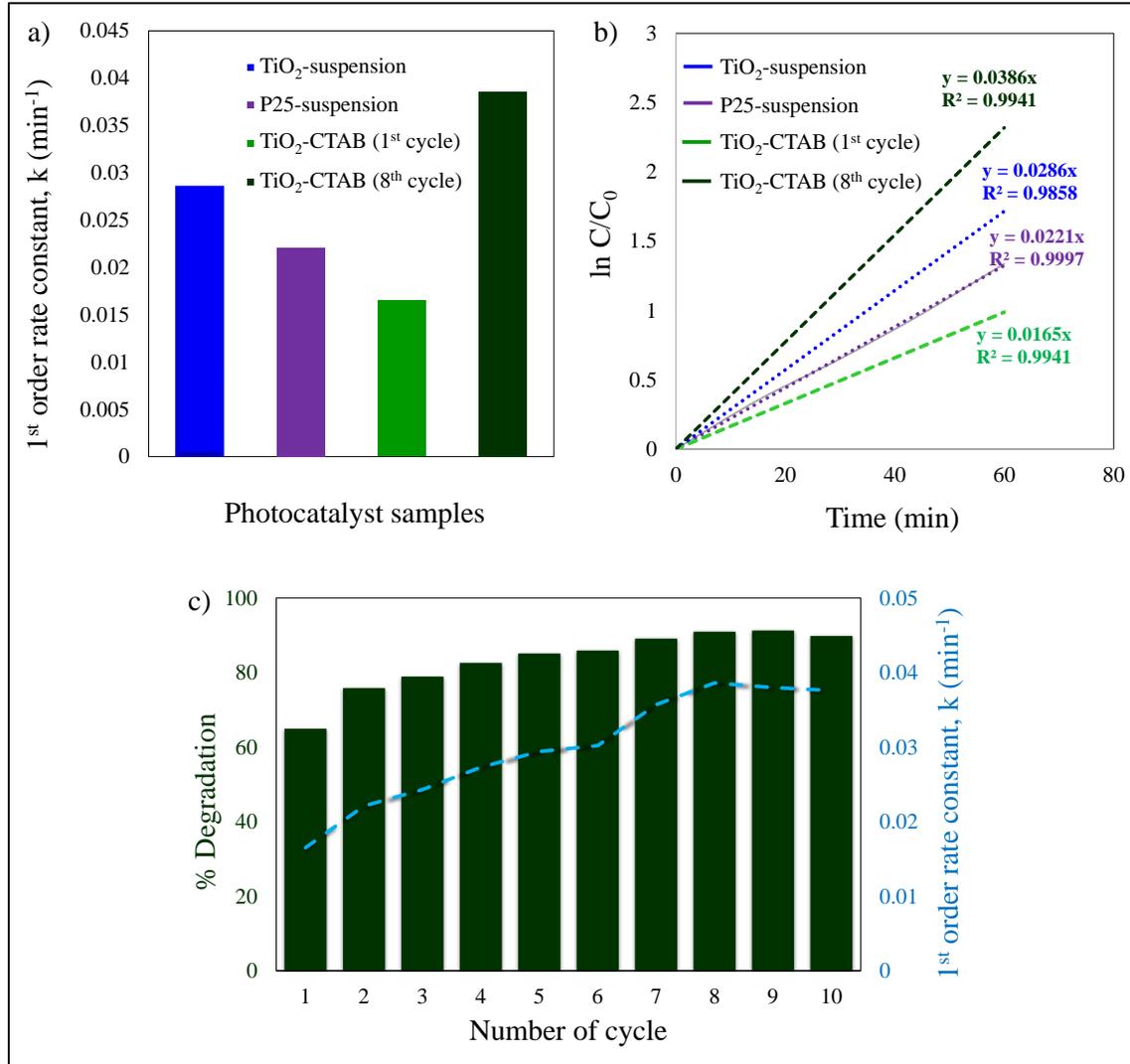


Figure 5: Photocatalytic degradation rate of photocatalysts a), linear regression plots of pseudo-first-order rate constant using Langmuir Hinshelwood kinetic model b), and c) reusability study of immobilised TiO₂-CTAB photocatalyst

CONCLUSION

This immobilised TiO₂ with additional surfactant was successfully prepared using the DSAT method. The addition of CTAB as surfactant into immobilised TiO₂ showed an even-surface coating with high adhesiveness onto the DSAT compared to PEG and SB. The XRD pattern of immobilised TiO₂-CTAB showed no phase and crystallinity changes due to the low temperature involved during preparation. Several

functional groups of CTAB and PVA were present in the immobilised TiO₂-CTAB, such as C-C stretching, C-H stretching, C-N stretching, C-C stretching, C-H bending, and C=O carbonyl, respectively. All samples' photocatalytic degradation of MB dye followed the pseudo-first-order rate constant with an R² greater than 0.900. The first cycle immobilised TiO₂-CTAB shows a lower photocatalytic degradation of MB compared to the suspension mode of TiO₂ and P25 due to low the surface-active site. However, the photoactivity of immobilised TiO₂-CTAB was increased after the eighth cycle, where the photodegradation rate was 24 and 42 % higher than TiO₂ and P25 in suspension mode, respectively. A detailed explanation of this observation should be further studied to justify the factor behind this significant increment.

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AUTHOR'S CONTRIBUTION

Muhammad Syahirul Ikhwan: Carried out the research, perform analysis, validation, wrote and revised the article - original draft. Nur Syazana Nazeri: Design the analysis and contributed data or analysis tools. Nadiah Sabihah Natar: Conceptualization. Nureel Imanina Abdul Ghani: Visualization. Muhammad Afiq Rosli: Conceptualization. Siti Raihan Hamzah: Visualization. Mohd Azlan Mohd Ishak: Writing – review and editing. Siti Nur Liyana Mamaud : provided the theoretical framework. Mohammad Saifuldin Mohd Azami: Data curation, review and proofread. Wan Izhan Nawawi: Data curation, funding acquisition, writing and supervised.

CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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