Design of photoreactor with high sunlight concentration for improved photocatalytic degradation of dye pollutant

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Abstract. A homemade reactor was designed and fabricated with the use of P25 Degussa TiO2 as the photocatalyst. P25 Degussa nanoparticle is a mixture of 75% anatase and 25% rutile. It is more efficient than pure anatase polymorphs because anatase had a larger band gap. This will increase the useful wavelength range of photocatalytic reaction and also the size of the rutile crystal lattice become smaller, thus enhance the photocatalytic reaction. The performance of the homemade reactor was evaluated with a different parameter like the different type of dyes, different dosage, different concentration and compare with the conventional method (beaker). The photolysis of methyl blue (MB), methyl orange (MO) and Rhodamine B (RhB) in the absence of photocatalyst recorded an overall efficiency of 64%, 56%, and 48% respectively. The photodegradation of dyes in the presence of photocatalyst achieved an overall efficiency of 85%, 49%, and 96%, respectively. The overall efficiency can achieve 100% after 2 h of reaction time with 2 g of P25 Degussa. The homemade reactor reached a better degradation rate than that of a conventional method (beaker).

1. Introduction
The dyes pollution is difficult to mineralize, treat or degrade as it is associated with suspended solid, non-biodegradable substances like additives, detergents, heavy metals and others. They are difficult to remove in conventional water treatment and some which design to have high solubility in water may transport easily underwater like river and groundwater [1]. Conventional wastewater treatment method such as adsorption, irradiation, filtration process, oxidative processes, coagulation and other processes are usually applied to degrade the organic dyes. Among these process, the advanced oxidation processes (AOPs) has gained increasing attention because it is environmental friendly and had potential to mineralize the organic dyes. Photocatalysis is one of the AOPs which is widely applied to decompose organic pollutants [2], water purification and also self-cleaning surface with the presence of semiconductor photocatalyst.

During heterogeneous photocatalysis, the use of the photocatalyst is important for the whole process. The photocatalyst is usually semiconductor materials like zinc oxide (ZnO), cadmium sulfide (CdS), graphitic carbon nitride (g-C3N4), and others. This is because they produce no residue, the chemical itself will not change, and the contaminant is attracted by the catalyst to the surface, continuously in low
Among those semiconductor catalysts, the most widely used is titanium dioxide (TiO$_2$). It is inert to chemical environment, stable in water or air, can be used in both homogeneous and heterogeneous catalysis and safe to use in many industries \[4\]. TiO$_2$ is chosen as photocatalyst to remove dye pollutant because it shows a high reactivity and stability when exposed to UV light. However, the bulk TiO$_2$ powder which had small surface area will less efficient in the degradation of dye pollutant. Besides that, the TiO$_2$ photocatalyst are difficult to be separated after treatment and the accumulation of TiO$_2$ may cause health issues to human. To reduce these limitations, photocatalyst which had relatively higher surface area, and any effective method to separate the photocatalyst after the treatment can be applied when designing the photoreactor.

Sunlight is used to illuminate the TiO$_2$ because it is abundant and readily available in Malaysia. It is also an energy saving sources of light when compare to other light sources like xenon lamp and mercury lamp. The photocatalytic performance of TiO$_2$ is restricted by its large band gap (3.2 eV) which allows it to harvest a minor portion of UV light (~5%) in solar spectrum to drive photocatalysis \[5\]. Hence, a homemade photoreactor with high sunlight concentration was designed to improve the photocatalytic performance of TiO$_2$. A feasibility study was done by varying the parameters of experimental condition such as effect of dosage of P25 Degussa TiO$_2$, effect of RhB dye concentration and effect of different type of dyes. Besides, a comparison between homemade reactor and conventional reactor was also carried out.

2. Materials and methods

TiO$_2$ Degussa P25 (Sigma Aldrich, > 99.5 %) was contained anatase and rutile phase in ratio of 3 to 1, it was used as the photocatalyst. MB dye (Sigma Aldrich, 85 %), MO dye (Sigma Aldrich, > 82 %) and RhB dye (Sigma Aldrich, > 95 %) was used as the pollutant model to investigate the photocatalytic reaction of the designed reactor.

2.1. Characterization of TiO$_2$ Degussa P25

The powder X-ray diffraction (XRD, PANalytical-Empyrean) patterns were obtained with Cu Kα radiation at a scanning speed of 0.02° s$^{-1}$. Fourier transform infrared (FTIR, Perkin Elmer Spectrum 400 spectrophotometer) spectra were perform with the samples dispersed in KBr and extreme drying within the range of 400–4000 cm$^{-1}$. Ultraviolet-visible diffuse reflectance spectra (DR 6000™ UV-Vis spectrophotometer (Hach) was used to determine the intensity of light passing through MB solution ($\lambda_{max}$= 664 nm). Ultraviolet-visible diffuse reflectance spectra (UV-DRS) were acquired using Shimadzu UV-2600 spectrophotometer equipped with integrating sphere attachment with BaSO$_4$ as a reference. High resolution scanning electron microscope images (SEM) were obtained at 200 kV.

2.2. Homemade reactor and photocatalytic activity

Aluminium foil wrapped the outer surface of the reactor to reflect or concentrate the sunlight to the reactor (figure 1). The baffle consists of the rigid foam that was made by polymer plastic. The pump was used to pump the dye solution upward and flowed into the reactor through a hole, then the baffle channelled the water flow. After that, the water flowed out from the reactor through a hole and back to the pump. The dyes solution was repeated for a few cycles until the treatment ended.

The performance of the homemade reactor was evaluated by the photodegradation of RhB dye under sunlight irradiation. It was allowed to recycle in the homemade reactor for 1 h in the dark to reach the adsorption-desorption equilibrium followed by the photodegradation under sunlight irradiation. 5 ml of sample was collected for each 30 min and taken into small centrifugal bottles. Then the absorbance was measured by the Cary 100 UV-vis spectrophotometer. The experimental condition to test the performance of homemade reactor is tabulated in table 1.
Figure 1. The setup of homemade reactor.

Table 1. Experimental condition to test the performance of homemade reactor.

| Exp. | Research                                      | Initial concentration (ppm) | Volume (L) | Dosage of P25 Degussa TiO$_2$ (g) |
|------|-----------------------------------------------|----------------------------|------------|-----------------------------------|
| 1    | Blank                                         | 10                        | 4          | 0                                 |
| 2    | Effect of dosage of P25 Degussa TiO$_2$       | 10                        | 4          | 0.5, 1, 2                         |
| 3    | Effect of concentration                       | 10, 15, 20                | 4          | 2                                 |
| 4    | Homemade reactor vs beaker                    | 10                        | 4          | 2                                 |

3. Results and discussion

3.1. Characteristics of TiO$_2$ Degussa P25

From figure 2, the SEM image reveals that P25 Degussa TiO$_2$ agglomerated and tightly packed together and had wide distribution of particles sizes. The P25 Degussa TiO$_2$ consists of high amount of titanium (Ti) which is 63.76%, and 32.34 % of oxygen (O). Figure 3 shows the XRD pattern of P25 Degussa TiO$_2$ which consists of two different crystal structures which are anatase and rutile. The peaks of anatase structure were observed at 25.26°, 37.92°, 48.02°, 53.28°, 55.24°, 62.94°, 70.18°, and 79.06° corresponding to miller indices (5 8 0), (1 1 2), (1 7 6), (1 2 2), (0 8 6), (0 7 8), (0 4 0), and (0 2 4) respectively. Whereas the rutile peaks were at 27.54°, 36.8°, 42.22°, 75.1°, and 82.98°, corresponding to miller indices (1 3 8), (0 5 4), (0 1 2), (0 6 4), and (0 2 0) respectively. According to Tauc plot, the band gap energy of the P25 Degussa TiO$_2$ was obtained through the intercept of the tangent of the curve to x-axis (photon energy) which is shown in figure 4. The obtained band gap for P25 Degussa TiO$_2$ is 3.25 eV.

Figure 2. The SEM image and EDX of P25 Degussa TiO$_2$. 
3.2. Photodegradation experiment
The photocatalytic activity of P25 Degussa TiO$_2$ in homemade reactor was observed from each parameter. The first experiment is to investigate the effect of different types of dyes on the photocatalytic degradation efficiency. From figure 5, it is observed that the photolysis of MB dyes degraded the fastest compared to that of RhB and MO dyes. This is because MB chromophore is thiazine group, which is less complex and easier to break the bonds such as C-C, C-N, C-S and C-O with aromatic groups [6]. Whereas the photolysis of RhB is the slowest. This is because the RhB dyes chromophore is xanthene group which is more complex and more bonds than MB dyes [7]. So, it require more time to break the bonds. The result of the blank photodegradation is tabulated in table 2.

| Type of dyes | P25 Degussa TiO$_2$ dosage (g) | Concentration (ppm) | Volume (L) | Overall efficiency (%) | Rate of degradation (%) |
|--------------|---------------------------------|---------------------|------------|------------------------|-------------------------|
| RhB          | 0                               | 10                  | 4          | 48                     | 6                       |
| MO           | 0                               | 10                  | 4          | 56                     | 8                       |
| MB           | 0                               | 10                  | 4          | 64                     | 9                       |

Figure 5. Blank photolysis of different type of dyes without the use of catalyst.

Figure 6. Effect of different dye towards the degradation efficiency.

Figure 6 and table 3 display the degradation rate of different dyes in the presence of photocatalyst in the dark adsorption and photocatalysis. Contrary to the blank photolysis, the RhB dye was degraded the fastest compared to that of MB and MO. The degradation rate of RhB dye was 96% after 2 h of sunlight illumination. The result was different from the photodegradation in the absence of photocatalyst in which
the MB dye was degraded the fastest. This is because many bubbles formed in RhB dyes. The bubbled which contain oxygen had increased the photodegradation as the presence of oxygen increased the production of the \( \cdot \text{OH} \) radicals. Hence, it resulted in higher photodegradation rate. The photodegradation efficiency of MO was 49% after 2 h, which was the slowest among the dyes. This is because the MO did not produce bubbles during the research.

In second experiment, the photodegradation rate increased in the presence of photocatalyst. Under sunlight irradiation, the P25 Degussa TiO\(_2\) which had wide particle size distribution as shown in SEM analysis increased the absorption spectral range from 300 nm based on UV-Vis absorption spectra analysis of P25 Degussa TiO\(_2\), which was higher than UV light (254 nm) [7]. It could lead to a higher generation of hydroxyl radicals, and hence a faster the photodegradation rate was observed.

| Type of dyes | P25 Degussa TiO\(_2\) dosage (g) | Concentration (ppm) | Volume (L) | Adsorption Efficiency (%) | Overall efficiency (%) | Rate of degradation (%) |
|--------------|----------------------------------|---------------------|------------|--------------------------|------------------------|------------------------|
| RhB          | 1g                               | 10                  | 4          | 2                        | 96                     | 32                     |
| MO           | 1g                               | 10                  | 4          | 39                       | 49                     | 1                      |
| MB           | 1g                               | 10                  | 4          | 7                        | 85                     | 24                     |

The third experiment is to evaluate the performance of homemade reactor with different dosage of P25 Degussa TiO\(_2\). RhB dye was used as pollutant model since the degradation rate of RhB dyes was the fastest. The photocatalytic degradation results of dyes using different dosage of P25 Degussa TiO\(_2\) (0.5, 1, and 2 g) is displayed in figure 7. It is observed that 2 g of catalyst degraded faster and can achieve up to 100% degradation of dyes after 2 h of sunlight irradiation. This is because the concentration is remain the same but the ratio of oxide radical species to dye molecule become higher due to the increase of dosage of catalyst [8]. When the dosage of catalyst increase, the O-H group also increase because P25 Degussa TiO\(_2\) contain O-H bonds which could increase the generation of hydroxyl radicals. The photodegradation of dye involves the breaking of O-H bonds to form hydroxyl radical. 0.5 g of catalyst in dyes solution degraded the slowest, it only achieved the degradation of 23% after 2 h of photocatalytic reaction. This is because dosage of P25 Degussa TiO\(_2\) had become less and the O-H bonds which contained in P25 Degussa TiO\(_2\) will also decrease and then cause the formation of hydroxyl radicals which was one of the key component in photodegradation decrease too. Hence, the photodegradation decrease as the dosage of P25 Degussa TiO\(_2\) decrease. The performance of photodegradation of different dosage of P25 Degussa TiO\(_2\) is tabulated at table 4.

**Table 3. Photodegradation of RhB, MO and MB dyes under sunlight irradiation.**

**Figure 7.** Effect of different dosage of P25 Degussa TiO\(_2\) towards the degradation of RhB dye.

**Figure 8.** Effect of different concentration of RhB dye towards the degradation of RhB dye.
Table 4. The photodegradation of RhB dye in different dosage of P25 Degussa TiO$_2$.

| P25 Degussa TiO$_2$ dosage (g) | Concentration (ppm) | Volume (L) | Adsorption Efficiency (%) | Overall Efficiency (%) | Rate of degradation (%) |
|-------------------------------|---------------------|------------|---------------------------|------------------------|-------------------------|
| 0.5                           | 10                  | 4          | 1                         | 23                     | 3                       |
| 1                             | 10                  | 4          | 33                        | 96                     | 32                      |
| 2                             | 10                  | 4          | 46                        | 100                    | 35                      |

The fourth experiment was carried out by using different concentration of dyes (10 ppm, 15 ppm and 20 ppm) in the presence of 2 g of P25 Degussa TiO$_2$. In figure 8, the dyes with 10 ppm and 2 g of catalyst degraded 100% after 2 h which is the fastest among the other concentration of dyes. This is because the generation of OH radicals at the surface of the catalyst can be controlled by concentration [9]. The lower the dye concentration, the higher the generation of OH radicals on the surface of catalyst [6]. Thus, the higher the degradation of dyes. While for the 20 ppm concentration of dyes, it was degraded 90% after 2 h. This was due to the increase in concentration will also have an increase in the number of dye molecules. The increase of dyes molecules leads to lower generation of radical species and causing the penetration of light into the dyes solution decrease [8]. Hence, the activation of catalyst became lower and this caused a lower photodegradation rate of dye. The performance of fabricated reactor with different concentration is tabulated at table 5.

Table 5. The photodegradation of dyes in different concentration.

| Catalyst dosage (g) | Concentration (ppm) | Volume (L) | Adsorption Efficiency (%) | Overall Efficiency (%) | Rate of Degradation (%) |
|---------------------|---------------------|------------|---------------------------|------------------------|-------------------------|
| 2                   | 10                  | 4          | 46                        | 100                    | 43                      |
| 2                   | 15                  | 4          | 26                        | 94                     | 29                      |
| 2                   | 20                  | 4          | 21                        | 90                     | 27                      |

The last experiment is to compare the conventional reactor (beaker) and homemade reactor. From figure 9, the homemade reactor degraded the RhB dyes faster than the conventional reactor in the absence or the presence of catalyst. In the absence of catalyst, the degradation rate of RhB dye in homemade reactor was 94% while the conventional one was 81%. In the presence of catalyst, the homemade reactor could degrade 95% of RhB dye while the conventional method achieved the degradation rate of 93%. This can conclude that the homemade reactor can slightly degrade the dyes solution faster than that of conventional method. This is due to conventional method had limitation in mass transfer of dyes because the sunlight was blocked from penetrating to the catalyst surface by the dyes [8]. While for homemade reactor, the dyes solution is recycled in the reactor and the limitation of mass transfer is diminished in homemade reactor. Besides that, the recycling continuous flow reactor is performed in turbulent regime, it can ensure the oxygen dissolves effectively in the dyes. The performance of homemade reactor and conventional reactor is tabulated at table 6.
Figure 9. Comparison of RhB dye degradation efficiency between conventional reactor and homemade reactor.

Table 6. The comparison between homemade reactor and conventional reactor.

| Type of reactor | Catalyst dosage (g) | Concentration (ppm) | Volume (L) | Adsorption efficiency (%) | Overall efficiency (%) | Rate of degradation (%) |
|-----------------|---------------------|---------------------|------------|---------------------------|------------------------|------------------------|
| Homemade        | 0                   | 10                  | 4          | 0                         | 94                     | 28                     |
| Beaker          | 0                   | 10                  | 4          | 0                         | 81                     | 19                     |
| Homemade        | 1                   | 10                  | 4          | 2                         | 96                     | 32                     |
| Beaker          | 1                   | 10                  | 4          | 3                         | 94                     | 23                     |

4. Conclusion
In the absence of P25 Degussa TiO$_2$, the degradation rate of RhB dye was the highest due to the formation of bubbles during the photolysis, whereas the degradation rate of MO dye was the lowest as MO dye was not stable and the bubbles were not formed, causing the decrease in accuracy of result. The higher dosage of P25 Degussa TiO$_2$ increased the photodegradation rate because the O-H in P25 Degussa TiO$_2$ increased the formation of hydroxyl radicals. The photodegradation rate decreased when concentration of dyes increased because the increase of dyes molecules led to lower generation of radical species. The degradation rate in homemade reactor was slightly higher than that of conventional beaker because homemade reactor diminished the limitation of mass transfer and ensured the oxygen dissolved effectively in the dyes.

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