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Photodegradation of Benzoic Acid Using Titanium Dioxide Catalyst Calcined At Various Temperatures

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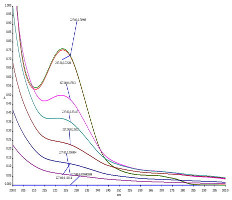
GRAPICAL ABSTRACT



UV Spectra of benzoic acid before and after reaction using 450℃ Degussa photocatalyst under 365 nm UV light irradiation

ABSTRACT

Removing the contaminants from the discharge of industrial, domestic and agricultural wastewater is a great challenge faced by scientists and environmentalists. Therefore, heterogeneous photocatalysis has become emerging technology to mineralize organic pollutants with the use of photocatalyst. In this research, photodegradation of benzoic acid (BA) under 365 nm UV light irradiation for 3 hours was investigated using commercial TiO_2 P25 Degussa, TiO_2 Aldrich and TiO_2 photocatalysts prepared by sol-gel method which were calcined at various temperatures of 450℃, 700℃, 800℃, 900℃, and 1000℃. The photocatalytic activity of the prepared catalysts was assessed by the photodegradation of $1.0x10^{-4}$ M BA using UV-Vis Spectrophotometer measured at λ_{max} 227.0 nm. The photocatalytic degradation was also conducted under various experimental condition of calcination temperature, initial concentration of substrate, oxidizing agent, pH and light source. The photodegradation efficiency decreased with the increased of calcination temperature due to the transformation of anatase to rutile phase. It was found that the degradation rate decreased with increasing initial concentration. Furthermore, only the original pH and addition of H_2O_2 and $K_2S_2O_8$ gave better degradation rates. The photodegradation of BA using sunlight and UV light was comparable. Lastly, the prepared photocatalysts were characterized by XRD, FESEM-EDX and BET surface area analysis. The data obtained proved that TiO_2 P25 Degussa calcined at 450℃ was the most efficient photocatalyst to degrade 92.08% BA at pH 4.8 with the presence of 57% anatase phase, 44.91 m^2/g optimum surface area, fine and uniform particle sizes which closely packed together with 29 – 32 nm average particle size of TiO_2.

Keywords: Photocatalysis, Benzoic acid, Calcination temperatures, UV light, Titanium Dioxide

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1. INTRODUCTION

Clean and non-polluted water is one of the basic requirements for all living organisms including human beings. But its availability is a major problem nowadays. Natural water is being contaminated by the discharge of industrial, domestic, and agricultural wastes. In the future, this problem will further increase due to global industrialization and population growth. Benzoic acid (BA) is an organic contaminant which is one of the most vulnerable water pollutants. It is mainly used as reaction intermediates, an agent for preservative, cosmetics and also can be present in industrial wastewater. Benzoic acid has impact on the environment in a number of ways and affects human health. Consequently, large amount of this pollutants effused into stream and soil, can give an adverse effects on aquatic life, land, animals and subsequently to human beings [1]. Therefore, wastewaters containing BA must be treated before discharge into water bodies.

The photocatalytic techniques or also called Advanced Oxidation Process (AOP's) is a promising technique, for photodegradation of various hazardous chemicals that are present in wastewaters. AOP's generate hydroxyl radical, a strong oxidant, which can completely degrade or mineralize the pollutants non-selectively into harmless products such as CO_2 and H_2O.

The most extensively used photocatalyst is titanium dioxide due to its non-toxic, inexpensive, abundance and chemical stability. TiO_2 as photocatalyst is able to mineralize organic pollutants to non-toxic substances such as CO_2, HCl and water. Moreover, the reaction can take place at room temperature [2]. TiO_2 semiconductor catalyst consists of three polymorphic forms, which are rutile, anatase and brookite. It is more dominant in the form of anatase and rutile. Anatase TiO2 has a band gap of 3.2 eV (385 nm), while the rutile phase has a smaller band gap of 3.0 eV (410 nm) [3].

According to the previous research, degradation of benzoic acid using ZnO powder synthesized by sol-gel method has shown 67.98% degradation after 2 hour under UV irradiation [4]. Interestingly, doping of Sn(10%)-doped BiOCl (bismuth oxychloride) has higher degradation percentage of BA than undoped BiOCl with 96% and 54% respectively [5].

In this study, commercial TiO_2 photocatalysts P25 Degussa and Aldrich and TiO_2 photocatalyst prepared by sol-gel method were used to investigate the photocatalytic degradation benzoic acid solution under UV light irradiation for 3 hours. TiO_2 photocatalysts were calcined at various temperatures in order to study the effect of calcination temperature which allowed obtaining morphological properties that enable their efficient use as photocatalysts. The photocatalytic activity was carried out under various experimental condition of calcination temperature, initial concentration of substrate, oxidizing agent, pH and light source as the variables to determine the best working condition.

2. EXPERIMENTS

This research was conducted in three different stages. The first stage was the heat treatment at various temperatures of commercial TiO_2 photocatalysts which are P25 Degussa and Aldrich and preparation of TiO_2 photocatalyst by sol-gel method. In the second stage, photocatalytic activity of benzoic acid (1.0×10^{-4} M) under UV light irradiation were studied using the prepared catalyst to determine the optimum condition. The absorbance value was analyzed using UV-Vis Spectrophotometer at λ_{max} 227.0 nm. The percentage of degradation was calculated using formula in Equation (1). The photocatalytic activity was also carried out under various experimental condition of calcination temperature, initial concentration of substrate, oxidizing agent, pH and light source as the variables to determine the best working condition. The last stage would be the characterization of the prepared catalyst by using XRD, FESEM-EDX and BET surface area analyses.

$$\% D = \frac{A_o - tA_t}{A_t} \text{ x } 100\% \qquad (1)$$

where % D is the percentage of degradation, A_0 is the initial absorbance of sample before irradiation under UV light and A_t is the absorbance of sample after irradiation under UV light.

3. RESULTS AND DISCUSSION

3.1 Characterization of Catalysts

3.1.1 X-ray Diffraction Analysis (XRD)

Figure 1 shows the diffractograms of XRD analysis for commercial TiO_2 photocatalysts calcined at various temperatures. Based on Figure 1, it can be observed that an increase in calcination temperatures plays a significant role in the phase transformation. At 450°C calcination temperature of TiO_2 Degussa photocatalyst, XRD pattern showed that anatase phase is dominant compared to rutile phase. At 700°C, rutile phase starts to dominate while some of the anatase phase can still be observed (Group research data). Meanwhile, with further increasing of temperature up to 1000°C, the intensities of anatase diffraction peaks were disappeared, while the intensities of rutile diffraction peaks became dominant. This is in agreement with previous research that reported the amorphous TiO_2 normally undergoes phase transformation into anatase at 380°C whereas an anatase-to-rutile phases transformation in the range from 600–700°C [6].

From Figure 2, XRD patterns of TiO_2 Adrich photocatalyst showed an anatase phase at calcination temperature of 450°C and 800°C. This was probably due to the high composition of anatase in TiO_2 Adrich photocatalyst which is 99% anatase. As the calcination temperature increased to 900°C, rutile phase starts to form while the anatase phase was still dominant. However, a major transformation into rutile phase was occurred as the temperature increased to 1000°C with little anatase phase can still observed. The increase in calcination temperature caused the transformation of anatase to rutile phase and the intensity of both anatase and rutile peaks gradually increases, indicating an enhancement of crystallization.

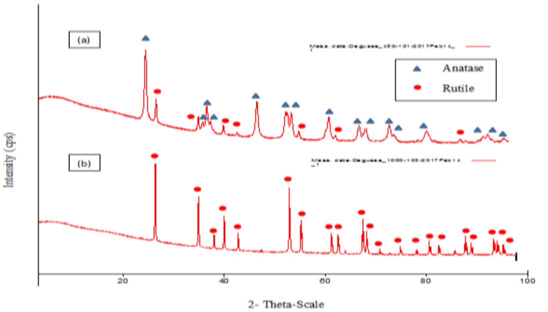

Fig. 1 The diffractograms of XRD for commercial TiO_2 Degussa photocatalysts calcined at (a) 450°C and (b) 1000°C

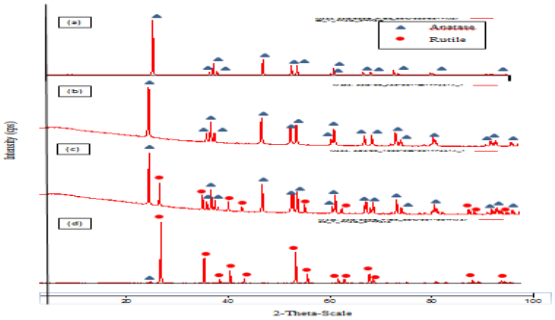

Fig. 2 The diffractograms of XRD analysis for commercial TiO_2 Aldrich photocatalyst calcined at (a) 450°C, (b) 800°C, (c) 900°C and (d) 1000°C

The percentage of anatase and rutile was calculated from XRD data using Equation 2 and tabulated in Table 1.

$$\text{Anatase (\%)} = \frac{I_A}{(I_{A+1.256I_R})} \; x \; 100 \qquad (2)$$

Where I_A and I_R corresponds to the intensity of anatase and rutile respectively in which the value for I_A and I_R were stated as below:

- 450°C TiO_2 Degussa photocatalyst, I_A = 38401 and I_R = 23065
- 1000°C TiO_2 Degussa photocatalyst, I_R = 29202

- 450℃ TiO_2 Aldrich photocatalyst, I_A = 47499
- 1000℃ TiO_2 Aldrich photocatalyst, I_A = 9076 and I_R = 50596.

Table 1 Percentage of anatase and rutile phase of commercial TiO_2 Degussa and Aldrich at calcination temperature of 450℃ and 1000℃

Photocatalysts	Before calcination		After calcination	
	Anatase (%)	Rutile (%)	Anatase (%)	Rutile (%)
450°C Degussa	75	25	57	43
1000°C Degussa	75	25	-	100
450°C Aldrich	99	1	100	-
1000°C Aldrich	99	1	65	35

3.1.2 FESEM-EDX

Figure 3 (a-d) shows the FESEM micrograph of the commercial 450℃ TiO_2 Degussa, 1000℃ TiO_2 Degussa, 450℃ TiO_2 Aldrich and 1000℃ TiO_2 Aldrich photocatalysts with scanning made from 25,000 , 50,000 , 80, 000 and 120,000 magnification and 2.0 kV scanning voltage with working distance of 8.1 mm. The micrographs show that 450℃ Degussa photocatalyst exhibit the smallest particle size which was ranging from 29 – 32 nm (Figure 3 (a)), followed by 450℃ Aldrich photocatalyst with 109 – 135 nm (Figure 3 (c)). The particle size of 1000℃ Aldrich photocatalyst was in the range of 164-225 nm ((Figure 3(d)). Meanwhile, 1000℃ Degussa was observed to have the largest particle size which was ranging from 172 – 399 nm (Figure 3 (b)).

Sharifuddin, 2011, found that smaller particle size of catalyst contributed to the higher surface area and more active sites present on the catalyst surface [7]. This statement was supported by the results from the photocatalytic degradation that showed both 450℃ Degussa and 450℃ Aldrich photocatalysts gave better performance on degrading benzoic acid solution compared to the other two photocatalysts. The micrograph also showed that as the calcination temperature increase, particle size increase as well. The FESEM images of the catalysts show that 450℃ Degussa and 450℃ Aldrich exhibits a fine and uniform particle sizes which agglomerate or closely packed together among particles. Thus, the photocatalysts would have better adsorption of UV light during photodegradation process. Meanwhile, FESEM micrograph of 1000℃ Degussa and 1000℃ Aldrich photocatalysts showed a non-uniform particles sizes.

Table 2 shows the atomic composition of elements presents on the surface of commercial TiO_2 photocatalysts (Degussa and Aldrich) which were calcined at 450℃ and 1000℃. It was observed that the percentage of titanium atoms was higher in those photocatalysts. However, the percentage of distributions of Ti atom and O atom were almost similar for all the photocatalysts. TiO_2 Aldrich photocatalyst calcined at 1000℃ has the highest atomic ratio of Ti species (57.9%) compare to the same photocatalyst calcined at 450℃ (52.6%) whereas 450℃ TiO_2 Degussa photocatalyst has the highest percentage of oxygen species. Other impurity peaks found in the spectrum (Figure 4 and 5 (a and b)) was from the platinum coating material.

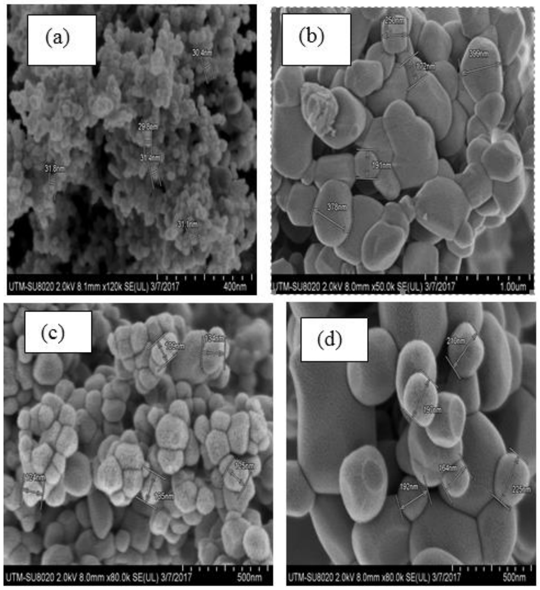

Fig. 3 FESEM micrographs of commercialized TiO_2 photocatalysts, (a) 450℃ Degussa, (b) 1000℃ Degussa, (c) 450℃ Aldrich and (d) 1000℃ Aldrich

Table 2 The atomic composition of elements presents on the surface of commercial TiO_2 photocatalysts

Photocatalyst	Atomic Ratio (%)	
	Ti	O
450℃ TiO_2 Degussa	50.8	49.2
1000℃ TiO_2 Degussa	57.0	43.0
450℃ TiO_2 Aldrich	52.6	47.4
1000℃ TiO_2 Aldrich	57.9	42.1

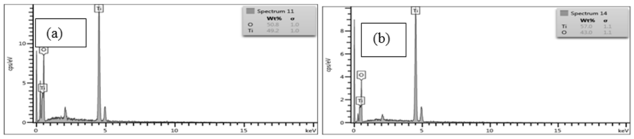

Fig. 4 EDX spectra of commercial TiO_2 photocatalysts (a) 450℃ Degussa and (b) 1000℃ Degussa

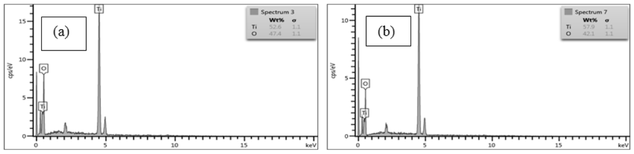

Fig. 5 EDX spectra of commercial TiO_2 photocatalysts (a) 450℃ Aldrich and (b) 1000℃ Aldrich

3.1.3 BET Surface Area Analyses

Table 3 shows the BET surface area for commercial TiO_2 P25 Degussa calcined at 450℃ and TiO_2 Aldrich photocatalysts calcined at 450℃. According to Vione *et al*., the initial surface area of TiO_2 P25 Degussa photocatalyst powder without undergoing calcination was 51.0 m^2/g [8]. From BET surface area results obtained, the surface area of TiO_2 Degussa photocatalyst calcined at 450°C was found to be 44.91 m^2/g. As the calcination temperature increases to 700°C, the surface area of 700°C TiO_2 Degussa photocatalyst decreases to 22.50 m^2/g (Group research data). This indicates that as calcination temperature increases, the surface area decreased.

Table 3 The surface area for commercial 450°C TiO_2 P25 Degussa and 700°C TiO_2 Aldrich photocatalysts

Type of Catalysts	BET Surface Area (m^2/g)
450°C Degussa	44.91
450°C Aldrich	17.35

3.2 Photodegradation of Benzoic Acid using Commercial TiO_2 Photocatalysts

Figure 6 shows the percentage degradation of benzoic acid using commercial TiO_2 photocatalysts which are P25 Degussa and Aldrich under UV light irradiation for 180 minutes. The experimental results showed that TiO_2 P25 Degussa photocatalyst had the higher degradation percentage with 57.93% than TiO_2 Aldrich photocatalyst with 55.30% degradation under UV irradiation of 180 minutes. It was observed that the TiO_2 photocatalyst supplied by Aldrich was less active than TiO_2 P25 Degussa. Commercial TiO_2 Aldrich photocatalyst contains 99% of anatase while TiO_2 P25 Degussa photocatalyst composed both of anatase and rutile crystallites, with 75% anatase and 25% rutile (Group research data). The co-presence of anatase and rutile crystallites in TiO_2 P25 Degussa photocatalyst helps to reduce the recombination rate of photogenerated electrons and holes, leading to more efficient electron-hole separation and greater photocatalytic activity compare to photocatalyst with rutile phase alone [9].

3.3 Photodegradation of Benzoic Acid using Commercial TiO_2 Photocatalysts Calcined at Various Temperatures

Figure 7 and Figure 8 show the degradation percentage of benzoic acid by using commercial TiO_2 photocatalysts, P25 Degussa and Aldrich which were calcined at 450°C, 700°C, 800°C, 900°C, and 1000°C for 5 hours and has been undergone UV irradiation for 180 minutes. From Figure 7, it was observed that TiO_2 P25 Degussa photocatalyst calcined at 450°C had the highest percentage of degradation with 92.08% followed by photocatalyst calcined at 800°C and 700°C with 50.32% and 44.7% respectively. The photocatalyst calcined at 1000°C had the insignificant percentage of degradation. Meanwhile, TiO_2 Aldrich photocatalyst calcined at 450°C had the highest percentage of degradation with 50.86% followed by photocatalyst calcined at 700°C and 800°C with 44.66% and 39.24% respectively. The photocatalyst calcined at 1000°C had the lowest percentage of degradation with 6.99% (Figure 8).

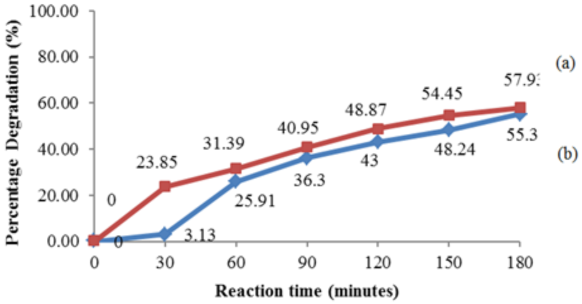

Fig. 6 The percentage degradation of benzoic acid using commercial (a) TiO_2 P25 Degussa and (b) TiO_2 Aldrich photocatalysts underUV light irradiation for 180 minutes

The trend indicates there is a decrease of degradation percentage of benzoic acid as calcination temperature increase. The photodegradation efficiency decreased with the increased of calcination temperature due to the crystallinity phase of TiO_2 photocatalyst. The characterization of photocatalyst using XRD showed that the transformation of anatase to rutile phase depends on calcination temperature. The higher the calcination temperature, less photocatalytic activity was observed as the crystallinity form of rutile TiO_2 increased.

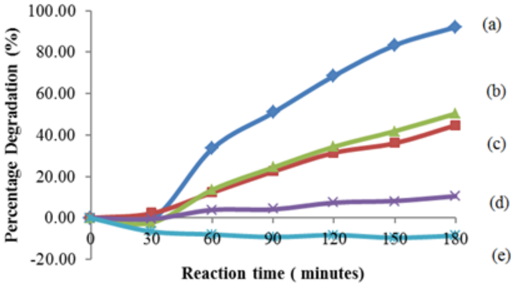

Fig. 7 P25 Degussa calcined at (a) 450°C, (b) 800°C, (c) 700°C, (d) 900°C and (e) 1000°C

Despite the larger experimental band gap of anatase (3.2 ev) compared with 3.0 ev of rutile [10], the activity of anatase TiO_2 is much higher than that of rutile phase although rutile is more thermodynamically stable. The surface area of TiO_2 decreases with calcination temperature due to the influence of agglomeration in TiO_2 photocatalyst. Crystallinity increases with calcination temperature and consequently reduced surface area leads to less efficient photocatalytic activity. Commercial TiO_2 P25 Degussa which was not calcined obtained less degradation percentage (55.3%) compared to 450°C TiO_2 P25 Degussa photocatalyst. This indicated that the heat treatment plays a vital role in the preparation of photocatalyst as it affects their morphology, crystallinity, porosity, surface area and induced phase transformation. The crystallinity would increases with calcination temperature and reduced surface area, consequently leads to less efficient photocatalytic activity. However, the heat treatment of commercial TiO_2 Aldrich does not show an increment in degradation rate as the photocatalyst without calcination have established an active anatase phase.

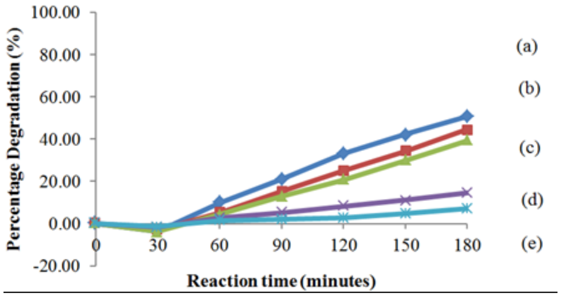

Fig. 8 The percentage degradation of benzoic acid using commercial TiO_2 Aldrich photocatalyst calcined at (a) 450℃, (b) 700℃, (c) 800℃, (d) 900℃ and (e) 1000℃

3.4 Photodegradation of Benzoic Acid using Single TiO_2 Photocatalyst Prepared by Sol-Gel Method

Figure 9 shows the percentage degradation of benzoic acid using TiO_2 photocatalyst synthesized by sol-gel method which was calcined at 450℃, 700℃, 800℃, 900℃ and 1000℃ for 5 hours. TiO_2 photocatalyst calcined at 450℃ has the highest percentage of degradation while other photocatalyst calcined at 700℃, 800℃, 900℃ and 1000℃ does not showed significant value. Different calcination temperatures caused the different in the photodegradation rate of benzoic acid under the same condition for irradiation under UV light. This is due to crystallinity phase of TiO_2photocatalyst exist in the catalyst structure. A fully anatase phase of TiO_2 photocatalyst calcined at 450℃ [11] gave a better degradation efficiency compared to other photocatalyst calcined at different calcination temperatures. TiO_2 photocatalyst calcined at 1000℃ [11] showed a complete transformation of anatase phase to rutile phase which responsible for the lower degradation rate and efficiency. Thus, the formation of rutile phase at temperature higher than 450℃ becoming less photoactive in degrading benzoic acid solution.

3.5 The Effect of Initial Substrate Concentrations

The effect of initial concentration of benzoic acid solution on the photocatalytic degradation rate was investigated over the concentration range of 0.5 x10 $^{-4}$ M to 4 x10 $^{-4}$ M. Figure 10 shows the percentage of degradation of different concentration of benzoic acid solution by using synthesized TiO_2 photocatalyst calcined at 450℃. The highest percentage of degradation (60.2%) was obtained at the concentration of 0.5 x10 $^{-4}$ M of benzoic acid solution. It can be observed that the percentage of degradation decreases with increasing initial concentration of the benzoic acid solution. On increasing the concentration of the benzoic acid solution until 4 x 10^{-4} M, the photodegradation became very slow, presenting a degradation of only 2.21% for benzoic acid solution.

As the initial concentration of the benzoic acid solution increased, more benzoic acid molecules were adsorbed on the surface on the catalyst and the generation of hydroxyl radicals was reduced since the active sites were occupied by benzoate ion, consequently affecting catalytic reaction.

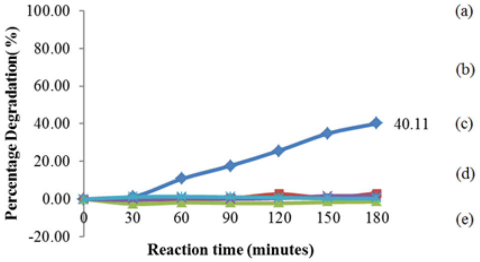

Fig. 9 The percentage degradation of benzoic acid using TiO_2 photocatalyst synthesized by sol-gel method calcined at (a) 450℃, (b) 700℃, (c) 900℃, (d) 1000℃ and (e) 800℃

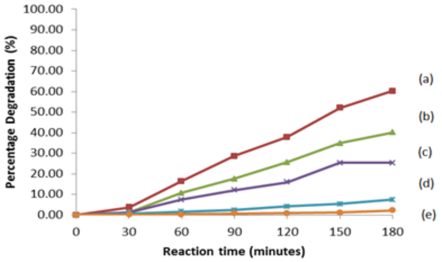

Fig. 10 The percentage degradation of various initial concentration of benzoic acid solution (a) 0.5 x 10^{-4} M, (b) 1 x 10^{-4} M, (c) 2 x 10^{-4} M, (d) 3 x 10^{-4} M and (e) 4 x 10^{-4} M using synthesized TiO_2 photocatalyst calcined at 450℃

3.6 The Effect of Oxidizing Agent

In this section, the effect of various oxidizing agents such as H_2O_2, $K_2S_2O_8$, $KMnO_4$ and $K_2Cr_2O_7$ on the photodegradation of benzoic acid was investigated by the addition of oxidizing agents and photocatalysts into benzoic acid solution (1x 10^{-4} M) and was irradiated under UV light for 180 minutes. These oxidants increase the number of trapped electrons, which prevents recombination and generates oxidizing radicals, which may, in turn, enhance the photocatalytic degradation of substrate.

Moreover, the capability of oxidizing agents to degrade benzoic acid solution also was related to their standard reduction potential ($E^{o}{}_{SRP}$) value [12]. Theoretically, $E^{o}{}_{SRP}$ value shows the capability for the oxidizing agents to undergo reduction process. Therefore, oxidizing agents with more positive value of $E^{o}{}_{SRP}$ would undergo reduction process easier and gave better degradation percentage compared to oxidizing agents with low value of E° $_{SRP}$. The E° $_{SRP}$ value for the oxidizing agents used in this study was shown in Table 4.

Table 4 E° $_{SRP}$ value for the oxidizing agents used [13]

Oxidizing agents	E° $_{SRP}$ (V)
H_2O_2	+1.77
$K_2S_2O_8$/ $S_2O_8^{2-}$	+2.01
$KMnO_4$/ MnO_4^-	+1.51
$K_2Cr_2O_7$	+1.33

By referring to above table, it was predicted that the order of oxidizing agents efficiency is $K_2S_2O_8 > H_2O_2 > KMnO_4 > K_2Cr_2O_7$.

From Figure 11(a), addition of hydrogen peroxide (H_2O_2) into benzoic acid solution using TiO_2 P25 Degussa photocatalyst calcined at 450℃ gave 90.33% of degradation. The percentage of degradation without the addition of H_2O_2 (92.02%) was higher compared to the addition of H_2O_2 means that H_2O_2 does not improved photodegradation process of benzoic acid acid using TiO_2 P25 Degussa photocatalyst as percentage degradation was already high.

The addition of hydrogen peroxide into benzoic acid solution using Aldrich photocatalysts calcined at 700℃ and synthesized TiO_2 450℃ photocatalyst gave higher photodegradation percentage of 69.83% and 57.01% respectively compared to percentage of degradation without the addition of H_2O_2. This showed that the addition of H_2O_2 can enhanced the photodegradation rate. The degradation of benzoic acid solution increased with the addition of H_2O_2 may be due to the formation of hydroxyl free radicals in photocatalytic processes. In photodegradation process, H_2O_2 produce more •OH radicals that can react with organic pollutants on catalyst surface. The mechanism for •OH radicals production were shown in Equation 3-5.

$$H_2O_2 + h\nu \rightarrow 2\ {\bullet}OH \tag{3}$$

$$H_2O_2 + e^- \rightarrow {\bullet}OH + OH^- \tag{4}$$

$$H_2O_2 + {\bullet}\ O_2^- \rightarrow {\bullet}OH + OH^- + O_2 \tag{5}$$

The experiments on the effect of oxidizing agents on photodegradation of benzoic acid solution were further investigated by using various oxidizing agents such as $K_2S_2O_8$, $KMnO_4$ and $K_2Cr_2O_7$. The addition of oxidizing agents to the benzoic acid solution was investigated with the presence of TiO_2 photocatalyst calcined at 450℃ irradiated under UV light. Figure 11(b) showed that only the addition of $K_2S_2O_8$ can enhance the photodegradation rate of benzoic acid solution with 49.28% while the other oxidizing agents does not show significant effect. The percentage of degradation by using $KMnO_4$ and $K_2Cr_2O_7$ were 35.41% and 26.50% respectively.

The order of effectiveness of the oxidizing agents in degrading benzoic acid was H_2O_2 (57.1%) > $K_2S_2O_8$ (49.28%) > $KMnO_4$ (35.41%) > $K_2Cr_2O_7$ (26.50%). The order of effectiveness of the oxidizing agents does not follow E° $_{SRP}$ except for the addition of $KMnO_4$ and $K_2Cr_2O_7$ into benzoic acid solution which has the lowest E° $_{SRP}$ and degradation percentage. Both $KMnO_4$ and K_2Cr_2O as oxidizing agents cannot enhance the photodegradation of benzoic acid solution. This is probably due to the low hydroxyl radical produced by $KMnO_4$ and $K_2Cr_2O_7$ which caused less degradation percentage. The mechanism for •OH radicals produced during the addition of $K_2S_2O_8$ in photodegradation process were shown in Equation 6 and Equation 7.

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4{\bullet}^- \tag{6}$$

$$SO_4{\bullet}^- + H_2O \rightarrow {\bullet}OH + SO_4^{2-} + H^+ \tag{7}$$

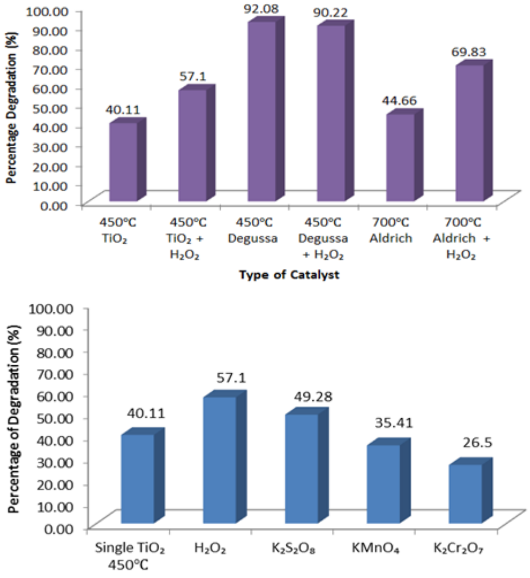

Fig. 11 (a) The percentage degradation of benzoic using various photocatalysts with addition of H_2O_2 and (b) The percentage degradation of benzoic acid using synthesized TiO_2 photocatalyst calcined at 450℃ with the addition of various oxidizing agents

3.7 The Effect of pH on Photodegradation of Benzoic Acid Solution

In this experiment, the initial pH of benzoic acid solution has been altered to pH of 2.5 and 10 using HCl and NaOH. The adjustment was made before the irradiation and is not controlled during the reaction. The original pH of benzoic acid solution is around 4.8 before any adjustment. It was found that there is change in pH of the solution after irradiation under UV light for pH 10 of benzoic acid whereas pH 2.5 of benzoic acid remains insignificant. The pH variation can in fact influence the adsorption of benzoate molecules onto the TiO_2 surfaces. From Figure 12, it can be observed that the initial pH of benzoic acid solution affects the photodegradation process. Benzoic acid solution at original pH of 4.8 had the highest percentage of degradation (44.7%) followed by pH 10 and pH 2.5 with 33.36% and 16.65% respectively.

Titanium dioxide exhibits an amphoteric character, so that either a positive or a negative charge can be developed on its [14]. The point of zero charge for TiO_2 P25 Degussa photocatalyst is at pH approximately 6. At pH above 6, the TiO_2 surface becomes negatively charged via deprotonation whereas at pH below 6, the TiO_2 surface becomes positively charged via protonation. Benzoic acid is a weak acid whose pka is 4.2. Once benzoic acid dissolved in distilled water, it exists in its anionic state and, therefore, an electrostatic attraction is expected to develop between the benzoic acid and the positively charged TiO_2 particles at pH < 6. At highly acidic conditions (pH =2.5), the decreased of the available active centers may occurs on the catalyst surface, which in turn causes a reduction of the adsorbed photons.

Benzoic acid adsorption onto catalyst does not favoured at alkaline conditions (pH=10) since both TiO_2 photocatalyst and substrate are negatively charged. Therefore, the degradation appears to proceed via reaction with hydroxyl radicals in the liquid bulk which are generated after adsorption of hydroxyl anions onto particle surface, followed by reaction with holes existing in exited semiconductor catalyst.

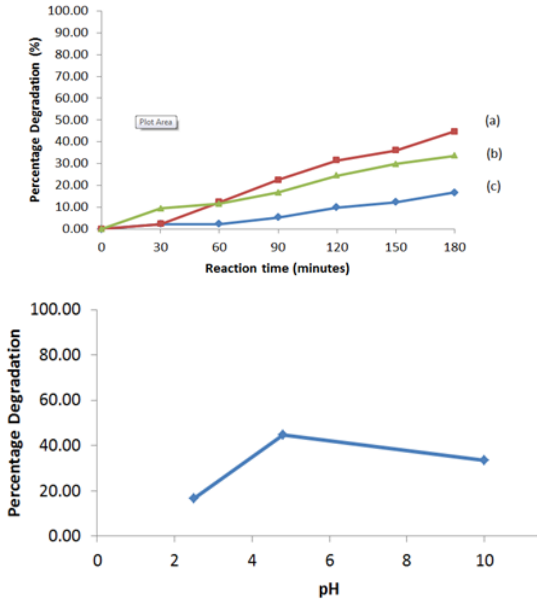

Fig. 12 Percentage Degradation of Benzoic Acid at various pH (a) 4.8, (b) 10 and (c) 2.5 under UV irradiation for 180 minutes

3.8 The Effect of Light Source on Photodegradation of Benzoic Acid Solution

The photodegradation of benzoic acid by using TiO_2 P25 Degussa photocatalyst calcined at 450℃ was conducted in the presence of natural sunlight as light source instead of UV light in order to investigate the capability of photocatalyst. The experiment was conducted on 21st February 2017 (Monday) from 10 am to 1 pm. The duration of time was suitable for photodegradation process due to strong intensity of sunlight source during noon. The percentage of degradation under UV lamp (365 nm) irradiation was 92.08% whereas percentage of degradation of benzoic acid using sunlight was 96.51% (Figure 13). Although the percentage degradation of benzoic acid using sunlight as light source is higher than percentage degradation of benzoic acid under UV lamp irradiation, the value obtained is comparable. Therefore, the use of natural sunlight creates great opportunities of practical applications.

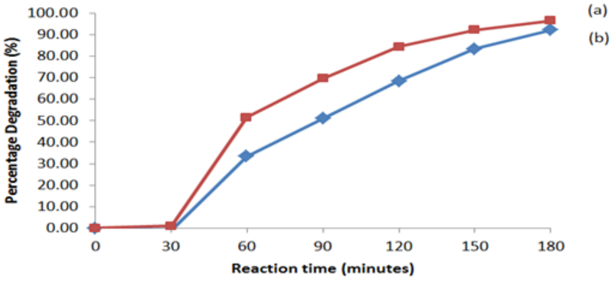

Fig. 13 The percentage degradation of benzoic acid under (a) sunlight and (b) UV light irradiation using commercial TiO_2 P25 Degussa photocatalyst calcined at 450℃

3.9 Controlled Reactions

The experiment on comparison of the different degradation condition, photolysis (no TiO_2/UV) and adsorption of benzoic acid on photocatalyst (TiO_2/ no UV) was conducted to demonstrate the importance of irradiating the aqueous system containing the TiO_2 catalyst and reactant with UV light. Also, the controlled experiment served as a purpose to test the stability of benzoic acid before undergoing photodegradation reaction. The photolysis was performed by irradiating the benzoic acid solution with UV light (365 nm, 6W) without the presence of photocatalyst while and adsorption reaction was conducted with the presence of synthesized TiO_2 photocatalyst calcined at 450℃ in a dark condition. From Figure 14, the percentage degradation of photocatalysis (40.11%) is much higher than photolysis (0.84%). However, for the adsorption experiment, the result shows that benzoic acid is not stable in dark condition which causes the absorbance increases and decreases. Therefore, the results proved that both photocatalyst and UV light plays a vital role in photodegradation process.

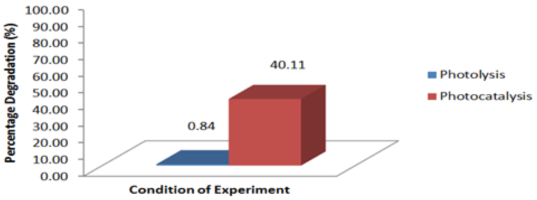

Fig. 14 The percentage degradation of benzoic acid under UV light irradiation using synthesized TiO_2 photocatalyst calcined at 450℃ (photocatalysis) and photolysis

4. CONCLUSION

In this research, photodegradation activity of benzoic acid was investigated using commercial, TiO_2 P25 Degussa, TiO_2 Aldrich and TiO_2 photocatalysts prepared by sol-gel method which were calcined at various temperatures of 450℃, 700℃, 800℃, 900℃, and 1000℃. The photocatalytic degradation under UV light irradiation was proven effective for the degradation of benzoic acid compared to photolysis. From the study, it was observed that the heat treatment plays a vital role in the preparation of photocatalyst as it affects their morphology, crystallinity, porosity, surface area and induced phase transformation. The crystallinity would increases with calcination temperature and reduced surface area, consequently leads to less efficient photocatalytic activity. The degradation rate decreased as the initial concentration increased due to the reduction of hydroxyl radical generation at the catalyst surface as the active sites are covered by benzoate ions. Only the addition of H_2O_2 and $K_2S_2O_8$ enhanced the photodegradation rate of benzoic acid. Moreover, modification of initial pH was found to be ineffective towards degradation of benzoic acid solution. Natural sunlight irradiation was proved to be suitable for the degradation of benzoic acid as 450℃ TiO_2 P25 Degussa photocatalyst was performed efficiently with percentage degradation of 96.51%. The data obtained proved that TiO_2 P25 Degussa calcined at 450℃ was the most efficient photocatalyst to degrade 92.08% BA at pH 4.8 with the presence of 57% anatase phase, 44.91 m^2/g optimum surface area, fine and uniform particle sizes which which or closely packed together among particles closely packed together with 29 – 32 nm average particle size of TiO_2.

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