# EFFECT OF HTAB CONCENTRATION ON THE SYNTHESIS OF NANOSTRUCTURED $TiO_2$ TOWARDS ITS CATALYTIC ACTIVITIES

## (Kesan Kepekatan HTAB Terhadap Sintesis $TiO_2$ Nanostruktur Ke Atas Aktiviti Pemangkinannya)

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**Abstract**

Titanium dioxide, $TiO_2$ photocatalyst was synthesised by microemulsion method under controlled hydrolysis of titanium butoxide, $Ti(O(CH_2)_3)CH_3$ in Hexadecyl Trimethyl Ammonium Bromide, HTAB. The effect of various concentrations of surfactant in the range between 0.01-1.0 M were focused on by investigating their morphology, crystallite size, crystalline phase and specific surface area. After observation on their degradation performance, 0.5 M concentration of HTAB presented as a optimum concentration to synthesis $TiO_2$ photocatalyst. These results also supported by XRD spectra which are exhibited size of photocatalyst in the range within 50-150 nm. As a result, the catalytic properties of the synthesised $TiO_2$ nanostructure was performed by exhibiting good behaviour in photocatalytically degraded atrazine, 2-chloro-4-(ethylamino)-6 (isopropylamino)-*S*-triazine to unharmful compounds in the environment.

**Keywords**: $TiO_2$, microemulsion, photodegradation, atrazine.

**Abstrak**

Fotopemangkin, titanium dioksida, $TiO_2$ telah disintesis melalui kaedah mikroemulsi di bawah kawalan hidrolisis titanium butoksida, $Ti(O(CH_2)_3)CH_3$ di dalam Heksadesil Trimetil Ammonium Bromida, HTAB. Kesan kepelbagaian kepekatan surfaktan dalam julat 0.01-1.0 M telah difokuskan di dalam kajian terhadap morfologi, saiz hablur, fasa kehablurannya dan luas permukaan spesifik. Selepas pemerhatian dan perbandingan dijalankan terhadap prestasi degradasinya, kepekatan 0.5 M HTAB telah menunjukkan kepekatan optimum untuk mesintesis fotopemangkin $TiO_2$. Keputusan ini juga telah disokong oleh spektra XRD yang mana telah mempamerkan saiz fotopemangkin adalah di dalam julat di antara 50-150 nm. Hasilnya, ciri-ciri mangkin $TiO_2$ nanostruktur yang telah disintesis menunjukkan sifat yang baik sebagai fotopemangkin bagi menguraikan atrazina, 2-kloro-4-(etilamino)-(isopropilamino)-*S*-triazina kepada sebatian-sebatian yang tidak berbahaya di dalam alam sekitar.

**Kata kunci**: $TiO_2$, mikroemulsi, fotopemangkinan, atrazina.

## Introduction

Titanium dioxide, $TiO_2$ photocatalyst has attracted great attention as a promising photocatalyst for photocatalytically degrade organic pollutant in the environment [1]. $TiO_2$ nanostructure is considered to be one of the promising materials due to its ideal physical and chemical properties such as environmental friendly, low cost, high oxidizing ability, long term stability and also exhibit high photocatalystic activity [2, 3]. However, their physical, chemical and photocatalytic activities are known to depend on its preparation methods such as by changing their calcinations temperature, time aging and pH of solution which may give affect on its performance [4, 5].

There are numerous methods known to synthesise $TiO_2$ including microemulsion which is believed to be very promising method to obtain nanosized $TiO_2$ particle with less agglomeration and flocculation. In addition, the surfactant in microemulsion will act as stabilized micro cavities to provide a cage-like effect that limits particle nucleation, growth and agglomeration [6]. However, the optimum concentration of surfactant in the microemulsion has become an argument among researchers because apparently it depends on the type of surfactant and preparation method that are used during synthesis process. The main objective of the study is to investigate the effect of various surfactant concentrations in synthesise $TiO_2$ towards degradation performance. The optimal surfactant concentration will promise great properties of $TiO_2$ nanoparticles and may have better capacity to degrade 2-chloro-4-(ethylamino)-6 (isopropylamino)-*S*-triazine or widely known as atrazine to unharmful compounds in the environment.

## Experimental

### Instruments

The physical properties of the synthesised $TiO_2$ were characterized by Scanning Electron Microscopy, SEM (JEOL JSM-6360 LA). The specific surface area of $TiO_2$ particles (BET method), specific pore volume and average pore diameter (BJH method) of the samples were determined by using nitrogen adsorption-desorption isotherms using Quantachrome Autosorb Automated Gas Sorption. Meanwhile, the particles size of the $TiO_2$ powders was determined by X-Ray Diffraction, XRD (Rigaku, Miniflex II Desktop X-Ray Diffractometer).

### Reagents

The reagents used were Hexadecyl Trimethyl Ammonium Bromide, HTAB (Sigma - Aldrich), titanium butoxide (purity 97%, Sigma-Aldrich), cyclohexane (Hamburg Chemical), NaCl (Merck Schuchartdt) and ammonium hydroxide, $NH_4OH$ (Mallinckrodt). In addition, for catalytic studies, the selected pesticide namely Atrazine (Sigma-Aldrich) was used as standard. All of these chemicals were used as received without further purification.

### General procedures

$TiO_2$ nanoparticles were prepared according to 6:3:1 proportion as proposed and carried out in previous studies [7]. Microemulsion A and B consist 60 ml cyclohexane (Hamburg Chemical) as oil phase and 30 ml Hexatrimethyl Ammonium Bromide, HTAB (Sigma - Aldrich) as surfactant by varying their concentration 0.01, 0.05, 0.1, 0.5 and 1.0 M. As starting material, 10 ml of titanium (IV) butoxide, $Ti(O(CH_2)_3)CH_3$ (purity 97%, Sigma-Aldrich) was added in microemulsion A, meanwhile ammonium hydroxide solution, $NH_4OH$ (Mallinckrodt) 2 M as reducing agent in reagent B. After 30 min of stirring separately, both microemulsion were mixed in a beaker (100 ml) and followed by vibrated homogeneously in ultrasonicator (JAC Ultrasonic Cleaner, JAC 2010, 240~/50Hz/30 A) for 1 hour. This step was carried out to prevent agglomeration of $TiO_2$ pigment in water.

Then, 10 ml of 5 M solution of sodium chloride, NaCl (Merck Schuchartdt) was added to microemulsion, followed by continuously vibrated in ultrasonicator for another 1 hour to ensure the mixture was completely mixed. The microemulsion, was then washed with 30 ml acetone before the product was annealed (Nabertherm, HTC 08/16, 400 V, 50/60 Hz) at 600º C for 4 hours. Next, the powders obtained were washed with 100 ml distilled water to remove the remaining NaCl, followed by dried in an oven at *ca.* 90°C for 12 hours to remove any excess water.

### Photocatalytic activity

The photocatalytic degradation of atrazine was performed by using 100 ml aqueous solution of atrazine (5 mg/l) (Sigma-Aldrich) and 0.1 g of synthesised $TiO_2$ catalyst. The degradation mixture were stirred magnetically and irradiated by UV-light (302 nm, 230 V~50 Hz) for 1 hour to ensure their optimum thermodynamic stability. Every 5 ml of the aqueous suspension was collected at each 30 minutes interval during the irradiation and then was filtered on 0.10 µm Milipore syringe filter (Whatman) to remove the catalyst. The samples were exposed for 4 hours under UV-light and analyzed by using UV-Vis spectrophotometer (UV-1601 PC, UV-Visible Spectrophotometer Shidmadzu) for the percentages of degradation determination.

## Results and discussion

### Morphological study

Figure 1 A to F indicate the SEM images of the $TiO_2$ powders prepared by microemulsion method at various HTAB concentration. From the observation of Figure 1 A to D, the particle are slowly become less agglomerates. Sample A was carried out without HTAB as a comparison with others to show the significant of surfactant existence in the synthesis process. Figure 1 A shows the effect of microemulsion without existence of surfactant. It can be observed that without existence of surfactant in microemulsion, there are no covers by surfactant on the surface to hydrolyze the products and hence, no nanosize $TiO_2$ can be obtained [8]. It is obviously noted that the ultrafine and nanosized particles cannot be achieved in the synthesis process without the present of surfactant.

However, at concentration of 0.5 M, the shape of $TiO_2$ particles becomes less agglomerates and uniformly shape. These observations are exposed to different water compositions in microemulsion which has played important roles. Therefore, according to Mohapatra *et al.,* 2006, at low HTAB concentration, the size of particles is increased. This might be due to the increasing size of water droplet which is produced by hydrolysis in the w/o microemulsion's water pool [9]. The high particles size of $TiO_2$ has caused by the increasing agglomeration process. The high agglomeration of particles is shown in Figure 1 A-D. However, one can observe that, their

agglomeration becomes gradually decrease with the decreasing of water content until it has reached the optimal concentration of HTAB which is 0.5 M.

Meanwhile, when HTAB concentration is more than 0.5 M, the particles become agglomerate again. Except for $TiO_2$ synthesised by 1.0 M of HTAB which has shown elongated structure compared to the other concentrations. This might be due to the viscosity of microemulsion has increased due to the high content of surfactant in microemulsion during synthetic steps. Hence, this condition caused the particles movement become difficult due to bridging of the surfactant and it was lead to the increasing of surface tension and particles size [10]. Therefore, the dispersion of powder in microemulsion is incompletely distributed and need to be improved under optimum concentration of HTAB, thus the ultrafine particles would be achieved.

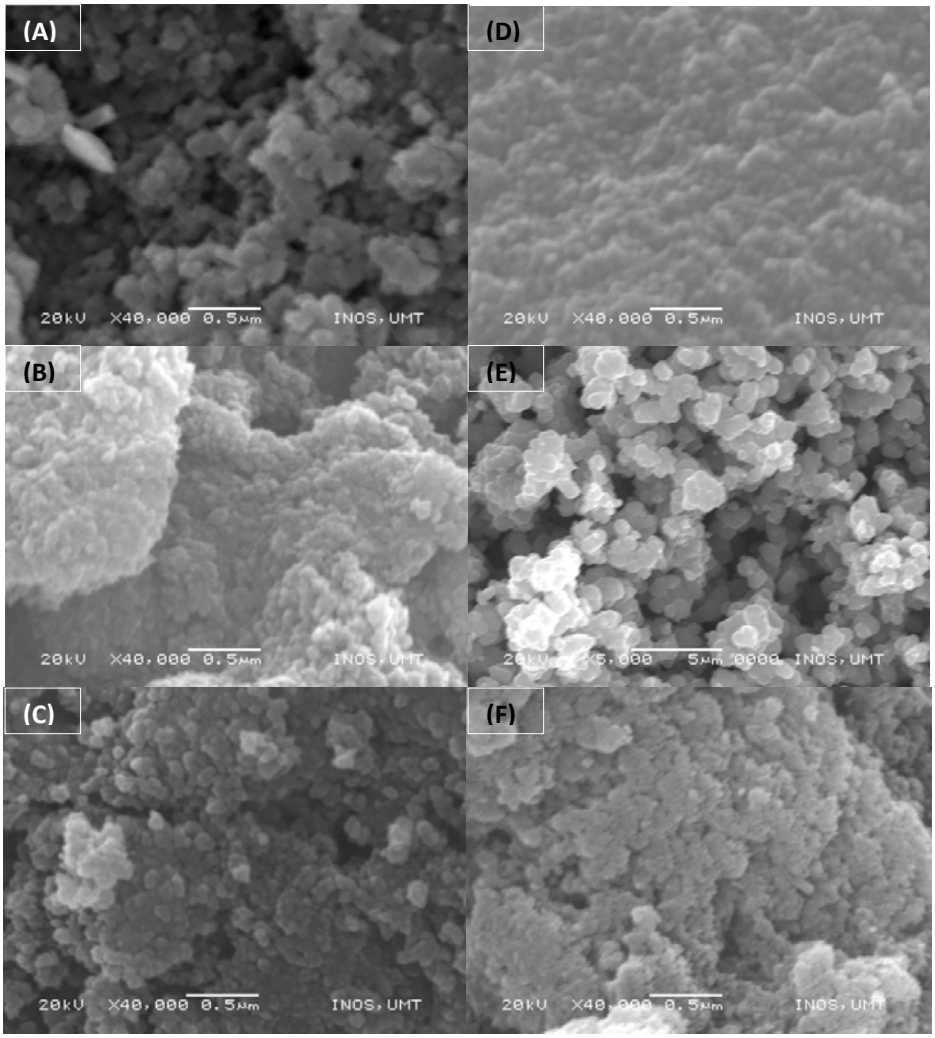


Figure 1: Morphological images effect of HTAB at (A) without HTAB, (B) 0.01, (C) 0.05, (D) 0.1, (E) 0.5 and (F) 1.0 M concentration.

**Crystal structure study**

Figure 2 indicates X-ray diffraction pattern of $TiO_2$ obtained from various HTAB concentrations. The XRD pattern revealed the effect of surfactant concentration on the phase change of $TiO_2$ nanoparticles. It is clearly shown that diffraction peaks from concentration 0.01 to 0.5 M gradually transform to anatase phase completely. The change in the width of these diffraction peaks is related to the variation changes of crystallite size of the

obtained powders. The major phase of all prepared particles is an anatase structure was observed at concentration 0.5 M HTAB. However, at concentration 1.0 M, the X-ray diffraction peak of the obtained $TiO_2$ powders becomes broader which is apparently revealing the particles size of $TiO_2$ to become increase again due to unsuitable and unideal concentration during synthesis process. The increase of the $TiO_2$ particle size might be due to agglomeration on their surface. This X-ray diffraction spectra data are comparable to SEM morphological image which has proved that the optimal surfactant concentration is crucial in order to synthesis $TiO_2$ at nanosize condition. Meanwhile, for synthesis $TiO_2$ without using HTAB surfactant (0.0 M) exhibits undesired peak was appear at angle 2Θ =22 degree corresponding to the high agglomeration due to without ultrafine synthesis medium.

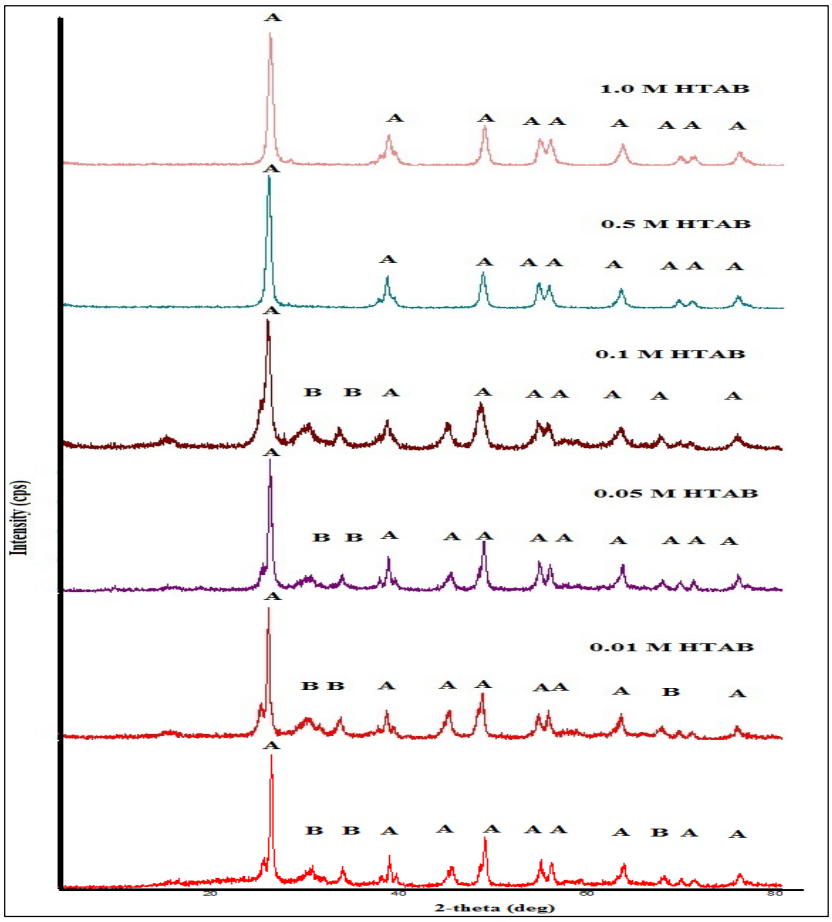


Figure 2: XRD spectra of $TiO_2$ nanoparticles synthesised at different HTAB concentration and were calcined at 500° C for 4 hours. (A: anatase, B: brookite).

Basically, the average particles size of $TiO_2$ is calculated by using Scherer's equation on each the highest intensity diffraction peaks by following equation:

$$D = \frac{K\lambda}{\beta}\cos\theta$$

…… Equation 1

Since D in the crystal size of the catalyst, λ the X-ray wavelength (1.54Å), β the full width half maximum, (FWHM) of the highest intensity diffraction peak, K is a coefficient (0.94 nm) and Θ is the diffraction angle. An average particles size of around 40-140 nm was obtained for nanoparticles. Based on these results, 0.5 M concentration of HTAB surfactant was successfully synthesised in the smallest particles size. It might be due to X-ray diffraction peaks intensities of obtained $TiO_2$ which was increased and the Full Width Half Maximum, FWHM peak at $2\Theta$=25.3° became narrower with decreasing the composition of water ratio [11]. The peak at $2\Theta$=25.3° was chosen as a standard peak due to their well crystallite peak for $TiO_2$ appeared. In addition, Figure 3 clearly shows the effect of HTAB concentration on particles size of $TiO_2$. This indicates the optimum value of HTAB concentration will determine the smallest size of particles. Hence, the best of particles size will be enhancing their percentage of degradation. Besides, physical properties of $TiO_2$ can be improved by varying their several parameters as well such as stirring time and pH of microemulsion in order to improve the performance of degradation process.

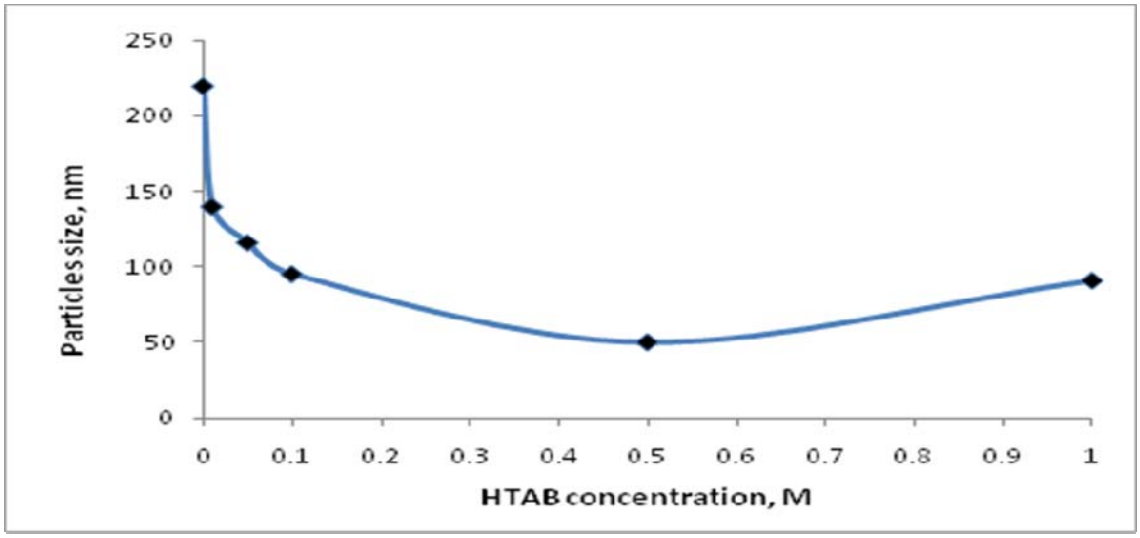


Figure 3: Variation in particles size of $TiO_2$ powders prepared at different surfactant concentration and were calcined at 500° C for hours.

**Surface area and pore volume analysis**

Surface area and pore volume are crucial aspect in term of photocatalytic studies. Table 1 summarises the crystallite size, surface area and pore diameter of $TiO_2$ photocatalyst when synthesised by varying their surfactant concentrations. The specific surface area slightly increases from 15.22 to 76.66 $m^2/g$ as the concentration of HTAB surfactant is increased from 0.01 M to 0.5 M. Nevertheless, the specific surface area of synthesised $TiO_2$ is decreased with HTAB concentration at 1.0 M. The $TiO_2$ prepared at 0.5 M concentration of HTAB and calcined at 500ºC for 4 hours exhibits the highest specific area of 76.66$m^2/g$.

Generally, the specific surface area depends on the size and shape of the particles. Somehow, the different of surface area which observed is owing to the agglomeration of the particles even though their particle shape and size is similar [12]. Hence, according to Lu *et al.,* 2008, by the increasing the particle size, apparently it will decrease the surface area [13]. In addition, the pore diameter of $TiO_2$ synthesised without HTAB surfactant was show the lowest specific surface area, which is 15.22 $m^2/g$. This resulted occurs due to absence of HTAB in the microemulsion during synthetic process. The presence of optimum concentration of HTAB not only controls the particles size and shape, but also increase the porosity of the materials [14].

Table 1: The profiles of the particles synthesised by varying their surfactant concentration in microemulsion and calcined at 500° C for 4 hours.

| HTAB concentration (M) | Crystallite size (nm)* | BET surface area ($m^2/g$) | BJH adsorption-desorption pore surface area ($m^2/g$) | Crystallite phase |
|---|---|---|---|---|
| 0.0 | 150.6 | 15.22 | 20.11 | Anatase, brookite |
| 0.01 | 139.5 | 20.75 | 36.91 | Anatase, brookite |
| 0.05 | 115.9 | 22.33 | 47.92 | Anatase, brookite |
| 0.1 | 95.1 | 57.53 | 62.77 | Anatase, brokite |
| 0.5 | 49.9 | 76.66 | 80.25 | Anatase |
| 1.0 | 90.8 | 41.76 | 38.47 | Anatase |

*Calculated by using Scherer equation.

While, the pore surface area of all synthesised $TiO_2$ was determined by using Barret-Joyner-Halenda (BJH) adsorption-desorption method. The addition of HTAB surfactant has resulted the pore surface area to increase of which is within 20 to 80 $m^2/g$. However, at the concentration of 1.0 M HTAB, the pore surface area drastically decrease to 38.5 $m^2/g$. The decreasing of pore surface area is due to less pores formed in the catalyst surface. This phenomenon was attributed to the restricting effect of the microemulsion due to over loaded amount of HTAB surfactant to control their excess growth. Thus, the growth speed and synergistic control of $TiO_2$ growth during synthetic process were inhibited and growth rate decreased accordingly [15]. Hence, the inhibition and restriction has caused the decreasing of surface area and pore surfacea area.

**Photocatalytic study**

The catalytic activity of catalysts which are synthesised by various surfactant concentrations in order to investigate their catalytic behaviour towards atrazine. Figure 4 shows the percentage of atrazine's degradation when exposed for 4 hours under UV irradiation. Photodegradation of atrazine by using $TiO_2$ synthesised without HTAB was only able to degrade at 27%. This degradation is lower compared to the others which may due to their specific surface area. The limit of specific surface area will act as adsorption surface to reduce molecular oxygen on the Ti (III) sites to the superoxide radical anion. The surface to bulk ratio for a nanoparticles material is much greater than for material with larger grains, which yields large interface interaction between the solid and gaseous or liquid medium [16].

The enhancement of photodegradation activity is improved in the presence of HTAB. According to Lu *et al.*, 2009, HTAB not only helps in the spherical particle formation but it is also increases the surface area and visible light absorption [17]. Therefore, it should be an effective photocatalyst in the presence of HTAB and the optimum concentration of HTAB will enhance the performance of photodegradation activity.

In this study, obviously the percentages of photodegradation were increasing by the decreasingly degree of agglomeration. Somehow, high degree of agglomeration will affect the catalyst's surface area which mean will resulted low performance of degradation. Hence, the percentages of photodegradation in the presence of the synthesised $TiO_2$ catalyst by 0.01, 0.05, 0.1 and 0.5 M of HTAB increased gradually from 35, 39, 44 and 60 %. These findings are supported by SEM observations, which show the agglomeration of $TiO_2$ catalyst's surface slowly decreased by the increasing amount of surfactant in the microemulsion. Furthermore, phase content that clearly observed from XRD pattern plays vital important role in enhancing the rate of photodegradation [18]. Thus, at 0.01, 0.05 and 0.1 M concentration of HTAB, the broader, less crystalline and less intensity peaks are observed compared to the XRD spectrum which obtained from 0.5 M concentration of HTAB. According to these results, the highly diffract peaks may be attributed to agglomeration process. Meanwhile, the well-crystallite pattern as represented by 0.5 M of HTAB is corresponding to the anatase phase crystalline structure of these aggregated particles. Whilst, the existence of broader and so-called noise peaks are believed to be

attributed as brookite phase. The mixture of phase content is influenced by the percentages of degradation which also to the respect of impurities presence in the sample.

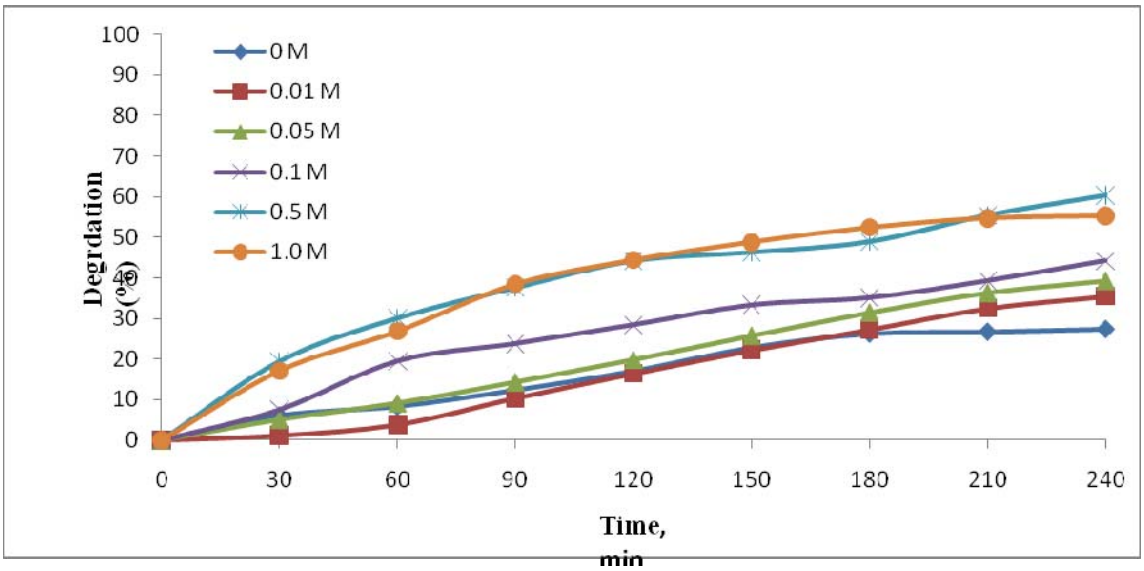


Figure 4: Effect of surfactant concentration towards percentages of photodegradation of atrazine by irradiated with UV for 4 hours.

Among all surfactant concentrations, 0.5 M surfactant shows the best photocatalytic activity by degrading 60 % of atrazine. Physical and chemical properties of all synthesised $TiO_2$ determined by SEM and XRD results proved that 0.5 M of HTAB has produced the aggregation of nanoparticles. The samples obtained at this concentration are all in the uniformly shape with the size particle in the average of 49.9 nm. This might be attributed to the narrower peaks, high crystalline and high intensity compared to the other peaks of other concentrations. The narrower peaks will produce high value of Full Width Half Maximum, FWHM value. Hence, by increasing the FWHM value the particles size will be decreased as suggested by Scherrer equation. In fact, less aggregation on surface of $TiO_2$ photocatalyst has caused the high specific surface area [19]. Hence, the interaction during photoreaction has taken place at maximum activity.

In addition, anatase crystallinity phase exhibits to produce high performance of degradation [20]. In addition, according to BET specific surface area has shows the surface area synthesised with 0.5 M of HTAB has the highest surface area compared with others. High surface area will enhancing the photodegradation process due to large surface area provided more area to react with atrazine and as well to produce hydroxyl radicals and superoxide radicals anions. Therefore, it can be assumed that the optimum concentration of surfactant in microemulsion leads to the formation of anatase phases. The nanoparticles in different phase formation observed as anatase phase is more stable at nanosized which resulted a higher photocatalytic activity compared to the bookite and rutile phase [21][22].

However, based on photodegradation result, it can be summarised that too high loading of surfactant in microemulsion will inhibit the formation of the desired nanoparticles. This is related to different size of water droplet in microemulsion with various concentration of HTAB [23]. In this report, 1.0 M HTAB is proven to contain an excessive amount of HTAB which prevent the formation of the ideally uniform shape. The observation was strongly agreed by SEM micrographs images, BET specific surface area and XRD spectrum result which show the degree of agglomeration of $TiO_2$ powders depends on the concentration of the aqueous solution. Thus, the most appropriate surfactant concentration in order to obtain spherical nanoparticles photocatalyst is 0.5 M HTAB.

## Conclusion

$TiO_2$ nanoparticles with optimum surfactant concentration were successfully prepared via microemulsion method. This investigation concludes that agglomeration of $TiO_2$ nanosized can be reduced by adding surfactant. However, the optimisation of surfactant concentration is essential for obtaining minimum $TiO_2$ particle sizes. The increase of surfactant concentration significantly decreased the particles size of the prepared $TiO_2$ by preventing agglomeration. The optimum concentration of surfactant needed is 0.5 M for synthesised $TiO_2$, which yield the size of the particles is 49.9 nm. As a result, photocatalytic activity of synthesised $TiO_2$ by optimum surfactant concentration was successfully 60 % degraded atrazine.

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