

Effect of Cu doping on structural properties and photocatalytic activity of TiO₂ nanoparticles synthesized by sol-gel method

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TiO₂ nanoparticles with varied content of Cu doping have been synthesized by sol-gel method with the addition of polyethylene glycol (PEG) as a template. The content of Cu doping significantly influenced the structure and morphology of TiO₂ nanoparticles. Increasing content of Cu doping caused a phase transformation of TiO₂ crystal from rutile to anatase. As well as the surface morphology of TiO₂ nanoparticles also significantly were affected by Cu doping, which the TiO₂ particles became more finer due to the Cu content increased. The effect of Cu doping on the photocatalytic activity of TiO₂ in degrading methyl violet (MV) dye was investigated. Photocatalysis test results confirmed that the content of Cu doping in the TiO₂ photocatalyst significantly affected the photocatalytic activity of TiO₂ for photodegradation of MV dye. Increasing content of Cu doping increased the degradation rate of MV dye. The TiO₂ photocatalyst with the highest Cu doping content (6.0 wt% Cu) has the best photocatalytic activity than the other TiO₂ photocatalyst, that is able to degrade MV dye up to 95% after 120 minutes of photocatalysis treatment with a degradation rate is 0.0214 ppm per minute. The pH of MV solution also influenced the photocatalytic activity of TiO₂, which the MV dye solution with higher pH has higher the photodegradation efficiency.

Key words: Cu doping, methyl violet dye, photocatalytic activity, TiO₂ nanoparticle.

Introduction

Dyes are the important component in the textile and paint industries. However, dyes can be a dangerous waste to the environment because of this organic compound is non-biodegradable and very difficult to be decomposed [1]. The type of the dye used in the textile industry today is extremely diverse, therefore textile waste handling becomes very complicated and requires several steps until the waste is completely safe to be released into the aquatic environment [2, 3]. One of the dyes often used in textile industry is methyl violet (MV) [4].

Dye waste produced by the textile industries can cause damage to the aquatic ecosystems because of the high concentration of organic compounds contained therein. The process of removal of textile dye becomes discussions and regulatory issues around the world [5]. Currently, a variety of techniques or methods of textile industry waste reduction has been developed, including the methods of adsorption [6]. However, these methods were less effective because of adsorbed dyes still accumulates in the adsorbent which someday will lead to new problems. In addition to these methods, other methods have also been developed to prevent the

pollution resulting from textile industrial dyes.

Three most prominent of all methods have been developing nowadays are the chemical degradation [7], biodegradation [8, 9] and photocatalytic degradation [3, 4, 10-13]. The last one uses semiconductor materials activated by a photon, as known as the photocatalyst. By the photocatalytic degradation method, the dye will be decomposed into components simpler and safer for the environment [14-16].

TiO₂ is a semiconductor material that is most often used as a photocatalyst to decompose dye since it was first discovered by Fujishima and Honda [14]. The photocatalytic activity of TiO₂ is known to be higher than other semiconductor materials. However, efforts remain to be done to increase its photocatalytic activity. Various ways can be done to improve the photocatalytic activity of TiO₂, including the addition of doping [17-19]. The goal is of course to enhance the kinetics of charges transfer that was generated through photon absorption to initiate catalytic reactions around the surface of TiO₂ particles which in turn produce free radicals that can degrade the dye pollutants. Another goal of doping addition is the photocatalyst can be activated by visible light [20-28].

There were many doping elements have been used to enhance photocatalytic activity of TiO₂. Among the doping elements that often used including nitrogen (18, 20), silver (11)), iron (21), carbon (17, 22), boron (23), bismuth (19, 24), and copper (25-28). The doping will

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improve the photocatalytic activity of the TiO_2 by enhancing the charges transfer between photocatalyst and the aqueous solution of MV dye [27, 28]. Doping also helps the adsorption of reductant and oxidant species and be a media for charges transfer from and to the photocatalyst surface.

The aim of this work is to enhance photocatalytic activity of TiO_2 in degrading the MV dye by addition of copper (Cu) doping. TiO_2 nanoparticles were synthesized from TiCl_4 by sol-gel method with the addition of polyethylene glycol (PEG) as a template. The template acts as a surfactant to disperse the TiO_2 particles in the precursor solution to prevent agglomeration so that can be obtained the nano-sized particles of TiO_2 with high surface area and porosity. Effect of pH of the dye solution to degradation efficiency of MV also studied.

Experimental Procedures

Synthesis of TiO_2 nanoparticles was carried out by sol-gel method with the addition of PEG as a template. 10 g PEG was dissolved in 60 ml ethanol solution and then stirred with a speed of 500 rpm using a magnetic stirrer for 30 minutes until the PEG dissolved completely. Then, gradually was added 10 ml TiCl_4 while still stirred, the solution was stirred for 8 hrs at room temperature to form a sol phase. The sol was divided into four portions, each used for different treatment, which was then called "precursors". Into the precursors were added $\text{Cu}(\text{NO}_3)_2$ as Cu doping source with a different variation of weight percentage (wt%). The first precursor without an addition of $\text{Cu}(\text{NO}_3)_2$, whereas the other three precursors were added $\text{Cu}(\text{NO}_3)_2$ with different weight percentage (wt%), respectively were 2 wt%, 4 wt%, and 6 wt%. Each precursor was stirred for 60 minutes. All precursors were dried on a hotplate at a temperature of 150°C for 3 hrs to remove the water content to form a powder and then annealed at a temperature of 450°C for 4 hrs. The crystal properties of TiO_2 powder samples were characterized by X-ray diffraction (XRD), whereas microstructure of TiO_2 was investigated by using a scanning electron microscopy (SEM).

To be applied as a photocatalyst in degrading MV dye, the TiO_2 powder was coated onto the glass slide substrate. TiO_2 films were prepared by the casting method from the TiO_2 powder that has been prepared by sol-gel method. TiO_2 paste was prepared by mixing 0.5 g of TiO_2 powder, 2 ml of distilled water, 2 ml of acetylacetone and 2 g of PEG, which was stirred for 1 hr until resulted in the paste. Prior to casting, the glass substrate (75 mm x 25 mm x 1.5 mm) is washed with ethanol, and then rinsed with DI water then dried. Three drops of TiO_2 paste were dropped onto the glass substrate and then coated using a glass rod to form a layer of TiO_2 . TiO_2 films were heated on a hotplate at 110°C for 15 minutes, for each coating. Then, the TiO_2

films were annealed at 450°C for 30 minutes, with the temperature rise of $5^\circ\text{C}/\text{min}$ in the furnace. The same treatment was carried out for each TiO_2 film as photocatalysts.

Photocatalysis test was carried out in a reactor made of a dark and opaque PVC cylinder, where light from outside is blocked to enter the reactor so that the reaction can take place effectively. As test solution, 500 mL MV solution with an initial concentration of 4 ppm was poured into the reactor. As an irradiation light source for photo-activation of TiO_2 photocatalyst was used 11-watt UV lamp with a wavelength of 365 nm that immersed in the center of the reactor. Transmission and distribution of light energy in the reactor must be homogeneous so that the UV lamp must be partially dipped into the test dye solution. The three TiO_2 films with a size of 75 mm (length) x 25 mm (wide) were placed at the bottom of the reactor, while 3 pieces affixed to the walls of the reactor. Photocatalysis treatment of MV dye solution was carried out for 120 minutes, where the solution was sampled every 30 minutes to measure its concentration by using UV-Vis spectroscopy.

Results and Discussion

Effect of Cu doping on the crystal properties of TiO_2 was studied by XRD analysis for each sample with a content variation of Cu doping. Four TiO_2 samples were characterized, each of which one sample without doping (undoped) and three samples with a content variation of Cu doping in weight percentages (wt%) respectively were 2 wt%, 4 wt%, and 6 wt%. The XRD pattern of each sample is shown in Fig. 1.

There is a significant difference in diffraction patterns due to the variation in Cu doping content in the TiO_2 samples indicating that the phase transformation of

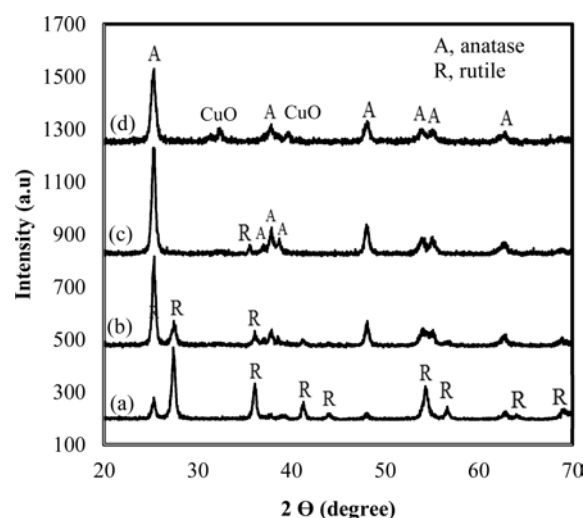


Fig. 1. XRD patterns of TiO_2 samples with different Cu content, (a) 0, (b) 2, (c) 4, and (d) 6 wt%.

TiO₂ crystals has taken place. The diffraction pattern of the undoped TiO₂ is shown in Fig. 2(a), where the rutile phase dominating the pattern compared to the anatase phase. Rutile peak at an angle 2θ around 27° corresponding to reflection plane (110) with the strongest intensity which is very dominant over the other peaks. Other rutile peaks which are also strong enough appeared respectively for reflection planes (101), (111), (201), (211), (220), (002), and (301). The reflection planes identified were matched with JCPDS No.21-1276. Whereas the anatase peak appeared only at angle 25° corresponding to reflection plane (101) with an intensity that is much lower than the peaks of rutile (JCPDS No. 21-1272). Therefore, it can be concluded that the undoped TiO₂ sample has a rutile phase. This result is unusual and in contrast to the results of other studies, in which the formation of rutile phase usually takes place at a higher temperature (600 °C), as reported by Tsai et.al. [28]. In this study, the rutile phase was formed at relatively low temperature, that is 450 °C.

Effect of Cu doping on the crystal properties of TiO₂ was studied. There are three content variations of Cu doping, respectively were 2 wt%, 4 wt%, and 6 wt%. The diffraction patterns of Cu-doped TiO₂ samples were shown in Fig. 2(b-d). TiO₂ doped with 2 wt% Cu began to be dominated by the anatase phase (Fig. 2(b)) compared to the undoped TiO₂ which dominated by rutile peaks. As can be seen in the diffraction pattern (Fig. 2(b)) in which the peaks of anatase stronger than the peak of rutile. The peak of anatase at reflection plane (101) is higher than the peak of rutile at reflection plane (110) in which higher in the undoped TiO₂. Other anatase peaks also began to emerge, although the peaks of rutile also still emerged but began to weaken compared to the undoped TiO₂ sample. Thus, the doping addition with 2 wt% Cu began affected the crystalline phase of TiO₂ by initiating the phase transformation from rutile to anatase.

The diffraction pattern of the TiO₂ doped with 4 wt% Cu (Fig. 2(c)) showed the peaks dominated by the anatase phase with very strong intensity and dominating in the diffraction pattern, especially for reflection plane (101). The other anatase peaks appeared for reflection planes (004), (220), (105), and (215), respectively. While the peaks of rutile weakened, even almost no longer appeared in the diffraction pattern. It means that the higher Cu content strongly affected the crystal phase of grown TiO₂, which the rutile phase reduced and the anatase phase increased.

Further doping with the high Cu content up to 6 wt% showed a very different diffraction pattern of TiO₂, as shown in Fig. 2(d). The diffraction pattern of TiO₂ sample doped with 6 wt% Cu is dominated by the anatase peaks. Almost all peaks in the diffraction pattern are belonging to anatase phase and did not leave the rutile phase at all. Thereby, TiO₂ doped with

6 wt% Cu resulted in a single phase of anatase. However, the high content of Cu doping resulted in the emergence of CuO phase in the diffraction pattern. The presence of the CuO phase slightly decreased the intensity of the diffraction of the anatase phase. The Peaks of monoclinic CuO appeared at 32.4° and 39° corresponding to the reflection planes (110) and (200) [25, 30, 31].

In general, the content variation of the Cu doping significantly influenced the crystal phase of grown TiO₂. These results differ from those obtained by Tsai et al. [28] and Yang et al. [27], where the addition of Cu doping up to 5 wt% almost does not change the crystal phase of TiO₂ [28]. In this study, the increase in the content of Cu doping caused phase transformation of TiO₂ from being dominated by rutile phase became entirely anatase phase on the addition of high content of Cu doping (6 wt%).

Based on the broadening of the diffraction pattern, the average crystallite size (ACS) of TiO₂ samples can be determined by using the Scherrer method with the following Eq. (1).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where k is a constant of 0.89; λ is the wavelength of X-ray source of CuK_α (1.54 Å or 0.154 nm), β is the full-width half maximum (FWHM) (rad) and θ is the angle of diffraction (rad). Broadening of the diffraction pattern correlated to the crystallite size of a material, where a broader diffraction pattern has smaller crystallite size.

The calculation results of ACS confirmed that fraction of Cu doping in TiO₂ sample significantly influenced the ACS of TiO₂. Effect of Cu doping content on the ACS of TiO₂ was summarized in Table 1. The ACS of the undoped TiO₂ sample is 17.6 nm that consistent with the broadening of the diffraction pattern of the sample. While the ACS of the TiO₂ doped with 2 wt% Cu is 17.9 nm. The ACS of the TiO₂ doped with 4 wt% Cu showed a smaller crystallite size of 14.3 nm. Further doping of TiO₂ up to 6 wt% Cu resulted in a smallest ACS of about 11.3 nm. Based on the ACS) of the TiO₂ samples in the range of 11-17 nm, we concluded that the grown TiO₂ samples have a nanocrystalline structure, where the increase in the content of Cu doping caused a decrease in crystallite size of TiO₂ significantly.

Table 1. Effect of content variation of Cu doping on the average crystal size (ACS) of TiO₂.

Cu content (% wt)	Average crystal sizes (nm)
0	17.6
2	17.9
4	14.3
6	11.3

The surface morphology of TiO_2 sample was characterized by SEM. The SEM images with a magnification of 20,000 times for all sample of TiO_2 are shown in Fig. 2, both for undoped and Cu-doped TiO_2 samples. The SEM image of the undoped TiO_2 is significantly different to the other TiO_2 samples which were doped with Cu. The surface morphology of undoped TiO_2 particles tends formed microspheres (Fig. 2(a)). On the image, there are larger sized particles with a diameter about of $3\ \mu\text{m}$ which were estimated as rutile particles, while the smaller particles surrounding were estimated as anatase particles. This conclusion was drawn based on the results of X-ray diffraction which the rutile phase dominating as compared to the anatase phase for the undoped TiO_2 .

Different from the surface morphology of undoped TiO_2 , an image of the microstructure of TiO_2 doped with 2 wt% Cu showed the finer particles, as shown in Fig. 2(b). In the SEM image, clearly looked the anatase particles finer than the rutile in the undoped TiO_2 , although it still looked the presence of rutile particles (microspheres) but no longer dominant. This image consistent with the XRD analysis which where the rutile phase was much reduced, even began dominated by the anatase phase with a smaller grain size. It can be stated that the addition of Cu reduced the presence of rutile phase significantly in the sample.

Further, the addition of Cu doping up to 4 wt% significantly altered the microstructure of TiO_2 , as shown in Fig. 2(c). In the SEM image, the surface morphology is clearly looked the TiO_2 particles with a more uniform size, the large granules that predicted as rutile particles did not exist as in the undoped TiO_2 . TiO_2 particles have been transformed into small granules as the anatase particles uniformly dispersed on the surface of the sample with a smaller size (finer).

A significant difference in the microstructure of TiO_2 with the further addition of Cu doping up to 6 wt%, as shown in Fig. 3(d). The image presents the microstructure of TiO_2 in which the appearance of particles are dispersed evenly with a nearly uniform size and smooth, which are believed to be the anatase particles. The rutile particles absolutely no longer present in the sample, consistent with XRD result. Thus, the addition of Cu doping up to 6 wt% significantly affected the microstructure of TiO_2 , where the increased in Cu content produced TiO_2 particles finer.

Based on the XRD pattern and SEM images, the addition of Cu doping taken from copper nitrate ($\text{Cu}(\text{NO}_3)_2$), overall proved that the increase of Cu content reduced rutile phase and changed the crystal properties and microstructure of TiO_2 . The addition of Cu doping up to 6 wt% is no longer showed rutile phase of TiO_2 . Rutile phase was transformed entirely into anatase phase with finer particles. That is, the addition of Cu doping resulted in a decrease in the content of rutile phase in the TiO_2 , even disappeared

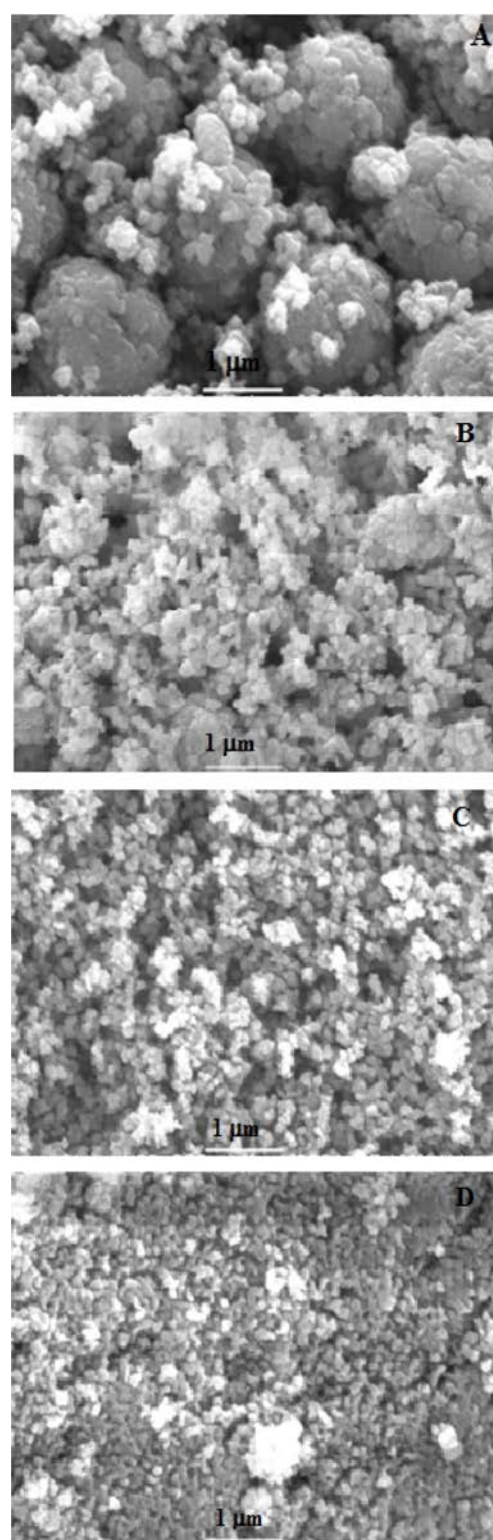


Fig. 2. SEM images of TiO_2 with addition of Cu content variation, (a) 0, (b) 2, (c) 4, and (d) 6 wt%.

altogether with the addition of Cu doping up to 6 wt%. On the other hand, the crystallite size of TiO_2 is also smaller as the increase in the content of Cu doping.

Photocatalytic activity of TiO_2 sample was tested in MV solution as dye pollutant model. Four TiO_2 samples

tested as photocatalysts with varied content of Cu doping respectively were undoped TiO₂ and TiO₂ doped with 2 wt%, 4 wt%, and 6 wt% of Cu content. Photocatalysis treatment was carried out in a reactor made of a dark and opaque PVC cylinder. Photocatalysis treatment was performed for 120 minutes with sampling every 30 minutes. The initial concentration of MV dye is 4 ppm. Determination of the concentration of the each MV sampling was conducted by UV-Vis spectroscopy method based on the standard curve of MV dye solution previously was taken.

The degradation pattern of MV dye after photocatalysis treatment follows the exponential relationship of concentration (C) with the time of photocatalysis treatment as the following Eq. (2),

$$C = C_0 \exp(-kt) \quad (2)$$

where C₀ is the initial concentration of MV dye solution, k is a constant (rate) of degradation, and t is the time of photocatalysis treatment. The negative sign in the equation states that the concentration of MV dye solution decreased with the time of photocatalysis treatment.

The degradation curves of MV dye for each TiO₂ photocatalysts were shown in Fig. 3. It can be seen that the degradation curves have a similar pattern for the four TiO₂ photocatalysts. Based on the degradation curves, it is known that the concentration of MV dye decreased exponentially with the time of photocatalysis treatment. Variation of Cu content in the TiO₂ photocatalysts effected the photodegradation characteristics of MV dye. The higher the Cu doping content in the TiO₂ photocatalyst, the faster the dye molecule concentration of MV dye decreased. TiO₂ photocatalyst doped with the highest Cu content (6 wt%) has the best photocatalytic activity with the curve steepness higher than the other photocatalysts. The degradation curves also showed that at the end of the photocatalysis treatment the lowest dye MV concentration left behind was obtained by utilizing a photocatalyst of Cu-doped TiO₂ by 6 wt% with a degradation ratio (C/C₀) of 0.05 that means 95% of MV dye has been degraded for the 120 minutes of photocatalytic treatment.

In general, it found that the concentration of MV dye decreased with the time of photocatalysis treatment with the different steepness of the curve for each TiO₂ photocatalysts used, especially for the first 30 minutes. The increase in a content of Cu doping increased the curve steepness that indicates the degradation rate increased with increasing Cu content in the TiO₂ photocatalysts. Thus it can be stated that Cu doping has taken an important role in enhancing photocatalytic activity of TiO₂. CuO clusters have successfully facilitated the charge transfer mechanisms at the interface between photocatalyst and dye solution that play a important role in the decomposition process of MV dye molecules on the surface of TiO₂ photocatalysts.

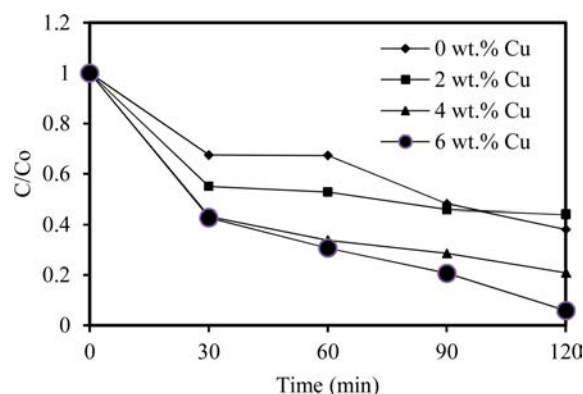


Fig. 3. Photocatalytic degradation of MV dye for TiO₂ with variation Cu content (0 wt%, 2 wt%, 4 wt%, and 6 wt%).

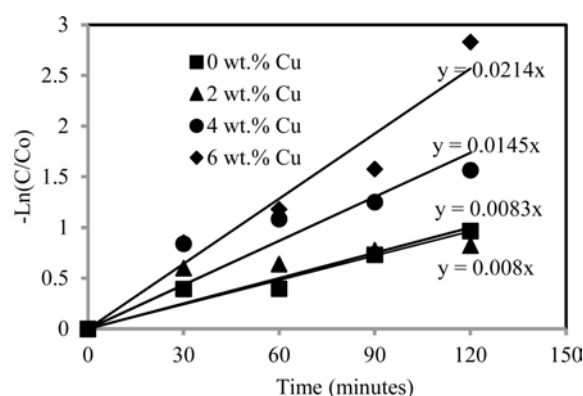


Fig. 4. Graphs of $-\ln(C/C_0)$ versus time for four different amounts of Cu doping content (0 wt%, 2 wt%, 4 wt%, and 6 wt%).

Table 2. Degradation rate of MV dye by different TiO₂ photocatalysts.

Cu content (% wt)	Degradation rate, k (min ⁻¹)
0	0.0080
2	0.0083
4	0.0145
6	0.0214

To determine the degradation constants or degradation rate, Eq. (2) has to be written in the form of the natural logarithm as the following Eq. (3).

$$-\ln\left(\frac{C}{C_0}\right) = kt \quad (3)$$

By plotting $-\ln(C/C_0)$ versus time of photocatalytic treatment using equation (3) to obtain linear curve from which can be determined a degradation rate for each photocatalysis treatment based on a slope of the curves. Fig. 4 shows the linear curves with different slopes indicating different degradation rates. Degradation rates of MV dye using four TiO₂ photocatalysts with different content of Cu doping were summarized in Table 2.

The slope of the curve increased with the increase of Cu content in the TiO₂ photocatalyst indicating that the

degradation rate increased. The addition of Cu in the TiO₂ sample is found increased the rate of transfer of photogenerated charges to initiate the reaction at the surface of the photocatalyst to produce free radicals in the environment that will degrade methyl violet (MV) [28].

This study proved that doping with Cu improved the photocatalytic activity of the TiO₂ photocatalyst. The addition of Cu doping rearranged the electronic configuration in the TiO₂ photocatalyst so that the TiO₂ had an ability to generate more charges species to initiate a catalytic reaction in the aqueous dye solution that improved the photocatalytic activity of TiO₂. Even, the addition of Cu doping into TiO₂ up to 6 wt% formed CuO clusters at the TiO₂ particles surface that where the CuO acted as a mediator for charges transfer from and to the photocatalyst that increased significantly the photocatalytic activity of TiO₂. Therefore, the TiO₂ photocatalyst doped with Cu by 6 wt% has the best photocatalytic activity found in this study.

Microstructure and pore distribution also significantly affected the photocatalytic activity of the TiO₂ photocatalyst. The addition of Cu doping to the TiO₂ photocatalyst resulted in a change in the microstructure of TiO₂, among which the TiO₂ particles became finer to form the nanoparticles. The addition of Cu doping also changed the pore distribution of TiO₂, the higher the Cu doping content the higher TiO₂ porosity. TiO₂ photocatalyst doped with 6 wt% of Cu has the smallest particle size and highest porosity than other photocatalysts so that has highest active area. The smaller the particle size and the more porous a photocatalyst the higher the catalytic activity, including photocatalytic activity.

Influence of pH of dye solution on the photodegradation efficiency of MV dye was investigated. Three variations of the pH-value of MV dye solution were tested their efficiency of photodegradation. Degradation efficiency of MV dye can be calculated using the following Eq. (4),

$$\eta = \left(1 - \frac{C}{C_0}\right) \times 100\% \quad (4)$$

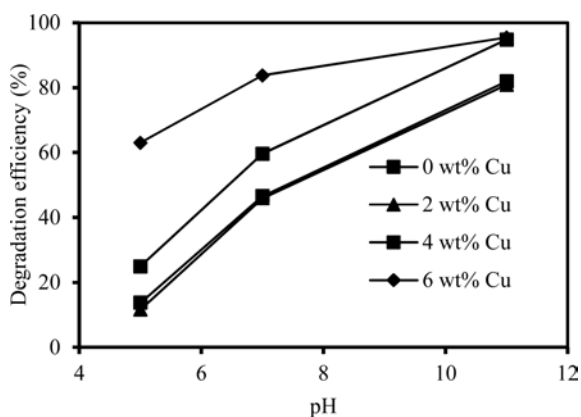


Fig. 5. Effect of pH on degradation efficiency of MV dye for TiO₂ photocatalyst with different Cu content (0 wt%, 2 wt%, 4 wt%, and 6 wt%).

where C and C₀ are the concentration at time t and at initial time, respectively.

Fig. 5 shows the relationship between photodegradation efficiency and pH of MV dye solution for four TiO₂ photocatalysts with a variation of the content of Cu doping. Generally, the curves show that photodegradation efficiency of MV dyes increased with pH of MV dye solution for the entire TiO₂ photocatalyst used. The highest photodegradation efficiency was found for TiO₂ photocatalyst with the highest content of Cu doping (6 wt%), especially at lower pH of MV dye solution.

The photodegradation efficiency of MV dye increased with the increasing pH value of the dye solution due to an increase of the hydroxyl ions (OH⁻) in the dye solution which induced more hydroxyl radical formation in the dye solution. Hydroxyl radical is one of the factors that determine the process of photocatalysis to decompose the dye pollutant. The high hydroxyl radicals in the dye solution will increase the rate of photodegradation such that the photodegradation efficiency increases as well.

Conclusions

Sol-gel method has been implemented to synthesize TiO₂ nanoparticles using PEG as polymerization agent. The ACS was obtained smaller than 20 nm based on broadening of diffraction pattern. The addition of Cu doping changed the crystal phase of TiO₂ that transformed the rutile phase into anatase. The rate of photodegradation was strongly influenced by the content of Cus doping in the TiO₂ photocatalyst. The addition of Cu doping greatly increased the photocatalytic activity of TiO₂, where photodegradation rate and efficiency of MV dye increased with the increasing content of Cu doping in the TiO₂ photocatalyst. It is concluded that the addition of Cu doping into the TiO₂ photocatalyst significantly increased the rate of charges transfer that was photogenerated from TiO₂ nanoparticles into the aqueous dye solution to induce the reduction reaction of water to produce free radicals in the aqueous environment that degraded methyl violet (MV) dye. Photodegradation efficiency of MV dye increased with a pH value of MV solution for the entire TiO₂ photocatalyst used which the highest efficiency belongs to TiO₂ photocatalyst with Cu content of 6 wt%.

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