



Enhancement of visible-light photocatalytic activity of Cu-doped TiO₂ for photodegradation of amoxicillin in water

E.T. Wahyuni^{1(*)}, P.Y. Yulikayani^{1,a}, N.H. Aprilita¹

¹Chemistry Department, Faculty of Mathematics and Natural Sciences, Gadjah Mada University
Sekip Utara, P.O. Box Bls. 21, Yogyakarta, Indonesia, 55281

^aMaster Student

Received 19 January 2020

Revised 31 March 2020

Accepted 1 April 2020

Keywords

- ✓ Doped,
- ✓ Copper,
- ✓ TiO₂,
- ✓ Amoxicillin,
- ✓ Degradation

endang_triw@ugm.ac.id ;

Phone: +6281328892114

Fax: +62274544188

Abstract

This paper presents a study on the doping TiO₂ with Cu referred as TiO₂-Cu, to enhance its visible light photocatalysis process for amoxicillin degradation. The doping was carried out by photodeposition of Cu²⁺ into TiO₂ structure. The effect of the amount of Cu doped on TiO₂ towards the characters and photoactivity was evaluated. The doped TiO₂ resulted was characterized by XRD and UV-Vis DR spectrophotometry methods. The activity of the photocatalyst was examined for degradation of amoxicillin in water with the presence of visible light. The results of the research, attributed that Cu doping on TiO₂ could uniquely improve the crystallinity of TiO₂, shifted the light absorption into visible region, and enhanced the photocatalytic activity on the amoxicillin degradation under visible light. The maximum shift and the highest enhancement of the activity were exhibited by Cu doped on TiO₂ as much as 4.56 mg g⁻¹. It was also found that the highest photodegradation (about 90%) of 10 mg L⁻¹ amoxicillin by TiO₂-Cu with 4.56 mg g⁻¹ of Cu doped, was achieved by 0.40 g L⁻¹ of the photocatalyst dose, in 24 h, and at pH 6.

1. Introduction

Photocatalyst of TiO₂ has been intensively studied because it has high stability toward biological and chemical effects, high activity, low cost and non-toxic property [1-7]. Photocatalysis process over TiO₂ under UV illumination has received considerable attention for degradation various organic pollutants [1-6] that is induced by OH radicals provided during the process. However, due to the wide band gap energy (E_g) that is 3.2 eV for rutile and 3.2 eV for anatase form [2, 7], the activity of TiO₂ is limited only under UV light, and very weak in the presence of visible light [7-21]. The UV light is only found about 5% of whole solar-light spectrum, preventing TiO₂ for applications in industries [7].

Many studies have reported enhancement of absorption in the visible range and photocatalytic activity of TiO₂ by doping with several metals such as Co, Ni, Mn, and Fe [7-8], Cr [9], Pt [10], Ag [10-11, 18], Au [12], and Cu [13-19]. Among various transition metals, it is noted that Cu²⁺-doped TiO₂ has attracted many interests due to its low cost, smaller ion radii allowing it to insert into TiO₂ lattice very easily [14], and ability in plausibly increasing TiO₂ activity under visible illumination [13-19].

Doping Cu on TiO₂ [13-19] has been carried out by hydrothermal [13-14], sol-gel [15-18], photodeposition [19-20], deep-coating [21], and evaporation [22] methods. The photodeposition or photoreduction based on the reduction of the metal ion under UV light over TiO₂, is one of the easiest methods to doping noble and transition metals on TiO₂ [20]. Compared with most other methods that need a high temperature, an additional redox agent, electric potential, or multi-step processing, the photo

reduction method requires only the irradiation of a light source [20]. However, only few reports employing photodeposition method for doping Cu in TiO₂.

In addition, the doped photocatalyst of TiO₂-Cu has been examined for catalyzing various processes like H₂ production [14], and degradation of oxalic and formic acids [15], phenol [16], and methylene blue dye [21], as well as for *E.coli* bacterial disinfection [22]. In contrast, photocatalyst of TiO₂-Cu has not been explored for degradation of pharmaceutical compounds, which have recently emerged as significant environmental pollutants. Accordingly, in this present research, TiO₂-Cu material for photocatalysis degradation of amoxicillin in the presence of visible radiation, is addressed.

Amoxicillin belonged to penicillin family, was selected to be an object in the current study, because it is one of the most consumed antibiotics worldwide [6,23-27], that is almost 90% excreted from the dosage consumed and disposed in urine [6,23-27]. Amoxicillin is frequently used as veterinary medicine for treatment of infections encountered in gastro-intestinal and systemic infections, and also commonly used as human prescription medicine to cure against infections caused by bacteria [6,23-27]. Due to its high stability, amoxicillin has been detected in the waste water of municipal [6,25-26], hospital and manufacture [26] in the level from µg/L to mg/L [6,24,26]. The release of antibiotics to the environment can enhance the bacterial resistant, which makes related treatment difficult [6,24-26]. The presence of amoxicillin in the environment act as an inhibitor of the photosynthesis mechanism of algae *Synechocystis sp.* [26], and showed toxic effects on human and ecological health [26-27]. Therefore, amoxicillin must be completely eliminated before reaching natural waters. Many studies have been dedicated to remove amoxicillin [26], and among them, degradation has received much attention. Amoxicillin degradation by photocatalysis over UV-A/TiO₂ [6,26], UV-A/ZnO [23], Sn/TiO₂ [24], TiO₂/Zeolite [25], and Pt and Bi co-doped TiO₂ under visible light [27] have become research of interest. However, to best of our knowledge the removal of amoxicillin in water by using a doped photocatalyst of TiO₂-Cu with the presence of visible light has not been reported.

Under the circumstance, in this present paper, preparation of Cu doped TiO₂ photocatalyst by photodeposition method under UV light, along with the characterizations and the photocatalyst activity test for amoxicillin photodegradation are systematically studied. In addition, to obtain maximum photodegradation efficiency, several operating variables including the initial concentration of amoxicillin, pH, photocatalyst dose, and illumination time were also optimized.

2. Material and Methods

2.1. Material and instruments

TiO₂, CuCl₂, amoxicillin, HCl, NaOH, and KMnO₄ in Analytical Grade were purchased from E. Merck, and were used without any purification. A Speccord Plus -UV/Visible spectrophotometer, a Perkin Elmer 311-AAS, Shimadzu 6000X-XRD, and Pharmaspec UV-1700 DRUV machines were operated for analysis and characterizations.

2.2 Preparation and characterization of doped photocatalyst

As much as 1 gram of TiO₂ was suspended in the 250 mL Cu²⁺ solutions with various concentrations (50, 75, 100, and 150 mg L⁻¹), then the suspensions were sonicated for 24 h, and then were irradiated with UV lamp in the correspond apparatus as seen in figure 1 for 24 h under magnetic stirring with the constant rate. When the processes finished, the solid of photocatalysts from the suspension were separated from their respective solutions by using centrifuge machine. The solutions were analyzed by using atomic absorption spectrophotometer (AAS) machine for determination of the concentrations of Cu²⁺ un-doped or left in the solution. Meanwhile the solids of TiO₂-Cu were dried at about 100 °C for 3 h. The photocatalysts of TiO₂-Cu with various amount of Cu were coded as TiO₂-Cu(1), TiO₂-Cu(2),

TiO₂-Cu(3), and TiO₂-Cu(4) referring the gradual increase of Cu doped on TiO₂. The prepared photocatalysts were characterized by means of X-ray diffraction (XRD) and diffuse reflectance UV-Visible (DRUV-Vis.) spectrophotometer instruments. The XRD patterns and the DRUV-Vis. spectra of all TiO₂-Cu samples and TiO₂ were recorded from 5 to 60° of the 2 theta and were scanned from 200-800 nm⁻¹ of the wavelength respectively.

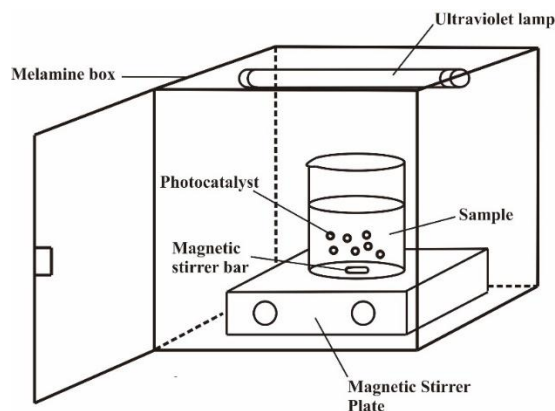


Figure 1: A set of apparatus for Cu²⁺ photoreduction and amoxicillin photodegradation processes

2.3. Assessment of TiO₂-Cu photoactivity for amoxicillin degradation

The amoxicillin photodegradation was carried out by batch experiment in an apparatus as illustrated Figure 1. In 2 Erlenmeyer flasks were filled with 100 mL of amoxicillin aqueous solution and then were added with 40 mg of TiO₂-Cu and un-doped TiO₂ respectively. Then the flasks were put on the photodegradation equipment (Fig.1), and the wolfram lamp as a visible light source was switched on. The visible light irradiations accompanied by stirring were conducted for 24 h. The concentrations of amoxicillin left in the solutions after photodegradation were determined by using visible spectrophotometry method, based on the reaction with KMnO₄ to form green solution of Mn₂O₄⁻. Then the absorbance of the green solutions were measured at 615 nm of the wavelength. The concentrations were obtained by plotting their absorbance into the respective standard curve. To find the amount of amoxicillin degraded, it was calculated by following a formulae below :

$$\frac{(Am)_i - (Am)_f}{(Am)_i} \times 100 \%$$

(Am)_i = The initial amount of amoxicillin before photodegradation (g)

(Am)_f = The final amount of amoxicillin after photodegradation (g)

The photodegradation procedure was repeated for a process by using TiO₂-Cu with various fractions of Cu doped, as well as for a process with different photocatalyst dose, illumination time and solution pH. For comparison, the same procedure was also applied for TiO₂-Cu under UV light illumination, as well as for TiO₂ with visible light.

3. Results and Discussion

3.1. The Characters of photocatalyst of TiO₂-Cu

3.1.1. The amount of Cu doped on TiO₂

The amount of Cu doped on TiO₂ prepared by various Cu²⁺ concentrations was displayed in figure 2. The figure attributes that increasing concentration of Cu²⁺ introduced, the considerably enhancement of Cu doped on TiO₂ is observed, but the Cu doped slightly increase for the concentration of Cu²⁺ higher than 75 mg L⁻¹. The doping should take place through photoreduction of Cu²⁺ in the solution by electron

provided by TiO₂ during the UV illumination, that was deposited on TiO₂, presented as reactions (1) to (2) :

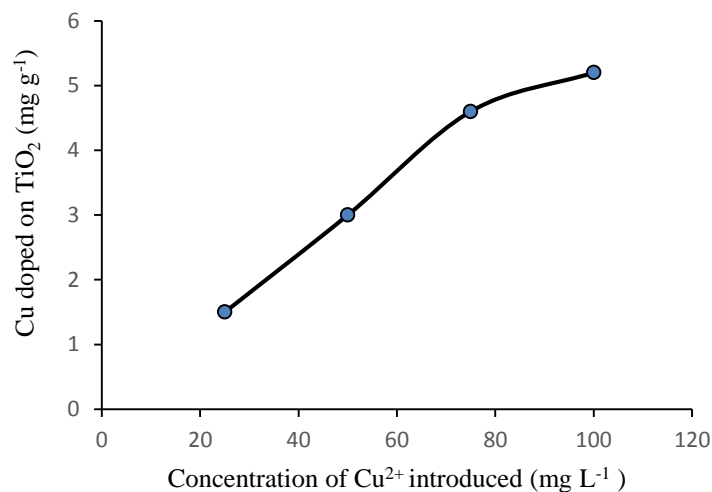


Figure 2: The influence of the Cu²⁺ concentration on the amount of Cu doped on TiO₂

Increasing amount of Cu²⁺ in the solution with adequate electrons from TiO₂ should result in more effective photodeposition. Interesting data is demonstrated for the highest initial concentration of Cu²⁺ that is the Cu doped on TiO₂ only slightly increased, compared to the low concentration. It is because more Cu solid resulted from the reduction has been deposited on and covered of the surface of TiO₂ that inhibited the contact between TiO₂ with UV light [15]. Consequently, small number of electrons must be provided, that led to the reduction of Cu²⁺ less effective.

3.1.2. The XRD data

In order to detect the effect of doping Cu on TiO₂ structure, their corresponding XRD patterns have been recorded and shown in figure 3. It is seen in the figure that TiO₂ reveals the presence of peaks at 25.25°, 37.52°, 48.02°, 53.58°, 54.88°, 62.61°, and 75.07° which are assigned to TiO₂ anatase, as referred by JCPDS with the number of 00-021-1272 [7,22]. The XRD patterns of all TiO₂-Cu samples are seen similar to that TiO₂, and no new peaks of Cu could be detected, even for the heaviest Cu-doped TiO₂. Some studies have found similar finding [7,13,17]. The absence of the Cu peaks may suggest that Cu is well dispersed in the TiO₂. The similarity in the Cu and Ti ionic radii (0.072 nm for Cu and 0.068 nm for Ti) allows the interstitial incorporation of the Cu dopant into the TiO₂ network [7,13,15]. However, researchers [11, 15] reported that no peaks of dopant were due to low concentration of dopant loading into TiO₂ structure, so that it was undetectable by the XRD instrument.

Furthermore, the unique data is assigned in the figure, that the doping Cu on TiO₂ could increase the XRD intensities of TiO₂. The increase of the line intensities represents the enhancement of the crystallinity. The enhancement may be induced by the matching size of Cu with the TiO₂ crystal lattice. A study also found similar data [21]. This result is notably unique than other metal doping on TiO₂ structure such as Co, Ni, Mn, and Fe [8], and Ag [11]. Since, generally, the crystalline of metal-doped TiO₂ significantly decreased due to distortion of TiO₂ lattice by metal dopant [8, 11]. Therefore, it can be noted that Cu doping is a beneficial factor for improving the crystallinity of TiO₂. Additionally, a gradual increase in the intensities is also observable with the enhancement of the doping concentration

from 1.5 to 3.13 mg g⁻¹. The increase suggests that more of Cu atoms are inserted in the crystal of TiO₂ [21]. The opposite effect is exhibited by Cu doped larger than 3.13 mg g⁻¹, that gives smaller TiO₂ crystallinity improvement. A possible reason of the trend is the formation of Cu aggregate with larger size that prevents it to insert into the TiO₂ lattice [11].

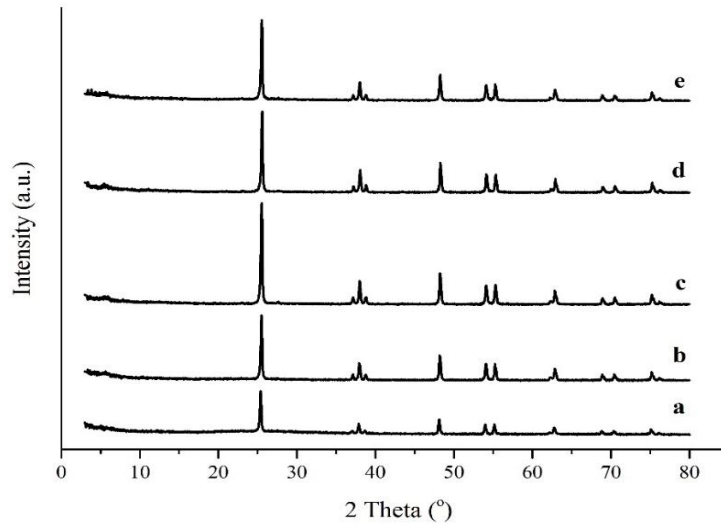


Figure 3: The XRD patterns of a) TiO₂, b) TiO₂-Cu(1), c) TiO₂-Cu(2), c) TiO₂- Cu(3), and d) TiO₂-Cu(4).

3.1.3. DRUV Spectra

The effect of Cu doping on the light absorption of TiO₂ was evaluated based on their corresponding reflectance spectra, that were displayed as figure 4. From the figure, the wavelength (λ) of their absorption edges were obtained based on the intersection from the straight line of the curve to the Y-axis = 0 [7, 22].

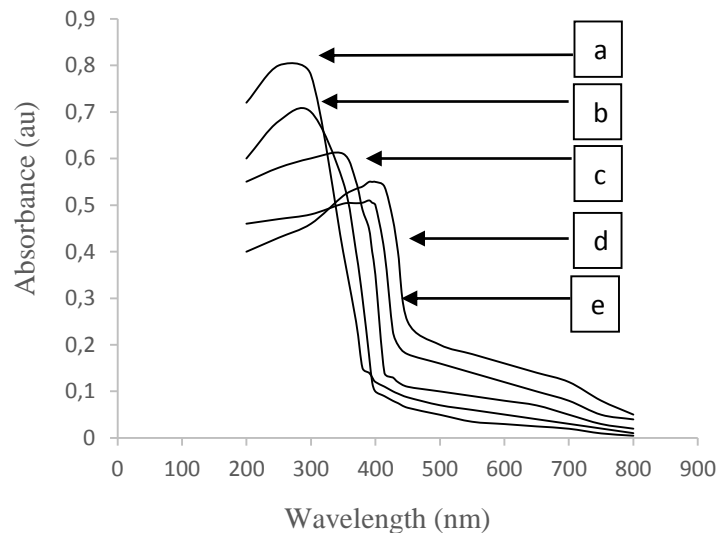


Figure 4: The DRUV spectra of a) TiO₂, b) TiO₂-Cu(1), c) TiO₂-Cu(2), d) TiO₂-Cu(3) and TiO₂-Cu(4)

Then the wavelengths were converted into band gap energy (E_g) by following the formulae of $E_g = 1240/\lambda$ [11], and their respective band gap energy values were presented in table 1. As seen in the table, that Cu doping has shifted the light absorption by TiO₂ to the longer wavelength (λ) emerging the visible radiation. Furthermore, the shifts plausibly increases with the enlargement of the Cu doped from 1.50 - 4.56 mg g⁻¹, but smaller shift is observed for further larger Cu doped of 4.56 - 5.20 mg g⁻¹.

The shift is resulted from the narrowing band gap energy (E_g) due to the insertion of Cu into the gap between conduction and valence bands [7,11,13]. Increasing shift represents that more amount of Cu has inserted into the gaps. However the larger amount of Cu might form aggregate with larger size that prevented them to insert into the lattice of TiO_2 crystal. It is obvious hence that this data is in a good agreement with their XRD patterns.

Table 1: The influence of Cu amount in TiO_2 -Cu on the absorption shift and band gap energies

Cu Doped on TiO_2 ($mg\ g^{-1}$)	λ (nm)	E_g (eV)
0	387.5	3.20
1.50	397.5	3.12
3.13	413.5	3.00
4.56	435.0	2.85
5.20	427.5	2.90

3.1.4. TEM images

The TEM images of the un-doped and doped photocatalysts are presented as figure 5. In the images of TiO_2 -Cu samples, dark spots are observable, that are not seen in TiO_2 image. Further, increasing Cu doped (figure 5 b to 5d), The dark spots clearly represent the Cu atoms doped on the TiO_2 structure, that well agrees with the previous data.

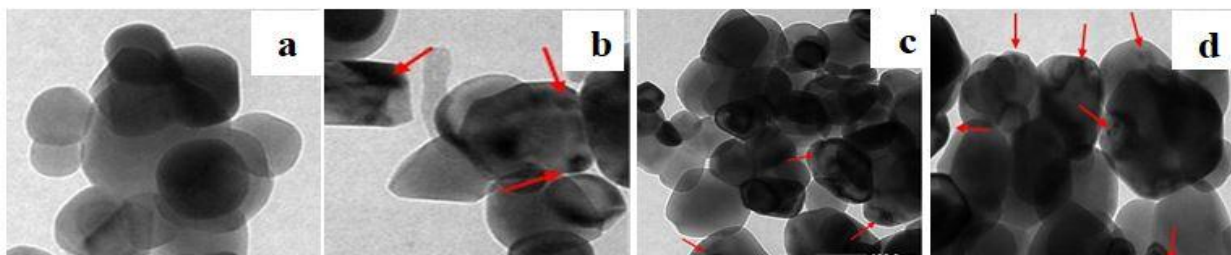


Figure 5: The TEM images of a) TiO_2 , b) TiO_2 -Cu(1), c) TiO_2 -Cu(2), and d) TiO_2 - Cu(3)

3.2. Photodegradation of amoxicillin over TiO_2 -Cu under visible light

3.2.1. Effect of Cu doping on the photocatalyst activity

The effect of Cu doping on the photocatalytic activity of TiO_2 has been assessed for amoxicillin degradation both under visible and UV light. For comparison, same processes with TiO_2 -Cu were also performed. The results are displayed as figure 6. As seen in the figure, photodegradation of amoxicillin can take place whether absence and presence of the photocatalysts, both under UV and visible light. The photodegradation under light illumination is induced by OH radicals acting as strong oxidizing agent. The process without photocatalyst is observed to be less effective, because only few OH radicals from H_2O photolysis might be available due to the weak photolysis process [11]. UV is stronger light than visible light, that can provide more OH radicals, in turns to result more effective degradation.

TiO_2 -Cu photocatalyst also exhibits higher activity under visible light in the photodegradation of amoxicillin compared to that of TiO_2 with same condition. The visible light with E_g (2.2 - 3.0 eV) that is near the E_g of TiO_2 -Cu (2.80 - 3.10 eV), is able to activate TiO_2 -Cu for the amoxicillin photodegradation. In contrast, the energy of the visible light is lower than the band gap energy of TiO_2 (3.2 eV), that inhibites it to excite an electron in un-doped TiO_2 . Therefore, the weak photocatalytic performance of TiO_2 is obviously resulted. In addition, the presence of Cu in the photocatalyst can capture the electron released by TiO_2 that further inhibit the recombination between electron and h^+ .

This condition allows more amount of OH radical are provided, that results in the higher photodegradation of amoxicillin.

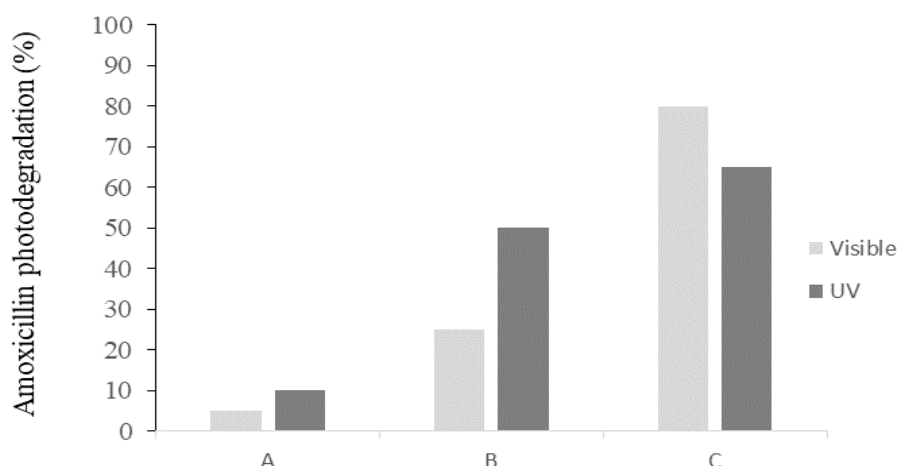


Figure 6: The efficiency of the amoxicillin photodegradation under UV and visible light with : A) No photocatalyst, B) TiO₂, and C) TiO₂-Cu(3). (Amoxicillin volume and concentration: : 100 mL and 10 mg L⁻¹, photocatalysts mass: 40 mg, time: 24 h, and pH: 6).

The photocatalytic degradation of amoxicillin over TiO₂-Cu under visible light is seen to be higher than that of under UV light. The amoxicillin molecules can be adsorbed by Cu particle in TiO₂-Cu, then it can be activated by visible light to form unstable molecules that allows degradation easily [7]. It is clear that the more effective photodegradation is not only induced by OH radicals, but it is also stimulated directly by visible light. On the other side, the lower photocatalytic activity of TiO₂-Cu in UV light may be corresponded to the fact that in TiO₂-Cu the Cu surface plasmon resonance cannot be excited by UV light [13]. This un-excited molecules can only release few electrons that leads to the low photodegradation. In contrast, TiO₂ with UV light can stimulate more photodegradation of amoxicillin than that of with visible light. The band gap energy of TiO₂ is 3.0-3.2 eV, that is equal to the UV region, allowing the light to excite TiO₂ to release electron and to form OH radicals. Meanwhile, due to its lower E_g, the visible light is unable to stimulate electron from TiO₂, causing lower photodegradation. In figure 7, increasing Cu content in TiO₂-Cu promotes the amoxicillin photodegradation as also shown in many works [7,11,17]. But further increase in Cu content could have detrimental effect on the photodegradation result. The optimum Cu content in TiO₂-Cu is found be at about 4.5 mg g⁻¹. The effect of Cu content in TiO₂-Cu on photocatalytic activity can be explained as follows. The appropriate amount of Cu doped on TiO₂ allows effective capture the photoinduced electrons. The photoinduced electrons during light irradiation results in negatively charged Cu. The photoinduced electrons can be immediately transferred to oxygen atoms of TiO₂. The electron transfer from the TiO₂ conduction band to metallic Cu particles at the interface is thermodynamically favorable because the Fermi level of TiO₂ is higher than that of Cu metals. It results in the formation of the Schottky barrier at metal-semiconductor contact region, which improves the charge separation. Accordingly, the recombination of the electron and the OH radicals can be inhibited more [13,15,24]. This condition explains the significant enhancement of the photocatalytic activity of TiO₂-Cu. The increase in Cu content would keep the photodegradation improves until it reaches its optimum level.

At high Cu loading above its optimum level, an excess amount of negatively charged Cu species are available. A significant amount of the negatively charged Cu particles allows Cu atoms to attract more

OH radicals. Accordingly it reduces charge separation efficiency or raises electron-hole recombination and decreases amoxicillin photodegradation [13,15]. An excess amount of Cu dopant can also produce the recombination center of photoinduced electron and hole pairs [13, 15, 24]. Recombination of e^- and h^+ pair reduces the rate of photocatalytic degradation. Another possible reason is due to the formation of Cu metallic clusters inside the TiO_2 crystal [7, 15, 17, 21]. The metal clusters Cu in TiO_2 -Cu can act as a barrier to obstruct light absorption by TiO_2 that may give small contact surface area of the photocatalyst. This prevents amoxicillin from contacting with the photocatalyst surface.

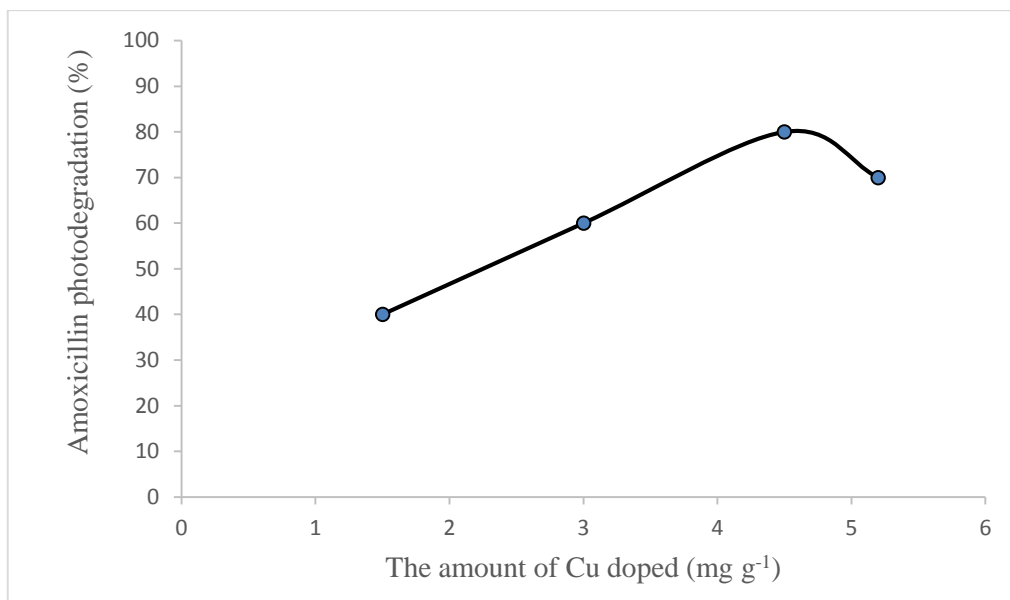


Figure 7: The effect of the amount of Cu doped on TiO_2 towards degradation efficiency of amoxicillin (Amoxicillin volume and concentration: 100mL and $10mg\ L^{-1}$, photocatalysts mass: 40mg, time: 24h, and pH: 6)

3. 2. 2. Effect of photocatalyst dose on the degradation efficiency of amoxicillin

The photodegradation improves with the increase in the photocatalyst dose, as illustrated by figure 8. The effectiveness of the photodegradation reduces when the photocatalyst dose is further increased.

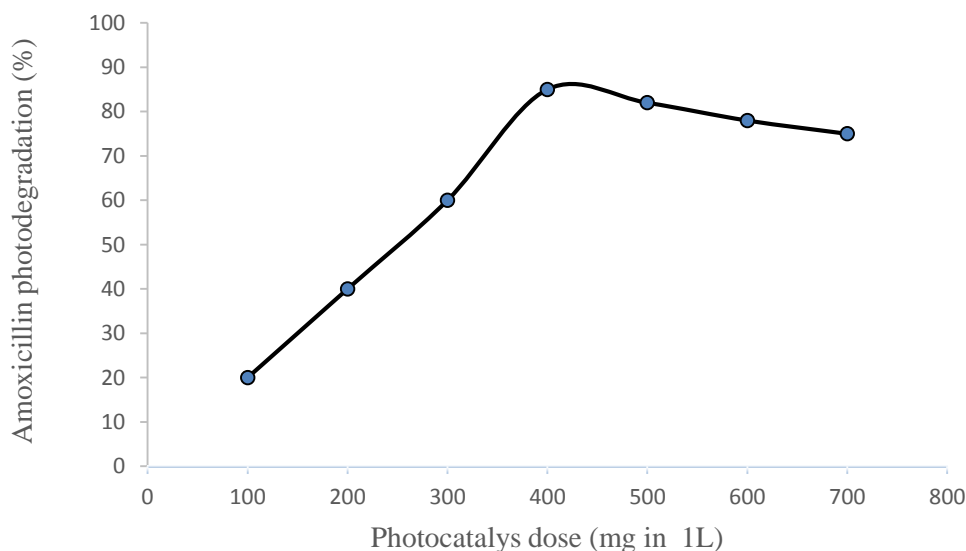


Figure 8: The effect of the photocatalyst dose on the degradation efficiency of amoxicillin (Cu doped in TiO_2 : $4.56\ mg\ g^{-1}$, amoxicillin volume and concentration: 100 mL and $10\ mg\ L^{-1}$, time: 24 h, and pH: 6)

The maximum photodegradation is obtained by using 40 mg photocatalyst/100 mL or 0.4 g/L. In other work, the same dose was also reported [24]. Such data can be explained based on the number of active sites available for photocatalytic reactions. More active sites of the photocatalyst are available when the dose of the photocatalyst increases.

However, the use of a large number of photocatalysts may cause agglomeration of the material to produce big particle size. The large particle size gives small surface area, which decreases the number of active sites on the surface. Another reason for the decrease in the degradation can be attributed to the increase in the turbidity of suspension due to more suspended photocatalyst solids. Such high turbidity causes the light scattering that leads to the blockage of photon absorption, providing less OH radicals in the solution [11, 24-26].

3. 2. 3. Effect of solution pH on the degradation efficiency of amoxicillin

pH is a variable controlling the charges of TiO₂ and amoxicillin, that determines the effectiveness of the adsorption amoxicillin on TiO₂ surface and further give an effect on the photodegradation efficiency [15]. The change of the photodegradation efficiency as the pH alteration is represented as figure 9. At low pH, the high amoxicillin removal is observed, then the photodegradation decreases, but then it enhances as the pH keeps to raise.

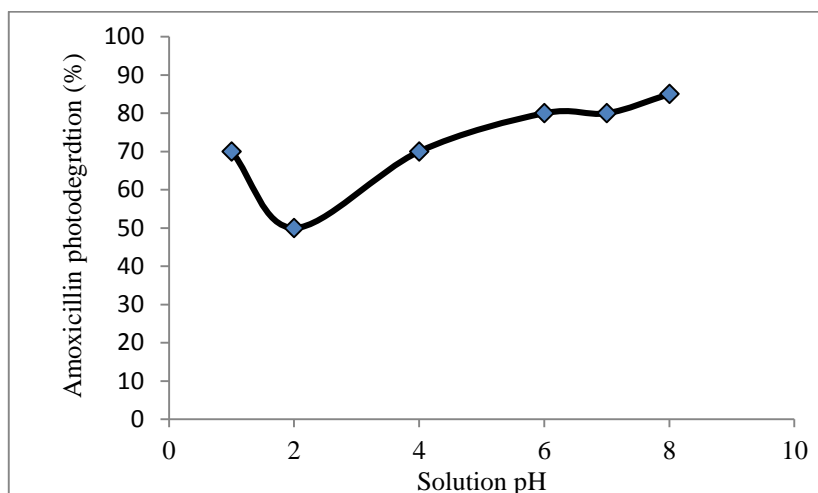


Figure 9: The effect of solution pH on the photodegradation of amoxicillin (Cu doped in TiO₂: 4.56 mg g⁻¹, amoxicillin volume and concentration: 100 mL and 10 mg L⁻¹, photocatalyst mass: 40 mg, and time: 24 h)

At low pH, TiO₂ is protonated by H⁺ in the solution to form positive charge at the surface (TiO₂H⁺), meanwhile amoxicillin owns both positive and negative charges in its structure [15]. This allows much amoxicillin can be adsorbed on the photocatalyst surface. The large amount of amoxicillin adsorbed should be effectively degraded by OH radicals at TiO₂ surface, but since the protonated of TiO₂H⁺ is less effective in the OH formation, only low photodegradation should be proceeded. The opposite result shows evident that at very low pH amoxicillin adsorption is more pronoun than its photodegradation. Then, a decrease in the photodegradation can be seen when the pH is increased to 4. It is due to the less protonation of TiO₂ and so decrease the adsorption, and at the same time TiO₂ is more effective in the OH formation to degrade amoxicillin [6, 15, 25]. Hence, at this pH, the prominent process in the amoxicillin decrease must be photodegradation. At pH 6 to 7, TiO₂ with pH zpc = 6.4 is formed dominantly that can provide more OH radicals [7], in accordance the high photogradation is assigned. At pH higher than 8, the negative charges are formed at the amoxicillin structure [25], that similarly occurs in TiO₂ to form TiO⁻, leading to the repulsion of the adsorption and the fewer OH radicals formed.

This condition should result in low degradation, but the contrary result is observable. The high removal of amoxicillin at higher pH is due to the hydrolysis [6,25,26], that reduces the amount of amoxicillin in the solution.

3.2.4. Effect of the illumination time on the degradation efficiency of amoxicillin

Reaction time dictates the effectiveness of the contact between light and TiO_2 and between TiO_2/OH radicals with amoxicillin, and turns to the degradation effectiveness. The effect of the time on the photodegradation is displayed as figure 10. Extension time to 24 h can raise the photodegradation, that is promoted by more effective contact among the substrates. However, longer irradiation than 24 h, the photodegradation is not dependence on the reaction time, since the photocatalyst is exhausted in releasing OH radicals [11, 15, 25].

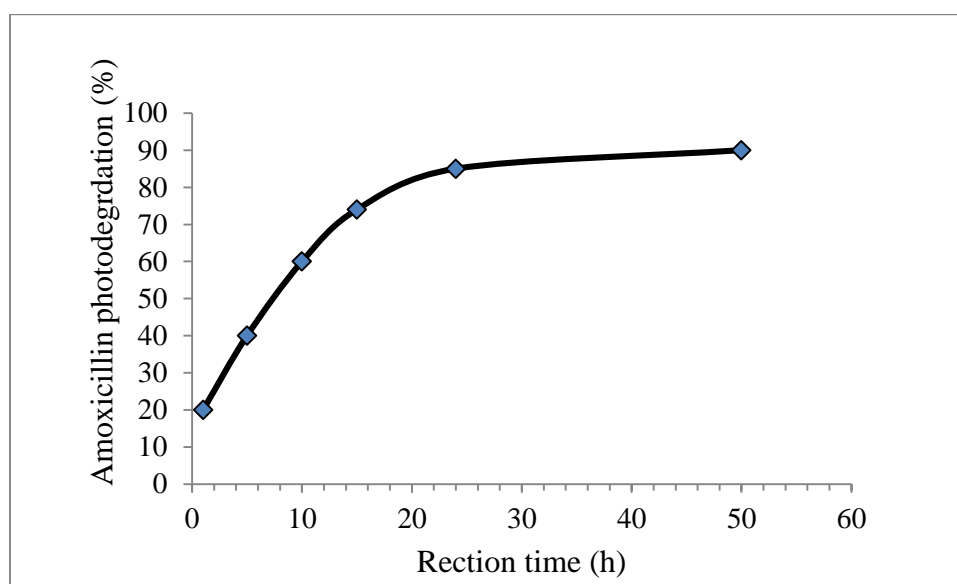


Figure 10: The effect of the reaction time on the amoxicillin photodegradation.

(Cu doped in TiO_2 : 4.56 mg g^{-1} , amoxicillin volume and concentration: 100 mL and 10 mg L^{-1} , and pH: 6)

3.2.5. Kinetics and Mechanism of the photodegradation

In general the rate of an organic compound, including amoxicillin, degradation is controlled by the amount of OH radicals and the initial concentration of amoxicillin. In fact, the number of OH radical is in the excessive that is assumed to be constant during the process [1, 6, 24]. In accordance the kinetic of amoxicillin degradation is modelled as the pseudo first-order, since the rate of the degradation is only dependence on the initial concentration of the amoxicillin. In order to find the rate constant (k), a curve of $\ln(C/C_0)$ versus time was constructed and displayed as figure 11. It can be seen in the figure, that the straight line was obtained with the linearity correlation (R^2) as much as 0.98. From the curve, we found the rate constant as much as $4 \times 10^{-4} \text{ min}^{-1}$, which seemed to be slower since the structure of amoxicillin is stable compared the finding reported by other studies [6, 24].

The mechanism of the amoxicillin degradation over OH radicals by adopting the mechanisms proposed previously [28-30], is presented as figure 12. The photodegradation is started from the breaking bond of the amoxicillin to form 2 big molecules accompanied by releasing smaller molecules including CO_2 , NH_4^+ , and H_2O [28]. One big molecule is phenol that can be further degraded into oxalic acid [30]. The other big molecule can also prior to degrade into oxalic and oxamic acids [29]. The final products from the degradation are smaller molecules of CO_2 , H_2O , HNO_3 [28-30]

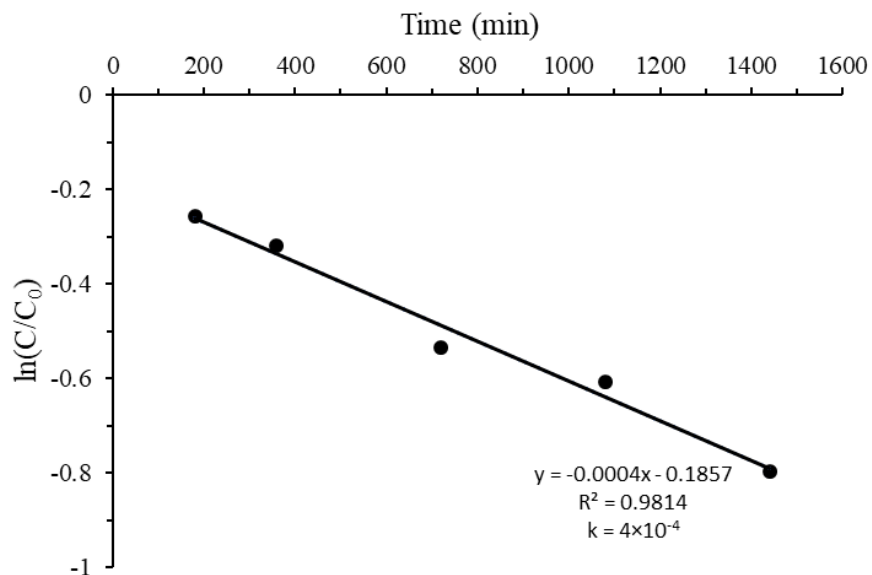


Figure 11: The kinetic model for amoxicillin degradation

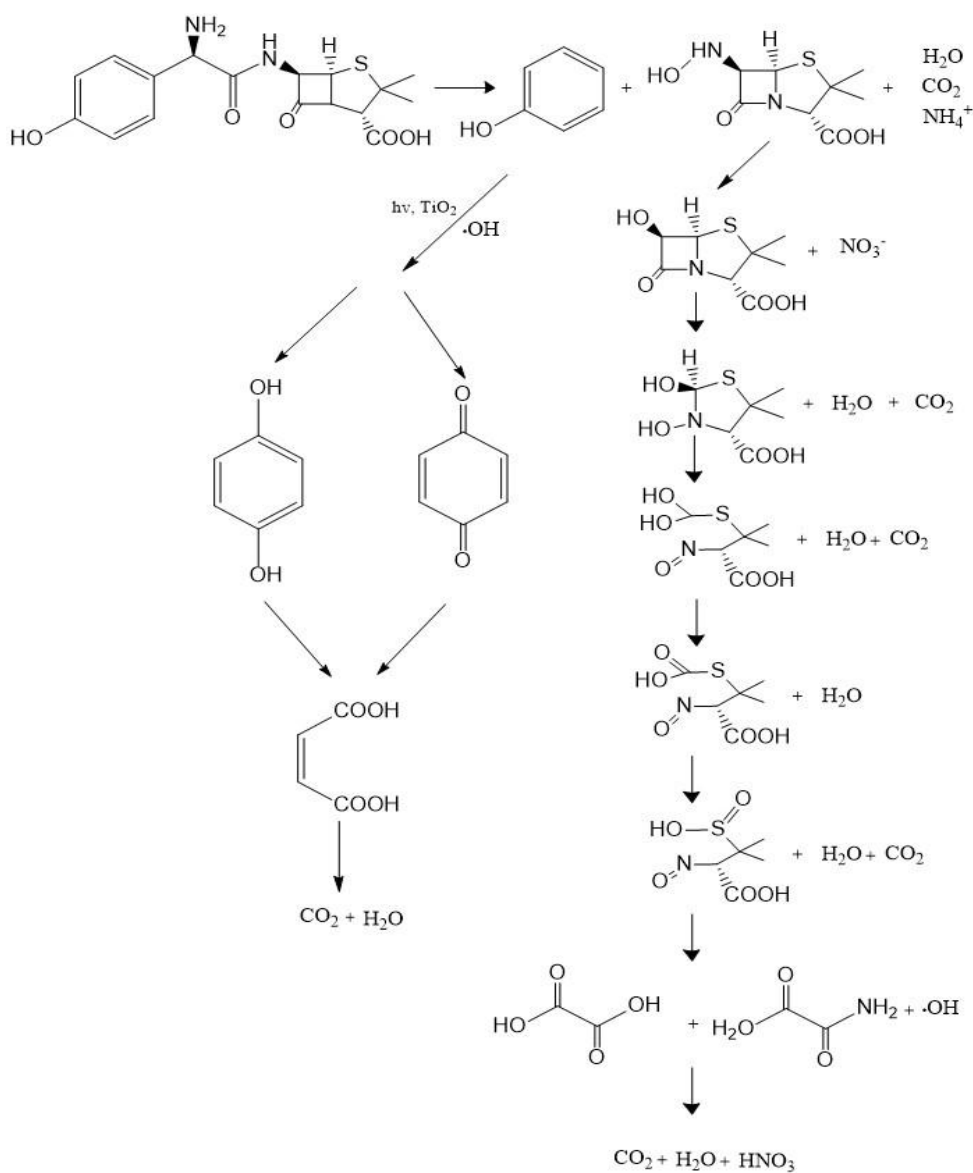


Figure 12: The mechanism of the amoxicillin photodegradation

Some studies reported that the doped photocatalysts generally showed well reusable [7-9,14], that could be applied in several photodegradation cycles. It is hoped that the doped photocatalyst of TiO₂-Cu prepared in this research has also good reusability, but it has not been evaluated, and so it is suggested to be further studied.

Conclusion

From the research results, it can be concluded that a visible responsive photocatalyst of TiO₂-Cu has been successfully prepared by using photoreduction method. The Cu doping was found to shift the light absorption of TiO₂-Cu into visible region, and the maximum shift was shown by the amount of Cu doped as much as 4.56 mg g⁻¹. The doping Cu on TiO₂ was found to increase its activity in the amoxicillin degradation under visible light. It is also shown that the amoxicillin degradation over TiO₂-Cu under visible light was more effective compared to the process under UV illumination. Furthermore, the highest efficiency of the photodegradation under visible light, that was about 90% for 100 ml of the amoxicillin 10 mg L⁻¹, was achieved by using photocatalyst of TiO₂-Cu containing Cu as much as 4.56 mg g⁻¹, 40 mg of the photocatalyst dose, during 24 h of the illumination time, and at pH 6. The amoxicillin photodegradation is well fitted with the pseudo-first order model with the rate constant as $4 \times 10^{-4} \text{ min}^{-1}$.

Acknowledgement-A great thank to Universitas Gadjah Mada for the financial support in the Research Project Grant through The Final Project Recognition (R.T.A.) schema with the No : 3193/UN.1/DIT-LIT/LT/2019 April 11 2019.

References

1. A. Hu, R. Liang, Zhang X, S. Kurdi, D. Luong, H. Huang., P. Peng, E. Marzbandrad, K.D. Oakes, Y. Zhou, M.R. Servos, Enhanced photocatalytic degradation of dyes by TiO₂ nanobelts with hierarchical structures, *J. Photochem. Photobiol. A-Chem.* 256 (2013) 7-15. <https://doi.org/10.1016/j.jphotochem.2013.01.015>
2. A. Gautam, A. Kshirsagar, R. Biswas, S. Banerjee, P.K. Khann, Photodegradation of organic dyes based on anatase and rutile TiO₂ nanoparticles. *RSC Adv.* 6 (2016) 2746-2759. [10.1039/C5RA20861K](https://doi.org/10.1039/C5RA20861K)
3. R.S. Dariani, A. Esmaeili, A. Mortezaali, S. Dehghanpour, Photocatalytic reaction and degradation of methylene blue on TiO₂ nano-sized particles, *Optik.* 127 (2016) 7143-7154. <https://dx.doi.org/10.1016%2Fj.ijleo.2016.04.026>.
4. A. Turki, C. Guillard, F. Dappozze, Z. Ksibi, G. Berhault, H. Kochkar, Phenol photocatalytic degradation over anisotropic TiO₂ nanomaterials: Kinetic study, adsorption isotherms and formal mechanisms. *Appl Catal B-Environ.* 163 (2015) 404-414. DOI: 10.1016/j.apcatb.2014.08.010
5. H. Ahmari, S.Z. Heris, M.H. Khayyat, Photocatalytic degradation of linear alkylbenzene sulfonic acid, *Res Chem Intermed.* 4 (2016) 6587-6606.
6. D. Dimitrakopoulou, I. Rethemiotaki, Z. Frontistis, N.P. Xekoukoulotakis, D. Venieri, D. Mantzavinos, Degradation, mineralization and antibiotic inactivation of amoxicillin by UV-A/TiO₂ photocatalysis. *J. Environ. Manage.* 98 (2012) 168-174. <https://doi.org/10.1016/j.jenvman.2012.01.010>
7. M. H. Razali, M. N Ahmad-Fauzi., A. R. Mohamed, S. Sreekantan, Morphological, structural and optical properties study of transition metal ions doped TiO₂ nanotubes prepared by hydrothermal method. *Int. J. Mater. Mech. Manuf.* 1 (4) (2013) 314-318. DOI: 10.7763/IJMMM.2013.V1.68

8. L-T Tseng, X. Luo, N. Bao, J. Ding, S.Li, J. Yi, Structures and properties of transition-metal-doped TiO₂ nanorods. *Mater.* 170 (2016) 142–146. <http://dx.doi.org/10.1016%2Fj.matlet.2016.02.0>
9. N. Khakpash, A. Simchi, T. Jafari, Adsorption and solar light activity of transition-metal doped TiO₂ nanoparticles as semiconductor photocatalyst. *J Mater Sci: Mater Electron.* 23 (2012) 659–667.
10. P. Ribao, M.J. Rivero, I. Ortiz, TiO₂ structures doped with noble metals and/or graphene oxide to improve the photocatalytic degradation of dichloroacetic acid. *Environ Sci Pollut Res.* 24 (2017) 12628–12637. <https://doi.org/10.1007/s11356-016-7714-x>.
11. E.T. Wahyuni, R. Roto, D. Novarita, K.P. Suwondo, B. Kuswandi, Preparation of TiO₂/AgNPs photodeposition method using Ag(I) present in radiophotography wastewater and their antibacterial activity in visible light illumination. *J. Environ Chem Eng.* 7 (2019) 10317
<https://doi.org/10.1016/j.jece.2019.10317>
12. A. Gultekin, Effect of Au nanoparticles doping on the properties of TiO₂ thin films. *Materials Science (Medžiagotyra).* 20 (1) (2014) 10–14. <https://doi.org/10.5755/j01.ms.20.1.3709>.
13. Y. Wang, W. Duan, B. Liu, X. Chen, F. Yang, J. Guo, The Effects of doping copper and structure on photocatalytic properties of TiO₂. *J. Nanomater.* (2014) 1–7.
<https://doi.org/10.1155/2014/178152>
14. M-C Wu, P-Y Wu, T-H Lin, T-F Lin, Photocatalytic performance of Cu-doped TiO₂ nanofibers treated by the hydrothermal synthesis and air-thermal treatment, *Appl Surf Sci.* 430 (2018) 390–398. <https://doi.org/10.1016/j.apsusc.2017.09.035>
15. P. Pongwan, K. Wetchakun, S. Phanichphant, N. Wetchakun, Enhancement of visible-light photocatalytic activity of Cu-doped TiO₂ nanoparticles. *Res Chem Intermed.* 42 (2016) 2815–2830. DOI 10.1007/s11164-015-2179-y. <https://doi.org/10.1007/s11164-015-2179-y>
16. G. Colon, M. Maicu, M.C. Hidalgo, J.A. Navio, Cu-doped TiO₂ systems with improved photocatalytic activity. *Appl. Catal. B Environ.* 67 (2006) 41–51.
<https://doi.org/10.1016/j.apcatb.2006.03.019>
17. S.K. Poznyak, V.I. Pergushov, I. Kokorin, I. Kulak, C.W. Schlapfer, Structure and electrochemical properties of species formed as a result of Cu(II) ion adsorption onto TiO₂ nanoparticles. *J. Phys. Chem. B*, 103 (1999) 13081315. <https://doi.org/10.1021/jp9840580>
18. S. Bhardwaj, B. Pal, Photodeposition of Ag and Cu binary co-catalyst onto TiO₂ for improved optical and photocatalytic degradation properties, *Adv Powder Technol.* 29 (9) (2018) 2119–2128.
<https://doi.org/10.1016/j.apt.2018.05.020>
19. A. J. J. Lennox, P. Bartels, M-M. Pohl, H. Junge, M. Beller, *In situ* photodeposition of copper nanoparticles on TiO₂: Novel catalysts with facile light-induced redox cycling, *J. Catal.* 340 (2016) 177–183. <https://doi.org/10.1016/j.jcat.2016.04.011>
20. Y. Lee, E. Kim, Y. Par, J. Kim, W.H. Ryu, J. Rho, K. Kim, Photodeposited metal-semiconductor nanocomposites and their applications. *J. Materiomics* 4 (2018) 8383, 84–92.
<https://doi.org/10.1016/j.jmat.2018.01.004>
21. I. Ganesh, P.P. Kumar, I. Annapoorna, J.M. Sumliner, M. Ramakrishna, N.Y. Hebalkar, G. Padmanabham, G. Sundararajan, Preparation and characterization of Cu-doped TiO₂ materials for electrochemical, photoelectrochemical, and photocatalytic applications. *Appl. Surf. Sci.* 293 (2014) 229–247. <https://doi.org/10.1016/j.apsusc.2013.12.140>
22. C. Karunakaran, G. Abiramasundari, P. Gomathisankar, G. Manikandan, V. Anandi. Cu-doped TiO₂ nanoparticles for photocatalytic disinfection of bacteria under visible light, *J. Colloid Interface Sci.* 352 (2010) 68–74. <https://doi.org/10.1016/j.jcis.2010.08.012>
23. B. Ambrosetti, L. Campanella, R. Palmisano, Degradation of antibiotics in aqueous solution by photocatalytic process: Comparing the efficiency in the use of ZnO or TiO₂. *J. Environ. Sci. Eng. A* 4 (2015) 273–281. <https://doi.org/10.17265/2162-5298/2015.06.001>

24. R. Mohammadi, B. Massoumi, M. Rabani, Photocatalytic decomposition of amoxicillin trihydrate antibiotic in aqueous solutions under UV irradiation using Sn/TiO₂ nanoparticles. *Int J Photoenergy*. (2012), 11 pages. <https://doi.org/10.1155/2012/514856>
25. D. Kanakaraju, J. Kockler, C.A. Mott, B.D. Glass, M. Oelgemöller, Titanium dioxide/zeolite integrated photocatalytic adsorbents for the degradation of amoxicillin. *Appl Catal B-Environ*, 166-167 (2015) 45-55. <https://doi.org/10.1016/j.apcatb.2014.11.001>
26. F.S. Moosavi, T. Tavakoli, Amoxicillin degradation from contaminated water by solar photocatalysis using response surface methodology (RSM), *Environ Sci Pollut Res*. 23 (2016) 23262–23270. <https://doi.org/10.1007/s11356-016-7349->
27. M. Salimi, M. Behbahani, H. R. Sobhi, M. Gholami, A. J. Jafari, R.R. Kalantary, M. Farzadkia, A. Esrafil, A new nano-photocatalyst based on Pt and Bi co-doped TiO₂ for efficient visible-light photo degradation of amoxicillin, *New J. Chem*. 43 (2019) 1562-1568. <https://doi.org/10.1039/C8NJ05020A>
28. D. Klauson, J. Babkina, K. Stepanova, M. Krichevskaya, S. Preis, , Aqueous photocatalytic oxidation of amoxicillin, *Catal. Today*. 151 (2010) 39–45
29. N.F.F. Moreira, C. A. Orge, A. R. Ribeiro, J. L. Faria, O. C. Nunes, M. Fe, R. Pereira, A. M.T. Silva, Fast mineralization and detoxification of amoxicillin and diclofenac photocatalytic ozonation and application to an urban wastewater, *Water Res*. 87 (2015) 87- 96.
30. T.T.T. Dang, S. T. T. Le, D. Channei, W. Khanitchaidecha, A. Nakaruk, Photodegradation mechanisms of phenol in the photocatalytic process, *Res. Chem. Intermed.*, 42 (2016) 5961–5974

(2020) ; <http://www.jmaterenvirosci.com>