



The Use of Silica Supported Nickel-Copper Oxide Catalyst for Photodegradation of Methylene Blue

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<http://dx.doi.org/10.13005/ojc/350423>

(Received: July 02, 2019; Accepted: August 06, 2019)

ABSTRACT

Photodegradation is a safe and low cost methods to clean water bodies from some organic pollutants. The method has been developed in term of increasing the efficiency of the degradation capacity of photocatalyst. The photocatalyst working under visible light is the most desirable. The preparation of silica supported nickel-copper oxide [(Ni-Cu) O_x @SiO $_2$] catalyst and the use of the catalyst in the photodegradation of methylene blue in the water were studied. The catalyst was prepared by impregnating the silica support into the mixture of nickel and copper salts, followed by calcination at 800°C for 4 hours. A series method of XRD, SEM- EDX, and UV-Vis, Diffuse Reflectance has been used to characterize the catalyst. The catalyst adsorption test was undertaken in the dark, and the catalyst activity test for photodegradation of methylene blue was conducted under the sunlight. The XRD diffractogram of as prepared (Ni-Cu) O_x @SiO $_2$ shows a weak-wide peak at $2\theta = 21.8^\circ$ indicating SiO $_2$ tridymite, and has a crystallite size of 10.38 nm. The combination method of SEM and EDX confirms the formation of (Ni-Cu) O_x @SiO $_2$. The (Ni-Cu) O_x @SiO $_2$ catalyst has a relatively low bandgap energy and shows a good activity for photodegradation of blue methylene under sunlight. The adsorption of the methylene blue on the (Ni-Cu) O_x @SiO $_2$ follows the Langmuir isotherm pattern.

Keywords: SiO $_2$, (Ni-Cu) O_x @SiO $_2$, Impregnation, Photocatalyst, Methylene blue.

INTRODUCTION

Textile industry is one of the fastest growing industries in Indonesia.¹ The rapid development of the textile industry poses a problem for the environment, especially the problem caused by textile dyeing liquid waste. The liquid waste contains toxic and dangerous compounds. The liquid waste in the waters can kill water organisms and block

sunlight from penetrating the aquatic environment, thus disrupting the biological processes.²

Discharged dyestuffs from textile industry are generally in the form of organic compounds that are bio-nondegradable and difficult to be decomposed.³ Dyes often used in the textile industry are methylene blue, methyl orange, and Congo red. Methylene blue is a cationic heterocyclic aromatic



compound commonly used as basic leather, cloth, and fabric coloring. The threshold limit value of methylene blue is 5-10 mg/L.

The conventional method for reducing the levels of methylene blue in water includes chlorination, ozonation, and adsorption using activated carbon.^{4,5} New methods which are easy to implement and relatively inexpensive need to be developed. One of these is photodegradation using a combination of semi-conductor photocatalyst and ultraviolet light.^{6,7} Harraz *et al.*, (2019) was successful in engineering the photodegradation of methylene blue under UV and visible light using $\text{TiO}_2@SiO_2$ photocatalyst.⁸ The photodegradation will be more costly effective if undertaken under the sunlight.⁹

The use of photocatalyst has advantages because it can mineralize the total organic pollutants including the textile waste (azo compounds), the cost of their use is cheap and the process is relatively fast, non-toxic and has long-term use capability.^{9,10} The ability of the photocatalyst can be improved by applying materials such as TiO_2 , ZnO , Fe_2O_3 , CdS , and ZnS which have semiconductor properties.¹¹⁻¹³ However, the materials have a relatively expensive price. Therefore, semiconductor materials need to be supported by inexpensive compounds such as silica (SiO_2).^{14,15}

Nickel and copper oxides are semiconductor materials. The bandgap energy of NiO and CuO is >3 eV and 2-3 eV, respectively.^{16,17} To lower the bandgap of SiO_2 which is about 9 eV the nickel and copper oxides may be supported on the surface of silica. Silica-supported nickel and copper oxides are expected to work as a photocatalyst of methylene blue under sunlight.

MATERIALS AND METHODS

Materials including SiO_2 (Merck & Co., 99.3%), $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck & Co., 99.99%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck & Co, 99-104%), and Methylene Blue, are used without any prior treatment.

The $(\text{Ni-Cu})\text{Ox}@SiO_2$ catalyst was prepared by mixing a proportional amount of $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and SiO_2 , and distilled water to a volume of 30 mL. The mixture was stirred using a magnetic stirrer and evaporated. Nearly dry mixture was added with ethanol, then methanol, stirred and filtered. The residue was air dried for 24 h and calcined at 800°C for 4 hours.

The XRD diffractogram of $(\text{Ni-Cu})\text{Ox}@SiO_2$ catalyst was obtained by using X-Ray. Diffraction Rigaku Multiflex, and $\text{Cu-K}\alpha$ radiation in the range 2θ from 5° - 80° . The UV-Vis spectrum of the samples were recorded as a function of wavelength using the UV-Vis 1700 Pharmaspec Spectrophotometer Specular Reflectance. The samples were put into cuvettes and the absorbances were measured in a wavelength range of 200-800 nm. The samples of $(\text{Ni-Cu})\text{Ox}@SiO_2$ were qualitatively analyzed using Scanning Electron Microscopy-Electron Dispersive X-Ray Analyzer JEOL JED-2300 working at 15 kV. Dark adsorption test was undertaken by mixing 0.1 g of the $(\text{Ni-Cu})\text{Ox}@SiO_2$ catalyst with 50 ml of 10 ppm methylene blue solution in a 100 mL Erlenmeyer. The mixture was stirred in a dark room. The absorption of the filtrate was measured at the time interval of 0, 5, 10, 15, 20, 25, 35, 65, 95, and 125 min and at a wavelength of 663 nm.

Photocatalyst activity of the $(\text{Ni-Cu})\text{Ox}@SiO_2$ under sunlight was measured by mixing 0.1 g of the catalyst with 50 ml of 10 ppm methylene blue solution in a 100 ml Erlenmeyer. The mixture was exposed under the sunlight, and the absorbance of the filtrate was observed after 0, 5, 10, 15, 20, 25, 35, 65, 95, and 125 min of the sunlight exposure, at a wavelength of 663 nm.

RESULTS AND DISCUSSION

The grayish white of $(\text{Ni-Cu})\text{Ox}@SiO_2$ catalysts were successfully synthesized. The XRD spectra indicate the presence of a broad-weak peak at $2\theta = 21.8^\circ$ (Fig. 1.), which is a diffraction of SiO_2 tridymite (JCPDS No. 39-1425). Crystal size of $(\text{Ni-Cu})\text{Ox}@SiO_2$ calculated using the Scherrer equation is 10.38 nm.^{18,19}

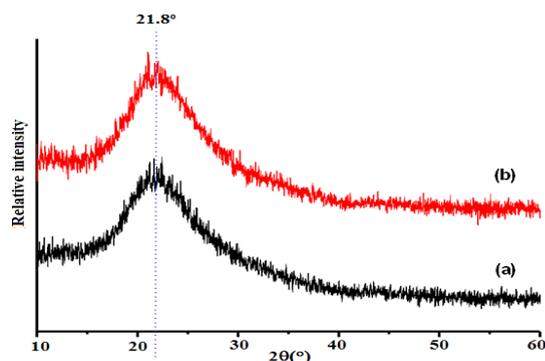
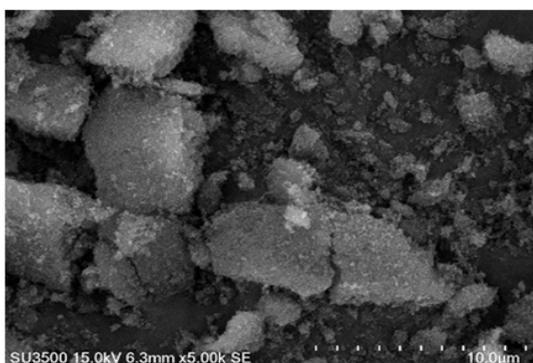


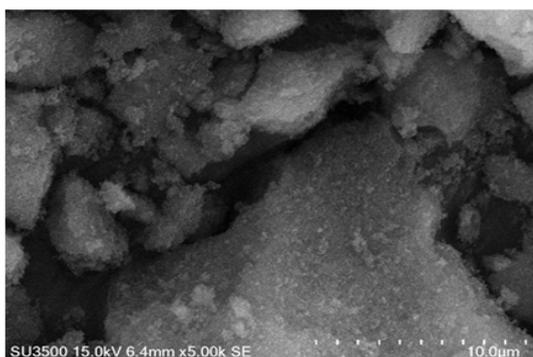
Fig. 1. The XRD diffractogram of $(\text{Ni-Cu})\text{Ox}@SiO_2$, Ni: Cu = (a) 0.2:0.1 and (b) 0.15:0.15

Unfortunately, the combination of SEM-EDX method is failed to prove the presence of both nickel and copper species on the surface of SiO₂.

The micrographs only indicate the silica species, that is SiO₂ having particle size of between 0.1 - 15 μm (Fig. 2). The EDX analysis suggests that both nickel and copper species are under limitation of EDX measurement (Figure 3).



(a)



(b)

Fig. 2. The SEM micrograph of (Ni-Cu)Ox@SiO₂, Ni:Cu = (a) 0.2:0.1 and (b) 0.15:0.15

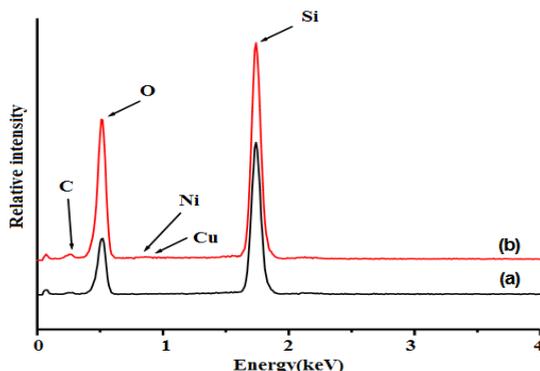


Fig. 3. The EDX spectra of (Ni-Cu)Ox@SiO₂, Ni:Cu = (a) 0.2:0.1 and (b) 0.15:0.15

UV-Vis Diffuse Reflectance method was applied to measure energy absorbance of samples at wavelength between 200-800 nm. It has been postulated that the UV spectrum ranges from 200-400 nm, while the visible spectrum ranges from 400-800 nm. All samples indicate peaks at UV and visible wavelength (Table 1). These prove that the nickel and copper species are supported on the surface of SiO₂, since SiO₂ absorbs the energy at low wavelength.

Table 1: Absorbances of (Ni-Cu)Ox@SiO₂ catalysts

(Ni-Cu)Ox@SiO ₂ , Ni:Cu =	λ (nm)	
	Visibel	UV
0.3:0.0	331	264
0.2:0.1	331	252
0.15:0.15	320	-

Bandgap energy affects the photocatalytic ability of (Ni-Cu)Ox@SiO₂ catalyst. The reflectance data (REF) of the diffuse reflectance UV-Vis measurement is used in the calculation using the Kubelka-Munk equation to obtain the bandgap energy (Eg) of (Ni-Cu)Ox@SiO₂.²⁰ The calculation of bandgap energy by the Kubelka-Munk method include a graph of the relationship between eV and (F (R_∞xhν))^{1/2} presented in (Figure 4).

(Figure 4) describes that bandgap energies of (Ni-Cu)Ox@SiO₂, Ni:Cu = 0.3:0.0, 0.2:0.1 and 0.15:0.15 are between 3.40-2.58 eV, 4.62-2.31 eV, and 3.34-2.41 eV, respectively. Steiner, *et al.*, (1992) found that NiO bandgap energy is ~4 eV,²¹ while the CuO has an energy bandgap between 1.85-2.4 eV and are effectively operated under UV and visible lights.²² This promises that the (Ni-Cu)Ox@SiO₂ catalyst is also effectively used under sunlight.

The absorption study of (Ni-Cu)Ox@SiO₂ on methylene blue is carried out in the dark room. This experiment facilitates the determination of the ability of the catalyst to absorb methylene blue without obstruction of light. The concentration of methylene blue before and after adsorption measured at any times is listed in (Table 2).

The (Ni-Cu)Ox@SiO₂ catalyst absorption capacity was calculated by using the Langmuir and

Freundlich equations.²³ A plot of the concentration of methylene blue adsorbed in each 1 g of catalyst (C/m) versus the final methylene blue concentration (C) is used to determine the Langmuir isotherm pattern, and a plot of the log amount of methylene blue adsorbed on every 1 g of catalyst ($\log X_m/m$) versus a log concentration of methylene blue after adsorption ($\log C_f$) is used to determine the pattern of Freundlich isotherm. Line equations are obtained from the plots of Langmuir and Freundlich isotherms

(Table 3). The values of R^2 of Langmuir adsorption isotherm pattern are higher than the value of R^2 of Freundlich adsorption isotherm pattern, leading the conclusion that the adsorption of methylene blue by the (Ni-Cu)Ox@SiO₂ follows the Langmuir isotherm pattern. This model assumes that there is only a surface layer (monolayer) and is homogeneous of (Ni-Cu)Ox on the surface of SiO₂ which can block adsorption into deeper layers.

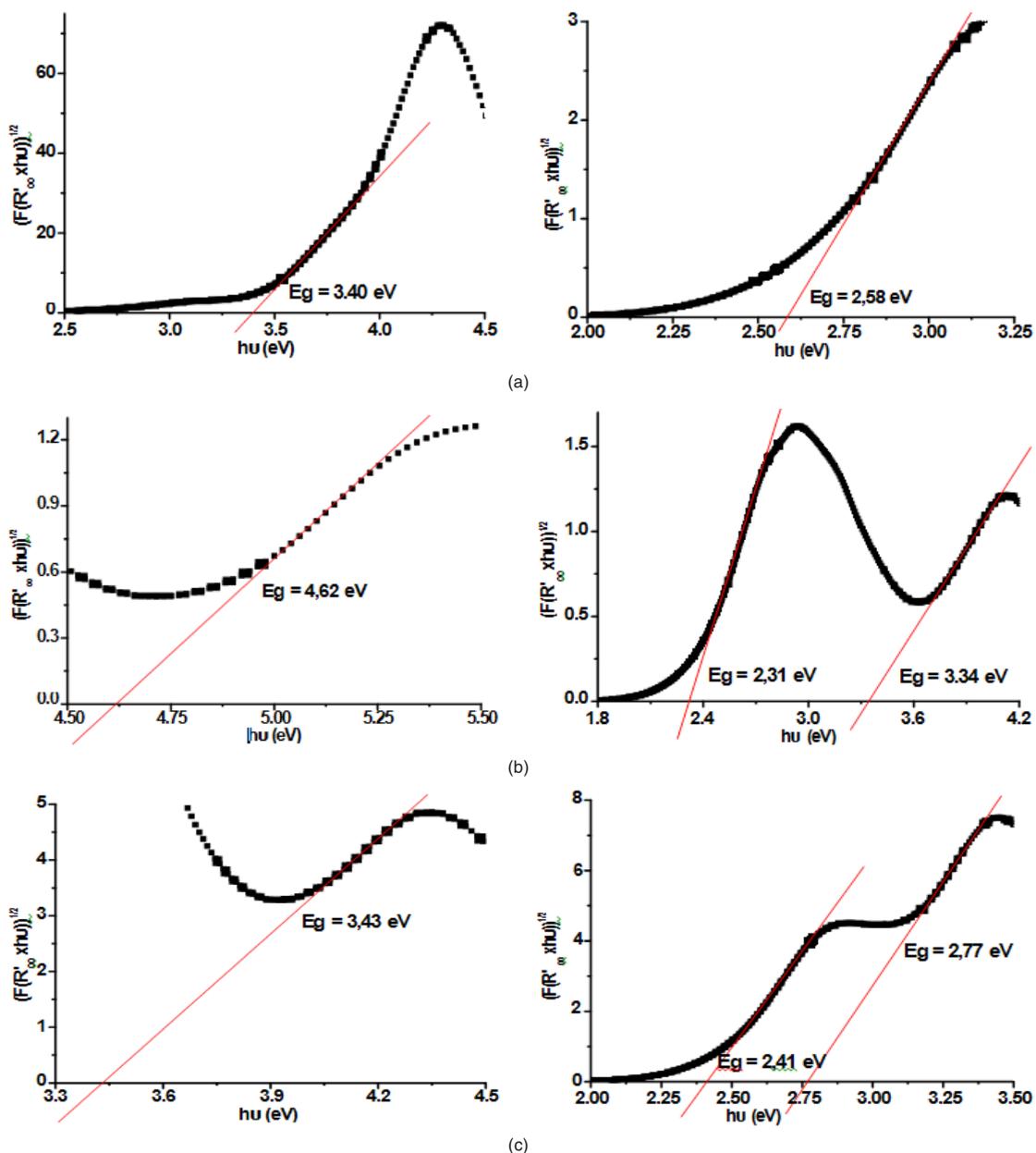


Fig. 4. The calculation of (Ni-Cu)Ox@SiO₂, Ni:Cu = (a) 0.3:0.0 (b) 0.2:0.1 and (c) 0.15:0.15, band gap energies

Table 2: The concentration of methylene blue after adsorption by (Ni-Cu)Ox@SiO₂

Time (min)	The concentration of methylene blue (ppm) after adsorption by (Ni-Cu)Ox@SiO ₂ , for Ni:Cu =		
	0.3:0.0	0.2:0.2	0.15:0.15
0	8.66727	8.66727	8.66727
5	5.49894	5.49894	5.49894
10	2.47603	2.37215	2.36176
15	1.88911	2.28905	2.13842
20	1.75926	1.87872	1.16714
25	1.74368	1.54630	1.11001
35	1.55669	1.52553	0.87628
65	1.43204	1.41126	0.55945
95	1.42684	1.37490	0.55438
125	1.01652	0.96977	0.54910

Table 3: Langmuir and Freundlich isotherm's line equations

(Ni-Cu)Ox@SiO ₂ , Ni:Cu=	Langmuir isotherm	Freundlich isotherm
0.3:0.0	y = 0.0743x - 0.0736 R ² = 0.9757	y = -0.5398x + 1.6498 R ² = 0.898
0.2:0.1	y = 0.0734x - 0.0719 R ² = 0.9695	y = -0.516x + 1.6422 R ² = 0.8789
0.15:0.15	y = 0.0665x - 0.0428 R ² = 0.955	y = -0.369x + 1.5679 R ² = 0.8247

The catalyst adsorption capacity can be calculated by using the line equation of the Langmuir isotherm pattern. The adsorption capacity of (Ni-Cu)Ox@SiO₂ catalyst is listed in Table 4. The decreasing of NiOx and the increasing of CuOx is related linearly with the increasing of the adsorption capacity of (Ni-Cu)Ox@SiO₂ catalyst to methylene blue.

Table 4: The adsorption capacity of (Ni-Cu)Ox@SiO₂ catalyst

(Ni-Cu)Ox@SiO ₂ , Ni:Cu=	Adsorption capacity (mol/g)
0.3:0.0	13.5870
0.2:0.1	13.9082
0.15:0.15	23.3645

The concentration of methylene blue isolated in the dark for 24 h is higher than for 2 h might be due to desorption process. The methylene blue in the solution was then exposed to sunlight for period of times. The concentration of methylene blue after exposed by sunlight at period of times is presented in (Fig. 5). The concentration of methylene blue is gradually decreased at the first 20 minutes. The concentration is then steady figuring that the photodegradation is finished. The percentages of methylene blue photodegraded under sunlight using (Ni-Cu)Ox@SiO₂, where Ni:Cu=0.3:0, 0.2:0.1 and 1.5:1.5 are 55.65%, 49.87%, and 52.11%, respectively.

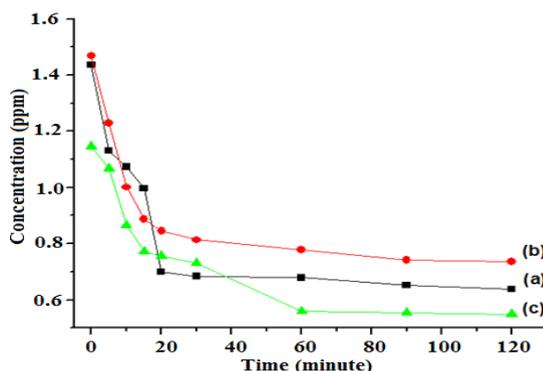


Fig. 5. The methylene blue photodegradation under sunlight using (Ni-Cu)Ox@SiO₂, where Ni:Cu= (a) 0.3:0, (b) 0.2:0.1 and (c) 1.5:1.5

The reaction order kinetics for photodegradation of methylene blue are presented in (Table 5). The highest R² values indicate the second reaction order. These is meant that the photodegradation reaction rate of methylene blue using the (Ni-Cu)Ox@SiO₂ catalyst under sunlight follows the second-order reaction.

Table 5. Methylene blue photodegradation order kinetics

(Ni-Cu)Ox@SiO ₂ , Ni:Cu=	Order	k	R ²
0.3:0.0	0	0.0036	0.5293
	1	0.0043	0.5565
	2	0.0053	0.5866
	0	0.0028	0.5148
0.2:0.1	1	0.0031	0.5812
	2	0.0036	0.6476
	0	0.0036	0.6903
	1	0.005	0.7631
0.15:0.15	1	0.005	0.7631
	2	0.0071	0.8169

The photocatalytic reaction takes place in a heterogeneous system and the reaction rate is influenced by the adsorbance of the reactants on the surface of the catalyst. The kinetic constant k_{obs} is the reaction rate constant that does not take into account the role of adsorption, so that when the adsorption process becomes a part that affects the photodegradation reaction, it is necessary to determine the actual reaction rate constant (k) which has corrected the k_{obs} with the adsorption constant (K) where $k_{obs} = kKL$. The kinetics parameters of the k_{obs} are determined by fitting the curve $1/C_1$ to the time due to the photodegradation reaction of methylene blue with (Ni-Cu)Ox@SiO₂ following a second-order reaction. Then the reaction rate constant (k) is determined based on the k_{obs} listed in (Table 6). The (Ni-Cu)Ox@SiO₂, Ni:Cu=0.15:0.15 shows the highest photodegradation reaction rate

constant of methylene blue under sunlight, which is $0.10677 \cdot 10^4 \text{ min}^{-1}$. This concludes that the (Ni-Cu)Ox@SiO₂, Ni:Cu=0.15:0.15 is most effectively used as a photocatalyst under sunlight.

Table 6: Methylene blue photodegradation kinetics using Ni-Cu oxide@SiO₂ catalyst

(Ni-Cu)Ox@SiO ₂ , Ni:Cu=	K_L	k_{obs} (min ⁻¹)	k (min ⁻¹)
0.3:0.0	$0.0743 \cdot 10^6$	0.0053	$0.07133 \cdot 10^4$
0.2:0.1	$0.0734 \cdot 10^6$	0.0036	$0.04905 \cdot 10^4$
0.15:0.15	$0.0665 \cdot 10^6$	0.0071	$0.10677 \cdot 10^4$

The photodegradation reaction rates of methylene blue are listed in (Table 7). The difference in Ni and Cu concentrations supported onto silica does not have a significant effect on the photodegradation reaction rate equation. This proves that the (Ni-Cu)Ox@SiO₂ catalyst is effective for photodegradation of methylene blue under sunlight.

Table 7: Methylene blue photodegradation rate

(Ni-Cu)Ox@SiO ₂ , Ni:Cu=	Reaction rate (ppm/minute)
0.3:0.0	$0.07133 \cdot 10^4 \times C^2$
0.2:0.1	$0.04905 \cdot 10^4 \times C^2$
0.15:0.15	$0.10677 \cdot 10^4 \times C^2$

CONCLUSION

The prepared (Ni-Cu)Ox@SiO₂ is representative for photodegradation of methylene blue. The nickel and copper oxides decrease the bandgap of silica making the catalyst suitable for photodegradation under visible and ultra violet lights. The catalyst adsorption follows the Langmuir isotherm pattern with adsorption capacity of (Ni-Cu)Ox@SiO₂ increases along with the increasing of copper oxide. The photocatalytic activity of the catalyst in the degradation of methylene blue under the sunlight follows a second order reaction rate.

ACKNOWLEDGMENT

This research was supported and fully funded by the Yogyakarta State University of Indonesia.

Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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