JURNAL KIMIA Valensi

Jurnal Kimia Valensi, Vol6(1), May 2020, 89-94
Available online at Website: http://journal.uinjkt.ac.id/index.php/valensi

The Use of Rice Husk Silica in Modified Zinc Oxide Photocatalysts to Reduce Chromium Concentration

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Received: August 2019; Revision: September 2019; Accepted: July 2020; Available online: May 2020

Abstract

Rice husk ash contains approximately 90-98% dry weight of silica and they have been reported to have several advantages compared to mineral silica. One of these is its application as a filler in ZnO photocatalysts using the sol-gel method. This study was, therefore, conducted to determine the effect of adding rice husk silica to increase the ability of ZnO/SiO_2 photocatalyst to reduce chromium concentration. Meanwhile, a previous effort has been made to degrade methylene blue dyes by 89%. This current research involved preparing rice husk charcoal using pyrolysis tubes after which they were extracted to produce silica while ZnO/SiO_2 composites were made at a 95/5, 90/10, and 85/15 (w/w) ratio and composite activity test was conducted to determine its ability to reduce chromium concentration from practicum discharge. The SEM-EDS results showed the formation of SiO_2 composites in ZnO while 82.6% decrease in total chromium concentration from waste was obtained after 2 hours irradiation with 95/5 composites using ultraviolet radiation.

Keywords: Photocatalysts, rice husk, SiO_2, ZnO/SiO_2.

DOI: *10.15408/jkv.v6i1.12324*

1. INTRODUCTION

The need for rice as a staple food by Indonesian has increased over the years and this has also led to an increase in the husk waste produced. These by products and wastes were reported not to be maximally utilized (Ismunadji, 1998). Meanwhile, burning rice husk ash at a high temperature of 500-600°C produces silica ash which is used in several chemical processes (Putro and Prasetyoko, 2007; Handayani *et al.*, 2015; Soeswanto and Lintang, 2011). Husk silica can be used as a filler in ZnO photocatalysts using the sol-gel method and the application of semiconductors as photocatalysts have become an interesting topic in recent times due to their ability to degrade surrounding compounds through the use of light (Guisnet and Gilson, 2002; Fatimah and Haris, 2014). The previous study investigated the production of photocatalysts by incorporating ZnO and SiO_2 from rice husk extraction which is useful to degrade methylene blue dyes and decrease chromium(VI) concentrations (Rakhmawaty *et al.*, 2016; Eddy *et al.*, 2018; Eddy *et al.*, 2019). This present research was, however, conducted to reduce the concentration of chromium using wastes in the laboratory.

2. MATERIALS AND METHODS

The tools used include glassware, buchner funnels, whatman filter paper No. 40, mercury lamps (HPL-N 125 W Philips), magnetic stirrer, mortar, analytical balance (Mettler Toledo, AB164-S), oven (Carbolite S30 2RR), glass plates, drop pipettes, sonicators (Ultrasonic bath Starsonic 18-35), furnace, Atomic Absorption Spectrophotometer (SSA) (Shimadzu AA 7000), Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) (Hitachi EDAX Team), and Particle Size Analyzer (PSA) (Beckman Coulter LS 13 320).

The materials used were distilled water, potassium carbonate (K_2CO_3 for analysis, Merck), 2 M sodium hydroxide (NaOH, 98%, pellets, Merck), rice husk from Jatiroke

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P-ISSN: 2460-6065, E-ISSN: 2548-3013

Village, Jatinangor District, Sumedang, zinc sulfate heptahydrate ($ZnSO_4.7H_2O$ for analysis, Merck), and practicum waste.

ZnO Synthesis

The process involved the dissolution of 4.3135 g of zinc sulfate heptahydrate in 30 mL methanol and stirred using a magnetic stirrer for 60 minutes. This was followed by the addition of 2M NaOH to the solution drop by drop while stirring to ensure the pH became 8 and was continuously stirred for 180 minutes. The precipitate solution was filtered and washed twice using distilled water and dried in an oven at 85 °C for 1 hour. The precipitated powder was later calcined in a furnace at 500 °C for 1 hour (Eddy *et al.*, 2019).

ZnO/SiO_2 Composites Production

The ZnO/SiO_2 composite was made from a mixture of 3 g ZnO and SiO_2 suspensions obtained from rice husk with the compositions varied at 5%, 10%, and 15% (w/w) and the photocatalyst made was 1 g. Moreover, the suspensions were stirred using a magnetic stirrer at 500 rpm for 2 hours, sonicated for 90 minutes, and coated on the surface of the 3 x 30 cm glass plate using a pipette. The glass plate was later dried in an oven at 40 °C for 12 hours, calcined at 450 °C for 1 hour, and washed using distilled water to release the ZnO/SiO_2 composite. The formed layer was then characterized using SEM-EDX and PSA.

Chromium Photocatalysis Test on Practicum Waste

The chromium photocatalysis test was conducted using a UV lamp (HPL-N 125 W Philips). This involved placing the glass plate in a tube and later filled with a lab waste solution containing chromium and irradiated using a UV lamp for 2 hours. Moreover, 3 mL of filtrate from the waste was obtained at 30 minutes interval to be analyzed using Atomic Absorption Spectroscopy. These tests were conducted on all the compositions of ZnO/SiO_2 composites and ZnO photocatalysts.

Adsorption Test

Adsorption test was conducted to determine the absorption of ZnO/SiO_2 composites and ZnO photocatalysts on the lab wastes containing the chromium. This involved the placement of a glass plate in a tube and then filled with the sample solution while stirring using a magnetic stirrer for 2 hours. Moreover, 3 mL of filtrate from the waste was obtained at 30 minutes interval to be analyzed using Atomic Absorption Spectroscopy. These tests were conducted on all the compositions of ZnO/SiO_2 composites and ZnO photocatalysts.

3. RESULTS AND DISCUSSION

Characterization Result

The characterization results have been reported in the previous study (Eddy *et al.*, 2019). Furthermore, SEM-EDS analysis was conducted to determine the surface morphology and thickness of the ZnO/SiO_2 composite layer on the glass plate using 85/15 (w/w) composition. Figure 1 shows the results with 1000, 2500, and 5000 times magnification. The 1000 magnification shows the composites stick evenly with low porosity and they started to become porous at 2500 and much more at 5000 times.

The 5000 times magnification presented in Figure 1 (C) shows the ZnO/SiO_2 composite consisted of a collection of fine and almost homogeneous bar grains and this means the glass surface was coated homogeneously and subtly. This regularity pattern indicates a good crystal quality in the microstructure properties of the coating.

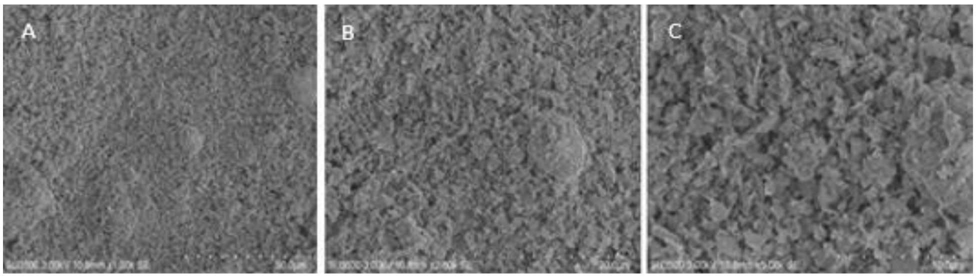
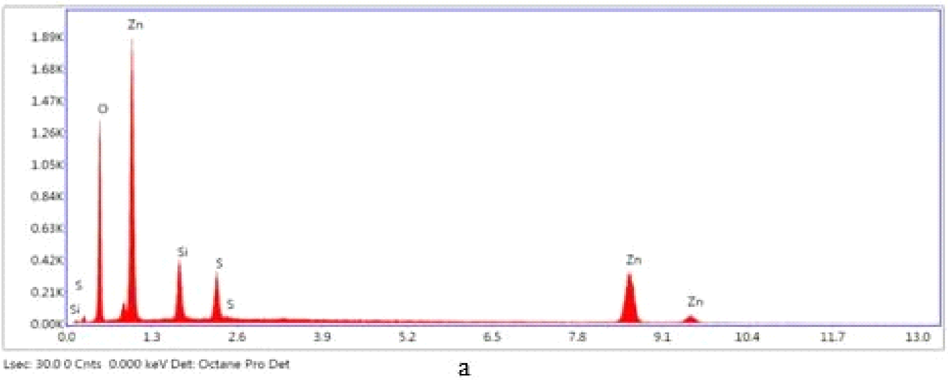


Figure 1. SEM image of ZnO/SiO_2 composite layer morphology (A). 1000 times (B). 2500 times. (C). 5000 times magnification



a

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
OK	35.94	64.91	438.18	8.51	0.1415	1.1493	0.9114	0.3425	1.0000
SiK	7.23	7.44	198.52	8.45	0.0362	1.0537	0.9667	0.4727	1.0054
SK	5.52	4.97	170.43	7.96	0.0382	1.0340	0.9816	0.6633	1.0102
ZnK	51.31	22.68	347.53	3.66	0.4682	0.8596	1.0460	1.0057	1.0553

b

Figure 2 EDS test result. (a). ZnO / SiO_2 composite EDS Spectrum; (b). ZnO / SiO_2 composite atoms

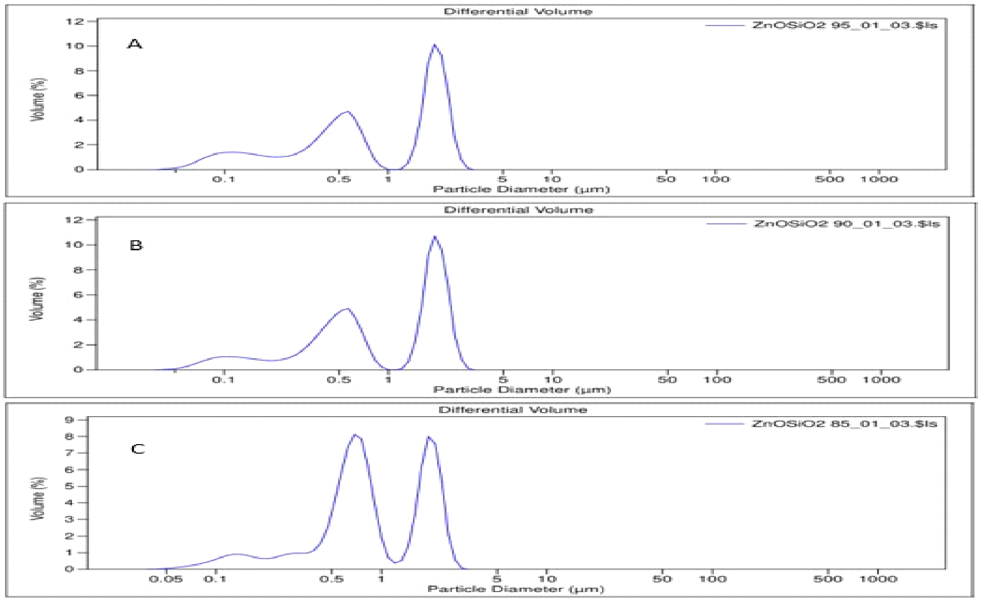


Figure 3. Particle size analyzer (PSA) test results for (a) 95/5 (w/w), (b) 90/10 (w/w), and (c) 85/15 (w/w).

The results of the ZnO/SiO_2 composite EDS spectrum test on the glass plate are shown in Figure 2 and the composite was found to be consisting of zinc (Zn), sulfur (S), silicon (Si), and oxygen (O). The mass of the 85/15 (w/w) composition was observed to contain 51.31% and 7.23% of Zn and Si by weight compared to the percentage difference which was calculated to be 68.21% and 7% respectively. These results, therefore, showed Zn composition calculated and the Si composition measured in the EDS test to be greater. This was associated with the natural occurrence of Zn clumping due to longer sonification which facilitates the release of ZnO and increases the porosity of the coating surface. Meanwhile, the porosity is directly proportional to the waste degrading effectiveness such that at higher porosity there is a lower ability to degrade and this caused by the reduced formation of hydroxyl radicals by the ZnO.

Table 1. The statistical average size of ZnO/SiO_2 composite particles calculated

Variation (w/w)	Mean (µm)	Mean/Median ratio (µm)	S.D (µm)	Mode (µm)
95/5	1.104	1.629	0.833	1.919
90/10	1.154	1.545	0.819	1.919
85/15	1.075	1.392	0.718	0.688

The atomic composition test showed the ZnO/SiO_2 composites have 22.68% zinc (Zn), 4.97% sulfur (S), 7.44% silicon (Si), and 64. 91% oxygen (O). The higher percentage of oxygen compared to zinc indicates some atomic impurities in the composites.

The Particle Size Analyzer (PSA) analysis was used to determine the particle size and this involved dispersing the particles in a liquid media to avoid agglomeration with the size of each of them measured using three distributions which are intensity, number, and volume. The overall sample condition of the 95/5, 90/10, and 85/15 (w / w) compositions of the composite are shown in Figure 3.

The results presented in Figure 3 (a) showed the average diameter size for 95/5 (w/w) was 1.629 µm with a standard deviation (SD) of 0.833 µm. This means its particle size ranges from 0.796 µm to 2.462 µm based on 1.629 ± 0.833 µm. Similarly, 90/10 (w/w) was shown in Figure 3(b) to range between 0.726 µm and 2.364 µm based on 1.545 ± 0.819 µm while 85/15 (w/w) composition presented in Figure 3 (c) and Table 1 was observed to have ranged from 0.674 µm to 2.11 µm based on the average diameter of 1.392 with an SD of 0.718 µm.

The 95/5 and 90/10 (w/w) compositions were also recorded to be 1.919 µm in size and this is the most commonly detected by the PSA particle detector while 85/15 (w/w) had 0.688 µm and has been reported to be the most often detected. Moreover, Figures 3 (a) and (b) show a high peak and this means the particles formed have almost the same size distribution while Figure 3 (c) shows two peaks indicating two different distributions.

Photocatalysis Test

Figure 4 shows the use of UV radiation for 120 minutes was more effective in reducing the chromium concentration in composites with 95/5 (w/w) composition to 82.6% compared to a 73.3% reduction recorded at 60 minutes as shown in Figure 5. This was observed to be more effective than the values recorded for 90/10 and 85/15 (w/w) at the same time. Moreover, the ZnO was 59.6%, 63.7%, and 52.1% respectively in the 60th minute and this decrease was influenced by using more than 5% of SiO_2 (w/w). This attached to the closure of ZnO photocatalyst by SiO_2 which led to the reduction in the numbers of the hydroxyl radicals formed. It is important to note that, as a semiconductor, ZnO produces holes and electrons when exposed to UV and its further reaction with water usually leads to the production of hydroxyl radicals which are useful in degrading organic compounds, dyes, or dissolved metals concentration also known as the reducing metals. The concentration reduction is associated with the decrease in the ZnO/SiO_2 composite absorbed into the photocatalysis process without UV irradiation. Therefore, the final reduction in chromium concentration can be calculated based on the difference between the two processes. Meanwhile, it is possible to explain the mechanism of the photocatalysis process using the reduction of chromium from VI to III through the application of AAS. It is, however, important to note that this method cannot determine the charge on the metal. This is in line with the reports of Naimah and Ermawati (2011), and Slamet and Danumulyo (2003). The reaction mechanism is as follows (Riyani and Setyaningtyas, 2016).

$$ZnO + h\nu \rightarrow ZnO\ (e^{-}CB + h^{+}VB) \quad (1)$$
$$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O \quad (2)$$
$$CrO_4^{2-} + 8H^{+} + 3e^{-} \rightarrow Cr^{3+} + 4H_2O \quad (3)$$

Cr (VI) in the sample is in a balanced state between chromate ions (CrO_4^{2-}) and dichromate ions ($Cr_2O_7^{2}$) as shown in the following equation (4):

$$2CrO_4^{2-} + 2H^{+} \rightarrow Cr_2O_7^{2-} + H_2O \quad (4)$$

Acidic solutions such as Cr (VI) in the form of $Cr_2O_7^{2-}$ are more dominant than CrO_4^{2-} and are expected to be reduced by electrons from the reaction between photocatalyst and photon to produce Cr (III) and H_2O.

Figure 4 also showed the use of ZnO/SiO_2 composites as a whole was more effective than ZnO photocatalysts without the addition of SiO_2. This is observed from the ability to reduce the concentration which was recorded for the ZnO photocatalysts to be only 42.8%, 52.1%, 53.8%, and 56.3% from the 30 to 120 minutes. This means adding SiO_2 as a filler was able to increase the activity of the original composite and this is in line with the findings of Soltani *et al.*, (2015) that attaching ZnO to the plates without SiO_2 was uneven and led to porosity in certain areas.

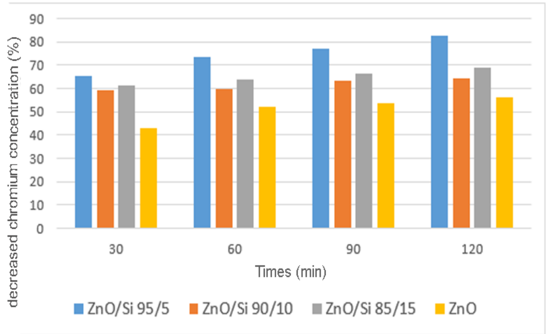


Figure 4: Diagram of the reduction in chromium concentration in laboratory waste using ZnO/SiO_2 composites

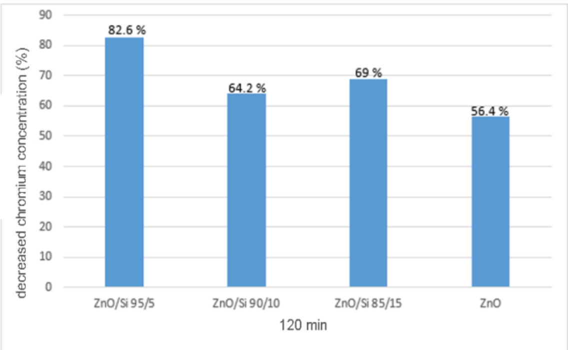


Figure 5: Diagram of a reduction in the concentration of chromium in laboratory waste within 120 minutes

Figure 5 shows the percentage reduction in chromium concentration using 95/5, 90/10, and 85/15 (w/w) compositions as well as ZnO photocatalysts with 120 minutes irradiation was 82.6%, 64.2%, 69%, and 56.4% respectively.

4. CONCLUSION

The addition of SiO_2 rice husk as filler in ZnO photocatalyst has the ability to mobilize particles on the glass plate surface evenly and form ZnO/SiO_2 composites with 95/5, 90/10, and 85/15 (w/w) compositions. Moreover, the homogeneous particle size for the 95/5 (w/w) was 1.919 µm and considered the most effective to reduce chromium concentrations from lab waste as observed in the 82.6% reduction recorded.

ACKNOWLEDGEMENT

The authors are grateful for the funding provided by the Ministry of Research, Technology, and Higher Education to the Master's Thesis Research No. 2886 / UN6.D / LT / 2019.

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