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Synthesis and Characterization of SiO_2/ZnO Nanocomposites from Zinc Waste and Mount Merapi Volcanic Ash

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Abstract

Research on the synthesis and characterization of SiO_2/ZnO nanocomposites from zinc waste and Mount Merapi volcanic ash has been carried out. The semiconductor used was ZnO using a SiO_2 as the host material. The use of SiO_2 was due to its high efficiency and abundant raw materials. This is because the eruption of Mount Merapi occurs regularly every four years. Apart from the abundant presence of SiO_2, the source of ZnO from lathe workshop waste is also easy to obtain. The research aims to reduce the volume of zinc waste from the lathe and volcanic ash, which was not optimized. Zinc waste and volcanic ash were synthesized into nanocomposites. Then the obtained nanocomposites were characterized to determine their effectiveness in degrading various wastes. The synthesis of SiO_2/ZnO nanocomposites was carried out using the sol-gel method as easy and highly effective. The method used is to transform zinc waste into $Zn(OH)_2$. The volcanic ash was extracted with KOH to form potassium silicate (K_2SiO_3). $Zn(OH)_2$, (K_2SiO_3) and HCl were reacted together when sonicated, then calcined at 550°C. The results showed that SiO_2/ZnO nanocomposites made from volcanic ash and zinc waste produced composite sizes with a size range of 100-200 nm and a uniform circular shape. FTIR analysis results show that SiO has the peaks at wavenumbers of 993.34 and 1109.07 cm^{-1}, while the ZnO peak is at wavenumbers of 443.63 cm^{-1}. The XRD diffractogram of SiO_2/ZnO nanocomposites shows peaks at 2θ of 30.42°, 31.56°, and 44.40°.

1. Introduction

The eruption cycle of Mount Merapi is routine every four years. Mount Merapi, which erupted in 2018, released various solid materials such as gravel and volcanic ash. The impact of this eruption has harmed humans and the environment. In addition to causing respiratory system disorders, if inhaled, volcanic ash can also cause increased turbidity in water and damage ecosystems. It needs extraordinary efforts to deal with volcanic ash in the short and long term [1]. The availability of volcanic ash that is large enough around the slope of Mount Merapi can be used as an adsorbent to purify wastewater. Volcanic ash contains large amounts of silica [2]. It is hoped that the abundant availability of volcanic ash in nature can be utilized properly and increase the practical value of volcanic ash. Previous studies have stated that the large silica content in volcanic ash can be used as an adsorbent [3] to reduce water pollution [4]. SiO_2/ZnO nanocomposites are semiconductors that can be synthesized from volcanic ash and zinc waste. SiO_2/ZnO nanocomposites can be used to degrade various wastes. The use of volcanic ash becoming SiO_2/ZnO nanocomposites is intended to increase the use-value of volcanic ash and zinc waste into products with higher economic value. The nanocomposites obtained can be used for water purification.

Semiconductor materials that are widely developed today are metal oxide semiconductor compounds. One of the metal-semiconductor materials is zinc oxide (ZnO). ZnO is a unique material that exhibits semiconductor, piezoelectric, and several pyroelectric properties. ZnO growth morphology has several groups, such as nanocombs, nanorings, nanohelixes, nanowires, and nanocages. For applications, ZnO nanostructures have are very beneficial in optoelectronics, sensors, transducers, photocatalysts, and biomedical sciences as they are environmentally friendly materials.

The sol-gel method is a method used to make solid material from nanoparticles or small molecules, which is mainly used for the fabrication of metal oxides such as silicon (Si) [5] and titanium (Ti) [6]. Several techniques or methods are used to synthesize nanocomposite photocatalyst materials, including the sol-gel method, grafting, and co-precipitation. The method used in this research is the sol-gel method. The process used a medium as a solution, which changed the phase into a sol and then formed a gel. The sol-gel method was used to synthesize Lithium Manganese Oxide Spinel ($LiMn_2O_4$) with a silicon series through the sol-gel process. XRD results showed that doped silicon samples could retain the spinel structure of $LiMn_2O_4$.$LiMn_2O_4$ [7]. In previous research, the sol-gel method has been chosen to synthesize composites since it was easy, effective, and efficient. The sol-gel method in previous studies has been applied to the synthesis of MgO-SiO_2 composites based on rice husk silica [8], TiO_2-kaolin composites [9], and titania-silica composites [10]. This method can be used to make SiO_2/ZnO composites made from zinc waste and volcanic ash, where these composites can be used for water purification.

2. Methodology

The synthesis of SiO_2/ZnO nanocomposites was carried out using the sol-gel method by reacting $Zn(OH)_2$ from zinc waste, K_2SiO_3 from volcanic ash from Mount Merapi, and HCl.

2.1. Materials and equipment

The raw materials are Mount Merapi volcanic ash taken directly from the village of Cangkringan, the Mbah Marijan bunker and the Gendol river flow, zinc waste for the lathe workshop, KOH (Merck), NaOH (Merck), HCl p.a. (Merck), H_2SO_4 pa (Merck), distilled water. The equipment for research was as follows: laboratory glassware, analytical balance (Mettler PE300), Oven (HERAEUS KR 170E), Sonicator (Elmasonic S 30 H), Furnace (Barnstead International Thermolyne), UV-Vis Spectrophotometer (SHIMADZU CORP. 80550), Fourier Transform Infrared/FTIR (SHIMADZU IR Prestige – 21), Scanning Electron Microscopy/SEM (Hitachi SU-70), X-ray diffraction/XRD (Philip Analytical X-Ray B. V), Centrifuge (Hettich CBA 200), reflux and other supporting laboratory equipment.

2.2. Preparation and Pre-Treatment of Raw Materials

Before raw materials were used, they must be treated to remove impurities. The raw material for volcanic ash was washed and then left overnight and separated from other materials such as sand, soil, and rock. The ashes were sun-dried to dry. After it was clean and dry, the volcanic ash was sieved with a 100-mesh sieve and then heated at 110°C for 15 minutes. The zinc waste in powder from the lathe was washed with soapy water to remove greasy dirt. Then the clean zinc waste was dried in the sun to dry. The clean and dry zinc waste was then sieved for 50 mesh.

2.3. Transformation of Zinc Waste into $Zn(OH)_2$

20 mL of concentrated sulfuric acid was added to 10 grams of waste zinc under gentle stirring with a stirring rod. The addition of concentrated sulfuric acid aims to dissolve zinc waste. The resulting filtrate was then re-reacted with 100 mL 6N NaOH dropwise and stirred slowly. The reaction products were left for 24 hours. The results obtained from this process were $Zn(OH)_2$ [11]].

2.4. Synthesis of Potassium Silicate (K_2SiO_3)

Ten grams of volcanic ash was extracted using 4N KOH with a weight ratio of 1: 1. The mixture of volcanic ash and KOH was refluxed for 5 hours, then cooled, and the filtrate was filtered as potassium silicate (K_2SiO_3) [12].

2.5. Synthesis and Characterization

25 mL of $Zn(OH)_2$ were reacted with 25 mL of K_2SiO_3 and 50 mL of 1 N HCl. The three reactants were added simultaneously, while sonication was carried out for 15 minutes at 35°C. The pH of the reaction results was measured with a pH meter. The solution obtained was left to stand for 24 hours. Furthermore, the gel was neutralized with hot distilled water and then evaporated until dry. The dry gel obtained was calcined at 550°C in a furnace for 3 hours [13]. Furthermore, the gel in the form of powder was characterized using SEM, FTIR, and XRD.

3. Results and Discussion

3.1. Transformation of Zinc Waste into $Zn(OH)_2$

The transformation of zinc waste into ZnO was obtained, as shown in Figure 1.

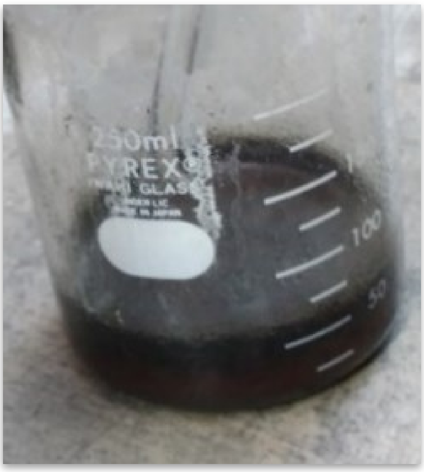


Figure 1. Transformation of $Zn(OH)_2$ solution from zinc waste with concentrated H_2SO_4

Figure 1 shows a blackish gray solution, and if it is left for 24 hours, it will change the phase from the solution into a gel phase. These results are in accordance with research published by Agustina [14]. Other studies [15, 16, 17, 18] also published using zinc acetate as a source of ZnO. The reactions that occur in the zinc waste transformation process are as follows:

$$ZnX_{2\,(s)} + H_2SO_{4\,(l)} \rightarrow ZnSO_{4\,(aq)} + 2HX_{\,(aq)}$$

$ZnSO_{4\,(s)} + 2HX_{\,(aq)} + 2NaOH_{\,(l)} \rightarrow Zn(OH)_2 + H_2O_{\,(l)} + Na_2SO_{4\,(l)} + 2X^-_{\,(l)}$

Research by Ati *et al.* [11] became the reference for this study. The amount of $Zn(OH)_2$ obtained from the transformation of zinc waste was 40% of the raw material used as zinc was only used as an anti-rust coating.

3.2. Synthesis of Potassium Silicate (K_2SiO_3)

The results of volcanic ash extraction are as shown in Figure 2.

Figure 2. K_2SiO_3 solution from volcanic ash extraction

The results of the volcanic ash extraction in Figure 2 show a brown solution. This brown solution follows the research results obtained by Agung M. *et al.* [19] and Niu *et al.* [20]. The reactions that occur in volcanic ash extraction are as follows:

$SiO_{2\,(s)} + 2KOH_{\,(l)} \rightarrow K_2SiO_{3\,(aq)} + H_2O_{\,(l)}$

The results of the extraction of volcanic ash to SiO_2 are under previously published studies [3, 12, 21]. The results of the volcanic ash extraction obtained SiO_2 content of 85% by weight. Compared with pure (analytical grade) K_2SiO_3 (Merck), the K_2SiO_3 results from volcanic ash extraction have a different shape. The K_2SiO_3 extracted result is a brown colored solution, while the pure (analytical grade) K_2SiO_3 (Merck) produces a colorless solution. The color difference is due to the volcanic ash containing 18.59% ferrous oxide (Fe_2O_3), which is also extracted when reacted with KOH. Future research is expected to extract pure SiO_2 in volcanic ash without impurities.

3.3. Synthesis Nanocomposite SiO_2/ZnO

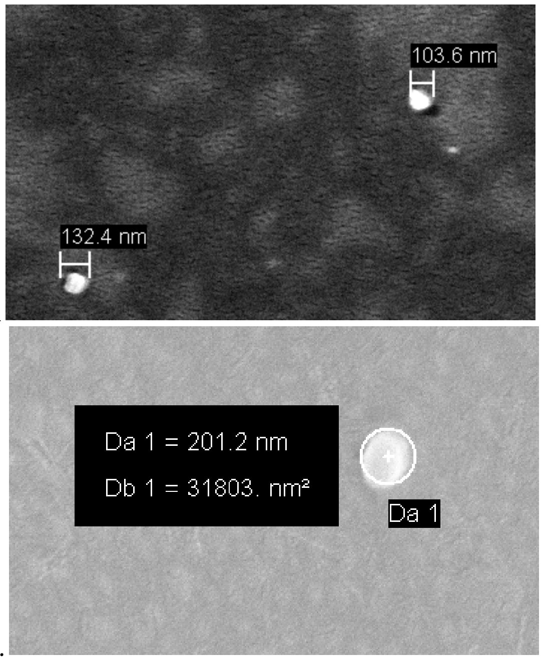
The SiO_2/ZnO nanocomposite synthesis was carried out by reacting K_2SiO_3 obtained from the volcanic ash extraction process with ZnO obtained from the transformation of zinc and HCl waste. After going through the sonication and calcination stages, the results were obtained, as shown in Figure 3.

Figure 3. Synthesis result of SiO_2/ZnO nanocomposites

Figure 3 shows a fine powder with a brown color. This powder is a SiO_2/ZnO nanocomposite. The color of the nanocomposites produced in this study is different from the results of previous studies, which was white [13, 17]. Impurities cause a color difference resulting in nanocomposites of the zinc waste. Zinc waste obtained from lathe workshops contains impurities as iron, which affects the resulting composite color.

3.4. Characterization composite SiO_2/ZnO

The SiO_2/ZnO composites from the synthesis of volcanic ash and zinc waste were then characterized using SEM, FTIR, and XRD analysis. The results of the characterization of SiO_2/ZnO composites using SEM are shown in Figures 4. The characteristics of SiO_2/ZnO nanocomposites can be seen in Figures 4. It can be seen that the uniformity of the crystals that make up a material. The morphology of the synthesis results has a variety of shapes in the form of a circle. The sol-gel method provides a fairly uniform size of uniformity [22]. In this study, the resulting composites ranged in size from 100-200 nm. These results are in line with research published by Mohamed and Aazam [18], which stated that the SiO_2/ZnO nanocomposite synthesis has a size range of 200-800 nm, and a 2015 study also stated that the SiO_2/ZnO nanocomposite had a size of 200 nm [22].



a

b.

Figure 4. SEM images of SiO_2/ZnO composites (a) size range 103-132 nm) (b) (size range 201.2 nm)

The results of FTIR analysis on SiO_2/ZnO nanocomposite are shown in Figure 5. SiO_2/ZnO nanocomposites have functional groups in the form of Zn-O and Si-O. FTIR test results showed silica in the nanocomposite as indicated by the appearance of SiO_2 spectra with wavenumbers of 993.34 cm^{-1} and 1109.07 cm^{-1}, while ZnO was at a wavenumber of 443.63 cm^{-1}. Another published study states that the wavenumber is 1087.85 cm^{-1} for the Si-O-Si group. The wavenumbers of 462.92 cm^{-1}, 570.93 cm^{-1}; 617.22 cm^{-1} and 671.23 cm^{-1} show stretching vibrations of the Zn-O groups [23]. Other studies have also stated that a strong SiO2 spectrum indicates the presence of silica, including the symmetric bending of Si-O-Si at a wavenumber of 786 cm^{-1} and Si-O-H at 956 cm^{-1}. The asymmetric bending and stretching vibrations of Si-O-Si are at wavenumbers 1095 cm^{-1} and 1211 cm^{-1} [23].

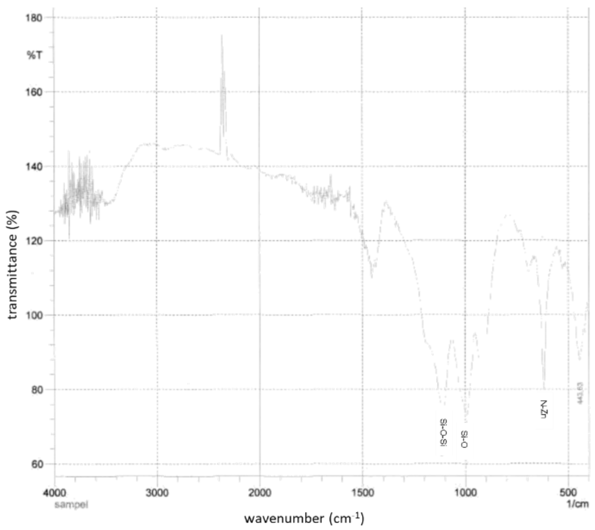


Figure 5. FTIR Spectra of synthesized SiO_2/ZnO nanocomposites

The XRD results of the SiO_2/ZnO nanocomposites are shown in Figure 6(c). The results show that the peaks of SiO_2/ZnO nanocomposites are 30.42°, 31.56°, and 44.40°. Figure 6(b) shows that pure ZnO has a peak at 2θ of 31.84°, 34.52°, 36.38°, 47.64°, 56.7°, 63.06°, and 68.1°. While the pure silica material (Figure 6(a)) has no peaks. Based on the three diffractograms, the SiO2 / ZnO nanocomposite has different peaks from the constituent materials. The results of the XRD characterization indicated that the results of this study were similar to those of the previous study, namely the peak was obtained at 2θ for ZnO at 31.97°; 34.63°; 36.46°; 47.77°; 56.80°; 63.06°; 68.12° and 69.26°. The SiO_2 peaks are at 28.82°, 32.84°, and 42.89° [13]. Another study stated that the 2θ peak in the SiO_2/ZnO composite was 32.0°; 34.6°; 36.4°; 47.7°; 56.8° and 63.0° [24]

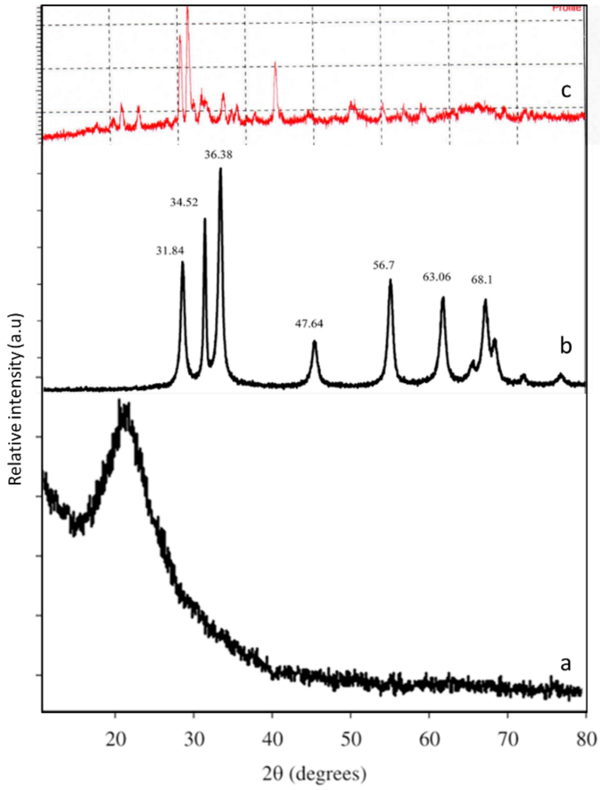


Figure 6. XRD diffractogram of (a) SiO_2/ZnO nanocomposites from volcanic ash and zinc waste (b) pure ZnO material [25] (c) pure silica material [26]

4. Conclusion

This study concluded that the SiO_2/ZnO nanocomposite synthesized from volcanic ash and zinc waste has a uniform shape, a circle with a size range of 100-200 nm. FTIR analysis results show that SiO is at wavenumbers of 993.34 and 1109.07 cm^{-1}, while ZnO is at wavenumbers of 443.63 cm^{-1}. The XRD diffractogram for SiO_2/ZnO nanocomposites shows that the peaks were at 2θ of 30.42°, 31.56°, and 44.40°.

References

[1] Rahayu Rahayu, Dwi Priyo Ariyanto, Komariah Komariah, Sri Hartati, Jauhari Syamsiyah, Widyatmani Sih Dewi, Dampak erupsi gunung merapi terhadap lahan dan upaya-upaya pemulihannya, *Caraka Tani: Journal of Sustainable Agriculture*, 29, 1, (2014), 61-72 https://doi.org/10.20961/carakatani.v29i1.13320

[2] Lisnawaty Simatupang, Devi Devi, The preparation and characterization of Sinabung volcanic ash as silica based adsorbent, *Jurnal Pendidikan Kimia*, 8, 3, (2016), 159-163 https://doi.org/10.24114/jpkim.v8i3.4478

[3] Muchammad Nizar, Z.A. Imam Supardi, Sintesis SiO_2 Berbahan Dasar Abu Vulkanik sebagai Adsorben Ion Pb [II], *Inovasi Fisika Indonesia*, 5, 1, (2016), 28-32

[4] Luca Lora, Galih Ramadhan, Pranoto, Candra Purnawan, Kombinasi Adsorben Alofan dan Abu Vulkanik Gunung Kelud Diaktivasi sebagai Penyerap Logam Berat Pada Limbah Cair Pengrajin Batik, *Seminar Nasional Teknologi Industri Hijau 2014*, Semarang, 2014

[5] M. Catauro, F. Papale, G. Roviello, C. Ferone, F. Bollino, M. Trifuoggi, C. Aurilio, Synthesis of SiO_2 and CaO rich calcium silicate systems via sol-gel process: Bioactivity, biocompatibility, and drug delivery tests, *Journal of Biomedical Materials Research Part A*, 102, 9, (2014), 3087-3092 https://doi.org/10.1002/jbm.a.34978

[6] Ruth Evelyn R. S. Lourenço, Amanda A. N. Linhares, André Vicente de Oliveira, Marcelo Gomes da Silva, Jurandi Gonçalves de Oliveira, Maria Cristina Canela, Photodegradation of ethylene by use of TiO_2 sol-gel on polypropylene and on glass for application in the postharvest of papaya fruit, *Environmental Science and Pollution Research*, 24, 7, (2017), 6047-6054 https://doi.org/10.1007/s11356-016-8197-5

[7] Shiqi Huang, Mostapha Dakhchoune, Wen Luo, Emad Oveisi, Guangwei He, Mojtaba Rezaei, Jing Zhao, Duncan T. L. Alexander, Andreas Züttel, Michael S. Strano, Kumar Varoon Agrawal, Single-layer graphene membranes by crack-free transfer for gas mixture separation, *Nature Communications*, 9, 1, (2018), 2632 https://doi.org/10.1038/s41467-018-04904-3

[8] Dian Dahliana, Simon Sembiring, Wasinton Simanjuntak, Pengaruh suhu sintering terhadap karakteristik fisis komposit MgO-SiO_2 berbasis silika sekam padi, *Jurnal Teori dan Aplikasi Fisika*, 1, 1, (2013), 49-52

[9] Dewi Fatmawati, Anthoni B Aritonang, Sintesis dan Karakterisasi TiO_2-Kaolin Menggunakan Metode Sol-Gel, *Jurnal Kimia Khatulistiwa*, 8, 2, 15-21

[10] Alfan Yusuf Putra Santoso, Muhammad Fayrus, Srie Muljani, Sintesis Komposit Titania-Silika dengan Proses Sol gel, *ChemPro*, 1, 1, (2020), 36-40 https://doi.org/10.33005/chempro.v1i01.37

[11] Laras Ati, Priyandika DR, Agus Yulianto, Mahardika Prasetya Aji, Uji Efektivitas Ekstraksi Limbah Seng menjadi Seng Oksida (ZnO) dengan Metode Presipitasi, *Jurnal Fisika*, 7, 2, (2017), 55-58

[12] U. Kalapathy, A. Proctor, J. Shultz, An improved method for production of silica from rice hull ash, *Bioresource Technology*, 85, 3, (2002), 285-289 https://doi.org/10.1016/S0960-8524(02)00116-5

[13] Zasrie Puti Oktaviani, Abdul Haris, Sintesis ZnO-SiO2 dan Aplikasinya pada Fotokatalisis Degradasi Limbah Organik Fenol dan Penurunan Kadar Cd (II) secara Simultan, *Jurnal Kimia Sains dan Aplikasi*, 19, 2, (2016), 45-49 https://doi.org/10.14710/jksa.19.2.45-49

[14] Siti Agustina, Proses Ekstraksi Seng Oksida Dari Seng Dross Menggunakan Metode Hidrometalurgi Sistim Terbuka, *Jurnal Kimia dan Kemasan*, 38, 2, (2016), 103-108 http://dx.doi.org/10.24817/jkk.v38i2.2704

[15] Roberto Colonia, Vanessa C Martínez, José L Solís, Mónica M Gómez, Síntesis de nanopartículas de ZnO2 empleando ultrasonido: caracterización estructural y morfológica para aplicaciones bactericidas, *Revista de la Sociedad Química del Perú*, 79, 2, (2013), 126-135

[16] Dessy Gilang Permata, Ni Putu Diantariani, Ida Ayu Gede Widihati, Degradasi fotokatalitik fenol menggunakan fotokatalis ZnO dan sinar UV, *Jurnal Kimia*, 10, 2, (2016), 263-269 https://doi.org/10.24843/JCHEM.2016.v10.i02.p13

[17] Sherly Kasuma Warda Ningsih, Sintesis dan Karakterisasi Nanopartikel ZnO doped Cu^{2+} Melalui Metoda Sol-Gel, *EKSAKTA: Berkala Ilmiah Bidang MIPA*, 18, 02, (2017), 39-51 https://doi.org/10.24036/eksakta/vol18-iss02/51

[18] R. M. Mohamed, E. S. Aazam, Enhancement of photocatalytic activity of ZnO–SiO2 by nano-sized Ag for visible photocatalytic reduction of Hg(II), *Desalination and Water Treatment*, 50, 1-3, (2012), 140-146 https://doi.org/10.1080/19443994.2012.708559

[19] Galang Fajar Agung M., Muhammad Rizal Hanafie Sy, Primata Mardina, Ekstraksi silika dari abu sekam padi dengan pelarut KOH, *Konversi*, 2, 1, (2013), 28-31

[20] Yanqing Niu, Yuan Lv, Xiao Zhang, Denghui Wang, Ping Li, Shi'en Hui, Effects of water leaching (simulated rainfall) and additives (KOH, KCl, and SiO2) on the ash fusion characteristics of corn straw, *Applied Thermal Engineering*, 154, (2019), 485-492 https://doi.org/10.1016/j.applthermaleng.2019.03.124

[21] Muchamad Rijal, Z.A. Imam Supardi, Pengaruh pH Silika Berbasis Abu Vulkanik terhadap Komposit SiO_2-Mgo sebagai Kandidat Seal Fuel Cells, *Inovasi Fisika Indonesia*, 5, 1, (2016), 23-27

[22] Rosi Selfia Putri, Ratnawulan Ratnawulan, Dani Gustaman Syarif, Pengaruh Penambahan ZrO_2 terhadap Karakteristik Termistor NTC Berbahan Dasar Fe_2O_3 dari Mineral Yarosit, *Pillar of Physics*, 10, 1, (2017), 86-93

[23] Choiril Azmiyawati, Endang Sawitri, Parsaoran Siahaan, Silica Magnetite Adsorbent: Effect of Drying Temperature of Silica Sol Gel on Magnetite Core Structure, *Jurnal Kimia Sains dan Aplikasi*, 21, 3, 149-154 https://doi.org/10.14710/jksa.21.3.149-154

[24] M. Y. Sari, E. B. Susatyo, Sintesis Kitosan-Silika Bead serta Aplikasinya untuk Menurunkan Kadar Ion Cr (VI) dalam Larutan, *Jurnal Mipa*, 40, 2, (2017), 104-110

[25] Snehal Yedurkar, Chandra Maurya, Prakash Mahanwar, Biosynthesis of zinc oxide nanoparticles using ixora coccinea leaf extract—a green approach, *Open Journal of Synthesis Theory and Applications*, 5, 1, (2016), 1-14 http://dx.doi.org/10.4236/ojsta.2016.51001

[26] Gobi Nallathambi, Thangavelu Ramachandran, Venkatachalam Rajendran, Rajagoundar Palanivelu, Effect of silica nanoparticles and BTCA on physical properties of cotton fabrics, *Materials Research*, 14, 4, (2011), 552-559 https://doi.org/10.1590/S1516-14392011005000086