MOLEKUL
eISSN: 2503-0310

Articles
https://doi.org/10.20884/1.jm.2022.17.3.5719

Easy Handling Preparation of Cubic Sulfur in Aqueous Extract of *Sapindus rarak* rinds

Charles Banon[1]*, Nesbah[1], Bambang Trihadi[1], Aswin Falahudin[1], Salprima Yudha S[1,2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Bengkulu
Jalan W.R, Supratman, Kandang Limun, Kota Bengkulu 38122, Indones
[2]Research Center of Sumatera Natural Products and Functional Materials, Universitas Bengkulu
Jalan W.R, Supratman, Kandang Limun, Kota Bengkulu 38122, Indonesia

*Corresponding author email: cbanon@unib.ac.id

Received May 13, 2022; **Accepted** September 23, 2022; **Available online** November 20, 2022

ABSTRACT. The aqueous extract of *Sapindus rarak* (*S. rarak*) was produced by heating its rinds in demineralized water at 80 °C. The main experiment was conducted at room temperature by mixing a solution of sodium thiosulfate with the extract obtained previously. After adding dilute hydrochloric acid (10%), fine granules gradually formed in the solution and precipitated when the reaction was stopped and allowed to stand for 24 h. The analysis results showed the consistency of the X-ray diffraction (XRD) peak of the obtained material with sulfur standards. When looked at the surface using scanning electron microscopy (SEM), sulfur was found to be cube-shaped. The formation of cuboidal elemental sulfur possibly occurs due to the covering of thiosulfate ions and elemental sulfur during and after the reaction. Organic compounds were found covering sulfur through elemental and functional group analyses using energy-dispersive X-ray (EDX) and Fourier-transform infrared (FTIR) spectroscopy, respectively

Keywords: Cubic form, natural surfactant, *Sapindus rarak*, saponin, sulfur

INTRODUCTION

The properties and utility of elemental sulfur have encouraged many researchers to modify the reaction conditions for a specific target regarding shape and size and to develop various interesting applications (McCue, & Anderson, 2014; Nguyen 2017; Ragab, & Saad-Allah, 2020; Saedi *et al*, 2020). Considerable focus has been placed on developing the green synthesis of elemental sulfur, including sulfur nanoparticles (SNPs), using plant and animal extracts (Suleiman et al., 2013; Paralikar and Rai, 2018). This is because certain organic compounds in plant extracts could significantly affect the reaction conditions, especially their reaction intermediates, ultimately providing specific characteristics to the corresponding SNPs (Ghotekar et al., 2020).

Some interesting results have been reported in this field. For example, the SNPs with a specific size were successfully synthesized using *Ficus bengalensis* at room temperature, with the as-prepared sulfur useful in reducing Cr (VI) to Cr (III) (Tripathi *et al.*, 2018). Other plant extracts have been used as a medium for SNP synthesis (average size = 50 nm), with the obtained SNPs effectively increasing the growth and health of certain plants (Salem *et al.*, 2016). Additionally, the number of hatched *Drosophila melanogaster* larvae has been effectively reduced with the SNPs synthesized using specific plant extracts (Araj *et al.*, 2015). *Allium sativum* aqueous garlic extract has also been found to help synthesize the SNPs. When the extract is used, the particle sizes in the SNPs are more evenly distributed than when the extract is not used (Khairan and Jalil, 2019).

Certain surfactants have also been reported for their effect on the characteristics of the produced sulfur. For example, Triton X-100 and butanol are effective as surfactants and co-surfactants in forming monoclinic sulfur particles from a sodium polysulfide solution (Soleimani *et al.*, 2013), respectively. The further research of the effects of the surfactants was conducted by modifying sulfur surfaces using water-soluble polyelectrolyte/surfactants (Turganbay *et al.*, 2019). Interestingly, saponin, a natural surfactant extracted from *Acanthe phylum bracteatum*, was also employed in synthesizing monodispersed SNPs (Kouzegaran and Farhadi, 2017). However, all these studies show that reported reaction conditions produce irregularities or spherical sulfur forms.

Meanwhile, the application of elemental sulfur as a catalyst was investigated in several important reactions, such as the oxidative trimerization of phenylacetonitriles (Nguyen and Retailleau, 2019), the coupling of dibenzyl disulfides with amines (Nguyen *et al.*, 2019), the stereo- and regioselective synthesis of heteropropellanes (Nguyen and Retailleau, 2019), and the reduction of hexavalent chromium (Tripathi *et* *al*., 2018). Interestingly, elemental sulfurized graphene was effective for the catalytic reduction of 4-nitrophenol to 4-aminophenol (Wang *et al*., 2014).

Based on the literature review on the importance of alternative synthesis methods in obtaining unique sulfur characteristics, this report proposes another alternative in elemental sulfur synthesis, using *Sapindus rarak* (*S. rarak*) rind extract, that produces cubic sulfur. The proposed alternative may also influence the choice of certain applications. The research is considered important because natural surfactants are continuously being developed to support sustainable chemistry, as natural surfactants are renewable and biodegradable. This is consistent with the principles of green chemistry, especially from two perspectives: whenever it is technically and economically possible, (1) a raw material or feedstock should be renewed instead of depleted, and (2) synthetic methods should be designed to use and make substances that are not harmful to people or the environment.

EXPERIMENTAL SECTION

Dried *S. rarak* fruits were peeled carefully and subsequently subjected to a juice mixture to form a sticky powder, of which 50 g was dispensed into boiled demineralized water (250 mL). The mixture was then heated for 1 h at 80 °C, cooled to room temperature, and slowly filtered to remove unwanted particles using Whatman® No. 1 filter paper. Approximately, 4.8 g of $Na_2S_2O_3$ salt was added to 80 mL of the as-prepared *S. rarak* extract in a beaker, with magnetic stirring subsequently performed for 10 min. The mixture was further stirred for 1 h, after which 150 mL hydrogen chloride (HCl, 10%) was added dropwise to the mixture until fine white particles appeared. Additional stirring was performed for 2 h, and the mixture was left to stand for 24 h to allow the fine sulfur particles to be deposited at the bottom of the beaker. The mixture was then separated using a centrifuge at a speed of 4600 rpm for 15 min before being washed with demineralized water. This process was repeated three times. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) (JEOL JSM 6510 LA), as well as a Fourier-transform infrared (FTIR) spectrometer (Compact FT-IR Alpha 2, Bruker) and an X-ray diffractometer (XRD) (XRD MiniFlex, Rigaku), were used to investigate the crystalline phase, morphology and elemental composition, and functional groups of the produced sulfur.

RESULTS AND DISCUSSIONS

The synthesis of the current sulfur particles was performed using *S. rarak* rinds (**Figure 1a**) and sodium thiosulfate ($Na_2S_2O_3$) (**Figure 1b**). The reaction between the *S. rarak* extract and $Na_2S_2O_3$ solutions was performed in the presence of diluted HCl, which, acting at room temperature without any additional compounds, produced fine yellow particles (**Figure 1c**). This result shows that the presence of the *S. rarak* extract could not prevent the reaction between the precursors, $Na_2S_2O_3$ and HCl. Instead, the presence of the extract made the resulting particles able to retain their particle form and struggle to form agglomerations.

The 2θ and intensity data of the XRD measurement were processed on an XRD diffractogram using Origin-2018 software. The XRD analysis results (**Figure 2**) showed that the peaks generated at 2θ = 15.5°, 23.1°, 25.9°, 27.8°, 28.7°, 34.2°, 42.7°, 51.3°, among others, on the XRD diffractogram of the as-prepared sulfur correspond with the diffraction pattern (Joint Committee on Powder Diffraction Standards, JCPDS No-34-0941) for standard monoclinic phase sulfur (Salem *et al*., 2016) and are consistent with the ICDD PDF card number 00-008-0247 (Suzanowicz *et al*., 2022). Based on the calculation using the XRD software (Integrated X-ray powder diffraction software: Rigaku PDXL2), the crystallite size was 37 nm and the crystallinity was 63%.

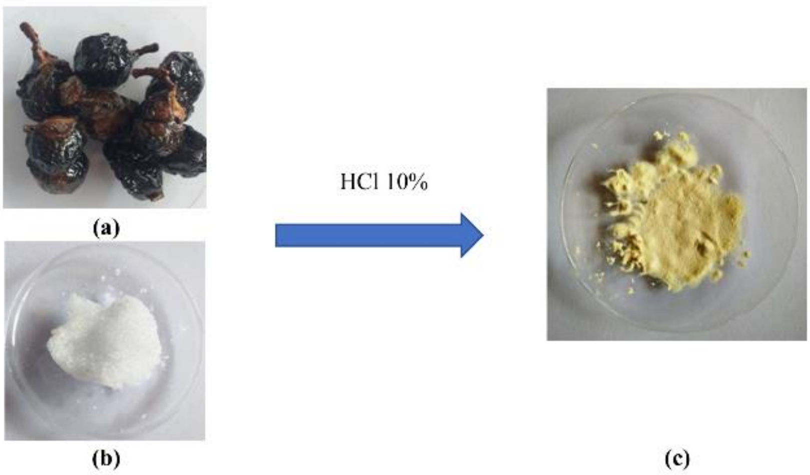


Figure 1. Schematic of sulfur particle synthesis using *S. rarak* rind extract (a) *S. rarak* fruits (b) $Na_2S_2O_3$ precursor (c) Sulfur particles

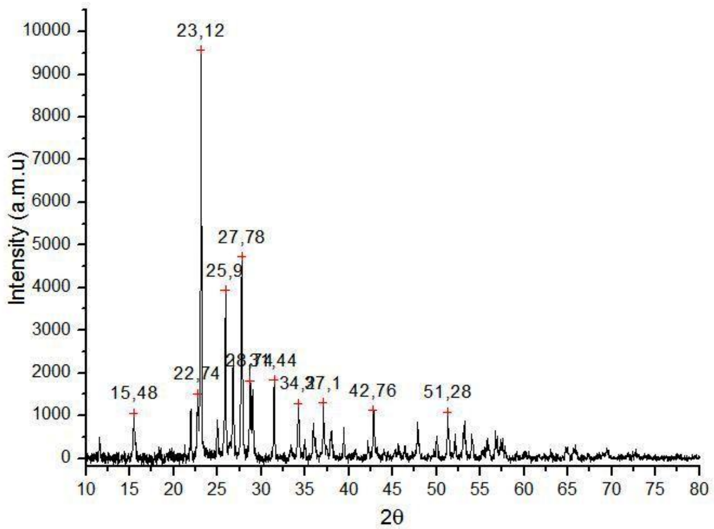


Figure 2. XRD pattern of as-prepared sulfur particles in *S. rarak* aqueous extract.

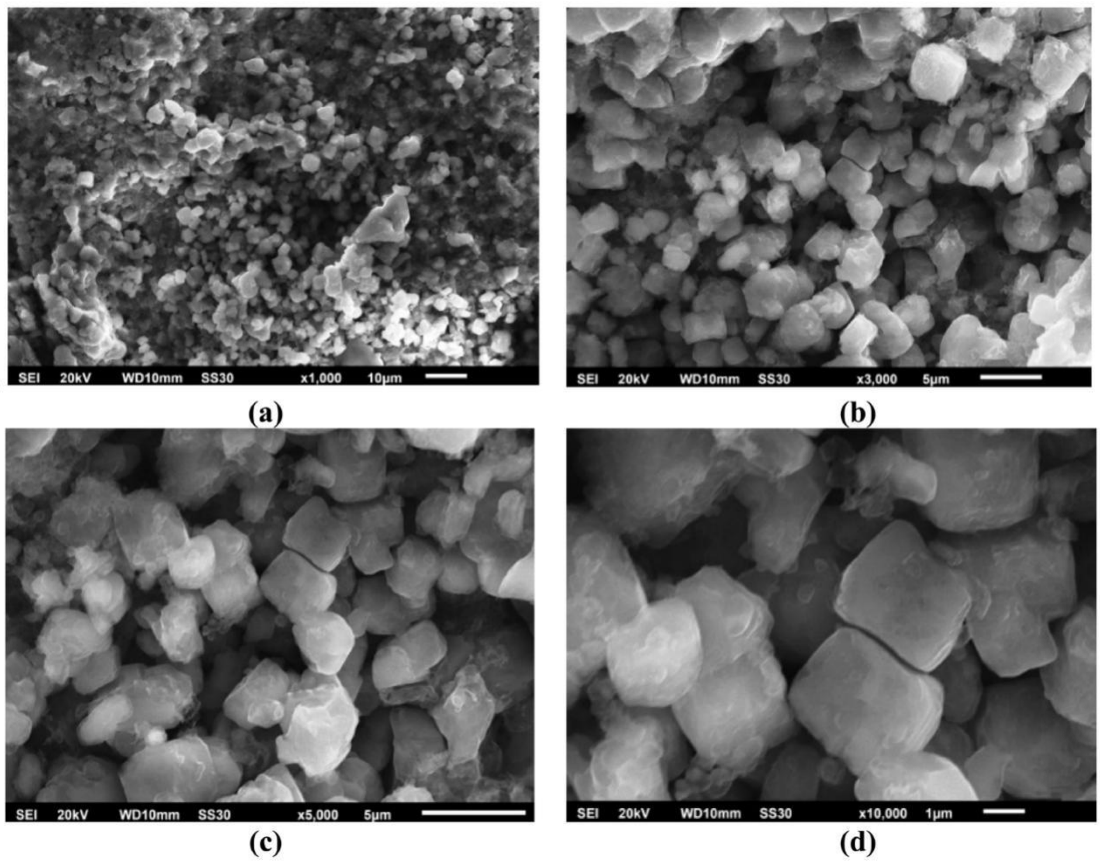


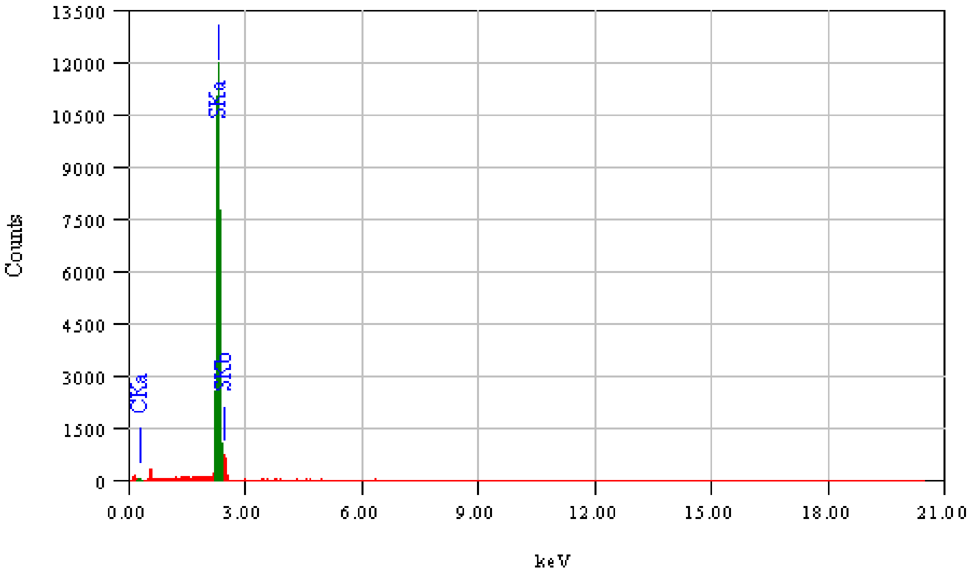
Figure 3. SEM pattern of as-prepared sulfur particles in *S. rarak* aqueous extract

SEM was used to investigate the sulfur morphology that had been obtained. The results are shown in Figure 3, which shows four types of magnification observed under an electron microscope. Figure 3a (magnification 1000×) shows that the sulfur particles are obtained as fine grains, which are difficult to detect and look like a mixture of spheres and other irregular shapes. However, when the observations were enlarged from 3000× to 10,000× (Figure 3b–3d), the results showed the presence of cuboidal sulfur particles. Therefore, Figure 3 shows that the as-prepared sulfur was in cubic form with a particle size of ~3 μm.

These particle forms are different from the reported sulfur, which was synthesized without any additional extract, in which the produced sulfur was not uniform, and the particle size was a bit large (Khairan and Jalil, 2019). Moreover, other studies show that synthetic surfactants, such as Triton X-100, sodium dodecyl sulfate, cetyl trimethylammoniumbromide, and sodium dodecyl benzene sulfonate, play an important role in mediating the formation of the spherical shapes of sulfur products (Chaudury *et al*., 2010). Furthermore, previous studies have explained the formation of the spherical shape of sulfur using other plant extracts that do not specifically contain natural surfactants (Paralikar et al., 2018; Ghotekar *et al*., 2020). Comparing the reported and current results showed that under the current reaction conditions, using the extract of *S. rarak*, which contains natural surfactants, can provide an alternative to obtaining sulfur particles in cubic form.

Further analysis was performed to determine the composition of the obtained products, including some impurities that were possibly attached to the main target material. Therefore, the sample was also subjected to EDX measurement, and the results are shown in **Figure 4**.

Figure 4 shows that the current procedure produces sulfur with high purity, judging by the clean appearance of the sulfur peak in the EDX analysis. However, carbon is also detected in the sample. The carbon could come from compounds in the *S. rarak* rind extract that were possibly attached to the as-prepared sulfur surface. This explanation is supported by other research results that used other plant extracts and found organic molecules in the sulfur product when EDX analysis was performed (Tripathi *et al*., 2018). Further analysis using FTIR spectroscopy afforded a spectrum as shown in **Figure 5**.



Element	K(eV)	% mass
C	0.277	39.58
S	2.307	60.42

Figure 4. EDX pattern and elemental composition of as-prepared sulfur particles in *S. rarak* aqueous extract.

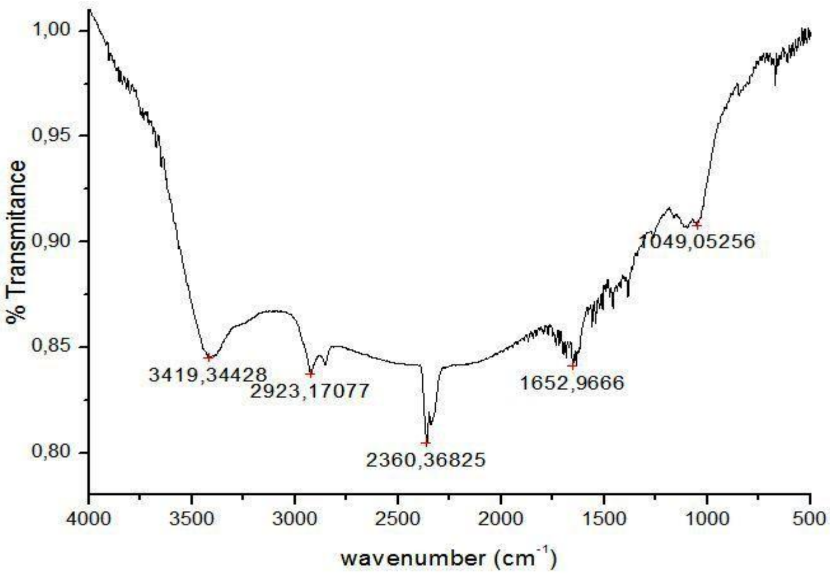


Figure 5. FTIR pattern of as-prepared sulfur particles in *S. rarak* aqueous extract

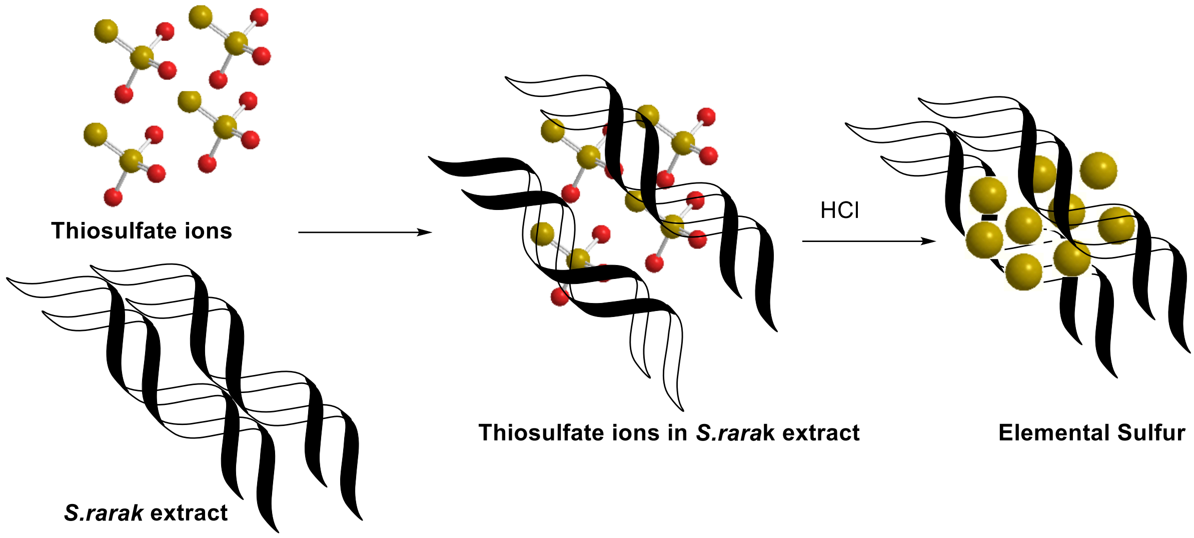


Figure 6. Plausible mechanism of elemental sulfur formation in the presence of *S.rarak* extract

Some peaks are typical for organic molecules (**Figure 5**), which might come from the *S. rarak* extract covering the produced sulfur surface. It is already known that aqueous extracts of *S. rarak* contain saponin-type surfactants (Wisetkomolmat *et al*., 2019; Rai *et al*., 2021). A peak at 3419 cm^{-1} indicated the characteristics of O–H, and that at 2923 cm^{-1} was for C–H. A peak at 1652 cm^{-1} was observed for the C=C functional group, and one at 1049 cm^{-1} was consistent with C–O–C aglycone of sapogenin. These peaks are consistent with the reported FTIR analysis of the *S. rarak* extract 3421, 2934, 1638, and 1047 cm^{-1} for O–H, C–H, C=C, and C–O–C sapogenin, respectively (Aryanti *et al*., 2021). These data confirm that the produced sulfur is still covered by saponin from *S. rarak*. This fact is consistent with the EDX analysis results. The appearance of various small peaks below 1000 cm^{-1} is predicted to correspond to elemental sulfur peaks (He *et al*., 2009; Tripathi *et al*., 2018; Bajpai and Dubey, 2021). Although the FTIR spectrum did not show the sulfur peaks clearly, it should be noted that the current material is elemental sulfur based on the XRD and EDX analyses.

The general reaction of the sulfur formation is shown in equation 1. Furthermore, HCl plays a major role in the disproportionation reaction of $Na_2S_2O_3$ to produce sodium chloride salt, which is soluble in the reaction mixture and partly produces sulfur dioxide gas. Correspondingly, sulfur particles slowly form at the bottom of the reaction vessel. The solid sulfur is separated easily from the reaction mixture using a centrifugation technique.

$$Na_2S_2O_3 + HCl \xrightarrow[S.\ rarak]{\text{Aqueous Extract}} NaCl + SO_2 + H_2O + S\downarrow \quad (1)$$

Although there is no clear evidence for the absolute reaction mechanism, the plausible mechanism of the current reaction was developed following the mechanism inspired by other research results (Tripathi *et al*., 2018; Ghotekar *et al*., 2020) and is summarized as shown in **Figure 6**.

Overall, based on **Figure 6**, the synthesis of elemental sulfur in this study begins with the covering of thiosulfate ions ($S_2O_3^{2-}$) in the solution by organic molecules present in the aqueous extract of *S. rarak*. The presence of HCl in the reaction mixture causes an attack on $S_2O_3^{2-}$ ions, which slowly produces grains of elemental sulfur, and the organic molecules switch from covering the $S_2O_3^{2-}$ to covering the resulting sulfur particles. This covering produces these fine particles, which are thought to produce cuboidal sulfur while simultaneously inhibiting the agglomeration process of these grains so that they remain as fine-sized particles. Saponins and other compounds in *S. rarak* primarily act as capping agents and affect the reaction between $S_2O_3^{2-}$ and dilute HCl. Finally, the reaction system results in the formation of sulfur cubes.

CONCLUSIONS

In this study, the role of *S. rarak* extract in influencing the stability of sulfur particles resulting from the reduction of $Na_2S_2O_3$ using dilute HCl was studied. The presence of the *S. rarak* extract affected the formation process of elemental sulfur in the reaction mixture by covering $S_2O_3^{2-}$ and the produced elemental sulfur. The covering of $S_2O_3^{2-}$ is thought to be one of the steps that affect the direction of the process toward the cube shape of the resulting sulfur. The fact that the obtained material is elemental sulfur was confirmed by XRD analysis and supported by EDX analysis, showing that the current sulfur was incorporated by organic molecules from *S. rarak*. The presence of organic molecules was also confirmed by FTIR analysis. This study found a new way to easily make sulfur cube-shaped.

AKNOWLEDGMENTS

We thank the Department of Chemistry at the Faculty of Mathematics and Natural Sciences of the University of Bengkulu in Indonesia for making it possible for us to do our experiment in the lab that belongs to the department. S.Y.S also gets administrative support from the Research Center of Sumatera Natural Products and Functional Materials (RC-SuNaPFuMa) at University of Bengkulu, Indonesia.

REFERENCES

Araj, S.-E.A., Salem, N.M., Ghabeish, I.H., & Awwad, A.M. (2015). Toxicity of nanoparticles against *Drosophila melanogaster* (Diptera: *Drosophilidae*). *Journal of Nanomaterials*, *2015*, 758132. DOI: https://doi.org/10.1155/2015/758132

Aryanti, N., Nafiunisa, A., Kusworo, T.D., Wardhani, D.H. (2021). Dye solubilization ability of plant derived surfactant from *Sapindus rarak* DC. extracted with the assistance of ultrasonic waves. *Environmental Technology & Innovation*, *22*, 101450. DOI: https://doi.org/10.1016/j.eti.2021.101450

Bajpai, S.K., & Dubey, D. (2021). Removal of oil from oil-in-water emulsion by poly (Sulfur/Soya Bean Oil) composite adsorbent: an equilibrium study. *Journal of Polymers and the Environment, 29*, 2385–2396. DOI: https://doi.org/10.1007/s10924-020-02032-y

Chaudhuri, R.G., Paria, S. (2010). Synthesis of sulfur nanoparticles in aqueous surfactant solutions. *Journal of Colloid and Interface Science*, *343*, 439–446. DOI: https://doi.org/10.1016/j.jcis.2009.12.004

Ghotekar, S., Pagar, T., Pansambal, S., & Oza, R. (2020). A Review on green synthesis of sulfur nanoparticles via plant extract, characterization and its applications. *Advanced Journal of Chemistry, Section B*, *2*(3), 128–143. DOI: https://doi.org/10.22034/AJCB.2020.109501

He, H., Zhang, C.-G., Xia, J.-L., Peng, A.-A., Yang, Y., Jiang, H.-C., Zheng, L., Ma, C.-Y., Zhao, Y.-D., Nie, Z.-Y., & Qiu, G.-Z. (2009). Investigation of elemental sulfur speciation transformation mediated by *Acidithiobacillus* ferrooxidans. *Current Microbiology 58,* ,300–307. DOI: https://doi.org/10.1007/s00284-008-9330-6

Khairan, K., & Jalil, Z.Z. (2019). Green Synthesis of sulphur nanoparticles using aqueous garlic extract (*Allium sativum*). *Rasayan Journal of Chemistry, 12*(1) 50–57. DOI: https://doi.org/10.31788/RJC.2019.1214073

Kouzegaran, V.J., & Farhadi, K. (2017). Green synthesis of sulphur nanoparticles assisted by a herbal surfactant in aqueous Solutions. *Micro & Nano Letters*, *12*(5) 329–334. DOI: https://doi.org/10.1049/mnl.2016.0567

McCue, A.J., & Anderson, J.A. (2014). Sulfur as a catalyst promoter or selectivity modifier in heterogeneous catalysis. *Catalysis Science & Technology*, *4*, 272–294. DOI: https://doi.org/10.1039/c3cy00754e

Nguyen, T.B. (2017). Recent advances in organic reactions involving elemental sulfur. *Advanced Synthesis & Catalysis*. *359*, 1066 –1130. DOI: https://doi.org/10.1002/adsc.201601329

Nguyen, T.B., & Retailleau, P. (2019). Sulfur-promoted DABCO-catalyzed oxidative trimerization of phenylacetonitriles. *Journal of organic chemistry*. *84*, 5907–5912. DOI: https://doi.org/10.1021/acs.joc.9b00408

Nguyen, T.B., Nguyen, L.P.A., & Nguyen, T.T.T. (2019). Sulfur-catalyzed oxidative coupling of dibenzyl disulfides with amines: access to thioamides and aza heterocycles. *Advanced Synthesis & catalysis*, *361*(8), 1787–1791. DOI: https://doi.org/10.1002/adsc.201801695

Nguyen, T.B., & Retailleau, P. (2019). Sulfur-catalyzed stereo and regioselective synthesis of heteropropellanes via oxidative condensation of cyclohexanones with 2-aminophenols. *Advanced Synthesis & catalysis*, *361*(15), 3588–3592. DOI: https://doi.org/10.1002/ADSC.201900436

Paralikar, P., & Rai, M. (2018). Bio-inspired synthesis of sulfur nanoparticles using leaf extract of four medicinal plants with special reference to their antibacterial activity. *IET Nanobiotechnology*, *12*(1), 25-31. DOI: https://doi.org/10.1049/IET-NBT.2017.0079

Ragab, G.A., & Saad-Allah, K.M. (2020). Green synthesis of sulfur nanoparticles using *Ocimum basilicum* leaves and its prospective effect on manganese-stressed *Helianthus annuus* (L.) seedlings. *Ecotoxicology and Environmental Safety, 191*, 110242. DOI: https://doi.org/10.1016/j.ecoenv.2020.110242

Rai, S., Acharya-Siwakoti, E., Kafle, A., Devkota, H.P. & Bhattarai, A. (2021). Plant-derived saponins: a review of their surfactant properties and applications. *Sci*, *3*(4), 44. DOI: https://doi.org/10.3390/sci3040044

Saedi, S., Shokri, M., & Rhim, J.-W. (2020). Antimicrobial activity of sulfur nanoparticles: Effect of preparation methods. *Arabian Journal of Chemistry, 13*, 6580–6588. DOI: https://doi.org/10.1016/j.arabjc.2020.06.014

Salem, N.M., Albanna, L.S., & Awwad, A.M. (2016). Green synthesis of sulfur nanoparticles using *Punica granatum* peel and the effects on the growth of tomato by foliar spray applications. *Environmental Nanotechnology, Monitoring & Management, 6*, 83–87. DOI: https://doi.org/10.1016/J.ENMM.2016.06.006

Salem, N.M., Albanna, L.S., Awwad, A.M., Ibrahim, Q.M., & Abdeen, A.O. (2016). Green synthesis of nano-sized sulfur and its effect on plant growth. *Journal of Agricultural Science, 8*(1), 188–194. DOI: https://doi.org/10.5539/jas.v8n1p188

Suleiman, M., Ali, A.A., Hussein, A., Hammouti, B., Hadda, T.B., & Warad, I. (2013). Sulfur nanoparticles: synthesis, characterizations and their applications. *Journal of Materials and Environmental Science*, *5*(6), 1029–1033

Soleimani, M., Aflatouni, F., & Khani, A. (2013). A New and simple method for sulfur nanoparticles synthesis. *Colloid Journal*, *75*(1) 112–116. DOI: https://doi.org/10.1134/S1061933X12060142

Suzanowicz, A.M., Lee, Y., Lin, H., Marques, O.J.J., Segre, C.U., & Mandal, B.K. (2022). A new graphitic nitride and reduced graphene oxide-based sulfur cathode for high-capacity lithium-sulfur cells. *Energies*, *15*, 702. DOI: https://doi.org/10.3390/en15030702

Tripathi, R.M., Rao, R.P., & Tsuzuki, T. (2018). Green synthesis of sulfur nanoparticles and evaluation of their catalytic detoxification of hexavalent chromium in water. *RSC Adances*, *8*, 36345–36352. DOI: https://doi.org/10.1039/C8RA07845A

Turganbay, S., Aidarova, S.B., Turganbay, G., Tileuberdi, Y., & Sheng-Li Chen. (2019)., Synthesis and characterization of sulfur nanoparticles with WSP/surfactants mixtures. *International Journal of Biology and Chemistry*, *12*(1), 146–152. DOI: https://doi.org/10.26577/ijbch-2019-1-i19

Wang, S., Zhang, J., He, D., Zhang, Y., Xu, H., Wen, X., Ge, H., Zhao, Y., & Wang, L. (2014). Sulfur-catalyzed phase transition in MoS under high pressure and temperature. *Journal of Physics and Chemistry of Solids*, *75*, 100–104. DOI: https://doi.org/10.1021/jp4076355

Wisetkomolmat, J., Suppakittpaisarn, P., & Sommano, S.R. (2019). Detergent plants of Northern Thailand: potential sources of natural saponins. *Resources, 8*(1), 10. DOI: https://doi.org/10.3390/resources8010010