

EXTRACT OF MANGOSTEEN PEEL (*Garcinia mangostana* L.) AS CALCIUM CARBONATE SCALE INHIBITOR

Suharso^{1,✉}, N.M. Chandra², A.A. Kiswandono¹, Tugiyono³ and Buhani¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Lampung, Lampung, Bandar Lampung, Indonesia, 35145

²Undergraduate Student of Chemistry, Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Lampung, Lampung, Bandar Lampung, Indonesia, 35145

³Department of Biology, Faculty of Mathematics and Natural Sciences, University of Lampung, Lampung, Bandar Lampung, Indonesia, 35145

✉Corresponding Author: suharso@fmipa.unila.ac.id

ABSTRACT

In this research, it has been conducted the participation of mangosteen peel (*Garcinia mangostana* L.) extract in the calcium carbonate (CaCO₃) growth solution to a green inhibitor of CaCO₃ scale establishment utilizing unseeded technique at various concentrations of calcium carbonate 0.075, 0.100, and 0.125 M and concentration ranges of inhibitor added were around 0, 50, 150, and 250 ppm. Analysis of functional groups contained in mangosteen peel extract was performed by infrared (IR) spectrophotometer. The result shows that the extract of mangosteen peel may be applied as a green inhibitor to block CaCO₃ scale formation with the highest Inhibitor Effectivity Percent (IEP) in blocking the CaCO₃ deposit formation of 95.68% at the condition of calcium carbonate growth solution of 0.100 M and the mangosteen peel extract concentration added of 250 ppm. The results based on a qualitative analysis using Scanning Electron Microscope (SEM) showed that calcium carbonate size without the addition of inhibitors is bigger than the addition of inhibitors.

Keywords: Calcium Carbonate, Green Inhibitor, Scale Formation, Mangosteen Peel Extract.

RASĀYAN *J. Chem.*, Vol.15, No. 3, 2022

INTRODUCTION

In recent decades, the use of natural materials or biomass for environmental control has increased rapidly. Utilization of natural materials or biomass can be aimed at controlling the disposal of industrial waste from hazardous toxic materials.¹⁻¹⁰ Utilization of natural materials from plant waste can also be intended as a substitute for chemical inhibitors which are toxic to the environment for the prevention of corrosion and inhibition of scale growth of inorganic materials.¹¹⁻¹³ Scale formation in cooling water system pipes is a classic problem that must be overcome.¹⁴⁻²⁰ The impact of this scale formation on the cooling water system pipes can interfere with industrial performance. Industry becomes inefficient because it can break down suddenly. To solve this problem, the researchers took advantage of green inhibitors to inhibit scale growth while maintaining environmental conditions to remain uncontaminated. The most common scale is the calcium carbonate scale. One of the green inhibitors of biomass waste that can be used to overcome the growth of calcium carbonate deposits which disturbs the circulation of the cooling water system in the industry is mangosteen peel waste. Like the green inhibitors of gambir extract, kemenyan extract, and liquid smoke of coconut shell, mangosteen peel extract may be applied as a green inhibitor to block calcium carbonate deposit growth.²¹⁻²⁵ The capability of mangosteen peel extract to prevent the growth of CaCO₃ crystals is because the mangosteen peel extract contains major chemical materials like tannins, phenolic acids, anthocyanins, and xanthenes. For this reason, in this study, the mangosteen peel extract was tested as a green inhibitor to block calcium carbonate deposit growth.²⁶⁻²⁹

EXPERIMENTAL

Materials and Instruments

The materials applied in this experiment were calcium chloride (CaCl₂) anhydrous (Merck, Germany), sodium carbonate (Na₂CO₃) (Merck, Germany), distilled water, filter paper, and the extract of mangosteen

peel. The tools applied for this experiment were glassware, water bath, plastic bottles, universal pH, magnetic stirrer, the analytical balance of the Ainswoth AA-160 brand, optical microscope, and scanning electron microscope (SEM) (JSM-6360la Jeol).

Preparation of Mangosteen Peel Extract

Mangosteen peel extract was made by cutting the peels of the mangosteen fruit which is still wet and then dried for 2 days in the sun, then placed in the oven for 4 hours to obtain a completely dry mangosteen peel. The dried mangosteen peel was ground to produce mangosteen peel powder. The mangosteen peel solution was made with a concentration of 1000 ppm, as much as 1 gram of mangosteen peel powder was immersed with distilled water up to a capacity of 1 liter in a vessel glass. The mixture was blended taking a magnetic stirrer for 2-3 hours at 90 °C and was continued by separating through filter paper. The mangosteen peel extract obtained was identified by using an IR spectrophotometer to recognize the functional groups that existed in the extract.

The Experiment of Mangosteen Peel Extract as Inhibitor to Calcium Carbonate Crystal Growth

The stages to test the mangosteen peel extract as an inhibitor to CaCO₃ crystal growth by the unseeded experiment method was carried out with the following series of experiments:

Determination of Calcium Carbonate Growth Rate without Inhibitors in Different Concentrations of Growth Solution with unseeded Experiment Method

The growth solution was made by dissolving 0.075 M calcium chloride and 0.075 M sodium carbonate each in distilled water to reach a capacity of 200 mL. Each solution was put into a beaker and blended taking a magnetic stirrer for 10-15 minutes at 90 °C to homogenize the solution. Next, the two solutions are mixed and stirred again for 10 minutes at 90 °C. Then, 50 mL of the solution mixture was placed into 6 plastic bottles each and inserted in a water bath for 10 min at 90 °C to attain equilibrium. The observations were carried out every five minutes. Within five minutes, one bottle was taken, the crystal that existed in the solution was separated by filter paper, and the crystals obtained were dried using the oven (105 °C) for 3-4 h. This experiment was repeated with variations in the concentration of calcium chloride and sodium carbonate solutions of 0.100 and 0.125 M. Furthermore, these crystals were weighed to determine the weight of the crystals formed and left to stand for 1 day to see the morphology of the crystals formed.

Determination of Calcium Carbonate Growth Rate with the Addition of Inhibitors in Different Concentrations of Growth Solution with unseeded Experiment Method

The growth solution was made by dissolving 0.075 M calcium chloride and 0.075 M sodium carbonate each in a solution of 50 ppm mangosteen peel extract to reach a volume of 200 mL. Each solution was put into a beaker and blended taking a magnetic stirrer for 10-15 minutes at 90 °C to homogenize the solution. Next, the two solutions were blended and mixed by a magnetic stirrer for 10 min at 90 °C. The homogenous solution obtained was put in 6 plastic bottles of 50 mL each, and inserted in a water bath (90 °C) for 10 min to attain equilibrium. Observations were carried out every five minutes. Within five minutes, one bottle was taken and the solution mixture contained in the bottle was filtered by filter paper. The crystal obtained was cleaned with water and dried in an oven for 3-4 hours at 105 °C. This experiment was repeated with variations in the concentration of calcium chloride and sodium carbonate solutions of 0.075, 0.100, and 0.125 M and various inhibitor concentrations of 0, 50, 150, and 250 ppm. Furthermore, the washed and dried crystals were weighed to determine the weight of the crystals formed and analyzed using SEM.

Data Analysis

The data resulted was analyzed by Microsoft Excel to identify the growth rate of calcium carbonate with or without the addition of mangosteen peel extract. The CaCO₃ crystal morphology in the absence and in the existence of mangosteen peel extract was characterized using SEM.

RESULTS AND DISCUSSION

Analysis of Mangosteen Peel Extract using Infrared (IR) Spectrophotometer

Analysis using an IR spectrophotometer serves to find out what functional groups are contained in the extract of mangosteen peel. Fig.-1(a) is an IR spectrum obtained for mangosteen peel extract. Before analyzing using an IR spectrophotometer, the solution of mangosteen peel extract measured the acidity

value using a universal pH and obtained a pH value of mangosteen peel extract of 5 indicating acidic solution can increase the solubility of calcium carbonate crystal. Some absorption bands that appear on the IR spectrum of Fig.-1(a) can indicate the existence of organic functional groups which are components in the extract of mangosteen peel. Based on the IR spectrum from Fig.-1(a), it exhibits the presence of a hydroxyl group (-OH) which appears in the area of 3410.15 cm^{-1} with a wide intensity. This group indicates the existence of tannic acid (tannin) as the major component of mangosteen peel extract. Wave number from the absorption band at 2924.09 cm^{-1} with sharp intensity represents the existence of aromatic C-H functional groups. These aromatic compounds come from the chemical content in the peel of the mangosteen fruit, such as tannins or catechins, flavonoids, and xanthenes, which mostly contain aromatic functional groups. The presence of this organic component is also reinforced by the emergence of the peak at 1056.99 cm^{-1} . The peak appears as a sign of the presence of a secondary alcohol C-O group. The presence of carboxylic acids indicates a solid, extensive band for the O-H stretch. The carboxylic acid O-H stretch emerges as a very extensive band in the range of $3200\text{-}2700\text{ cm}^{-1}$, concentrated at around 2900 cm^{-1} . This indicates the existence of protocatechuic acid (3,4-dihydroxybenzoic acid) in the mangosteen peel extract.³⁰ When compared with the IR spectrum of areca nut seeds (*Areca catechu*, L), it may be deduced that mangosteen peel extract contains chemical substances such as tannin, flavonoids, xanthenes, protocatechuic acid, and others as similar results found by Suttirak & Manurakchinakorn.³⁰ This can be seen from several peaks which appear as characteristics of each group contained in the compound. The IR spectrum of areca nut seed extract is shown in Fig.-1(b).

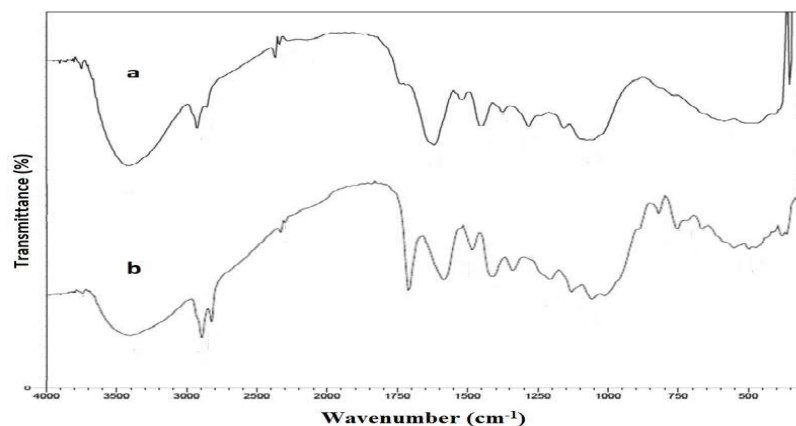


Fig.-1: IR Spectrum of (a) Mangosteen Peel Extract (b) Tannic Acid from Areca Nut Seeds

Crystallization Experiment

The crystal growth rate of calcium carbonate is influenced by several factors, such as growth solution concentration, inhibitor concentration, growth time, temperature, and pressure. It is known that the pH of the sodium carbonate solution at 0.075 M is 11 while the pH of the calcium chloride solution at 0.075 M is 5 before heating. After that, the calcium carbonate mixture solution formed which has been heated has a pH value of 11, as it is known that the raising in the growth rate of calcium carbonate crystals occurs at alkaline pH. In this study, the CaCO_3 crystal growth rate was only seen from the concentration of growth solution, inhibitor concentration, and growth time. Fig.-2 is a graph comparing the CaCO_3 crystal growth rates versus various growth solution concentrations in the absence of inhibitors. In Fig.-2, it may be seen that the growth pattern of CaCO_3 crystal nuclei with a concentration of calcium carbonate growth media of 0.075; 0.100; and 0.125 M has different growth rates with a growth time of 15, 20, 25, 30, 35, and 40 minutes. Based on the graph, it is concluded that the rate of crystal growth is in line with the rise in the concentration of the growth solution.

In this study, observations were made on the CaCO_3 crystal growth rate by adding an inhibitor of mangosteen peel extract at varying concentrations of 0, 50, 150, and 250 ppm in growth solutions of calcium carbonate with variations in the concentration of 0.075, 0.100, and 0.125 M at $90\text{ }^\circ\text{C}$ with the method without the addition of crystal seeds (unseeded experiment) as shown in Figs.-3, 4, and 5. The produced data represent that mangosteen peel extract could block the calcium carbonate crystal growth. The existence

of the inhibitor concentration added to the calcium carbonate growth solution was able to increase the inhibitor's ability in deterring the growth of CaCO_3 precipitation. The percentage value of the effectiveness of the inhibitor (IEP) of mangosteen peel extract in deterring the growth of CaCO_3 precipitation may be computed using the following Equation-1: The IEP data obtained can be seen in Tables-1, 2, and 3.

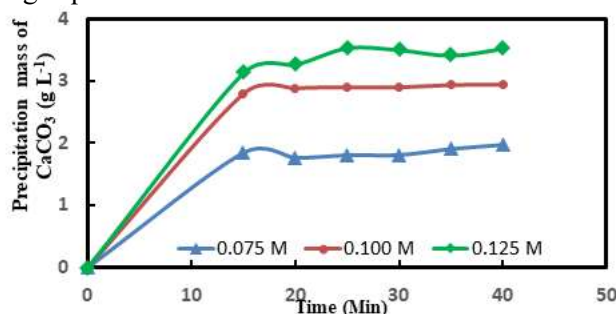


Fig.-2: Precipitation Mass of Calcium Carbonate versus Time at Different Growth Solution Concentrations

The ability of the mangosteen peel extract inhibitor to hinder CaCO_3 scale growth was obtained in the range of 66-96% (Table-1 and 2) relying on the inhibitor concentration added and the concentration of calcium carbonate growth solution. Generally, the ability of the inhibitor from natural ingredients is directly proportional to the inhibitor concentration added. However, the ability of the inhibitor decreases as the concentration of the growth solution increases. This was also found in several previous studies.³¹⁻³³

$$\text{Inhibitor Effectivity Percent (IEP)} = 100\% \times (C_a - C_b) / (C_0 - C_b)$$

Where:

IEP = Inhibitor Effectivity Percent (%)

C_a = crystal weight in the presence of inhibitor at equilibrium (g L^{-1})

C_b = crystal weight in the absence of inhibitor at equilibrium (g L^{-1})

C_0 = initial crystal weight (g L^{-1})

To visually prove the ability of mangosteen peel extract to inhibit CaCO_3 scale growth, the CaCO_3 crystals gained were investigated by SEM (Fig.-6). The images point out that there is no significant morphological change in calcium carbonate crystals (Fig.-6b). However, in general, the CaCO_3 crystal size decreased in the presence of mangosteen peel extract. Based on this fact, the dominant inhibitory mechanism that occurs is the threshold inhibition mechanism where the inhibitor plays a role in increasing the solubility rate of CaCO_3 in solution so that the amount of CaCO_3 deposits formed is less. This fact is also shown from the data on the growth kinetics of CaCO_3 crystals shown in Figs.-2, 3, and 4. The inhibition mechanism by complex formation between inhibitor compounds and calcium ions can also occur in the presence of a threshold inhibition mechanism. In the chelate formation mechanism, the inhibitor binds to cationic species (calcium ions) to react with carbonate ions. The effect of the complex formation mechanism also results in increased solubility of calcium carbonate in solution so that scale formation is inhibited. Observing the change in the morphology of CaCO_3 crystals, the crystal distortion mechanism in this case also had an effect on the presence of mangosteen peel extract on the growth of calcium carbonate crystals.

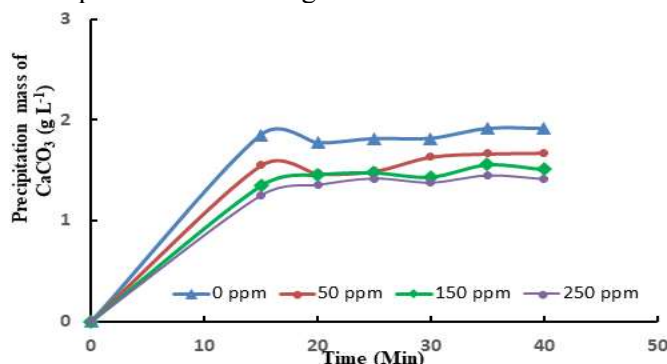


Fig.-3. Graph of Calcium Carbonate Crystal Growth with Inhibitor at 0.075 M

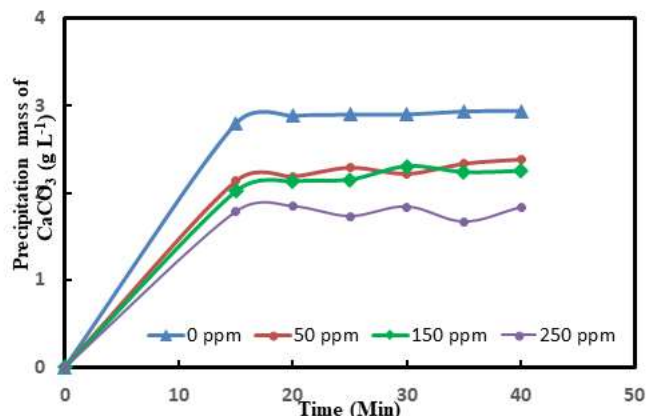


Fig.-4. Graph of Calcium Carbonate Crystal Growth with Inhibitor at 0.100 M

According to the investigation by SEM (Fig.-6), the change in surface morphology of CaCO_3 crystals at a concentration of 0.075 M in the unseeded experiment method in the absence of mangosteen peel extract looks cleaner than in the presence of 150 ppm of mangosteen peel extract. The surface of CaCO_3 crystals in the existence of inhibitor looks damaged. From these results, it can also be seen that the CaCO_3 crystals without inhibitors look thicker and bigger than the CaCO_3 crystals that have been added to the mangosteen peel extract to be smaller in size.

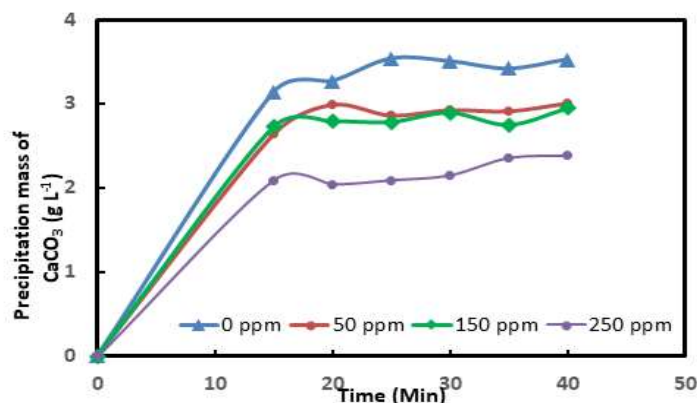


Fig.-5: Graph of Calcium Carbonate Crystal Growth with Inhibitor at 0.125 M

Table-1: Inhibitor Effectivity Data at 0.075 M

No.	Inhibitor added (ppm)	Inhibitor Effectivity (%)
1	0	0
2	50	65.75
3	150	71.17
4	250	75.53

Table-2: Inhibitor Effectivity Data at 0.100 M

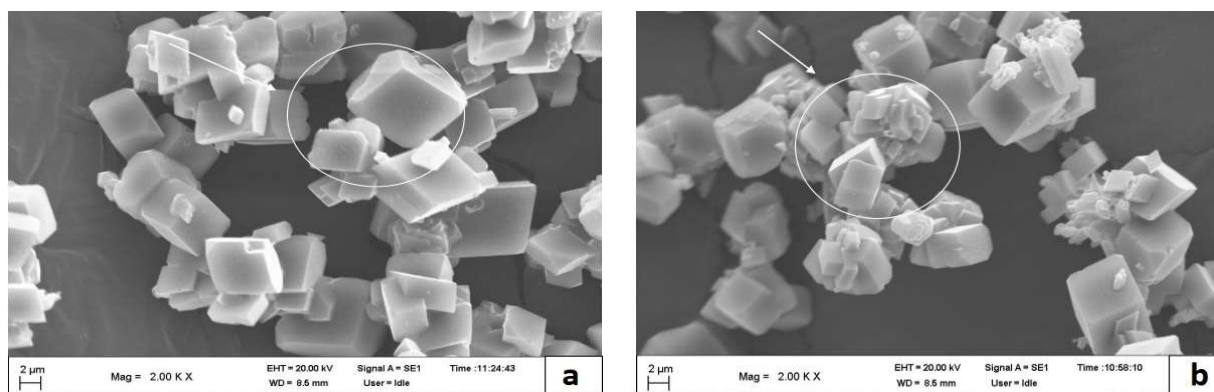
No.	Inhibitor added (ppm)	Inhibitor Effectivity (%)
1	0	0
2	50	69.08
3	150	74.62
4	250	95.68

This is because the surface of the crystals added to the inhibitor occurs by the adsorption process by molecules or organic groups conceived in the mangosteen peel extract against the CaCO_3 crystal surface.¹⁴⁻¹⁶ The results of these observations indicate that the existence of mangosteen peel extract may function as an inhibitor. This can be explained by the concentration of Ca^{2+} in the CaCO_3 crystal without the addition

of an inhibitor, the concentration of Ca^{2+} metal contained in the CaCO_3 crystal is greater so that when the crystal is fired by electron radiation, the crystal produces a clearer image and the morphology is denser. In CaCO_3 crystals whose growth has been inhibited by inhibitors of mangosteen peel extract shows a fairly clear image and the morphology is smaller and brittle, this is due to the reduced concentration of Ca^{2+} metal in CaCO_3 crystals due to the bond between Ca^{2+} metal and several active groups of chemical materials conceived in mangosteen peel extract. In addition, CaCO_3 crystals with a lower concentration of Ca metal when fired by electron radiation rays produce images and morphology that are quite changed.

Table-3: Inhibitor Effectivity Data at 0.125 M

No.	Inhibitor added (ppm)	Inhibitor Effectivity (%)
1	0	0.00
2	50	58.24
3	150	72.32
4	250	79.89

Fig.-6: The CaCO_3 Crystal at a Concentration of 0.075 M (a) with Inhibitor and (b) without Inhibitor

CONCLUSION

Mangosteen peel extract could be utilized as an inhibitor to prevent the shaping of CaCO_3 crystal growth. The inhibitor effectivity of mangosteen peel extract in preventing the shaping of CaCO_3 crystal growth is approximately 58-96 % depending on the concentration of calcium carbonate growth solution and added inhibitor concentration. In general, the crystal sizes of calcium carbonate in the participation of mangosteen peel extract are smaller than in the absence of mangosteen peel extract based on SEM analysis.

ACKNOWLEDGEMENT

Many thanks to the Ministry of Education, Culture, Research, and Technology, Republic of Indonesia, and the Institute of Research and Community Service-University of Lampung for supporting this project.

REFERENCES

1. V. Ramya, D. Murugan, C. Lajapathirai, P. Saravanan, and A. Sivasamy, *Journal of Environmental Chemical Engineering*, **7**, 1(2019), <https://doi.org/10.1016/j.jece.2018.11.043>
2. Buhani, Suharso, I. Aditiya, R.A. Kausar, Sumadi, and Rinawati, *Sustainable Environment Research*, **29**, Article 27, (2019), <https://doi.org/10.1186/s42834-019-0027-2>
3. N. Singh, and C. Balomajumder, *Journal of Water Process Engineering*, **9**, 233(2016), <https://doi.org/10.1016/j.jwpe.2016.01.008>
4. Buhani, Rinawati, Suharso, D.P. Yuliasari, and S.D. Yuwono, *Desalination and Water Treatment*, **80**, 203(2017), <https://doi.org/10.5004/dwt.2017.20932>
5. L.R. Martins, J.A.V. Rodrigues, O.F.H. Adarme, T.M.S. Melo, L.V.A. Gurgel, and L.F. Gil, *Journal of Colloid and Interface Science*, **494**, 223(2017), <https://doi.org/10.1016/j.jcis.2017.01.085>
6. Buhani, Suharso, M. Rilyanti, M. Sari, and Sumadi, *Desalination and Water Treatment*, **218**, 352(2021), <https://doi.org/10.5004/dwt.2021.26978>

7. Suharso and Buhani, *Asian Journal of Chemistry*, **23(3)**, 1112(2011)
8. Buhani, F. Hariyanti, Suharso, Rinawati, and Sumadi, *Desalination and Water Treatment*, **142**, 331(2019), <https://doi.org/10.5004/dwt.2019.23533>
9. R.V. Kandisa, N. Saibaba KV, K.B. Shaik and R. Gopinadh, *Rasayan Journal of Chemistry*, **14(3)**, 1528(2021), <https://doi.org/10.31788/RJC.2021.1436307>
10. Buhani, Suharso, and Sumadi, *Asian Journal of Chemistry*, **24(1)**, 133(2012)
11. H. Wang, M. Gao, Y. Guo, Y. Yang, and R. Hu, *Desalination*, **398**, 198(2016), <https://doi.org/10.1016/j.desal.2016.07.035>
12. M.K. Nayunigari, A. Maity, S. Agarwal, and V.K. Gupta, *Journal of Molecular Liquids*, **214**, 400(2016), <https://doi.org/10.1016/j.molliq.2015.11.034>
13. S. Jyothi, K. Rathidevi, D. Jalajaa, and P.S. Ratnakumar, *Rasayan Journal of Chemistry*, **12**, 272(2019), <https://doi.org/10.31788/RJC.2019.1214097>
14. Suharso, Buhani, S.D. Yuwono, and Tugiyono, *Desalination and Water Treatment*, **68**, 32(2017), <https://doi.org/10.5004/dwt.2017.20311>
15. Suharso, M. Padli, Tugiyono and Buhani, *Rasayan Journal of Chemistry*, **14(1)**, 141(2021), <https://doi.org/10.31788/RJC.2021.1415947>
16. G. Liu, M. Xue, and H. Yang, *Desalination*, **419**, 133(2017), <https://doi.org/10.1016/j.desal.2017.06.017>
17. Suharso, Buhani, T. Suhartati, *Indonesian Journal of Chemistry*, **9**, 206(2009), <https://doi.org/10.22146/ijc.21531>
18. R. Menzri, S. Ghizellaoui, and M. Tlili, *Desalination*, **404**, 147(2017), <https://doi.org/10.1016/j.desal.2016.11.005>
19. Suharso, Buhani, and L. Aprilia, *Asian Journal of Chemistry*, **26**, 6155(2014), <https://doi.org/10.14233/ajchem.2014.16899>
20. H. Zhang, X. Luo, X. Lin, P. Tang, X. Lu, M. Yang, and Y. Tang, *Desalination*, **381**, 1(2016), <https://doi.org/10.1016/j.desal.2015.11.029>
21. Suharso, Buhani, S. Bahri, and T. Endaryanto, *Desalination*, **265**, 102(2011), <https://doi.org/10.1016/j.desal.2010.07.038>
22. Suharso, T. Reno, T. Endaryanto, and Buhani, *Journal of Water Process Engineering*, **18**, 1(2017), <https://doi.org/10.1016/j.jwpe.2017.05.004>
23. Suharso, Buhani, H.R. Utari, Tugiyono, and H. Satria, *Desalination and Water Treatment*, **169**, 22(2019), <https://doi.org/10.5004/dwt.2019.24664>
24. Suharso, N.A. Sabriani, Tugiyono, Buhani, T. Endaryanto, *Desalination and Water Treatment*, **92**, 38(2017), <https://doi.org/10.5004/dwt.2017.21478>
25. Suharso, E. Setiososari, A.A. Kiswandono, Buhani, and H. Satria, *Desalination and Water Treatment*, **92**, 29(2017), <https://doi.org/10.5004/dwt.2019.24707>
26. W. Pothitirat, M.T. Chomnawang, R. Supabphol, and W. Gritsanapan, *Fitoterapia*, **80**, 442(2009), <https://doi.org/10.1016/j.fitote.2009.06.005>
27. R. Zadernowski, S. Czaplicki, and M. Naczka, *Food Chemistry*, **112**, 685(2009), <https://doi.org/10.1016/j.foodchem.2008.06.030>
28. Y. Palapol, S. Ketsa, D. Stevenson, J.M. Cooney, A.C. Allan, and I.B. Ferguson, *Postharvest Biology and Technology*, **51**, 349(2009), <https://doi.org/10.1016/j.postharvbio.2008.08.003>
29. A.S. Zarena, and S.K. Udaya, *Journal of Natural Products*, **2**, 23(2009)
30. W. Suttirak, and S. Manurakchinakorn, *Journal of Food Science and Technology*, **51(12)**, 3546 (2012), <https://doi.org/10.1007/s13197-012-0887-5>
31. H. Zahlan, W.S. Saeed, R. Alrasheed, N.M. Alandes, and T. Aouak, *Materials*, **12(22)**, 3800(2019), <https://doi.org/10.3390/ma12223800>
32. G. Liu, M. Xue, Q. Liu, and Y. Zhou, *Clean Technologies and Environmental Policy*, **19**, 917(2017), <https://doi.org/10.1007/s10098-016-1258-0>
33. G. Liu, M. Xue, Q. Liu, Y. Zhou, and J. Huang, *Tenside Surfactants Detergents*, **53(3)**, 235(2016), <https://doi.org/10.3139/113.110428>

[RJC-6910/2021]