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# A COMPARISON OF THE EFFECTIVENESS OF ONE AND TWO STAGES, THE PRECIPITATION METHOD IN THE PURIFICATION PROCESS OF SALT SOLUTION

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## ABSTRACT

A comparison of the effectiveness in the purification process of salt solution investigates using one-stage and two-stage two methods for the precipitation of removal of sulfate ($SO_4^{2-}$), calcium ($Ca^{2+}$), and magnesium ($Mg^{2+}$) ions. The concentration of three ions in 27 - 30 % w/v salt solution was determined before and after purification. The sulfate ion levels were measured using a UV-Vis Spectrophotometer, while calcium and magnesium ions used Induced Coupled Plasma (ICP). Apart from that, NaCl levels were also measured using Argentometric titration. The removal of three ions at one stage of the precipitation process was examined using 20 % w/v barium chloride ($BaCl_2$), 20 % w/v sodium hydroxide (NaOH), and 20 % w/v sodium carbonate ($Na_2CO_3$), successively and after 12 hours left the mixture was separated by the filtering process. Meanwhile, the removal of ions at two stages of the precipitation process is divided into two-step precipitation processes. The first process was examined by precipitation of $SO_4^{2-}$ and $Mg^{2+}$ ions using 20 % w/v $BaCl_2$ and 20 % w/v NaOH successively, and after 12 hours, the mixture was separated by a filtering process. The second process was studied by precipitation of $Ca^{2+}$ ion using 20 % w/v $Na_2CO_3$, and after 12 hours, the mixture was separated by the filtering process again. The result showed that adding $BaCl_2$, NaOH, and $Na_2CO_3$ solution in two kinds of process could decrease ions concentration. The concentration of $SO_4^{2-}$, $Mg^{2+}$, and $Ca^{2+}$ ions after purification by one-stage precipitation process are 446.67 ppm, 7.00 ppm, and 14.33 ppm, respectively, while the concentration of $SO_4^{2-}$, $Mg^{2+}$, and $Ca^{2+}$ ions after purification by two-stage of precipitation process are 5.83 ppm, 5.67 ppm, and 15.00 ppm, respectively. The result demonstrated that using two stages of the purification process can decrease $SO_4^{2-}$ ion in salt solution more effectively because the salting-in effect of barium sulfate ($BaSO_4$) precipitates in brine and $Na_2CO_3$ solution has not occurred.

**Keywords**: Effectiveness, One and Two Stages, Purification, Removal of Ions, Salt Solution
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## INTRODUCTION

Sodium Chloride (NaCl) is a strategic commodity. In the chemical industry, salt is the primary raw material for the production of chlorine gas ($Cl_2$), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium sulfate ($Na_2SO_4$), sodium carbonate ($Na_2CO_3$), and sodium bicarbonate ($NaHCO_3$).[1] Some types of salt suitable for use are analytical grade salt, pharmaceutical salt, miscellaneous salt, industrial salt, consumption salt, and salts for making salted fish-tanning skin.[2,3] Analytical grade salt is high-purity with a 99.5 - 100.5% NaCl content and a low concentration of other compounds. The salt is widely used for laboratory purposes, such as chemical reagents, standard solutions, and microbiological media. Analytical grade salt specifications refer to Sigma Aldrich, Merck, and Fisher Scientific standards. Meanwhile, pharmaceutical salt is used in the pharmaceutical industry to manufacture cosmetics and solutions for injection. Table-1 shows NaCl, calcium, magnesium, sulfate, and water quality requirements for analytical grade and pharmaceutical salt.[4,5]
Generally, to increase salt quality, it is necessary to have the stages of the purification process to increase NaCl content and reduce impurities of ions such as $SO_4^{2-}$, $Mg^{2+}$, $Ca^{2+}$, and $K^+$. Several studies have been investigated to improve the quality of salt using precipitation with NaOH, $Na_2CO_3$, and poly aluminium chloride[6], hydro extraction[7,8], coagulation process [9-12], HDPE membrane [13], and greenhouse prism[14], evaporation and purification with recrystallization and chemical methods by the addition of chemicals $Ca(OH)_2$, NaOH, and $Na_2CO_3$[15], separation and purification from desulfurization wastewater of thermal power plantE3S[16] but the results are only able to produce industrial and food-grade salt. Generally, analytical grade and pharmaceutical NaCl production require a purification process technology commonly carried out by precipitation and ion exchange methods.


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Table-1: The Quality of Requirements for Analytical Grade and Pharmaceutical Salt

| Parameter | Analytical | Pharmaceutical |
|---|---|---|
| NaCl, % | 99.50 – 100.50 | 99.50 – 100.50 |
| Magnesium and alkaline-earth metals calculated as Ca, ppm | < 100 | < 100 |
| Sulfate, ppm | < 10 | < 200 |
| Calcium, ppm | < 20 | < 50 |
| Magnesium, ppm | < 10 | < 50 |
| Potassium, ppm | < 50 | < 500 |
| Water content, % | 0.50 | 0.50 |

The salt of analytical grade and pharmaceutical products were also investigated using precipitation and partial crystallization process from "garam krosok" as raw material.[17] In the production process of both salts studied previously, the purification process for removing the calcium, magnesium, and sulfate impurity ions is carried out using a one-stage precipitation method. In the process, it turned out that there were still obstacles. An increase in sulfate levels returns to the purified solution after the storage, filtering process, and final product. The phenomenon is presumably due to the redissolving barium sulfate precipitate during storage. Therefore, in this research, sulfate, calcium, and magnesium content has been evaluated in the salt purification process using two methods of precipitation processes, namely one-stage and two-stage precipitation, respectively. The research objective is to obtain the best and most efficient purification process and improve the existing purification process.

## EXPERIMENTAL

### Materials

The raw and refining materials consist of crude salt, namely "garam krosok," industrial-grade of $Na_2CO_3$ (PT. Brataco), industrial-grade of NaOH (PT Asahi Mas Indonesia), industrial-grade of 32% HCl (PT. Asahi Mas Indonesia), industrial-grade of $BaCl_2$ (from China). While the materials for analysis include $AgNO_3$ p.a (Merck), NaCl p.a. (Merck), $K_2CrO_4$ p.a (Merck), Na-EDTA p.a. (Merck), EBT indicator (Merck), murexide indicator (Merck), 36% w/v HCl p.a. (Merck), NaOH p.a. (Merck), blue thymol bromine indicator (Merck), $NH_4OH$ pa. (Merck), $NH_4Cl$ p.a (Merck), $Na_2SO_4$ p.a. (Sigma - Aldrich), $BaCl_2$ p.a. (Merck), oxalic acid p.a. (Merck).

### Instrument

Equipment used in the research included an Inductively Coupled Plasma (ICP) for calcium and magnesium content analysis, a UV-Vis spectrophotometer for sulfate content analysis, and laboratory glassware, such as burettes, volumetric flasks, and volumetric pipettes for analyzing NaCl content through Argentometric titration.

### Purification Process

The purification stages for this process will be used as follows: (a) crude salt was dissolved with water to obtain a brine solution with NaCl content of about 27 – 30 % w/v; (b) the brine solution was then filtered to remove insoluble impurities; (c) analysis of NaCl, $SO_4^{2-}$, $Mg^{2+}$, and $Ca^{2+}$ content is carried out on the sample of the initial brine solution; (d) purification and filtering process; (e) analysis of NaCl, $SO_4^{2-}$, $Mg^{2+}$, and $Ca^{2+}$ content is carried out on the sample of the brine solution after the purification and filtering stages, (f) crystallization, and (g) separation and drying process, (h) analysis of NaCl, $SO_4^{2}$, $Mg^{2+}$, and $Ca^{2+}$ content is carried out on the sample of NaCl product. The purification process is carried out by precipitation of sulfate ions using 20 % w/v $BaCl_2$ solution, magnesium ions using 20 % w/v NaOH solution, and calcium ions using 20 % w/v $Na_2CO_3$ solution by two different purification processes, namely one stage and two stages processes precipitation, respectively. The detailed stages of the two purification methods are shown in Fig.-1 and Fig.-2.

## RESULTS AND DISCUSSION

### Analysis of Salt Raw Material and 30% of Salt Solution

Analysis of the content of impurity ions in salt raw material is needed to assess the concentrations of chemicals required during the refining process. Table-2 shows the analysis results of the NaCl content and the main impurities of the salt raw material.

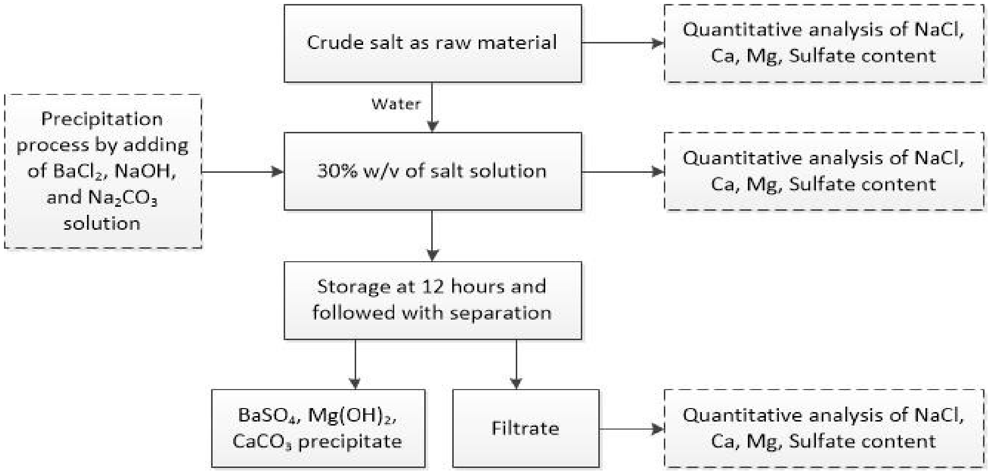


Fig.-1: Schematic Diagram of Purification by One Stage of Precipitation

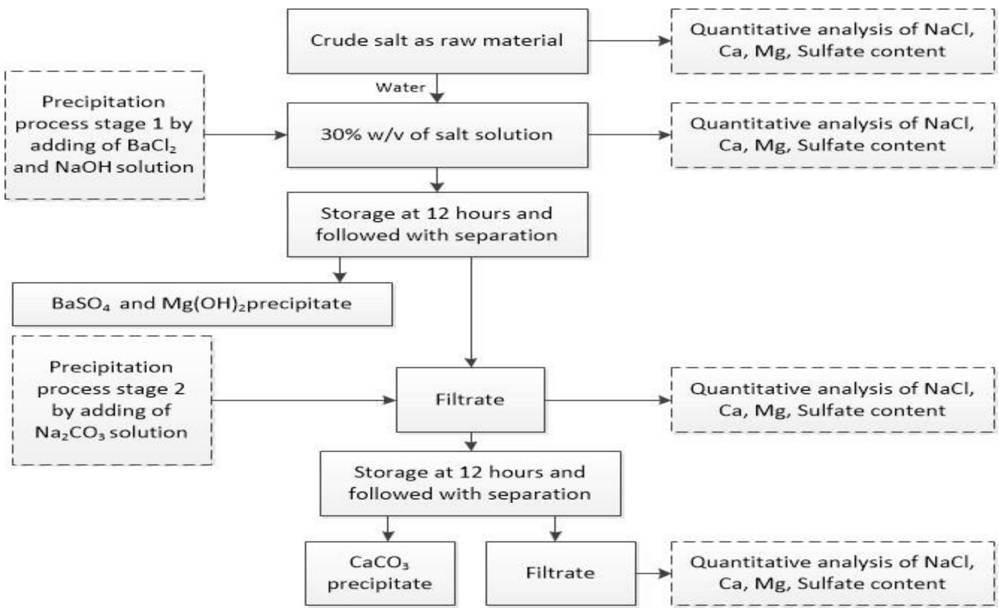


Fig.-2: Schematic Diagram of Purification by Two Stages of Precipitation

Table-2: The Results of the Analysis of the Raw Materials Salt

| Test Parameter | Unit | Test Results |
|---|---|---|
| Shape, color, taste, and appearance | - | Medium to large solid crystals, cube-shaped, dull-white, salty |
| Solubility | - | Soluble in water, a small part of water-insoluble, turbid solution |
| Identification | - | Show reaction with the sodium and chloride ion test |
| NaCl | % | 87.30 |
| Calcium (Ca) | ppm | 3,100 |
| Magnesium (Mg) | ppm | 755 |
| Sulfate ($SO_4^{2-}$) | % | 1.20 |
| Water content | % | 7.45 |
| Insoluble water content | % | 1.50 |

The results show that raw salt materials have 88.50% NaCl content. The content of impurities in calcium, magnesium, and sulfate is high. This result indicates that the raw material still has a low NaCl content and high impurities. The content of insoluble impurities and water is low to facilitate the separation of contaminants during the filtering process to get a clear salt solution. For industrial salt production (CAP quality, pharmaceutical, and pro analysis), the higher the NaCl content and the lower the impurity compound in salt raw material will be advantageous because the less material needed for the refining process and the higher the product yield produced. The salt is dissolved in water to obtain a salt solution with a concentration of about 27 - 30% w/v. Table-3 shows the results of testing several main parameters of the salt solution.

Table-3: Analysis Results of a 27 % w/v Salt Raw Material Solution

| Test Parameter | Unit | Test Results |
|---|---|---|
| Clarity of solution in water | - | The solution is turbid and contains insoluble impurities |
| Identification | - | Show reaction with the sodium and chloride ion test |
| NaCl | gram/L | 270 |
| Calcium | ppm | 1,050 |
| Magnesium | ppm | 280 |
| Sulfate | ppm | 3,500 |
| Barium | qualitative | Negative |
| pH | - | 7.00 |

Table-4 shows the result analysis of the brine solution after the purification process with one stage of the precipitation method. The purification results with one-stage precipitation showed that calcium, magnesium, and sulfate content had decreased during the precipitation process with concentrations of 8 ppm, 13.33 ppm, and 7.33 ppm, respectively. Figure-3 shows the sulfate, calcium, magnesium, and NaCl content after 12 hours of storage in one precipitation stage. However, the sulfate content in the brine solution increased to 446.67 ppm after being stored for 12 hours and the filtration process, while the calcium and magnesium ion content did not show changes. This result was studied at three replications with no different content, so the results were considered valid.

Table-4: Result Analysis of Brine Solution After Purification by one Stage of Precipitation

| Sample | Test parameter | Batch 1 | Batch 2 | Batch 3 | Average | SD |
|---|---|---|---|---|---|---|
| Brine solution after precipitation | Sulfate, ppm | 10 | 6 | 8 | 8.00 | 2.00 |
| | Calcium, ppm | 15 | 10 | 15 | 13.33 | 2.89 |
| | Magnesium, ppm | 5 | 8 | 9 | 7.33 | 2.08 |
| | NaCl, % gram/L | 265 | 260 | 268 | 264.33 | 4.04 |
| Brine solution after storage at 12 h and filtration of the precipitate | Sulfate, ppm | 430 | 450 | 460 | 446.67 | 15.28 |
| | Calcium, ppm | 15 | 10 | 18 | 14.33 | 4.04 |
| | Magnesium, ppm | 5 | 6 | 10 | 7.00 | 2.65 |
| | NaCl, % gram/L | 260 | 255 | 260 | 258.33 | 2.89 |
| Salt product | Sulfate, ppm | 200 | 250 | 210 | 220.00 | 26.46 |
| | Calcium, ppm | 10 | 8 | 15 | 11.00 | 3.61 |
| | Magnesium, ppm | 9 | 5 | 6 | 6.67 | 2.08 |
| | NaCl, % w/w | 99.55 | 99.60 | 99.40 | 99.52 | 0.10 |

The increased sulfate concentration in brine is the salting in the effect of $BaSO_4$(s) at the concentrated solution of brine/NaCl solution and $Na_2CO_3$.[18,19] "Salting in" is a common phenomenon in electrolyte solutions, whereby the solubility of one chemical substance increases due to the presence of another salt. The "salting in" $BaSO_4$ phenomenon in the one–stage purification process is shown in Fig.-4. The tiny amount of barium sulfate released into the solution forms barium, and sulfate ions depend on the molar salt concentration, brine type, temperature, and pressure. The evidence of solubility of barium sulfate due to "salting in" is also marked by the positive qualitative test of barium ions, and the high sulfate ion concentration results in the filtrate and salt product are 446.67 ppm and 220.00 ppm, respectively.

Table-5 shows the result analysis of the brine solution after the purification process with two stages of the precipitation method. The result of the two-stage purification shows that in the first step, magnesium and sulfate ion content decreased after precipitation with $BaCl_2$ and NaOH at concentrations of 7 and 6 ppm, respectively. At the same time, the calcium content does not reduce because calcium has not reacted with $BaCl_2$ and NaOH reagents. After storage for 12 hours and filtration, the magnesium and sulfate ion content remained relatively unchanged. In the second precipitation step, after reacting with $Na_2CO_3$, the calcium ion concentration can be reduced to 10 ppm.

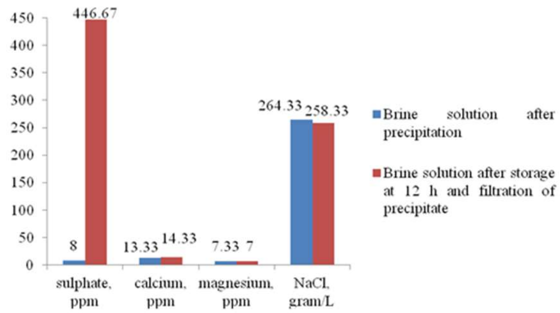


Fig.-3: Content of Sulfate, Calcium, Magnesium, and NaCl after Purification by one stage of Precipitation

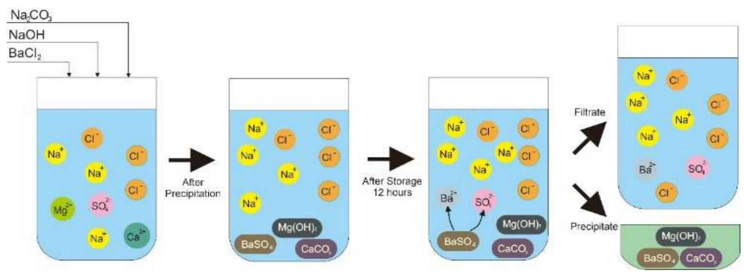


Fig.-4: The "salting in" Phenomenon in One Stage of Precipitation

Table-5: Result Analysis of Brine Solution after Purification by Two Stages of Precipitation

| Sample | Test parameter | Batch 1 | Batch 2 | Batch 3 | Average | SD |
|---|---|---|---|---|---|---|
| Brine solution after first-stage precipitation, storage at 12 h, and filtration | Sulfate, ppm | 5 | 5.5 | 7 | 5.83 | 1.04 |
| | Calcium, ppm | 890 | 900 | 875 | 888.33 | 12.58 |
| | Magnesium, ppm | 8 | 12 | 9 | 9.67 | 2.08 |
| | NaCl, % gram/L | 265 | 260 | 265 | 263.33 | 2.89 |
| Brine solution after second-stage precipitation, storage at 12 h, and filtration | Sulfate, ppm | 5 | 5.5 | 7 | 5.83 | 1.04 |
| | Calcium, ppm | 10 | 20 | 15 | 15.00 | 5.00 |
| | Magnesium, ppm | 5 | 6 | 6 | 5.67 | 0.58 |
| | NaCl, % gram/L | 255 | 250 | 258 | 254.33 | 4.04 |
| Salt product | Sulfate, ppm | 8 | 5 | 7 | 6.67 | 1.53 |
| | Calcium, ppm | 10 | 12 | 9 | 10.33 | 1.53 |
| | Magnesium, ppm | 9 | 10 | 10 | 9.67 | 0.58 |
| | NaCl, % w/w | 100.5 | 100.1 | 99.85 | 100.15 | 0.33 |

In contrast, magnesium and sulfate ion content after 12 hours of storage and filtering showed the same content. Figure-5 shows sulfate, calcium, magnesium, and NaCl content after 12-hour storage of first-stage and second-stage precipitation in the two-stage method. The illustration of the two stages of the precipitation process in the salt purification process is shown in Fig.-6.

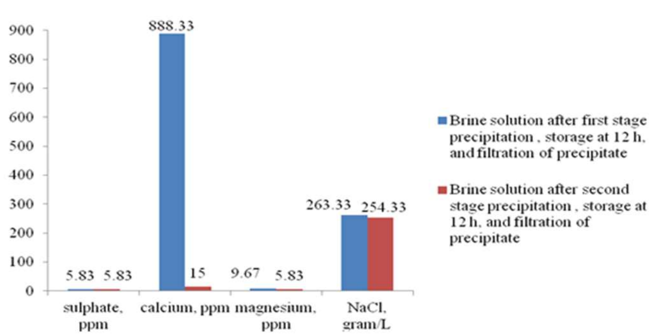


Fig.-5: Content of Sulfate, Calcium, Magnesium, and NaCl after Purification by Two Stages of Precipitation

The study results show three replications with no different content, so the results were considered valid. In this process, the content of three ions has fulfilled the requirements, so the resulting salt product also meets the requirement.

Table-6 and Fig.-7 show the results of the analysis of the quality of the salt produced after the crystallization process using the brine solution, which is this product with the one-stage and two-stage precipitation methods. The salt product with a one-stage purification method contains NaCl, calcium, magnesium, and water that meet the requirements. However, the sulfate concentration is still greater than required because the feed solution uses brine with high sulfate content. At the same time, the salt product with a two-stage purification method contains NaCl, calcium, magnesium, and sulfate, which meet the requirements.

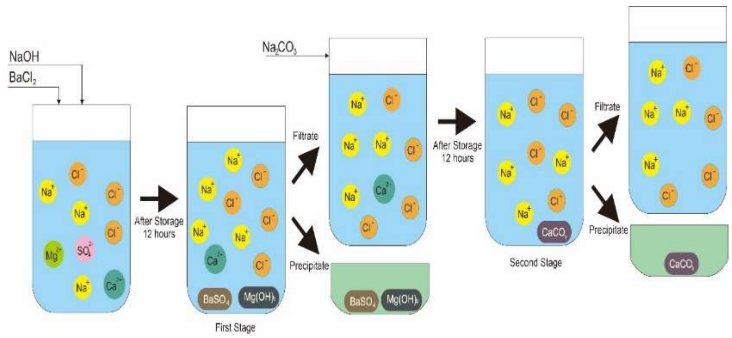


Fig.-6: The Illustration of a Two-Stage Method in Salt Purification

Table-6: Result in the Analysis of other Parameters at NaCl Product After Purification and Crystallization

| Test parameter | NaCl with One-stage precipitation | NaCl with Two-stages precipitation |
|---|---|---|
| Shape, color, taste, and appearance | Small crystals, cube-shaped, white, salty | Small crystals, cube-shaped, white, salty |
| Solubility in water | Soluble in water, clear solution | Soluble in water, clear solution |
| Identification | Show reaction with the sodium and chloride ion test | Show reaction with the sodium and chloride ion test |
| Water content, % | 0.40 | 0.35 |
| Barium (qualitative test) | positive | negative |

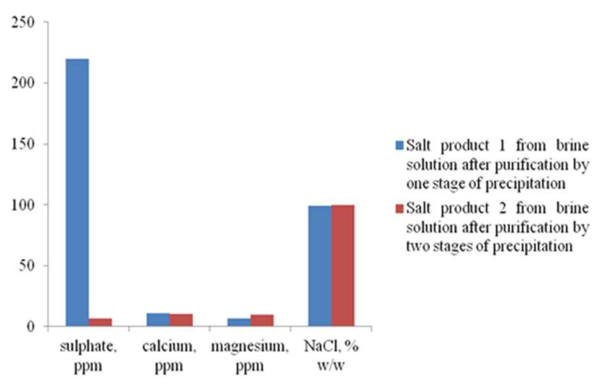


Fig.-7: Content of Sulfate, Calcium, Magnesium, and NaCl in the Salt Product After Purification by One- Stage and Two Stages of the Precipitation Process

## CONCLUSION

Based on the results of this study, the process of purification of salt solution with two stages of precipitation is more effective when compared to one stage of precipitation to increase NaCl content and reduce sulfate, calcium, and magnesium content. On the other hand, a study with one-stage precipitation showed an increase in barium and sulfate ion concentration at brine after purification and product. In addition, the "salting in" $BaSO_4$ in concentrated brine and $Na_2CO_3$ solution affects the quality of the brine solution and salt product.

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## CONFLICT OF INTERESTS

The authors, at this moment, declare that they do not have any conflict of interest.

## AUTHOR CONTRIBUTIONS

E. Rismana and S. Kusumaningrum contributed equally to this work as the main contributors. All authors agreed to the final version of this manuscript. The research profile of the authors can be verified from their ORCID ids, given below:

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