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Influence of gambier extract modification as inhibitor of calcium sulfate scale formation

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ABSTRACT

Scale formation is a serious problem in many industries, especially in oil and gas industries. Therefore, in order to control the problems, this research studied the effect of the addition of gambier extract modified with kemenyan extract on the growth of calcium sulfate ($CaSO_4$) scale formation as a green inhibitor. The crystallization experiments were carried out by using unseeded experiment method at temperature of 90°C. The $CaSO_4$ crystals obtained with and without the addition of inhibitor were analyzed by scanning electron microscopy (SEM), particle size analyzer (PSA), and X-ray diffraction (XRD). The results of this experiment show that the addition of the combination of gambier and kemenyan extract with ratio of 5:9 can inhibit the growth of $CaSO_4$ crystals with the inhibition effectivity of 39.88%. These results were supported from the SEM and PSA data showing that the crystal size and particle size distribution of the $CaSO_4$ in the addition of the inhibitor are smaller than without the addition of inhibitor. In addition, analysis using XRD showed that $CaSO_4$ crystals undergo a change in crystalline phase with the addition of inhibitors.

Keywords: $CaSO_4$; Green inhibitor; Scaling; Gambier extract, Kemenyan extract

1. Introduction

In cooling water system, calcium sulfate ($CaSO_4$) often found as mineral deposits which is a problem for industries. The mineral deposits not only lowers heat exchanger performance by increasing resistance to heat transfer but also wastes energy due to increased pumping power, causing enormous economic losses [1–7]. In order to control these deposits, a number of chemical compounds have been studied to obtain an effective inhibitor to inhibit scale formation [8–11].

The use of biomass from agricultural and plantation products is not only applied as an adsorbent [12–15] but can also be used as a corrosion and scaling inhibitor [16,17]. The gambier (*Uncaria gambier* Roxb leaves) and kemenyan (*Styrax benzoin* Dryand) extracts have been reported as green inhibitor of calcium carbonate ($CaCO_3$) [18,19]. The modification of the gambier extract with the addition of citric and benzoic acid has been also studied in inhibiting scale formation of calcium carbonate [20]. The role of citric and benzoic acid added in the mixtures was to maintain quality of gambier extract from chemical damage.

In this research, it was studied the modification of gambier and kemenyan extracts as green inhibitor to control the scale formation of calcium sulfate ($CaSO_4$) with various concentrations of gambier and kemenyan extracts. The kemenyan extract from Sumatra benzoin tree used in this experiment has main chemical compounds such as benzoic

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and cinnamic acid that can replace citric and benzoic acid to maintain the quality of the mixtures. The use of the kemenyan aims to reduce production costs of the inhibitor mixtures.

2. Experimental procedure

2.1. Materials and instrumentation

The instrument used in this experiment consisted of analytical balance (Kenr & Sohn GMBH ABT 220-4M, Germany), oven (Thermo Fisher Scientific, United Kingdom), water bath (Haake S21, Thermo Fisher Scientific, USA), plastic bottle, magnetic stirrer, chemical glass, Fourier transform infrared (FTIR) spectrophotometer (Shimadzu FTIR-8400, Japan), scanning electron microscopy (SEM) (JSM 6360 LA, JEOL, Japan), particle size analyzer (PSA) (the Beckman Coulter LS 13 320 MW, manufactured in USA), and X-ray diffraction (XRD, Philip Analytical, manufactured in Netherlands).

$CaCl_2$ anhydrate, CH_3CH_2OH, CH_3OH, acetone, and Na_2SO_4 were ordered from commercial product of Merck, Germany. The gambier and kemenyan extract were prepared with the raw materials obtained from local market in Bandar Lampung, Indonesia.

2.2. Preparation of gambier and kemenyan extract

The gambier extract was made by pounding gambier until smooth, so that it can be used to obtain gambier powder. A total of 10 g of the gambier powder was dissolved in water to a volume of 1 L. The solution was stirred using a magnetic stirrer for 3 h at a temperature of 90°C and then the solution was filtered using filter paper. The filtered solution was a gambier extract stock solution with a concentration of 10,000 ppm. The same procedure was carried out to make kemenyan extract with a concentration of 10,000 ppm [18,19].

2.3. Testing the use of a mixture of gambier and kemenyan extract as an inhibitor of $CaSO_4$ crystal formation with the unseeded experiment method

2.3.1. Without the addition of inhibitors

The growth solution of 0.05 M $CaSO_4$ was made from mixing a solution of 0.100 M $CaCl_2$ and 0.100 M Na_2SO_4 each in 200 mL of distilled water at a temperature of 90°C, the mixture was stirred using a magnetic stirrer for 15 min and it was divided into eight plastic bottles of each 50 mL. The plastic bottles containing the solution were placed into the water bath at temperature of 90°C. Observations were carried out for 2 h, and every 15 min one bottle was taken to weigh the crystals formed by filtering the solution in the bottle using filter paper, washing with distilled water, and drying using an oven at 105°C for 3 h. The precipitate formed was weighed, then analyzed using a SEM instrument, PSA, and XRD.

2.3.2. With the addition of inhibitors

The inhibitor solution was made by mixing 200 mL gambier extract with 200 mL of kemenyan extract with a varied concentration ratio. The combinations of gambier and kemenyan extract were tested for its effectiveness by varying the concentration of the mixture of gambier and kemenyan extract in which the concentration of gambier extract was made fixed. Comparison of the concentration of mixture of gambier and kemenyan extracts can be seen in Table 1. The mixture solution of gambier and kemenyan extract was stirred using a magnetic stirrer for 15 min at a temperature of 90°C, cooled and then stored in a dark bottle. Each mixture was tested for its effectiveness in inhibiting the scale formation of $CaSO_4$ in a growth solution of 0.05 M $CaSO_4$.

The growth solution of 0.05 M $CaSO_4$ was made by mixing each 200 mL solution of 0.100 M $CaCl_2$ and 0.100 M Na_2SO_4 which has been added by the inhibitor of a mixture of gambier and kemenyan extracts with a concentration comparison of 5:1. The mixture was stirred by magnetic stirrer for 15 min at temperature of 90°C and it was separated into eight plastic bottles and kept in the water bath at the same temperature. Every 15 min one bottle was taken to weigh the crystals formed by filtering the solution in the bottle using filter paper, washing it with distilled water, and drying it using an oven at 105°C for 3 h. These experiments were repeated with the mixture of gambier and kemenyan extract with the concentration ratio of 5:3, 5:5, 5:7, and 5:9. The precipitate formed was weighed; then the most effective was selected to be analyzed using instruments of SEM, PSA, and XRD.

2.4. Data analysis

To find out the effectiveness of inhibitors in inhibiting the scale formation of $CaSO_4$, Eq. (1) [21] given as follows can be used:

$$\text{Effectiveness of inhibitors } (\%) = 100 \times \frac{(\mathrm{Ca} - \mathrm{Cb})}{(\mathrm{Cc} - \mathrm{Cb})} \tag{1}$$

where Ca = $CaSO_4$ concentration after added inhibitor at equilibrium (g/L); Cb = $CaSO_4$ concentration without inhibitor at equilibrium (g/L); Cc = initial $CaSO_4$ concentration (g/L).

3. Results and discussion

3.1. Characterization of inhibitor extracts using FTIR spectrophotometer

Analysis using FTIR spectrophotometer served to determine the functional groups contained in the gambier and kemenyan extracts. The IR spectrum obtained for the

Table 1
Concentration comparisons of gambier (G) and kemenyan (K) extract mixtures

No.	Comparison G:K	Concentration (ppm)	
		G	K
1	5:1	250	50
2	5:3	250	150
3	5:5	250	250
4	5:7	250	350
5.	5:9	250	450

gambier, kemenyan, and gambier–kemenyan extracts is presented in Fig. 1. From Fig. 1c, the emergence of a number of absorption bands related to functional groups that are owned by organic components in the gambier extract can be observed. The presence of hydroxyl (–OH) groups can be observed with the appearance of absorption bands in the area of 3,417.86–3,363.86 1/cm with a very wide intensity. The hydroxyl (–OH) absorption band in Fig. 1c appears at 3,385.07 1/cm; this corresponds to the main component of the gambier extract such as tannic acid (tannins) which is very rich in hydroxyl groups. The absorption band at wave number 2,933.3 1/cm shows the presence of aromatic C–H functional groups derived from the chemical content in the gambier extract, such as tannins. The wave number 1,627.92 1/cm shows the presence of carbonyl (C=O stretch) functional groups found in catechins (catechin anhydride) from the gambier extract. The presence of C=C groups on aromatic compounds is seen by the appearance of peaks at wave numbers 1,467.83 and 1,523.76 1/cm.

In Fig. 1b it can be observed the emergence of a number of absorption bands related to functional groups possessed by organic components in extracts of the kemenyan. In Fig. 1b strong width uptake at 3,367.1 1/cm shows the O–H group. Uptake in 1,691.57 1/cm is characteristic of the carbonyl group (C=O) from the carboxylic acid. Group of (–C=C–) in aromatic compounds are seen by the appearance of peaks at wave numbers 1,514.12 to 1,450.47 1/cm with sharp and strong intensity. Based on the reference data, the carbonyl group in benzoic acid appears at wave numbers 1,600, O–H at 3,200–2,400, –C=C– aromatic at 1,500–1,410 and C–H (monosubstituted benzene) at 680–600 1/cm. Whereas in cinnamic acid, the carbonyl group appears at wave number 1,691.57, O–H at 3,367.71, –C=C– aromatic at 1,633.71 1/cm.

In this study, the inhibitor used was a mixture of gambier and kemenyan extract so that the extract mixture was also analyzed using an FTIR spectrophotometer as shown in Fig. 1a. Based on the FTIR analysis, there is a slight shift in absorption such as the hydroxyl (–OH) absorption band seen at wave number 3,388.93 1/cm, the functional group of carbonyl (C=O stretch) seen at wave number 1,624.06 1/cm, the functional group of –C=C– aromatic seen at wave number 1,517.98 and 1,462.04 1/cm. These results are consistent with IR spectrum of kemenyan and gambier resulted from previous researches [19,22]. The characterization results show that in a mixture of gambier and kemenyan extracts, there are several chemical compounds that have active functional groups that can be used as inhibitors of $CaSO_4$ scaling.

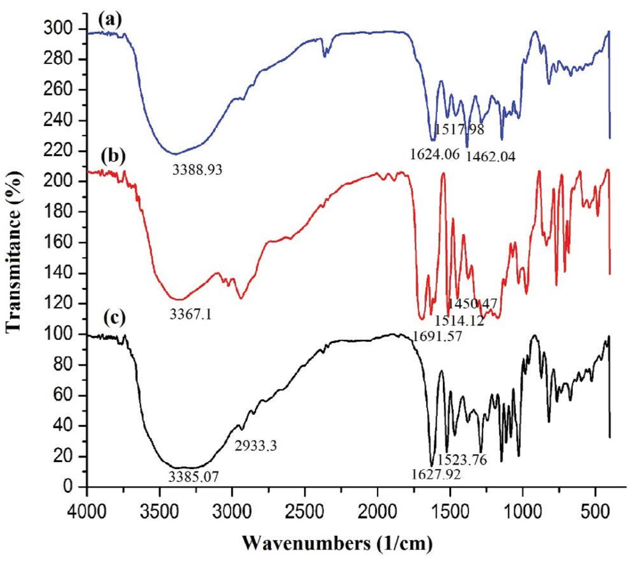

Fig. 1. IR spectrum of (a) gambier–kemenyan (5:9), (b) kemenyan, and (c) gambier extracts.

3.2. *Testing of inhibitor mixtures in inhibiting $CaSO_4$ scale formation*

The observation of the effect of the use of a mixture of gambier (G) and kemenyan (K) extract as an inhibitor of $CaSO_4$ scale formation at the concentration of 0.05 M with and without inhibitors of the gambier and kemenyan extract mixtures is shown in Fig. 2.

Based on observational data obtained in Fig. 2, calculations can be performed using Eq. (1) to obtain the effectiveness of inhibitors of the mixture of the gambier and kemenyan extract as shown in Table 2.

The data obtained in Table 2 show that a mixture of gambier and kemenyan extract in a growth solution of 0.05 M $CaSO_4$ was able to inhibit the growth rate of $CaSO_4$ crystals. The addition of the inhibitors of the mixture of gambier and kemenyan extracts with a concentration ratio of 5:9 had the greatest effectiveness of 39.88%.

The crystal morphology of $CaSO_4$ was observed by SEM analysis, and the results can be seen in Fig. 3. Based on the results of SEM analysis in Fig. 3, it can be observed that there was a change in the size of $CaSO_4$ crystals in the unseeded experiment method using inhibitors of the gambier and kemenyan extract mixtures with a ratio of 5:9 at a magnification of 1,000×. From the results of surface morphology analysis, it can be seen that $CaSO_4$ crystals without inhibitors have a larger and longer size compared with $CaSO_4$ crystals which have been added with inhibitors of gambier

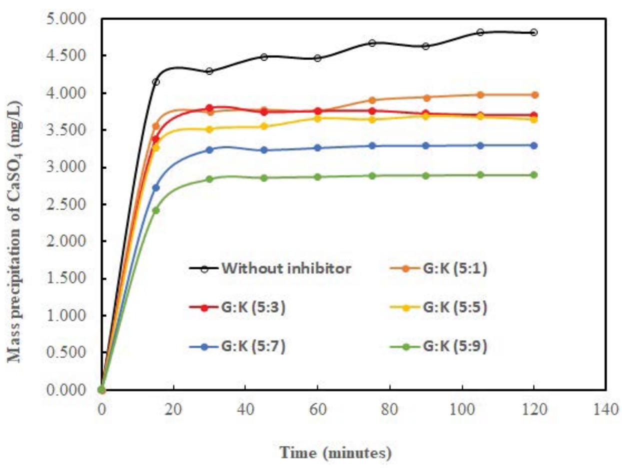

Fig. 2. Precipitation mass change of $CaSO_4$ at the concentration of growth solution of 0.05 M vs. time without and with the addition of inhibitor at various concentrations.

Table 2
Effectiveness of inhibitor (%) at the concentration of growth solution of 0.05 M with the various concentration of inhibitor added

Ratio of concentration (G:K) (ppm)	Effectiveness of Inhibitor (%)
5:1	17.35
5:3	22.98
5:5	24.23
5:7	31.48
5:9	39.88

and kemenyan extract mixtures which are smaller and shorter in size. Thus it can be stated that the addition of inhibitors causes changes in the size of $CaSO_4$ crystals and inhibitors also can change in the morphology of $CaSO_4$ crystals. The morphology of $CaSO_4$ crystal in the absence of inhibitors was larger needle-like gypsum crystals. While the morphology of $CaSO_4$ crystal in the presence of inhibitors was dominated by bassanite phase. The addition of the inhibitors in the growth solution of $CaSO_4$ causes a change in the crystalline phase of most $CaSO_4$ crystal from the gypsum ($CaSO_4 \times 2H_2O$) to the bassanite ($CaSO_4 \times 0.5H_2O$) phase (Fig. 3).

In order to support the data obtained through SEM images, the calcium sulfate crystals obtained with and without the addition of inhibitors were characterized using powder XRD. The XRD pattern of the calcium sulfate analyzed is displayed in Fig. 4. The XRD pattern obtained shows that the data resulted by XRD support the SEM data as seen in Fig. 3. The results of the analysis using XRD showed that with the addition of inhibitors, the presence of bassanite (B) dominated the crystalline phase of calcium sulfate compared with gypsum (G). Addition of inhibitors also to the calcium sulfate growth solution presents an anhydrous anhydrite ($CaSO_4$) crystal phase (A) as shown in Fig. 4. The gypsum phase is a type of hard scale phase. This phase is a crystalline phase that is difficult to clean. Whereas the bassanite and anhydrate phases are crystalline phases which are easier to clean (soft scale).

The results of this analysis also prove that the addition of inhibitors can slow the formation of $CaSO_4$ crystal nuclei. Addition of inhibitors can reduce the size of $CaSO_4$ crystals rather than without the addition of inhibitors. Smaller crystal sizes indicate that inhibitors work to reduce the formation of $CaSO_4$ crystals

Crystal size changes that occur in $CaSO_4$ crystals without inhibitors and with inhibitors are due to the role of inhibitors which inhibit the surface of $CaSO_4$ crystals through adsorption on the surface of the crystal or crystal nucleus. Thus, the inhibition mechanism that occurs is thought to be through the inhibitor adsorption of a mixture of the gambier and kemenyan extract to the surface of $CaSO_4$ crystals so that the crystal nucleus as a new growth unit derived from growth solution is blocked by inhibitors of the gambier and kemenyan extract and it cannot attach to the active growth site on the crystal surface $CaSO_4$ for growth. The inhibition of growth units by inhibitors causes the growth rate of $CaSO_4$ scale to slow down. The inhibition of $CaSO_4$ crystal growth will result in changes in crystal size of $CaSO_4$. This is in line with the research of Sikirić and Milhofer, who examined the effect of organic molecules on the crystallization of biomineral in solutions that showed changes in the growth rate and scale morphology of biomineral crystals due to the addition of organic molecules with certain functional groups [23].

To further prove changes in the size of $CaSO_4$ crystals without and with the addition of G:K inhibitors, an analysis using a particle size analyzer (PSA) was performed on $CaSO_4$ crystals obtained as seen in Fig. 5. Particle size distribution of $CaSO_4$ with the addition of G:K inhibitors becomes smaller than without the addition of inhibitors as shown in Fig. 5. In the graph without the addition of inhibitors (Fig. 5), it is known that the $CaSO_4$ crystal size diameter has a mean and median of 118.8 and 119.6 nm, respectively. After the

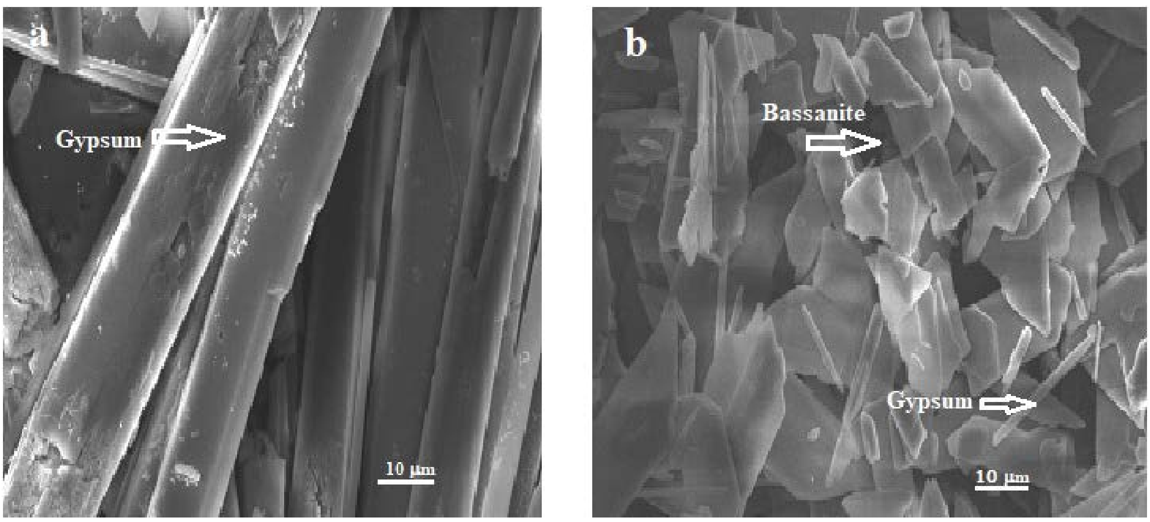

Fig. 3. Morphology of $CaSO_4$ crystals (a) without inhibitors and (b) with inhibitors of the mixture of gambier and kemenyan extracts with a ratio of 5:9 at magnification of 1,000×.

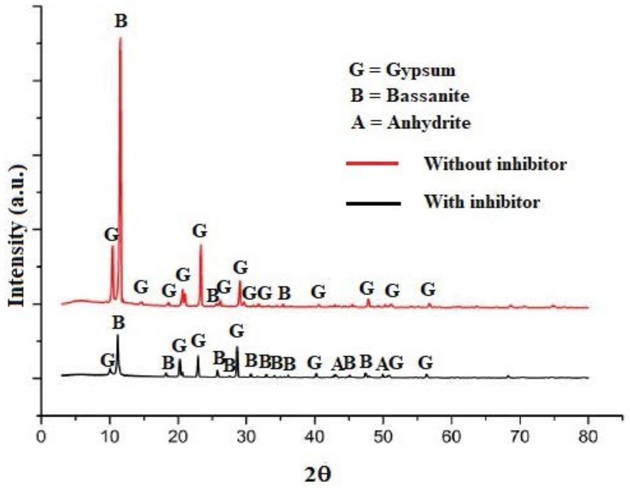

Fig. 4. XRD patterns of the calcium sulfate in the absence and presence of inhibitor mixtures (G:K = 5:9).

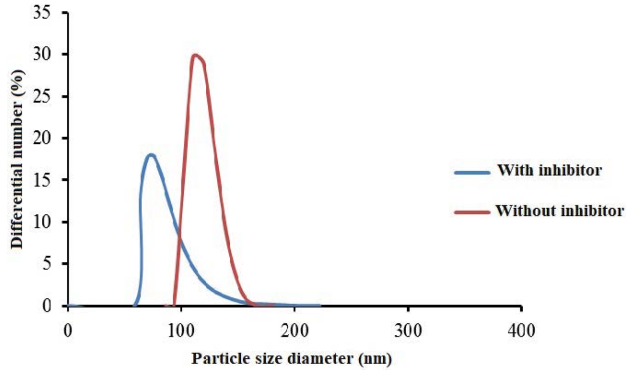

Fig. 5. Particle size distribution of $CaSO_4$ crystals with and without inhibitor of G:K (5:9) at the concentration of $CaSO_4$ growth solution of 0.05 M.

addition of a mixed inhibitor of GK (5:9), the $CaSO_4$ crystal size diameter has a mean and median of 83.9 and 82.1 nm, respectively.

Inhibitor can affect the nucleation and growth of $CaSO_4$ crystals, for example, by forming complexes or chelating agents with the active ions in the growth solution of $CaSO_4$. Inhibitor can also affect the nucleation and growth of $CaSO_4$ crystals by adsorbing to active crystal sites and inhibiting nucleation or crystal growth of $CaSO_4$. In the case of this experiment, the use of gambier and kemenyan extract mixture as inhibitor of $CaSO_4$ crystal allows the formation of complexes with Ca^{2+} ions as well as the inhibition of the growth of calcium sulfate crystals through adsorption on the $CaSO_4$ crystal surface. This is caused by the presence of chemical compounds such as tannic acid, catechin, quercetin, p-coumaryl cinnamate, cinnamic acid, p-coumaryl benzoate, isovanillin and benzoic acid which are contained in the gambier and kemenyan extract which have active groups as carboxylate and ketone group that can bind to Ca^{2+} ions. The presence of tannic acid, catechin, and quercetin as an organic molecule rich in –OH groups can adsorb onto the surface of $CaSO_4$ crystals, change the crystal morphology of $CaSO_4$, and finally inhibit the growth rate of $CaSO_4$ crystal. Similar results were also found in the addition of inhibitors of organic molecules causing a slowdown in the growth of $CaSO_4$ crystals as well as a change in the phase of $CaSO_4$ crystals [6,23–27]. Comparison of several inhibitors from other researchers is listed in Table 3. In general, the scale inhibition performance depends also on the concentration of growth solution and the type of inhibitor itself. Some commercial inhibitors (poly(itaconic acid-co-sodium vinylsulfonate and acrylic acid–oxalic acid–allylpolyethoxy carboxylate–8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (pyranine)) work very effectively at high concentrations of solution growth (Table 3). But some inhibitors such as phosphonate (P-Nate), polyacrylate, and polyaspartic acid are less effective at low concentrations of growth solutions as displayed in Table 3. In this case, the concentration of $CaSO_4$ growth solution is 0.05 M;

Table 3
Comparison of several inhibitors in inhibiting $CaSO_4$ crystal formation

Inhibitors	Growth solution concentration of Ca^{2+} (M)	Concentration of inhibitor (ppm)	Efficiency of inhibitor (%)	References
Gambier (G) and kemenyan (K) extract	0.0500	G: 250	17–40	This work
Poly(itaconic acid-co-sodium vinylsulfonate)		K: 50–450		
Acrylic acid–oxalic acid–allylpolyethoxy carboxylate–8-	0.3500	200–600	33–54	[27]
hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (pyranine)	0.0500–0.0750	4	87–96	[6]
Poly(acrylic acid)	0.0500	1–4	18–88	[6]
Homopolymer of polymaleic acid	0.0180	4	67	[6]
Terpolymer of polymaleic acid	0.0180	4	37	[6]
Copolymer of polymaleic acid	0.0180	4	12	[21]
Phosphonate	0.0180	4	5	[21]
Polyacrylate	0.0180	4	13	[21]
Polyepoxysuccinic acid	0.0003–0.0015	10	73–97	[28]
Polyaspartic acid	0.0150	4	25	[29]

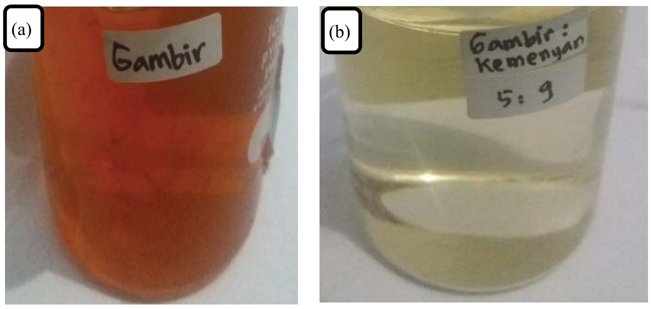

Fig. 6. Change of gambier extract (a) without the addition of kemenyan extract and (b) with the addition of kemenyan extract after being left alone for 2 weeks.

this concentration is enough higher. If it is compared with other inhibitors in Table 3, this inhibitor is still reasonable considering that from the side of the inhibitor price, it will be much cheaper for industrial applications. It may be predicted that this inhibitor can be used effectively for the concentration of growth solution lower than 0.05 M. Unfortunately in our experiments, the use of too low concentrations was difficult to do in observing changes in the weight of the crystals formed. As it is known that the performance of inhibitor will increase when the concentration of growth solution decreases. This case was observed at the addition of acrylic acid–oxalic acid–allylpolyethoxy carboxylate–8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (pyranine) (AA–APEM–APTA) in inhibiting of $CaSO_4$ crystal growth with decreasing of the concentration of Ca^{2+} and evidently the concentration of Ca^{2+} as the growth solution of $CaSO_4$ crystal decreased by 50%, the inhibition effectiveness of (AA–APEM–APTA) raised by 9% [6].

3.3. Quality of the inhibitor mixtures

In addition to the inhibition of the growth of $CaSO_4$ crystals, the addition of kemenyan extract in gambier extract can slow down the damage of gambir extract. This can be seen in Fig. 6 which shows that the gambier extract before kemenyan extract added within 2 weeks showed the growth of fungi and impurities, while the gambier extract mixed with extract of kemenyan was clear without impurity and no fungal growth was found. The kemenyan extract can slow the growth of fungi because it contains benzoic acid and cinnamic acid which can be used as antimicrobial and antifungal. In addition, the addition of kemenyan extract in gambier extract can increase the quality of the inhibitor mixture. The kemenyan extract can be used to substitute chemical compound as benzoic and citric acid in modification of gambier extract as scaling inhibitor as previous reported [20]. The use of kemenyan extract as a mixture has its own advantages because it is relatively much cheaper than the chemical compounds of citric and benzoic acid. In addition, the use of kemenyan extract can reduce the price of inhibitors.

4. Conclusions

A mixture of the gambier and kemenyan extract acts as an inhibitor of calcium sulfate ($CaSO_4$) scale formation. The gambier and kemenyan extracts in the ratio of the mixture concentration of 5:9 have good quality of an inhibitor mixtures as an inhibitor of $CaSO_4$ scale formation with the effectiveness of 39.88% in a growth solution of 0.05 M. The results of SEM observations showed a significant change between $CaSO_4$ crystal without and with the addition of mixed inhibitors of gambier and kemenyan extract. The crystal morphology of $CaSO_4$ with the addition of this inhibitor has a smaller and shorter size compared with the crystal morphology of $CaSO_4$ without the addition of inhibitors.

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