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kemenyan (*Styrax benzoin* Dryand) extract as green inhibitor of calcium carbonate ($CaCO_3$) crystallization

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ABSTRACT

To study the effect of kemenyan extract from *Styrax benzoin* Dryand resin as green inhibitor on calcium carbonate ($CaCO_3$) scale formation, experiment has been carried out using a bottle roller bath method at temperature of 80°C and at various growth solutions from 0.050 to 0.100 M. The extraction result of the kemenyan was characterized using Fourier transform infrared spectroscopy to identify functional groups found in the kemenyan extract. The morphology of $CaCO_3$ crystal obtained was analyzed using SEM and the particle size distributions of the $CaCO_3$ crystals produced were measured by a particle size analyzer. The result of the experiment showed that kemenyan extract can be used as a green inhibitor of calcium carbonate scale formation. The presence of kemenyan extracts in the various growth solutions of $CaCO_3$ 0.050, 0.075, and 0.100 M gives percentage of inhibition ability from 12% to 77% in inhibiting the formation of the $CaCO_3$ scale. The ability of the kemenyan extract to inhibit the growth rate of $CaCO_3$ crystallization depends on amount of the inhibitor concentration added and the growth solution concentration as a crystal growth media under these experiment conditions.

Keywords: kemenyan extract; $CaCO_3$ crystal; Green inhibitor

1. Introduction

Use of additives in inhibiting the inorganic material scale formation is used more increasingly in many industries involving salt water in cooling system of boiler. The additives are utilized because of simple and economic application. Additives are able to change a crystal morphology [1], to inhibit or as inhibitor of crystal formation [2], or both. Therefore, negative effect of the inorganic material scale formation can be controlled earlier. Because of these negative impacts, Indonesian Oil Company (Pertamina) has spent US$ 6–7 million to renew every pipeline at the Pertamina Geothermal Power Plant every 10 years [3].

Nevertheless, the use of scale inhibitor containing compounds of sulfonate and phosphonate polymer more to inhibit the inorganic material scale formation in several industries in Indonesia such as steam power plant (PLN/ Indonesian Electricity Company) and geothermal power plant (Pertamina Geothermal Power Plant) is not environmentally friendly. The majority of industrial wastes are thrown away into aquatic environments. Of course, the use of these compounds causes environmental contamination and affects ecological equilibrium in the aquatic environments.

Thus, the use of a green inhibitor which is environmentally friendly and economic in inhibiting the inorganic material scale formation is a main choice for recently used inhibitors applied widely by industries containing chemical compounds such as organophosphate and organophosphonate

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which are toxic and destructive for the environment as well as expensive [4–19]. For this aim, the researchers reported their inventions of development, modification, and application of the green inhibitor from various natural chemical compounds in various journals [3,8,11,12,15].

In this research, use of extract from kemenyan plant (*Styrax benzoin* Dryand) of Sumatra benzoin tree containing main chemical compounds such as benzoic acid, *cinnamic acid*, *p*-coumaryl cinnamate, *p*-coumaryl benzoate, and isovanillin as an inhibitor of $CaCO_3$ scale formation was investigated [20–23]. The experiments were carried out using bottle roller bath method, a crystal morphology was analyzed using scanning electron microscopy (SEM), and particle size distributions to study particle size diameter were performed with a particle size analyzer (PSA) [3,18].

2. Experimental procedure

2.1. Materials and instrumentation

Analytical balance (Kenr & Sohn GMBH ABT 220-4M), oven (Fisher Scientific), magnetic stirrer, bottle roller bath, glass reactor, overhead stirrer, water bath, Fourier transform infrared spectroscopy (FTIR) (Prestige–21, Shimadzu, Japan), PSA (Sedigraph III 5120, Micrometrics, USA), and SEM (JSM 6360 LA, JEOL, Japan) were used as instrument in this research.

The white kemenyan was taken from traditional market in Bandar Lampung and the chemical used in this experiment such as calcium chloride, acetone, sodium carbonate, ethanol, and methanol were purchased from commercial product of Merck, Germany.

2.2. Preparation of white kemenyan extract

The kemenyan (resin of *Styrax benzoin* Dryand from Sumatra benzoin tree) is graded based on the size of pieces. kemenyan farmers or sellers classify it into four different levels in the trade, from 1 (very large pieces and without foreign particle) to 4 (very small size and close to powder). In this research, it was selected the fresh white kemenyan with grade of 1 purchased directly from seller in Bandar Lampung City, Sumatera, Indonesia. To obtain the kemenyan extract as scaling inhibitor, the white kemenyan of grade 1 was pounded into powder. 50 g of powdered white kemenyan was heated in water with total volume of 1 L at a temperature of 50°C for 1 h and it was kept for 1 night. Then, it was filtered and the filtrate was identified by FTIR to investigate the functional groups playing a role from some chemical compounds such as benzoic acid, *cinnamic acid*, *p*-coumaryl cinnamate, *p*-coumaryl benzoate, and isovanillin in the kemenyan extract as reported by previous researchers [20]. The extract was used as the inhibitor in this research.

2.3. Crystallization experiments

The growth solution of $CaCO_3$ 0.050 M was prepared with mixing 200 mL of 0.100 M $CaCl_2$ anhydrate solution and 200 mL of Na_2CO_3 0.100 M in 500 mL of Nalgene polypropylene bottle at temperature of 80°C. The mixture was stirred by magnetic stirrer up to homogeneous solution and filtered by 0.45 μm Millipore filter. The growth solution was placed into 250 mL Nalgene polypropylene bottle each of 50 mL for seven bottles. These bottles were left in the bottle roller bath at temperature of 80°C. The bottle roller bath was used to rotate bottles containing the growth solution of $CaCO_3$ crystals and seed crystal of $CaCO_3$ with or without inhibitor to study the effect of inhibitor on the growth rate of the $CaCO_3$ crystal at the specific temperature and rotation. The bottle roller was adjusted to rotate at 40 revolutions/min. Over the 70 min experiment, a bottle was taken every 10 min. The precipitate was washed thoroughly with deionized water and dried at a temperature of 105°C in the oven for 1 d. The weight of the crystals was measured and the amount precipitated was calculated as data of precipitation mass change to count the growth rate of $CaCO_3$ precipitation. The experiments were repeated for different growth concentrations of 0.075 and 0.100 M with the same treatment like previous experiment of 0.050 M.

2.4. Experiment of kemenyan extract as inhibitor

The experiment to study the influence of inhibitor addition was performed by adding the kemenyan extract of various concentrations 0, 50, 150, 250, and 350 ppm in the growth solution of 0.050, 0.075, and 0.100 M. The procedure applied was similar with the procedure done in the crystallization experiment without kemenyan extract addition. The precipitation mass obtained was analyzed to investigate the effect of the kemenyan extract addition on the $CaCO_3$ scale formation. Inhibitor effectiveness (%) could be measured based on Eq. (1) [24]:

$$\text{Inhibitor effectiveness (\%)} = 100 \times \{(C_x - C_y)/(C_z - C_y)\} \quad (1)$$

where C_x = $CaCO_3$ concentration with inhibitor at equilibrium (g/L); C_y = $CaCO_3$ concentration without inhibitor at equilibrium (g/L); C_z = initial $CaCO_3$ concentration (g/L).

2.5. Data analysis

Acquired data of precipitation amount vs. time at various concentrations of growth solution and the addition of kemenyan extract additive were analyzed by MS Excel 2007. The effectiveness of kemenyan extract in hindering the $CaCO_3$ scale formation was determined by the amount of precipitation obtained and particle size distribution of $CaCO_3$ crystal. The particle size distributions of $CaCO_3$ crystal were identified by PSA and the morphology of crystal was analyzed by SEM.

3. Results and discussion

3.1. Functional group characterization of kemenyan extract

Extraction result of kemenyan was characterized using IR to analyze some functional groups found in the kemenyan extract. The result of IR analysis for the kemenyan extract is displayed in Fig. 1. In the IR spectrum (Fig. 1), the appearance of absorption bands linked with the functional groups of organic compounds in the kemenyan extract can be seen. Broad absorptions in the wave number 3,200–3,387 1/cm with a strong and wide intensity identify adsorption of O–H alcohol. These absorption areas also indicate O–H of carboxylate from cinnamic and benzoic acid. The existence of weak absorption at 2,800 1/cm gives indication of C–H aldehyde functional group from isovanillin and the absorption at 1,689.64 1/cm with sharp and strong intensity proves the existence of carbonyl group (C=O). The presence of –C=C– from aromatic compound can be identified with the absorption band at around 1,512.19–1,450.47 1/cm with sharp and strong intensity and strengthened in the area of 3,000 1/cm. These functional groups are matched to main compounds of kemenyan extract which are soluble in water especially cinnamic acid, benzoic acid, and isovanillin (Fig. 2).

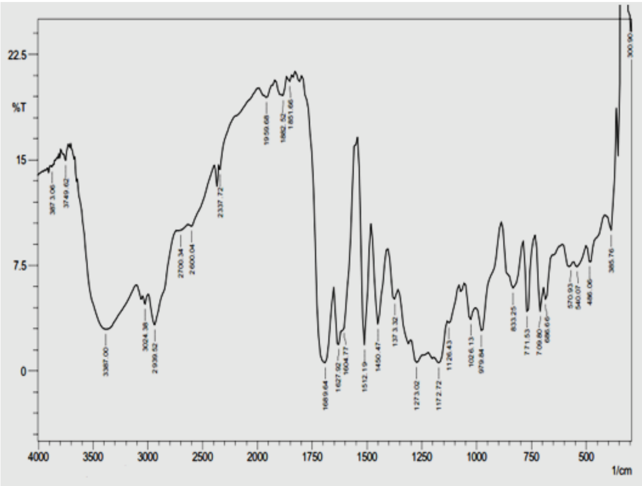


Fig. 1. IR spectrum of kemenyan extract.

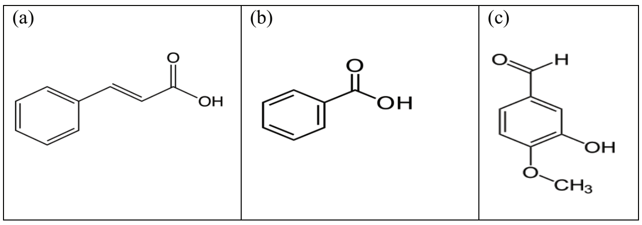


Fig. 2. Chemical structure of (a) cinnamic acid, (b) benzoic acid, and (c) isovanillin.

Table 1
Growth rate of $CaCO_3$ precipitation with various concentrations

Time (min)	Amount of precipitation (g/L)		
	0.050 M	0.075 M	0.100 M
0	0.0000	0.0000	0.0000
10	0.1004	0.1353	0.1878
20	0.1083	0.1453	0.1907
30	0.1094	0.1553	0.1914
40	0.1092	0.1582	0.1864
50	0.1061	0.1585	0.1892
60	0.1071	0.1585	0.1877
70	0.1027	0.1584	0.1888

3.2. *Experiment of kemenyan inhibitor*

Observation result data of the $CaCO_3$ crystal growth rate at different concentrations can be seen in Table 1, while the data of the $CaCO_3$ crystal growth rate at different growth solution concentration and different inhibitor concentrations are displayed in Tables 2–4. In Table 1, it can be observed that as the growth solution concentration increases, the amount of crystal precipitation will also raise. This fact shows that the growth rate of the $CaCO_3$ crystal is bigger with the increasing of the growth solution concentration (Fig. 3).

Table 2
Effect of kemenyan extract addition on $CaCO_3$ scale formation at growth solution concentration of 0.050 M

Time (min)	Amount of precipitation (g/L)				
	0 ppm	50 ppm	150 ppm	250 ppm	350 ppm
0	0.0000	0.0000	0.0000	0.0000	0.0000
10	0.1004	0.0619	0.0711	0.0320	0.0198
20	0.1083	0.0668	0.0751	0.0383	0.0179
30	0.1094	0.0789	0.0811	0.0523	0.0133
40	0.1092	0.0715	0.0782	0.0558	0.0163
50	0.1061	0.0784	0.0753	0.0375	0.0225
60	0.1071	0.0783	0.0764	0.0411	0.0216
70	0.1027	0.0809	0.0763	0.0452	0.0237

Table 3
Effect of kemenyan extract addition on $CaCO_3$ scale formation at growth solution concentration of 0.075 M

Time (min)	Amount of precipitation (g/L)				
	0 ppm	50 ppm	150 ppm	250 ppm	350 ppm
0	0.0000	0.0000	0.0000	0.0000	0.0000
10	0.1353	0.1007	0.1179	0.0767	0.0841
20	0.1453	0.1147	0.1161	0.0722	0.0803
30	0.1553	0.1184	0.1251	0.0806	0.0802
40	0.1582	0.1138	0.1207	0.0813	0.0841
50	0.1585	0.1148	0.1235	0.0778	0.0818
60	0.1585	0.1183	0.1233	0.0843	0.0901
70	0.1584	0.1198	0.1213	0.0798	0.0893

Table 4
Effect of kemenyan extract addition on $CaCO_3$ scale formation at growth solution concentration of 0.100 M

Time (min)	Amount of precipitation (g/L)				
	0 ppm	50 ppm	150 ppm	250 ppm	350 ppm
0	0.0000	0.0000	0.0000	0.0000	0.0000
10	0.1878	0.1642	0.1400	0.1160	0.0862
20	0.1907	0.1706	0.1419	0.1191	0.0896
30	0.1914	0.1671	0.1465	0.1235	0.0896
40	0.1864	0.1717	0.1428	0.1203	0.0945
50	0.1892	0.1641	0.1432	0.1248	0.1013
60	0.1877	0.1645	0.1461	0.1379	0.0961
70	0.1888	0.1667	0.1489	0.1297	0.1016

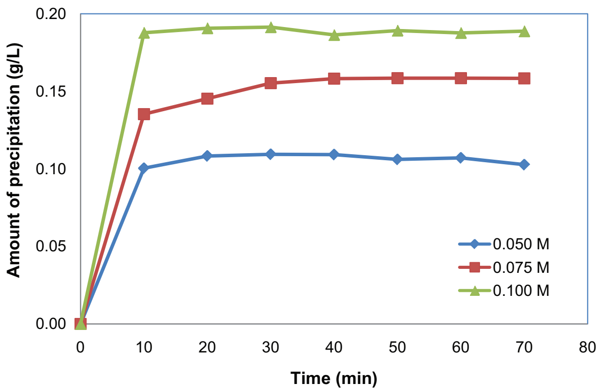


Fig. 3. Growth rate of $CaCO_3$ crystal at various growth solution concentrations.

Effects of the kemenyan extract addition at various concentrations of 0–350 ppm on the $CaCO_3$ crystal precipitation at the various growth solution concentrations of 0.050, 0.075, and 0.100 M in the absence of seed crystal can be observed in Figs. 4–6. From Figs. 4–6, generally it can be stated that the higher the concentration of the kemenyan extract added the bigger the ability of inhibition of the $CaCO_3$ scale formation. In the presence of 350 ppm of the kemenyan extract in the growth solution of $CaCO_3$ 0.050 M, inhibition of the growth rate of the $CaCO_3$ scale formation is significantly around 76.92% (Table 5). These facts also occur at the concentration of 0.075 and 0.100 M each of 49.62% and 46.19% in the presence of the kemenyan extract inhibitor from 250 and 350 ppm (Tables 6 and 7). This result is also compared with the experiment of copolymer modified with the palygorskite as inhibitor for calcium carbonate scale [25].

In order to prove deeply the effect of inhibitor addition (kemenyan extract) on the $CaCO_3$ crystal growth, it is investigated the growth of $CaCO_3$ crystal with using SEM (Figs. 7–9). From these observations with using SEM, the addition of the inhibitor in the growth solution of $CaCO_3$, the kemenyan extract can reduce the growth rates of the $CaCO_3$ crystals. These evidences can be seen in Figs. 7–9, the addition of the kemenyan extract made morphology size of the $CaCO_3$ crystals smaller than without the addition of the kemenyan extract.

The next evidence to investigate the effect of the kemenyan extract in hindering the growth rate of $CaCO_3$ crystal is with analyzing the particle size distribution of the $CaCO_3$ crystals obtained using PSA. Analysis of these particle size distributions was performed upon the $CaCO_3$ crystal formation in the absence of inhibitor and compared with in the presence of inhibitor. Analysis results are displayed in Figs. 10 and 11. Analysis result of particle size distributions shows that the addition of the kemenyan extract generally inhibits the growth rates of the $CaCO_3$ crystals. In the presence of 350 ppm of the kemenyan extract in the growth solution of $CaCO_3$ crystal 0.100 M can reduce the averages of the $CaCO_3$ crystal particle sizes from 12.72 to 9.70 μm (Fig. 10). Furthermore, the addition of the kemenyan extract 350 ppm in 0.075 M growth solution of $CaCO_3$ is able to decrease the averages of $CaCO_3$ crystal particle sizes distribution from 10.47 to 8.03 μm (Fig. 11). From the series of the experiments performed, in general, kemenyan extract plays a role as inhibitor in inhibiting the growth rate of the $CaCO_3$ scale formation and it can be compared with

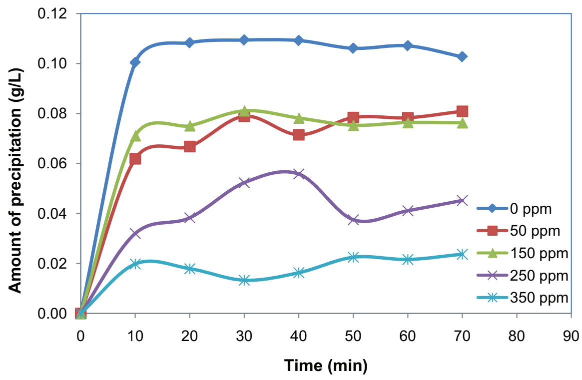


Fig. 4. Effect of kemenyan extract addition on $CaCO_3$ precipitation at growth solution concentrations of 0.050 M.

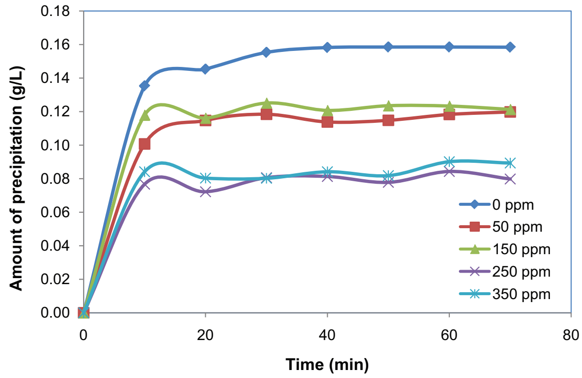


Fig. 5. Effect of kemenyan extract addition on $CaCO_3$ precipitation at growth solution concentrations of 0.075 M.

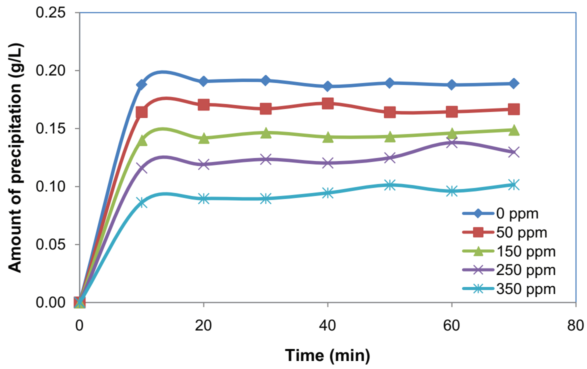


Fig. 6. Effect of kemenyan extract addition on $CaCO_3$ precipitation at growth solution concentrations of 0.100 M.

Table 5
Effectiveness of kemenyan extract in inhibiting growth rate of $CaCO_3$ scale at growth solution concentration of 0.050 M

Inhibitor concentration (ppm)	Inhibitor efficiency (%)
0	0.00
50	21.23
150	25.71
250	55.99
350	76.92

Table 6
Effectiveness of kemenyan extract in inhibiting growth rate of $CaCO_3$ scale at growth solution concentration of 0.075 M

Inhibitor concentration (ppm)	Inhibitor efficiency (%)
0	0.00
50	24.37
150	23.42
250	49.62
350	43.62

Table 7
Effectiveness of kemenyan extract in inhibiting growth rate of $CaCO_3$ scale at growth solution concentration of 0.100 M

Inhibitor concentration (ppm)	Inhibitor efficiency (%)
0	0.00
50	11.71
150	21.13
250	31.30
350	46.19

another scale inhibitor like *Gambier* extract [3], copolymer modified with palygorskite [25], acrylic acid–allylpolyethoxy carboxylate [26], a novel fluorescent-tagged scale inhibitor [27], and water-soluble anhydride containing alternating copolymers [28].

The scale process of microsolubility salts like $CaCO_3$ in cooling water system is just the process of crystallization; calcium carbonate scale formation consists of two steps: nucleation and growth [27]. Thus the mechanism of inhibition in this experiment is inhibitor containing carboxyl group adsorb on the scale surface causing inhibition of scale nuclei formation. The more kemenyan extract added in the growth solution, the more the carboxyl group existing in kemenyan extract will react to Ca^{2+} ion to inhibit the formation of $CaCO_3$ nuclei. In this case, it will occur that nucleation step of the $CaCO_3$ will be hardly formed in the experiment solution. This can identified with investigating the morphology of $CaCO_3$ crystal in the absence and in the presence of inhibitor (Figs. 8 and 9). The morphology of the $CaCO_3$ crystal in the presence of inhibitor changes to be smaller in size proving the inhibitor playing a role. This result is consistent with the result obtained from the previous experiment [26,29,30].

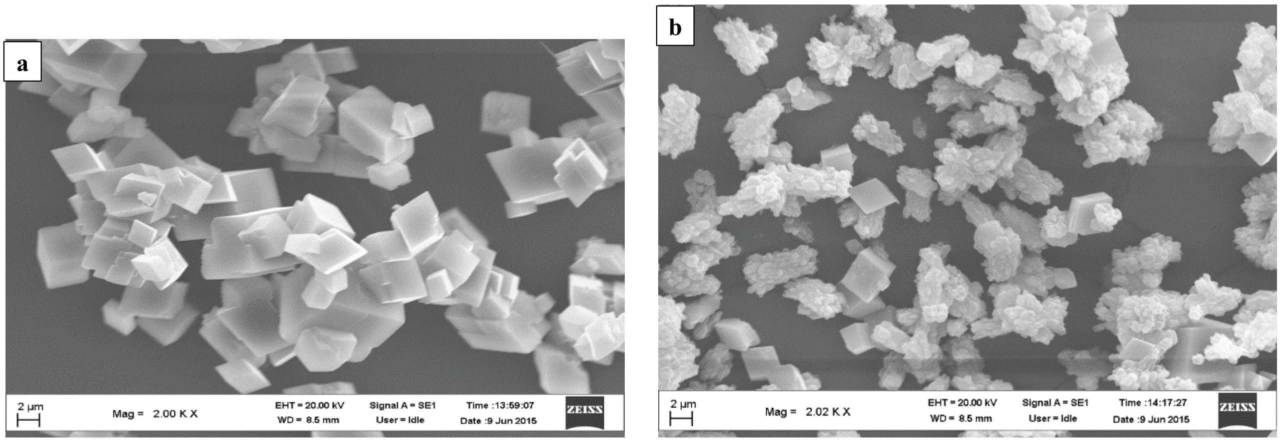


Fig. 7. Morphology of $CaCO_3$ crystal at growth solution concentration of 0.050 M (a) without and (b) with the addition of inhibitor 350 ppm.

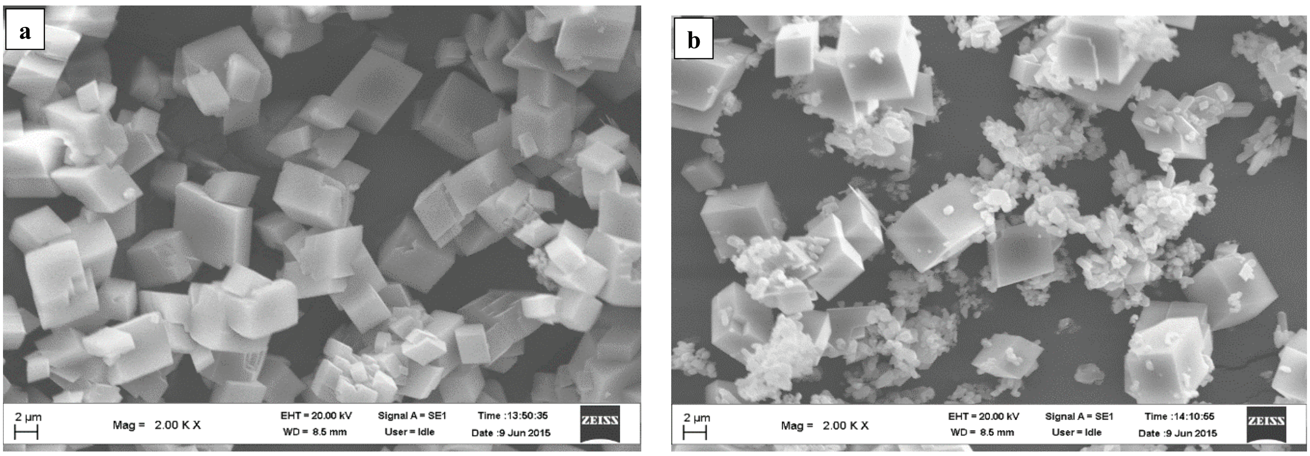
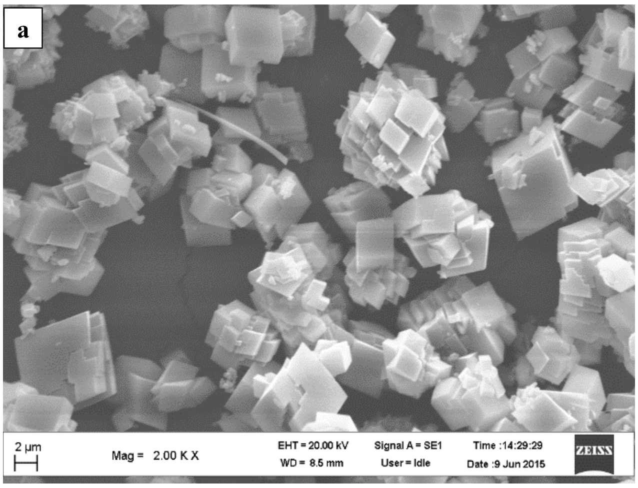


Fig. 8. Morphology of $CaCO_3$ crystal at growth solution concentration of 0.075 (a) without and (b) with the addition of inhibitor 250 ppm.



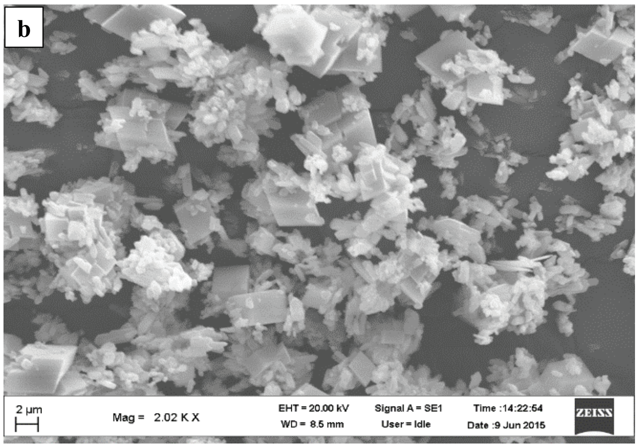


Fig. 9. Morphology of $CaCO_3$ crystal at growth solution concentration of 0.100 M (a) without and (b) with the addition of inhibitor 350 ppm.

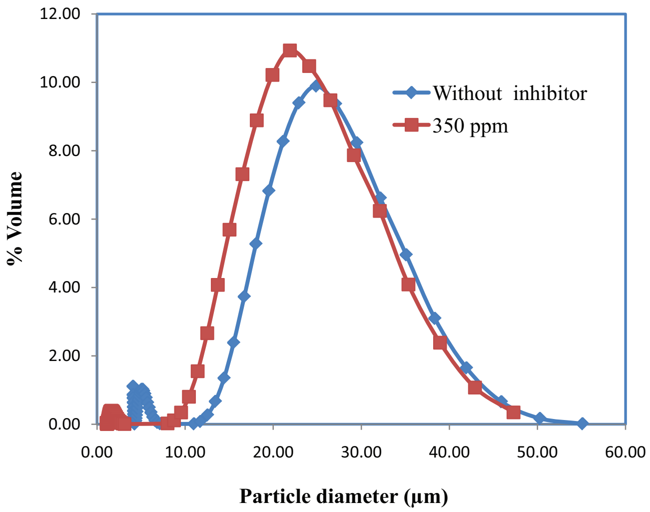


Fig. 10. Particle size distribution of $CaCO_3$ crystals without and with the addition of 350 ppm kemenyan extract at growth solution concentration of 0.100 M.

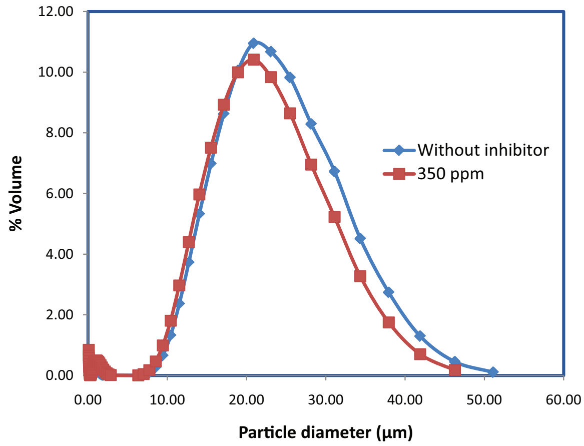


Fig. 11. Particle size distribution of $CaCO_3$ crystals without and with the addition of 350 ppm kemenyan extract at growth solution concentration of 0.075 M.

The inhibitor effectiveness is affected by the concentration of Ca^{2+} ion in the growth solution; usually the higher the concentration of Ca^{2+} ion in the growth solution, the higher the inhibitor needed to inhibit the formation of the $CaCO_3$ crystal. Table 8 shows the comparison of inhibitor efficiency from several researchers. The inhibitor of citric acid with the concentration of Ca^{2+} ion in the growth solution 0.0019 M needed 1–10 ppm to inhibit the formation of the $CaCO_3$ with the inhibitor efficiency of 25%–30% [31]. While, the polyepoxysuccinic acid with the concentration of Ca^{2+} ion in the growth solution from 0.001 to 0.005 M involved 10 ppm of this inhibitor to gain the inhibitor efficiency of 90% [32]. The results of these experiments obtained the inhibitor efficiency of 12%–77% with the concentration of Ca^{2+} ion from 0.05 to 0.10 M and inhibitor added of 50–350 ppm. If these results are compared with the previous researches as listed in Table 8, these results are still reasonable.

4. Conclusions

The extract of the kemenyan resin can be used as a green inhibitor of the $CaCO_3$ scale formation. The addition of the kemenyan extract in the various growth solutions of the $CaCO_3$ 0.050, 0.075, and 0.100 M was able to inhibit significantly the growth rates of the $CaCO_3$ precipitation with the percentage of inhibition ability from 12% to 77%. The inhibition ability depends on the inhibitor concentration added and growth solution concentration as crystal growth media under these condition experiments.

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Table 8
Comparison of inhibitor efficiency in inhibiting $CaCO_3$ formation from several researchers

Name of inhibitors	Concentration of Ca^{2+} as growth solution (M)	Inhibitor concentration (ppm)	Inhibitor efficiency (% IE)	References
kemenyan extract	0.050–0.100	50–350	12–77	This work
Modified Gambier	0.100–0.600	50–300	12–92	[18]
Gambier extracts	0.100–0.600	50–250	60–100	[3]
Citric acid	0.002	1–10	25–30	[31]
Homopolymer of polymaleic acid	0.003	4	67	[24]
Terpolymer of polymaleic acid	0.003	4	73	[24]
Copolymer of polymaleic acid	0.003	4	18	[24]
Polycarboxylic acid	0.003	4	70	[24]
C-methyl-4,10,16,22-tetrametoxy calix[4]arene	0.100	10–100	34–100	[30]
Poly(aspartic acid)	0.006	12	80	[11]
Polyepoxysuccinic acid	0.001–0.005	10	90	[32]
Soybean extract–based polymer from sea weeds	0.300	10	16.7	[33]
Calix[4]resorcinarene	0.100–0.600	25–75	38–94	[34]

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