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: Modification of Gambier Extacs as Green Inhibator of Calcium Carbonate (CaCO₃) Scale Formation : Suharso, Tiand Reno, Teguh Endarvanto, Burhan : Pertanian : Journal of Water Process Engeneering : http://repository.lppm.unila.ac.id/id/eprint/6975 Waktu Perbitan : Bandar Lampung, 27 April 2017

Mengetahui: WakilDekan I BidangAkademikdan KerjasamaFakultas Pertanian Universitas Lampung, m

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Bandar Lampung, 05 Juli 2019 Penulis,

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Mengesahkan: Ketua Lembaga Penelitian dan Pengabdian kepada Masyarakat Universitas Lampung,

Warsono, Ph.D NIP.196302161987031003

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Contents lists available at ScienceDirect





Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Modification of Gambier extracs as green inhibitor of calcium carbonate (CaCO₃) scale formation



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ARTICLE INFO

Keywords: Scale inhibitor CaCO₃ Gambier extract modification

ABSTRACT

The addition of the Gambier extract (*Uncaria gambier* Roxb leaves) modification (Gambier:benzoic acid:citric acid/2:1:2) as a green inhibitor on the formation of $CaCO_3$ scale at various concentrations was carried out using a seeded experiment method. The experiments were performed with observing the precipitation change of the $CaCO_3$ crystals growth obtained. In order to prove the efficiency of the inhibitor in inhibiting the formation of the $CaCO_3$ crystals, the changes of the crystal morphology were investigated by scanning electron microscopy (SEM) and the changes of the crystal size distribution were analyzed by particle size analyzer (PSA). The research results showed that the Gambier extract modification was able to inhibit the formation of the $CaCO_3$ scale indicated with the morphology change of the $CaCO_3$ crystals and smaller crystal size distribution after the addition of this inhibitor.

1. Introduction

Scale formation causes a serious issue encountered by many industries in Indonesia and other countries such as; the industry of oil or gas production, water transport, power generation, and batch precipitation [1–6]. Faced with this issue; PT Pertamina Geothermal Energy (PGE) which is one of subsidiary of Indonesian Oil Company (PT. Pertamina) has spent US\$ 6–7 million to rejuvenate the pipe installation of the Geothermal Energy Industry for 10 years. In order to solve this problem, several researchers studied many additives to prevent the scale formation or to modify the crystal morphology [7–12]. The addition of the additive in a growth solution of the scale formation is looked a cheaper method and an effective enough to inhibit the scale formation of an inorganic material.

Gambier extract from Uncaria gambier Roxb leaves was reported as a green inhibitor of $CaCO_3$ scale formation [13]. Nevertheless, the Gambier extract has several problems, such as; it is easily moldy and cannot be stored for a long time. In order to control these problems, the Gambier extract was mixed with citric and benzoic acid. Previous research reported that the citric and benzoic acid can play a role as an inhibitor also to inhibit the scale formation [14–16]. In addition, these mixtures are potential as a green inhibitor of the scale formation because they have some chemical compounds such as tannic acid, catechin, and quercetin [13] which are effective inhibitors of scale formation of $CaCO_3$ beside the citric and benzoic acid. Other advantation of $CaCO_3$ beside the citric and benzoic acid.

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http://dx.doi.org/10.1016/j.jwpe.2017.05.004

Received 4 February 2017; Received in revised form 27 April 2017; Accepted 3 May 2017 2214-7144/ © 2017 Elsevier Ltd. All rights reserved.

tages of these mixtures are cheaper and they can be applied as a green inhibitor like other materials which have been used previously [17–27] to keep our environment.

The effects of the Gambier extract modification as the inhibitor of $CaCO_3$ scale formation at various concentrations from 0 to 300 ppm on the precipitation rate of calcium carbonate was observed at temperature of 80 °C and at a growth solution of 0.1, 0.3 and 0.6 M under seeded experiment. The seeded experiments were applied by previous researchers to investigate the inhibition of the calcite crystal growth with using phosphonates additive and they monitored the rate of crystallization by measuring the concentration of calcium ion as a function of time [28]. In this experiment, the rate precipitation of the calcium carbonate seed crystals was monitored by weighing the amount of the calcium carbonate precipitated as function of time [13]. The precipitation obtained was characterized using scanning electron microscopy and particle size distribution to give an overview of its composition, size and morphology of the CaCO₃ crystals was analyzed by particle size analyzer.

2. Experimental procedure

2.1. Preparation of Gambier extract modification

Preparation of Gambier extract modification was made with the ratio of 2:1:2 (Gambier:benzoic acid:citric acid). The benzoic and citric



Fig. 1. The qualitity of Gambier extract (1) and modified Gambier (2) in the room temperature at (a) First day, (b) 7 days, (c) 14 days, (d) 25 days, (e) 14 days (drawn closer), and (f) 25 days (drawn closer).

acid used was produced by commercial products of Merck, Germany. Gambier was prepared from dry leaves of *Uncaria Gambir* Roxb from West Sumatra, Indonesia. The amount of 2 g powdered Gambier, 1 g benzoic acid, and 2 g citric acid was placed into a 1 L volume glass added water up to 1 L. The mixtures were heated at temperature of 80 °C for 1 h and left for 1 night. Then, the mixtures were filtered and the filtrate was used as an inhibitor of CaCO₃ scale formation. Similar with previous research, the Gambier extracts was identified containing 40% of tannic acid, 25% of catechin, and 12% of quercetin [13].

2.2. Seed crystal production

The crystal seeds of CaCO₃ were made with mixing each CaCl₂ anhydrate solution (1 M) and Na₂CO₃ solution (1 M) in 50 mL of water. The CaCl₂ anhydrate and Na₂CO₃ used was purchased by commercial products of Merck, Germany. The mixture was stirred by magnetic stirrer and it was left for 2 h to produce seed crystals continued with separating the seed crystals from the liquor by filtration through a 0.45 μ m Millipore filter. The seed crystals obtained were cleaned thoroughly with water and dried at room temperature for at least two days. This work was replicated a bunch of times to produce the required amount of the CaCO₃ seed crystals for the work.

2.3. Experiments of crystallization

An amount of 200 mL of $CaCl_2$ anhydrate solution (0.2 M) was mixed into 200 mL of Na_2CO_3 solution (0.2 M) in 500 mL Nalgene polypropylene bottles followed by shaking to produce a homogeneous

solution. This procedure was to prepare the growth solution of 0.1 M CaCO₃. The homogeneous solution produced was separated through a 0.45 μ m Millipore filter. The solution was fed into 250 mL Nalgene polypropylene bottles, each containing 50 mL consisted of 7 bottles. The bottles were fed back to the bottle-roller bath adjusted the temperature at 80 °C and the rotating at 40 rev min⁻¹ continued with adding together 100 mg of the CaCO₃ seed crystals into each bottle. Over the 90 min the experiment run, each bottle was picked up for every 15 min. The crystals obtained were cleaned thoroughly with water and placed in oven at temperature of 105 °C for one day. The weight of the CaCO₃ crystals obtained from each bottle was measured and the amount precipitated of CaCO₃ crystals was calculated.

For each crystallization experiment, a blank containing no inhibitor was performed in conjunction with the presence of inhibitor. The similar experiments were carried out for concentration variety of $CaCO_3$ growth solutions for each 0.3 and 0.6 M. Following the similar experiment applied for the 0.1 M $CaCO_3$ growth solution concentration, a growth solution concentration of 0.3 M $CaCO_3$ was made with mixing 200 mL of $CaCl_2$ anhydrate solution (0.6 M) and 200 mL of Na_2CO_3 solution (0.6 M), and a growth solution of 0.6 M $CaCO_3$ was made with mixing 200 mL of 1.2 M $CaCl_2$ anhydrate solution and 200 mL of 1.2 M Na_2CO_3 solution.

2.4. Presence of additives

The influence of various additive concentrations was observed by adding different amount of the additive (0, 50, 100, 200 and 300 ppm) in the similar treatment. The weight of the crystals was measured and

the amount precipitated was calculated.

2.5. Data analysis

The data produced as amount of precipitate versus time at various concentrations of growth solution and in the presence of additive, each was plotted as an amount of precipitate versus time using MS Excel 2010. The effectiveness of the additive in inhibiting the rate of the CaCO₃ scale formation were able to be identified from the mass of precipitate obtained and the morphology of the CaCO₃ observed by SEM (JSM 6360 LA, Made in Japan). The distribution of particle size from the CaCO₃ crystal precipitate resulted was also investigated by particle size analyzer (Sedigraph III 5120-Micrometrics).

3. Results and discussion

The quality of the Gambier extract and modified Gambier (Gambier extract:benzoic acid:citric acid) with the composition ratio of 2:1:2 in 1 L of water solution can be observed in Fig. 1. In this figure, it can be seen that the quality of the Gambier extract decreased after 14 days left in the room temperature. On the day of 14, the Gambier extract become moldy and on the day 25, the number of fungus contained in the Gambier extract was increased. The existence of the fungus in the Gambier extract may cause the chemical compounds as main component playing a role in inhibiting of the CaCO₃ scale formation having damaged. While the quality of the modifed Gambier in the addition of benzoic and citric acid after 25 days was still good enough. This modifed Gambier added benzoic and citric acid with the composition ratio of 2:1:2 was used in this experiment as a green inhibitor of the formation of CaCO₃ crystals.

The observations of the CaCO₃ formation rate at different concentrations were displayed in Fig. 2. These observations were performed at temperature of 80 °C and the growth solution concentration of 0.1, 0.3, and 0.6 M with adding 2 g crystal seeds in 1 L growth solution. The results showed that the growth rates of the CaCO₃ crystals were linear with the growth solution concentrations. The bigger the growth solution concentration of 0.6 M with the precipitation change occurred at growth solution concentration of 0.6 M with the precipitation amount increasing was approximately 0.6 g. The raising of the precipitation as a crystal deposit. The increasing change of precipitation amount from the concentration of 0.1, 0.3, and 0.6 M can be seen in Fig. 2.

Effect of the inhibitor mixture addition (Gambier:benzoic acid:citric acid/2:1:2) on the formation of the $CaCO_3$ crystal at various growth solution concentrations can be observed clearly in Figs. 3–5. From these figures, it can be seen that the inhibitor mixture was able to inhibit the formation of the $CaCO_3$ crystal based on the concentration of growth solution and the amount of the inhibitor added. The data show that at the concentration of 0.1 M, inhibitor ability inhibits the formation of



Fig. 2. The growth rate of CaCO₃ precipitation at various growth solution concentartion.



Fig. 3. Effect of inhibitor added on the formation of $CaCO_3$ precipitation at the growth solution concentration of 0.1 M.



Fig. 4. Effect of inhibitor added on the formation of $CaCO_3$ precipitation at the growth solution concentration of 0.3 M.



Fig. 5. Effect of inhibitor added on the formation of $CaCO_3$ precipitation at the growth solution concentration of 0.6 M.

the $CaCO_3$ higher than at the concentration of 0.3 and 0.6 M.

In order to investigate the inhibitor efficiency in inhibiting the rate of $CaCO_3$ scale formation may use equation reported by previous research [29] as this below;

PercentageofInhibitorEfficiency(%IE) =
$$100 \times \frac{(C_a - C_b)}{(C_c - C_b)}$$
 (1)

Where:

 C_a = Precipitation amount of CaCO₃ after added inhibitor at equilibrium (g/L).

 C_b = Precipitation amount of CaCO₃ without inhibitor at equilibrium (g/L).

 C_c = Initial precipitation amount of CaCO₃ (g/L).

From the calculations using Eq. (1) were obtained% IE from variety of the growth solution concentrations and the amount of inhibitor added as listed in Tables 1–3. From these tables, it can be stated that the

Table 1

Inhibitor efficiency in inhibiting the scale formation of \mbox{CaCO}_3 at the growth solution concentration of $0.1\,\mbox{M}.$

Inhibitor Concentrations (ppm)	Percentage Inhibitor Efficiency (% IE)
0	0.00
100	20.22
200	71.34
300	91.46

Table 2

Inhibitor efficiency in inhibiting the scale formation of ${\rm CaCO}_3$ at the growth solution concentration of 0.3 M.

Inhibitor Concentrations (ppm)	Percentage Inhibitor Efficiency (% IE)	
0 50 100 200 300	0.00 12.08 51.55 58.56 67.99	

Table 3

Inhibitor efficiency in inhibiting the scale formation of $\rm CaCO_3$ at the growth solution concentration of 0.6 M.

Inhibitor Concentrations (ppm)	Percentage Inhibitor Efficiency (% IE)		
0	0.00		
50	11.75		
100	21.48		
200	42.28		
300	55.03		

Table 4

Inhibitor Efficiency in inhibiting CaCO₃ crystal of different inhibitors, experiment methods, and growth solution concentrations.

Name of Inhibitors	Inhibitor Concentration (ppm)	Inhibitor Efficiency (% IE)	References
Modified Gambier	50-300	12–92	This work
Gambier extracts	50-250	60–100	[13]
Polymaleic acid	1-4	20-100	[18]
Homopolymer of polymaleic acid	4	67	[29]
Terpolymer of polymaleic acid	4	73	[29]
Copolymer of polymaleic acid	4	18	[29]
Polycarboxylic acid	4	70	[29]
Metallocene complexes	10	27–66	[30]
C-methyl-4,10,16,22- tetrametoxy calix[4] arene	10–100	34–100	[31]

inhibitor can inhibit the formation of the CaCO₃ crystals with% IE of 11.75–91.46% depending on the growth solution concentration and the amount of inhibitor added. The highest% IE of 91.46% occurred at the growth solution concentration of 0.1 M with the amount of the inhibitor added 300 ppm. While, the lowest% IE of 11.75% occurred at the growth solution concentration of 0.6 M with the presence of the inhibitor 50 ppm. In addition, the inhibitor ability in inhibiting the formation of the CaCO₃ scale formation is still strong enough at the amount of inhibitor added 300 ppm and the growth solution concentration of 0.6 M with the% IE of 55%. Therefore, it can be concluded that the inhibitor can still work at the higher growth solution concentration of 0.6 M. The Inhibitor Efficiency (% IE) from this experiment and several inhibitors from the previous research results in inhibiting the calcium carbonate crystal growth with the addition of



Fig. 6. Morphology of CaCO₃ crystals (a) in the absence of inhibitor (b) in the presence of inhibitor 300 ppm at the concentration of growth solution of 0.1 M (Magnification $2500 \times$).

homopolymer of polymaleic acid (PMA-1), terpolymer of polymaleic acid (PMA-2), copolymer of polymaleic acid (PMA-3), polycarboxylic acid (EM), polyacrylate (PAA), and phosphonate can be seen in Table 4 [18,29–31]. The Inhibitor Efficiency (% IE) from the inhibitors derived from the polymaleic acid, polycarboxylic acid, polyacrylate, and phosphonate groups in inhibiting the formation of calcium carbonate crystals was around 20–100% [18,29,30].

For further identification of the inhibitor effect on the CaCO₃ crystal growth, SEM analysis was performed toward morphology and crystal surface of the crystal resulted. SEM analysis results toward morphology and crystal surface of the CaCO₃ crystals with and without inhibitor displayed in Figs. 6 and 7. From these figures, it can be observed that the presence of the inhibitor not only changes the morphology of CaCO₃ crystals but also inhibits the growth of the CaCO₃ crystal. The size of CaCO₃ crystal with the presence of inhibitor (Figs. 6 and 7) was smaller compared with in the absence of inhibitor. Thus, Figs. 6 and 7 are visual evidences of the effect of adding the inhibitor on the $CaCO_3$ scale formation. The morphology change of CaCO3 crystal was because of crystal distortion. In the crystal distortion mechanism, the inhibitor added into the CaCO₃ growth solution affected the ordering and growth reaction of crystals and induced an irregular, noncrystalline shape. The inhibitor also delayed the crystal growth of the usually highly ordered CaCO₃ crystal. The inhibitor molecules especially tannin from the Gambir extract adsorbed onto the active growth sites of the CaCO₃ seed crystals, resulting in the blockage and inhibition of further growth [32]. This inhibitor effect can be seen in Figs. 6 and 7.

Further evidence of the inhibitor efficiency can be observed with analyzing the particle size distribution of the $CaCO_3$ crystal produced with and without inhibitor added into the growth solution of the $CaCO_3$ crystals (Figs. 8 and 9). The observation results from Figs. 8 and 9 show



Fig. 7. Morphology of CaCO₃ crystals (a) in the absence of inhibitor (b) in the presence of inhibitor 300 ppm at the concentration of growth solution of 0.6 M (Magnification $2500 \times$).



Fig. 8. Particle size distribution of $CaCO_3$ crystals in the absence of inhibitor and in the presence of 300 ppm of inhibitor at the growth solution concentration of 0.1 M.

that the average of the particle size distribution of the CaCO₃ crystals in the presence of inhibitor decreased dramatically. In the growth solution of 0.1 M, the average of particle size distribution of CaCO₃ crystals in the absence of inhibitor was around 10.6 μ m. After the inhibitor added into the growth solution of CaCO₃ crystal, the average of particle size distribution of the CaCO₃ crystals was 5.01 μ m. While, in the growth solution of 0.6 M, the average of particle size distribution of the CaCO₃ crystals in the absence of inhibitor was 17.3 μ m. When the inhibitor added into the growth solution of the CaCO₃ crystal, the average of particle size distribution of CaCO₃ crystals dropped to 8.5 μ m. Thus, it can be concluded that generally the addition of inhibitor into the growth solution of the CaCO₃ crystal can inhibit the CaCO₃ scale formation. The particle size distribution data produced from the CaCO₃



Fig. 9. Particle size distribution of $CaCO_3$ crystals in the absence of inhibitor and in the presence of 300 ppm of inhibitor at the growth solution concentration of 0.6 M.

crystal formation were acordance with the previous result using Gambier extract as inhibitor of the $CaCO_3$ scale formation [13].

As seen in Tables 1–3 and Figs. 3–5, the inhibition on CaCO₃ scale formation substantially increased when the inhibitor concentration increased. This case can be interpreted that after the scale inhibitor was added into the solution, chelating reaction among the carboxyl from citric and benzoic acid, and Ca2+ ions occurred in aqueous solution. And also, chelating reaction can be occurred between the hydroxyl from tannic acid, catechin, and quercetin (from the Gambier extracts as the main chemical compounds) and Ca² ions, as well as scale inhibitor-Ca was adsorbed on the surface of CaCO₃ crystal. The microcrystalline of CaCO₃ with the similar charges repelled each other, prevented the formation of crystal nucleus, and reduced the CaCO₃ crystal growth rate. The similar case occured in the presence of curcumin-malic acid in controlling of scale in industrial cooling water treatment [4]. In addition, the CaCO₃ crystal growth in the presence of inhibitor could not form the regular crystal as seen in Figs. 6 and 7, therefore inhibiting the formation of the CaCO3 scale. Thus, the percentage inhibitor efficiency increased as the inhibitor concentration level raised from 50 to 300 ppm. At the CaCO₃ growth concentration of 0.1 M, the percentage of inhibitor efficiency in the inhibitor presence of 100 ppm was around 20% and it increased to be 71 and 92% when the inhibitor presence was increased to be 200 and 300 ppm respectively. The similar cases were also occurred at the CaCO₃ growth concentration of 0.3 and 0.6 M. However, the percentage of inhibitor efficiency in the CaCO₃ growth concentration of 0.3 and 0.6 M is lower than at the CaCO₃ growth concentration of 0.1 M at all inhibitor concentration levels added (Tables 2 and 3). The differences of the percentage of inhibitor efficiency at the same concentration level were due to different concentrations of the CaCO₃ growth concentration. The higher the concentration of the CaCO₃ growth solution is the higher the growth rate of CaCO₃ crystal. At the CaCO₃ growth concentration of 0.3 and 0.6 M, the ability of the inhibitor to inhibit the formation of CaCO₃ crystals will be slower compared at the CaCO₃ growth concentration of 0.1 M. The percentage of inhibitor efficiency decreased with the increasing of the CaCO3 growth solution concentration because the increase of CaCO₃ growth solution concentration facilitated the formation of the CaCO₃ scale crystal, accelerated the crystallization process, and reduced the ability of inhibitor to inhibit the formation of the CaCO3 scale. Therefore, the inhibition of inhibitor at the addition of 300 ppm in the CaCO₃ growth solution concentration of 0.1, 0.3, and 0.6 is 92, 68 and 55%, respectively. These experiment results are also comparable to those studied for the calcium carbonate crystallization in the presence of green inhibitor of polymaleic acid [18], green inhibitors of thiamine and pyrodoxine [33], several comercial inhibitors produced by industry [34], and calix [4] resorcinarene [35].

The inhibitor efficiency depends on the concentration of the growth solution, in general the higher the concentration of the growth solution is the higher the inhibitor added. In this experiment, the growth solution concentrations of $CaCO_3$ were 0.1-0.6 M with the percentage inhibitor efficiency of 12-92% and the inhibitor added up to 300 ppm. These results are still comparable with in the case of calcium carbonate crystal growth inhibition test at the calcium ion concentration (as growth solution) of 125 mg/L (0.003 M) and the inhibitor of polycarboxylic or polymaleic acid compounds added of 4 ppm [29]. Previous reserchers reported also the use of citric acid as inhibitor of calcium carbonate at the concentration of calcium ion 0.0019 M with the citric acid added 1–10 ppm and the inhibitor efficiency of around 25–30% [36]. If it is compared these experiments, the doses of inhibitor added is still reasonable. Similar results with similar experiment conditions were shown in Table 4 with the addition of Gambier extract [13] and C-methyl-4,10,16,22-tetrametoxy calix[4]arene [31].

4. Conclusion

The modification of the Gambier extracts with the addition of benzoic and citric acid with the composition ratio of Gambier extract: benzoic acid:citric Acid/2:1:2 in 1 L of water solution as green inhibitor increased the quality of this mixture. This mixture was able to inhibit the formation of CaCO₃ scale at various inhibitor concentrations of 50–300 ppm and growth solution concentrations of 0.1–0.6 M using seeded experiment method with the Inhibitor Efficiency (% IE) of 12–92%. The inhibitor used also changed the morphology of CaCO₃ crystals and it made the crystal size of CaCO₃ crystals to be smaller in their crystal size distribution after addition of this inhibitor.

Acknowledgments

The authors would like to appreciate the Directorate of Research and Community Services, Directorate General of Strengthening Research and Development, Ministry of Research, Technology and Higher Education of the Republic of Indonesia (Kemristekdikti) for supporting this research through Research Grant of Sciences and Technology Development Research (IPTEK) with contract number: 80/UN26/8/LPPM/2016, 13 April 2016.

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