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 effectiveness 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
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 (Kern & 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 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

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 CaSO₄ crystal formation with the unseeded experiment method

2.3.1. Without the addition of inhibitors

The growth solution of 0.05 M CaSO₄ was made from mixing a solution of 0.100 M CaCl₂ and 0.100 M Na₂SO₄ 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 the most effective was selected to be analyzed using instruments of SEM, 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 concentrations 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 CaSO₄ in a growth solution of 0.05 M CaSO₄.

The growth solution of 0.05 M CaSO₄ was made by mixing each 200 mL solution of 0.100 M CaCl₂ and 0.100 M Na₂SO₄ 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 CaSO₄ Eq. (1) [21] given as follows can be used:

\[
\text{Effectiveness of inhibitors} (\%) = 100 \times \left( \frac{C_c - C_b}{C_c - C_b} \right)
\]

where \(C_a = \text{CaSO}_4\) concentration after added inhibitor at equilibrium (g/L); \(C_b = \text{CaSO}_4\) concentration without inhibitor at equilibrium (g/L); \(C_c = \text{initial CaSO}_4\) 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

<table>
<thead>
<tr>
<th>No.</th>
<th>Comparison G:K</th>
<th>Concentration (ppm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G</td>
</tr>
<tr>
<td>1</td>
<td>5:1</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>5:3</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>5:5</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>5:7</td>
<td>250</td>
</tr>
<tr>
<td>5</td>
<td>5:9</td>
<td>250</td>
</tr>
</tbody>
</table>
The inhibition of CaSO$_4$ scale formation by a mixture of gambier and kemenyan extracts was studied. FTIR analysis was used to determine the presence of functional groups in the extracts. The infrared spectra of the extracts showed the presence of hydroxyl (–OH) groups, aromatic C–H functional groups, and carbonyl (C=O) functional groups. The mixture of gambier and kemenyan extracts showed slight changes in the absorption bands, indicating the presence of active functional groups.

3.2. Testing of inhibitor mixtures in inhibiting CaSO$_4$ scale formation

The effectiveness of the inhibitor mixtures was evaluated using Eq. (1) and presented in Table 2. The mixture of gambier and kemenyan extracts in a growth solution of 0.05 M CaSO$_4$ was able to inhibit the growth rate of CaSO$_4$ crystals. The addition of inhibitors with a concentration ratio of 5:9 had the greatest effectiveness of 39.88%.

The crystal morphology of CaSO$_4$ was observed using SEM analysis. The SEM images showed a change in the size of CaSO$_4$ crystals in the seeded experiment method using inhibitors with a concentration ratio of 5:9. From the SEM analysis, it was observed that CaSO$_4$ crystals without inhibitors had a larger and longer size compared with CaSO$_4$ crystals with inhibitors.

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.
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\(_4\) × 2H\(_2\)O) to the bassanite (CaSO\(_4\) × 0.5H\(_2\)O) 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. 4. 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×.](image)
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;

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

Table 3

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

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.
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 gambier 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 previously 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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