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Piper betle leaf extract as a green inhibitor of calcium sulphate ($CaSO_4$) scale formation

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Abstract. The addition of *Piper betle* leaf extract with the concentration of 450 ppm as a green inhibitor of $CaSO_4$ scale formation at the concentration of growth solution of 0.05 M and temperature of 90°C was carried out using a seeded experiment method. The experiments were performed with observing the precipitation change of $CaSO_4$ crystals growth obtained. In order to prove the efficiency of the inhibitor in inhibiting the formation of $CaSO_4$ crystals, the changes of the crystal morphology were investigated by scanning electron microscopy (SEM). The research results showed that *Piper betle* leaf extract was able to inhibit the formation of $CaSO_4$ scale indicated with the morphology change of the $CaSO_4$ crystals after the addition of this inhibitor. The ability of *Piper betle* leaf extract as an inhibitor of the formation of $CaSO_4$ is 47.07%.

1. Introduction

The serious problem faced by the geothermal power plant was formation of scale on the walls of the fluid flow thus disrupting heat transfer causing reduction of fluid flow efficiency. The impact was more severe because it was destruction of tools due to corrosion. This was due to the scale buildup so the losses incurred are huge. That causes most of the cost of maintenance of equipment intended to replace or repair components damaged by scale buildup [1]. Pertamina Geothermal Energy (PGE) Company, one of the subsidiaries of Pertamina Company, has to spend US $ 6-7 million to build a steam geothermal well drilling plant. The well can only be used for 10 years due to scale formation which inhibits fluid flow so it was no longer effective. This was an interesting study for researchers as well as a challenge to find a solution to this problem.

One of the scale forming compounds which was a problem in the geothermal steam drilling industry is calcium sulfate ($CaSO_4$). This compound is usually produced in areas that have high sulfur content. Several methods have been proposed to overcome the formation of $CaSO_4$ scale. One method that was considered effective and inexpensive was the use of anti-scaling additives. Some additives that have been investigated for their use as crustal inhibitors include: gambir extract [2], kemenyan (*Styrax benzoin* dryand) extract [3], calixarene [4-5], catechin, quercetin and tannic acid [6].

Research to find $CaSO_4$ scale inhibitors needs to be carried out. One of which it is by utilizing the wealth potential of Indonesia's biodeversity. One of Indonesia's native plants that have the potential as $CaSO_4$ inhibitors is *Piper betle*. Currently *Piper betle* leaf extract has been used for various purposes including, ingredients for making bath soap, toothpaste, feminine cleaning products, and others. In addition, researchers from various countries have also done a lot of research on the use of *Piper betle* leaf extract, which is as an antioxidant and anti-inflammatory [7-8], protective against oxidative stress due to cadmium (Cd) and dysfunction liver in mice [9], biocompatible green synthesis media of gold nanoparticles [10] and inhibitors of xanthin oxidation [11].

Piper betle leaf extract containing active compound such as hydroxychavicol, fatty acids and hydroxy esters of fatty acids [12]. So nucleophilic functional groups of these compounds are expected to inhibit the growth of $CaSO_4$.

2. Experimental procedure

2.1. Preparation of Piper betle leaf extract

Preparation of *Piper betle* leaf extract was made by dissolving of 1 g dry *Piper betle* leaf powder in water with total volume of 1 L at temperature of 90°C for 1 h and it was kept for 1 night. Furthermore, 1000 ppm of *Piper betle* leaf extract solution obtained was diluted to 450 ppm.

2.2. Preparation of seed crystal

Seed crystal was prepared by mixing $CaCl_2$ anhydrate solution (1 M) and Na_2SO_4 solution (1 M) each in 500 mL water. The mixture was shaken to form seed crystals. Then, the seed crystals were separated from the liquor by filtration through a 0.45 μm Millipore filter, washed thoroughly with deionized water and dried in oven at temperature of 150 °C until dry.

2.3. Crystallization experiment

A growth solution of 0.05 M $CaSO_4$ was prepared by mixing 200 mL of $CaCl_2$ anhydrate solution (0.10 M) and 200 mL of $NaSO_4$ solution (0.10 M) each in 500 mL Nalgene polypropylene bottles at a temperature of 90 °C. The mixture was shaken to form a homogeneous solution. Then, the solution was filtered through a filter paper. The solution was placed into 250 mL Nalgene polypropylene bottles, each containing 50 mL (7 bottles). The bottles were returned to the water bath at a temperature of 90 °C and 200 mg of seed crystals was placed into each bottle. Over the 75 min experiment, a bottle was taken every 15 min. The precipitate was washed thoroughly with deionized water and dried at a temperature of 105 °C in the oven until dry. The weight of the crystals was measured and the amount precipitated was calculated. With each crystallization observation, a blank containing no additives was carried out in conjunction with the additive experiments.

2.4. Addition of additives

The effect of adding additive was determined by adding additive of 450 ppm into a growth solution of 0.05 M $CaSO_4$ which has been added of 200 mg of seed crystals. The weight of the crystals was measured and the amount precipitated was calculated.

2.5. Data analysis

Data were obtained as the amount of precipitate versus time at of 0.05 M concentrations of the growth solution and of 450 ppm additive added, and it was plotted as the amount of precipitate versus time using MS Excel 2010. The effectiveness of additive in inhibiting the rate of $CaSO_4$ scale formation can be determined from the mass of precipitate obtained and the morphology of $CaSO_4$ analyzed by SEM.

3. Result and discussion

The observation results of *Piper betle* leaf extract inhibitor effect at a concentration of 450 ppm and on the growth solution with a concentration of 0.05 M are shown in Table 1 and Figure 1. Based on the data obtained in Table 1 and Figure 1 it can be concluded that the additives in 450 ppm concentration and 0.05 M growth solution were able to inhibit the growth rate of $CaSO_4$ crystals. The additive ability to inhibit the formation rate of $CaSO_4$ crystals is 47.07%. This can be seen in Figure 1 obtained from the analysis in Table 1.

Table 1. Change of $CaSO_4$ precipitation mass with the addition inhibitor at a concentration of 450 ppm and on the growth solution with a concentration of 0.05 M

Time (min)	Precipitation mass change (g/L)	
	0 ppm	450 ppm
0	0.2000	0.2000
15	0.2790	0.2520
25	0.3286	0.2868
35	0.3113	0.2821
45	0.3239	0.2877
55	0.3482	0.2880
65	0.3472	0.2779
75	0.3342	0.3030

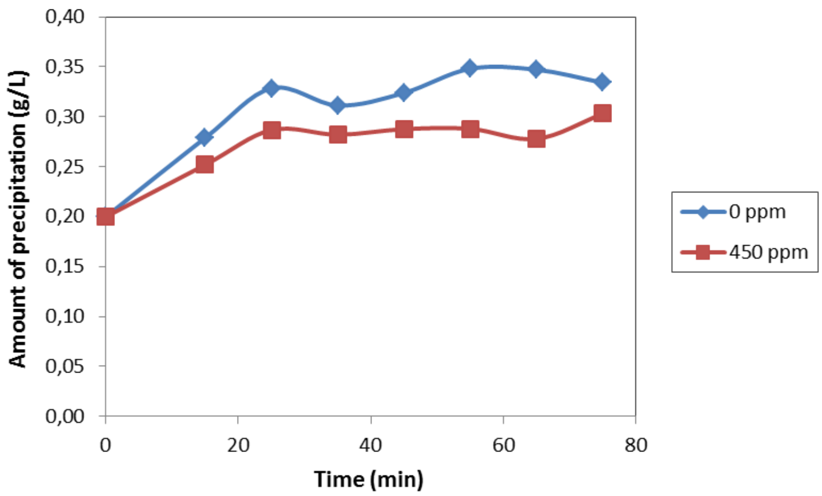


Fig. 1. The effect of inhibitor added on the precipitation of $CaSO_4$ at a growth solution of 0.05 M.

Based on Figure 1 it can be seen that the amount of $CaSO_4$ precipitate increases with the increasing of contact time until it reaches equilibrium. The inhibition of $CaSO_4$ growth by *Piper betle* leaf extract can be seen from the reduced amount of $CaSO_4$ which settles in the solution added to the inhibitor. The optimum inhibition of $CaSO_4$ by *Piper betle* leaf extract occurred at 65 minutes of contact time.
The effectiveness of *Piper betle* leaf extract inhibitors in inhibiting $CaSO_4$ growth can be calculated using the following equation:

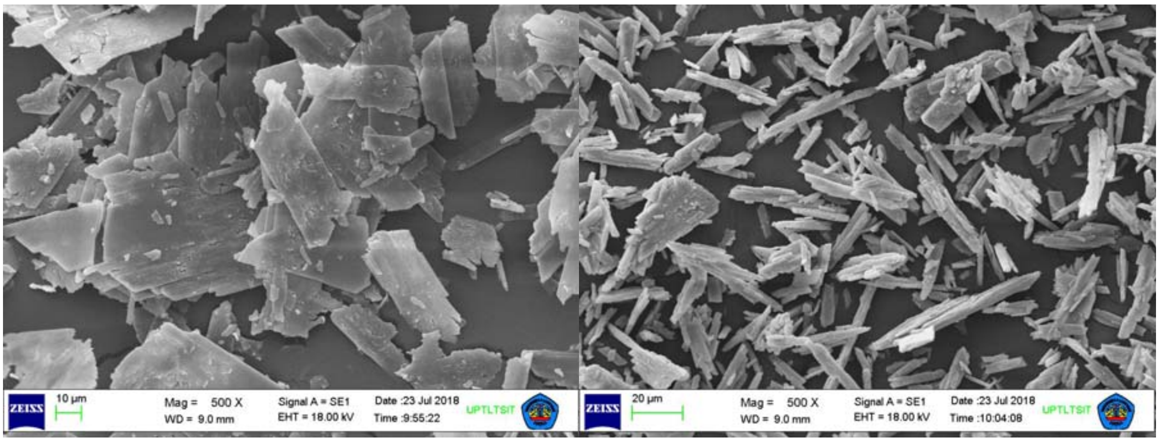
$$\text{Percentage of Inhibitor Efficiency (\%IE)} = \frac{C_a - C_b}{C_o - C_b} \times 100\%$$

Where:
C_a = Precipitation amount of $CaSO_4$ after added inhibitor at equilibrium (g/L)
C_b = Precipitation amount of $CaSO_4$ without inhibitor at equilibrium (g/L)
C_o = Initial precipitation amount of $CaSO_4$ (g/L)
Percentage of Inhibitor Efficiency (IE%) is a measure of the ability of an inhibitor to inhibit crystal growth. The greater the IE% value, the better the inhibitory power.
Based on these equations, inhibitor efficiency of *Piper betle* leaf extract at a concentration of 450 ppm and the concentration of 0.05 M growth solution with an inhibition time of 0-75 minutes can be seen in Table 2.

Tabel 2. Inhibitor efficiency in inhibiting the scale formation of $CaSO_4$ at a concentration of 450 ppm and the concentration of 0.05 M growth solution.

No	Time of Inhibition (min)	Inhibitor Efficiency (%)
1	0	0
2	15	34.18
3	25	32.50
4	35	26.23
5	45	29.21
6	55	40.62
7	65	47.07
8	75	23.24

To observe the morphological changes of $CaSO_4$ sediment particles, the particles of $CaSO_4$ was observed by SEM, and the results can be seen in Figure 2. Based on the analysis using SEM, it can be seen that morphological changes and also changes in size of $CaSO_4$ crystal before and after added *Piper betle* leaf extract inhibitors. Based on Figure 2, it was predicted that the $CaSO_4$ crystal growth was inhibited by *Piper betle* leaf extract through an adsorption mechanism. The active compound in *Piper betle* leaf extract will be adsorbed by the surface of $CaSO_4$ crystal so that it can inhibit the growth of the next scale [13].



(a) (b)

Fig. 2. Morphology of $CaSO_4$ crystals (a) in the absence of inhibitor (b) in the presence of inhibitor 450 ppm at the concentration of growth solution of 0.05 M (Magnification 500×)

4. Conclusion

Piper betle leaf extract can act as an inhibitor of $CaSO_4$ deposit formation. Inhibition mechanism of $CaSO_4$ by *Piper betle* leaf extract through the adsorption mechanism. The inhibitor effectiveness of *Piper betle* leaf extract at a concentration of 450 ppm and the concentration of growth solution of 0.05 M is 47.07%.

5. References

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