***JKPK (JURNAL KIMIA DAN PENDIDIKAN KIMIA)**, Vol. 8, No.2, 2023*
Chemistry Education Study Program, Universitas Sebelas Maret
https://jurnal.uns.ac.id/jkpk
pp. 235-247
ISSN 2503-4146
ISSN 2503-4154 (online)

Ability Test of C-4-Methoxyphenyl-Calix[4]resorcinarene as An Inhibitor of Calcium Carbonate ($CaCO_3$) Crust Growth at Various Concentration

Suryadi Budi Utomo*, Lathifah Ramadhani, Kisti Makrifatul Hanifah, Zamira Zia'ul Huda, Elfi Susanti V.H, Sri Retno Dwi Ariani, Sri Mulyani, and Muhammad Hizbul Wathon

Bachelor Program of Chemistry Education, Faculty of Teacher Training and Education, Universitas Sebelas Maret, Indonesia

ARTICLE INFO

Keywords:
C-4-methoxyphenyl-calix[4]resorcinarene;
Inhibitor;
$CaCO_3$ scale;
Concentrations;
scale formation rate;
various times.

Article History:
Received: 2023-05-30
Accepted: 2023-08-11
Published: 2023-08-31

**Corresponding Author*
*Email:*sbukim98@staff.uns.ac.id

doi:10.20961/jkpk.v8i2.74326

ABSTRACT

The primary objective of this study was to evaluate the capacity of C-4-methoxyphenyl-calix[4]resorcinarene in impeding the development of $CaCO_3$ crust at varying concentrations of the inhibitor and different durations of contact. The research employed a seeded experimental approach using a 0.1 M $CaCO_3$ growth solution maintained at 80 °C. The concentrations of C-4-methoxyphenyl-calix[4]resorcinarene introduced into the $CaCO_3$ growth solution were 0, 5, 10, 20, and 40 ppm. The experimental procedure commenced with preparing crystal seeds, which is pivotal for gauging crystal growth rates. Results obtained from crystal weighing and morphological analysis through Scanning Electron Microscopy (SEM) indicated that C-4-methoxyphenyl-calix[4]resorcinarene effectively impeded the pace of $CaCO_3$ scaling. The inhibitory efficacy of C-4-methoxyphenyl-calix[4]resorcinarene as a $CaCO_3$ scaling inhibitor was contingent on well-regulated temperature during the heating phase. The inhibition effectiveness was positively correlated with the inhibitor's concentration; higher concentrations yielded superior suppression of $CaCO_3$ scaling. Optimal scale reduction was observed at an inhibitor concentration of 10 ppm during a 20-minute contact period. These findings underscore the promising potential of C-4-methoxyphenyl-calix[4]resorcinarene as a viable inhibitor for mitigating scaling growth rates in various industrial fluid systems and related contexts.

How to cite: S. B. Utomo, L. Ramadhani, K. M. Hanifah, Z. Z. Huda, E. Susanti V.H, S. R. D. Ariani, S. Mulyani, & M. H. Wathon, "Ability Test of C-4-Methoxyphenyl-Calix[4]resorcinarene as An Inhibitor of Calcium Carbonate (CaCO3) Crust Growth at Various Concentration", *JKPK (Jurnal Kimia dan Pendidikan Kimia)*, vol. 8,no.2, pp. 221-233, 2023. http://dx.doi.org/10.20961/jkpk.v8i2.66855

INTRODUCTION

Deposition of inorganic substances on equipment within the oil industry has frequently posed challenges [1]. Inorganic sedimentation is common within the distribution of crude oil [2]. The formation of deposits results from solutions becoming supersaturated, coupled with undesired interactions among ions [3]. Once the solution surpasses its saturation point, solid particles adhere to the inner surface of pipelines, eventually forming deposits [4]. Over time, these deposits become progressively harder to eliminate, leading to pipeline blockages [5,6]. Neglecting these deposits can reduce heat exchange efficiency, overheating, and decrease flow rates due to narrowed pipe diameters. Consequently, more energy is required to maintain transfer rates, increasing energy consumption. Elevated pressure within the pipeline can also inflict damage, resulting in heightened maintenance costs [7].

Several approaches have been employed to mitigate the development of deposits by pH regulation. Introducing acid or creating an acidic environment reduces pH, thereby maintaining calcium carbonate deposits' solubility. However, the introduction of acidic substances can trigger corrosion. Certain acidic substances, including sulfuric acid and hydrochloric acid, possess hazardous attributes [1]. Employing anti-deposition additives derived from inorganic compounds, amino acids, water-soluble polymers like poly aspartate, and other agents such as phosphonates and carboxylates represents a feasible and cost-effective alternative to avert deposit formation.

Numerous investigations have delved into the potential of calixarene derivatives as inhibitors against $CaCO_3$ crust formation. For instance, Suharso et al. [8,9] examined the inhibitory role of C-methyl 4,10,16,22-tetramethoxycalix[4]arene in countering the formation of both $CaCO_3$ and $CaSO_4$ scales. The most effective inhibition against $CaSO_4$ scale growth was observed at 80 ºC with an optimal concentration of 50 ppm. Nevertheless, synthesizing this particular calyx[4]arene compound posed challenges, involving multiple reaction steps and non-renewable source-derived phenol as the key ingredient. Furthermore, investigations using calixarene for similar applications remain relatively scarce. Thus, this study endeavors to explore the inhibitory potential of C-4-methoxyphenyl-calix[4]resorcinarene—a distinct class of calix[4]arene, specifically a resorcinol derivative—in countering calcium carbonate ($CaCO_3$) scale growth at varying concentrations. Notably, the synthesis of C-4-methoxyphenyl-calix[4]resorcinarene can be achieved through a simplified single-step reaction between resorcinol and p-anisaldehyde under acidic conditions [10,11].

The current research investigated a calixarene derivative known as C-4-methoxyphenyl-calix[4]resorcinarene [10,11] for its potential as an inhibitor against the $CaCO_3$ crust. This compound acts as an additive to hinder the growth rate of calcium carbonate crust. A notable advantage of this calix[4]resorcinarene is its stability even under elevated temperatures. This derivative demonstrates extractant ligand capabilities and possesses sites for binding metal cations [12,13,14]. Furthermore, the carboxylic acid functional group of the derivative compound, C-4-methoxyphenyl-calix[4]resorcinarene, exhibits effective complexation with group IA and IIA metal ions [14], along with its potential as an antibacterial agent [15,16].

METHODS

The materials used in this work involve $CaCl_2$ anhydrous, Na_2CO_3, C-4-methoxyphenyl-calix[4]resorcinarene, acetone, and aquabidest. The equipment used in this experiment were an electronic balance, beaker, glass measuring beaker, watch glass, stirrer, hot plate, magnetic stirrer, stative and clamp, pipettes, filter paper, thermometer, erlenmeyer, oven, and water bath. FT-IR Spectrophotometer Shimadzu Prestige-21 and SEM JSM-6360 apparatus were used for instrumental measurements.

1. Crystal Seed Preparation

Preparing crystal seeds was initiated by creating separate solutions of 1 M anhydrous $CaCl_2$ and 1 M Na_2CO_3, each dissolved in 100 mL of aquabidest. These solutions were combined and heated in a water bath set at 80 °C. Subsequently, the solution underwent stirring via a magnetic stirrer for 10 minutes or until a state of homogeneity was achieved, forming crystal deposits.

Once the solution had attained homogeneity, it underwent filter paper filtration, effectively segregating the $CaCO_3$ crystal seeds from the filtrate. The collected crystal sediment was retained for further use, while the filtrate was discarded. The obtained $CaCO_3$ crystal seed sediment underwent a washing process involving adding 5 mL of aquabidest and 3 mL of acetone.

After washing, the $CaCO_3$ crystal seed sediment was dried in an oven at 100°C for 1 hour. This sequence of actions was repeated iteratively until a sufficient quantity of $CaCO_3$ crystal seeds had been amassed, suitable for utilization in the subsequent crystal growth experiment.

2. Determination of $CaCO_3$ Crystal Growth Rate Without Inhibitor

The process was initiated by combining 400 mL of 0.1 M anhydrous $CaCl_2$ with an equal amount of 0.1 M Na_2CO_3 solution. Subsequently, the mixture was heated in a water bath set at 80°C while simultaneously stirring using a magnetic stirrer. This stirring was continued for 10 minutes or until the solution achieved a state of homogeneity. Once homogeneity was attained, the solution underwent filter paper filtration, facilitating the separation of $CaCO_3$ seed crystals from the filtrate.

The obtained filtrate was then carefully distributed into 7 Erlenmeyer flasks, each containing 100 mL of solution, within a water bath at 80°C. Following this, 400 mg of $CaCO_3$ crystal seeds were introduced into each Erlenmeyer flask, and for a 5 ppm concentration variation, 0.5 mg of the C-4-methoxyphenyl-calix[4]resorcinarene inhibitor compound was included. This inhibitor compound was wrapped in filter paper and suspended in the soaking solution. The inhibition process was conducted across contact durations of 10, 20, 30, 40, 50, and 60 minutes to identify the optimal timeframe during the initial stages.

A similar procedure was performed for distinct inhibitor concentrations, precisely 10, 20, 30, and 40 ppm. The resultant $CaCO_3$ crystals were meticulously filtered and subjected to a washing procedure involving the gradual addition of 5 mL of aquabides followed by 3 mL of acetone. Subsequently, the crystals were dried in an oven at 100°C for 1 hour. Following this drying phase, the crystals were weighed to ascertain the sedimentation growth rate in the presence of the inhibitor.

3. Determination of $CaCO_3$ Crystal Growth Rate in the Presence of Inhibitor

The process was initiated by combining 400 mL of 0.1 M anhydrous

$CaCl_2$ with an equal amount of 0.1 M Na_2CO_3 solution. Subsequently, the mixture was heated in a water bath set at 80°C while simultaneously stirring using a magnetic stirrer. This stirring was continued for 10 minutes or until the solution achieved a state of homogeneity. Once homogeneity was attained, the solution underwent filter paper filtration, facilitating the separation of $CaCO_3$ seed crystals from the filtrate.

The obtained filtrate was then carefully distributed into 7 Erlenmeyer flasks, each containing 100 mL of solution, within a water bath at 80°C. Following this, 400 mg of $CaCO_3$ crystal seeds were introduced into each Erlenmeyer flask, and for a 5 ppm concentration variation, 0.5 mg of the C-4-methoxyphenyl-calix[4]resorcinarene inhibitor compound was included. This inhibitor compound was wrapped in filter paper and suspended in the soaking solution. The inhibition process was conducted across contact durations of 10, 20, 30, 40, 50, and 60 minutes to identify the optimal timeframe during the initial stages.

A similar procedure was performed for distinct inhibitor concentrations, specifically 10, 20, 30, and 40 ppm. The resultant $CaCO_3$ crystals were meticulously filtered and subjected to a washing procedure involving the gradual addition of 5 mL of aquabides followed by 3 mL of acetone. Subsequently, the crystals were dried in an oven at 100°C for 1 hour. Following this drying phase, the crystals were weighed to ascertain the sedimentation growth rate in the presence of the inhibitor.

RESULTS AND DISCUSSION

1. C-4-methoxyphenyl-calix[4]resorcinarene in Inhibiting the Growth of Crust Calcium Carbonate ($CaCO_3$)

The research findings depicted in Table 1 and Figure 1 illustrate that the growth of $CaCO_3$ crust without the presence of an inhibitor displays an upward trend with escalating time, reaching an optimal point at the 20-minute mark. Subsequently, the growth trajectory exhibits a descending tendency and remains relatively consistent. The maximum $CaCO_3$ crust growth observed without an inhibitor occurred at 20 minutes, measuring 0.404 g (Table 1 and Figure 1).

The introduction of the C-4-methoxyphenyl-calix[4]resorcinarene inhibitor generally reduces the precipitation of $CaCO_3$ crystals from the solution. A gradual reduction is noticeable within the initial 0-20 minute interval, as discerned from Figure 1, particularly within inhibitor concentrations of 5-20 ppm. However, with higher inhibitor concentrations, a relatively fluctuating decrease is observed, and interestingly, there appears to be a marginal increase in crust mass by 0.002 grams and 0.003 grams. This growth in mass might be attributed to desorption, wherein ions previously bound to the active groups within the inhibitor are released from the $CaCO_3$ crust. Adsorption, on the other hand, occurs when adsorbed ions solely adhere to the surface of the adsorbing particle [18]. Various factors influencing adsorption and desorption encompass contact time, solvent concentration, sediment solute concentration, solute speciation, organic and inorganic content, temperature, grain size, acid concentration (pH), and salinity [17].

Based on the description above, it can be inferred that the C-4-methoxyphenyl-calix[4]resorcinarene inhibitor effectively curtails the growth of the CaCO3 scale at lower concentrations, particularly those below 20 ppm. The optimal contact duration is 20-40 minutes, with 20 minutes suitable for a concentration of 10 ppm and 40 minutes for a concentration of 20 ppm.

Table 1. Mass of $CaCO_3$ crust at every inhibitor concentration.

Time (minutes)	Mass (gram)				
	0 ppm	5 ppm	10 ppm	20 ppm	40 ppm
0	0.392	0.392	0.392	0.392	0.392
10	0.394	0.392	0.372	0.387	0.376
20	0.404	0.371	0.332	0.385	0.386
30	0.394	0.372	0.387	0.381	0.394
40	0.396	0.365	0.389	0.353	0.385
50	0.396	0.377	0.394	0.386	0.388
60	0.395	0.367	0.376	0.390	0.395

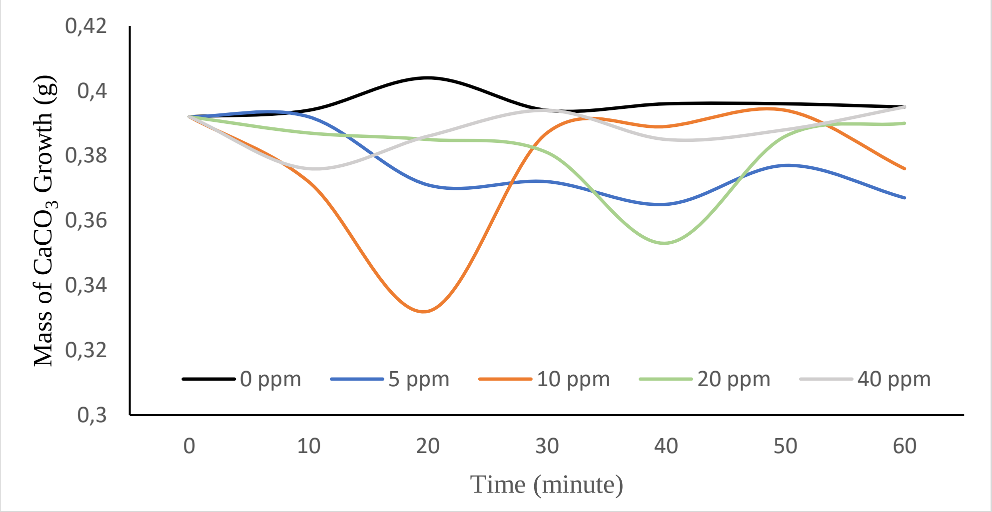


Figure 1. Mass of $CaCO_3$ crust growth in 0.1 m growth solution with inhibitor concentration and time variations.

The findings align with the research conducted by Suharso et al. [16], which demonstrated that the inhibitory capacity of C-methyl-4,10,16,22-tetramethoxy-calix[4]arene on the growth of $CaCO_3$ crust at inhibitor concentrations of 10, 50, and 100 ppm. Moreover, another study by Suharso et al. [20] focusing on 5,11,17,23-tetra(dimethylamino)methyl-4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetramethyl calix[4]arene (TDMACMKR), demonstrated its inhibitory effect on $CaCO_3$ crust growth. This effect was observed across varying growth solution concentrations (0.1 M, 0.3 M, and 0.6 M) and inhibitor concentrations (25 ppm, 50 ppm, and 75 ppm).

2. The Effect of C-4-methoxyphenyl-calix[4]resorcinarene Concentration on the Growth of Calcium Carbonate ($CaCO_3$) Crust

Based on the outcomes presented in Figure 2, the most significant reduction in $CaCO_3$ crust with each inhibitor occurred at the 20th minute, measuring 0.033 grams, 0.072 grams, and 0.018 grams, respectively. However, for the 20 ppm inhibitor, the most substantial reduction in the crust was observed at the 40th minute, amounting to 0.043 grams. The inhibitory effectiveness of the inhibitor demonstrated a decline after the 20th minute for concentrations of 5 ppm, ten ppm, and 40 ppm. In comparison, for the 40 ppm concentration, the reduction occurred after the 50th minute. This finding indicates that the optimal time for inhibiting $CaCO_3$ crust formation is at the 20th minute for inhibitor concentrations of 5 ppm, 10 ppm, and 40 ppm and at the 40th minute for a concentration of 20 ppm. Additionally, it is evident that at the 50th and 60th minutes, concentrations of 20 ppm and 40 ppm inhibitors displayed similar points of absorption.

Table 2. The reduced mass of $CaCO_3$ crust after adding the inhibitor.

Time (minutes)	Mass (gram)			
	5 ppm	10 ppm	20 ppm	40 ppm
10	0.002	0.022	0.007	0.018
20	0.033	0.072	0.019	0.018
30	0.022	0.007	0.013	0.000
40	0.031	0.007	0.043	0.011
50	0.019	0.002	0.010	0.008
60	0.028	0.019	0.005	0.000

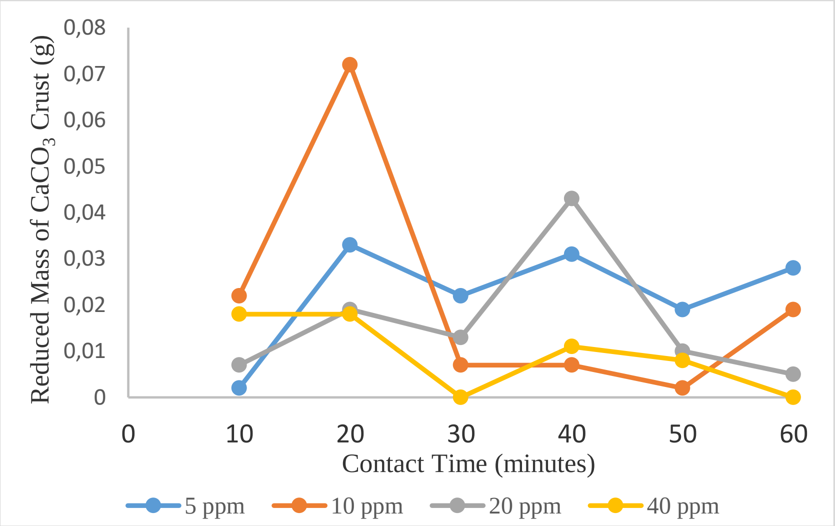


Figure 2. Difference of $CaCO_3$ crust mass against time.

In this experimental study, adding a CMFKR inhibitor at a concentration of 10 ppm proved to be more effective and optimal. Despite not affecting the surface area, increasing the inhibitor concentration rendered the 10 ppm concentration more proficient in adsorption and $CaCO_3$ crust reduction than the 40 ppm concentration. On the other hand, the 5 ppm inhibitor concentration appeared to be too low.

Theoretically, higher inhibitor concentrations correlate with enhanced inhibitory capacity in curbing the growth rate of the $CaCO_3$ crust.

The concentration of 40 ppm was deemed excessively high, considering that the filter paper's surface area remained constant. Consequently, the binding strength of Ca^{2+} ions to the active groups of the inhibitor could have been more robust. Thus, the absorption of the $CaCO_3$ crust demonstrated suboptimal results. Had the surface area been directly proportional to the concentration, the absorption of $CaCO_3$ crust at 40 ppm concentration might have been more productive. A similar principle was observed in ammonia desorption from activated charcoal, where an increased dosage led to higher ammonia concentrations in the solution [19]. This outcome can be attributed to the excellent ratio of activated charcoal mass to the solution, enhancing the contact field area. The extent of the adsorbent area plays a pivotal role in determining the absorption capacity. A larger adsorbent area corresponds to heightened adsorption capability. The augmented active site and increased area during contact with metal ions amplify the adsorbability of metal ions, resulting in improved adsorption efficiency.

The research findings highlighted that CMFKR inhibitors tended to absorb crust at low concentrations, particularly at 20 ppm concentration, notably at the 40th minute. Notably, the seed crystals underwent partial dissolution in the solution. This phenomenon suggests that the additive can enhance the solubility of $CaCO_3$ crystals within the solution, thereby impeding crust formation [15]. Moreover, the addition of C-methyl-4,10,16,22-tetramethoxy-calix[4]arene inhibitor in concentrations ranging from 10 to 100 ppm escalated the inhibitor's efficacy against the growth of $CaCO_3$ sediment by 33% to 100%. Notably, the introduction of a 50 ppm concentration of C-methyl-4,10,16,22-tetramethoxy-calix[4]arene inhibitor resulted in nearly a 50% reduction in the growth rate of $CaCO_3$ sediment compared to cases without C-methyl-4,10,16,22-tetramethoxy-calix[4]arene.

3. FTIR Analysis of C-4-methoxyphenyl-calix[4]resorcinarene Before and After Being Used as an Inhibitor of Calcium Carbonate ($CaCO_3$) Crust

The FTIR analysis conducted on C-4-methoxyphenyl-calix[4]resorcinarene before its utilization as a $CaCO_3$ crust inhibitor (depicted in Figure 3) reveals the presence of various molecular components within the compound. These components include OH bonds, functional groups linked to oxygen, CH sp^2 stretching, CH sp^3 stretching, CH sp^3 bending, aromatic carbonyl (C=C-C aromatic), aromatic bonds represented as CH sp^2, methylene C-H bending, CH methine bridge, and CH sp^3 bending, indicating the presence of methoxy groups. Thus, the FTIR analysis aids in the identification of the functional groups encompassed by the C-4-methoxyphenyl-calix[4]resorcinarene inhibitor compound. The specific functional group information is outlined in Table 3.

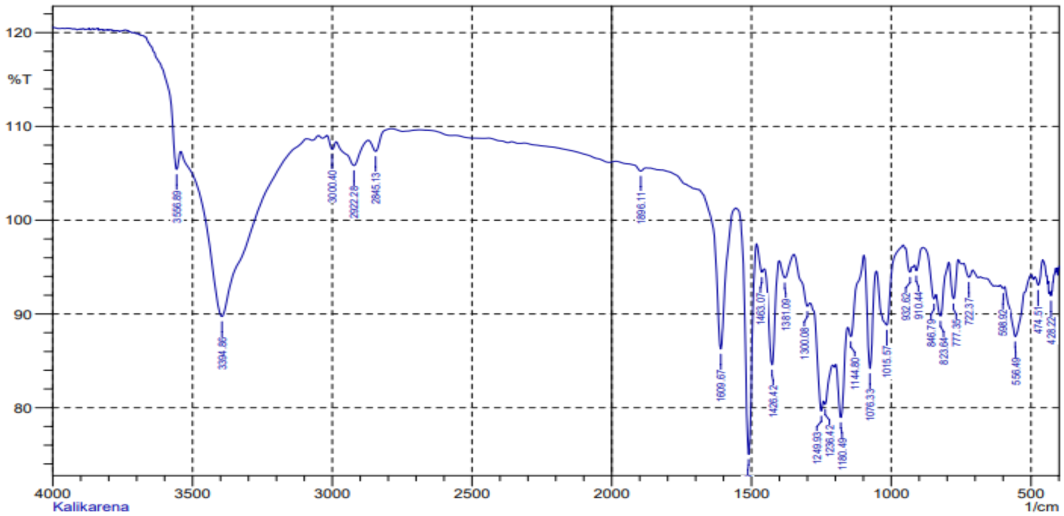


Figure 3. Characteristic of C-4-Methoxyphenyl-calix[4]resorcinarene before being used as an inhibitor of $CaCO_3$ crust using FTIR analysis.

Table 3. FTIR analysis of C-4-methoxyphenyl-calix[4]resorcinarene inhibitor compound.

No	Functional Group	Peak (cm^{-1})	Theoretic Peak (cm^{-1})
1.	OH (alcohol)	3394.86	3400-2400
2.	C=C-C (aromatic)	1609.67	1615-1580
		1510.33	1510-1450
3.	CH *methine bridge*	1426.42	~1420
4.	Methoxy	1144.80: ether	1300-1000
		1381.09: CH sp^3 bending	1450-1375

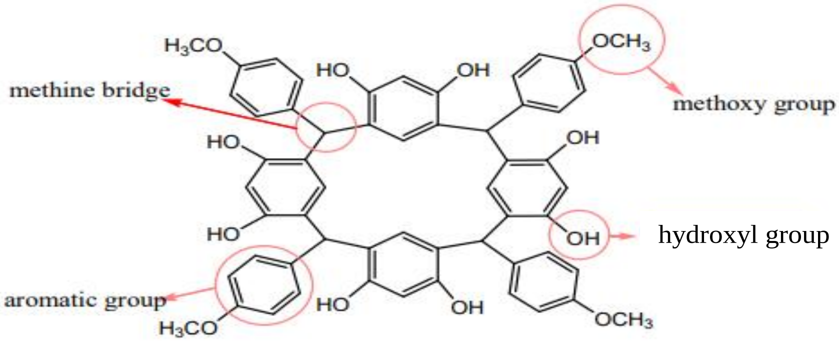


Figure 4. Groups in C-4-methoxyphenyl calix[4]resorcinarene inhibitor.

For each functional group's structural depiction discovered through the FTIR analysis of the C-4-methoxyphenyl-calix[4]resorcinarene inhibitor, refer to Figure 4. Certain functional groups, including methoxy, hydroxyl, and aromatic entities, are strongly presumed to be pivotal in inhibiting $CaCO_3$ crust formation.

The FTIR analysis of C-4-methoxyphenyl calix[4]resorcinarene after its utilization as a $CaCO_3$ crust inhibitor (depicted in Figure 5) demonstrates the presence of specific molecular attributes.

These include an OH bond, functional groups linked to oxygen, CH sp^2 stretching, CH sp^3 stretching, aromatic carbonyl (C=C-C aromatic), an aromatic bond in the CH sp^2 form, methylene C-H bending, CH ethane bridging, an ether group, and sp^3 bending, thereby confirming the identification of the methoxy moiety.

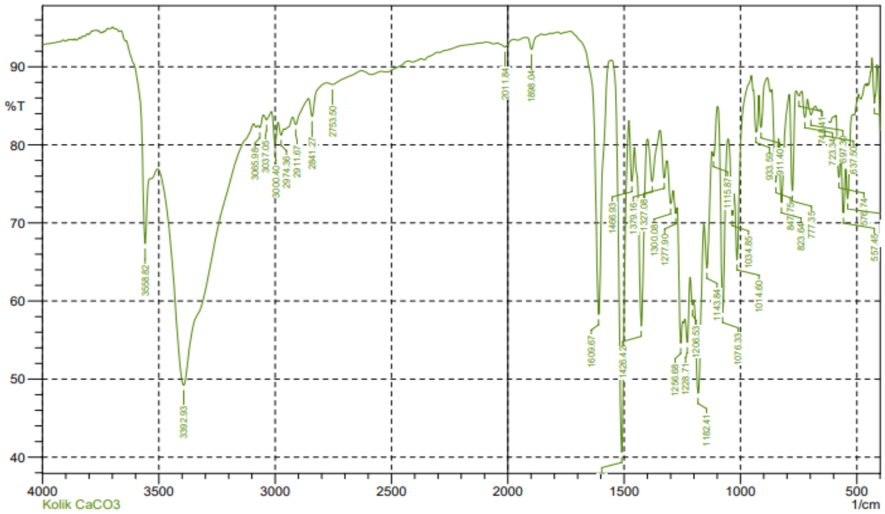


Figure 5. Characteristic of C-4-methoxyphenyl calix[4]resorcinarene after being used as an inhibitor of $CaCO_3$ crust using FTIR analysis.

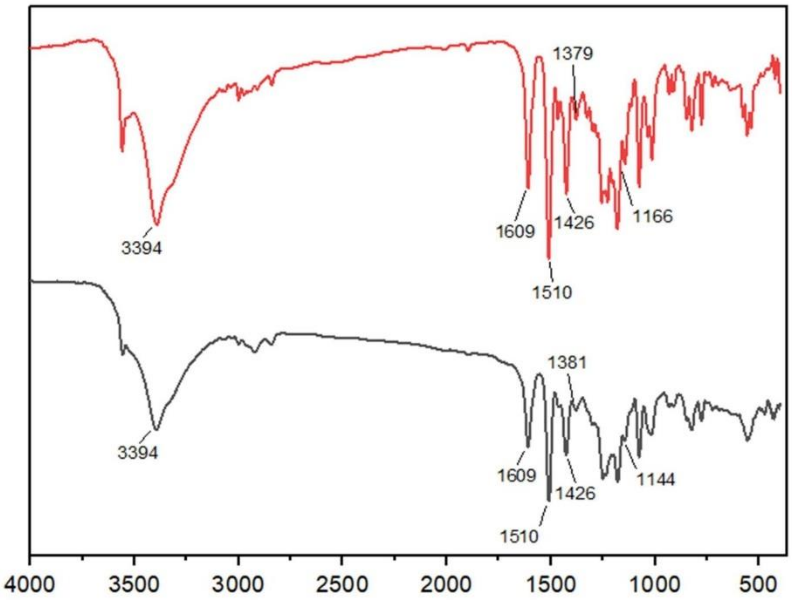
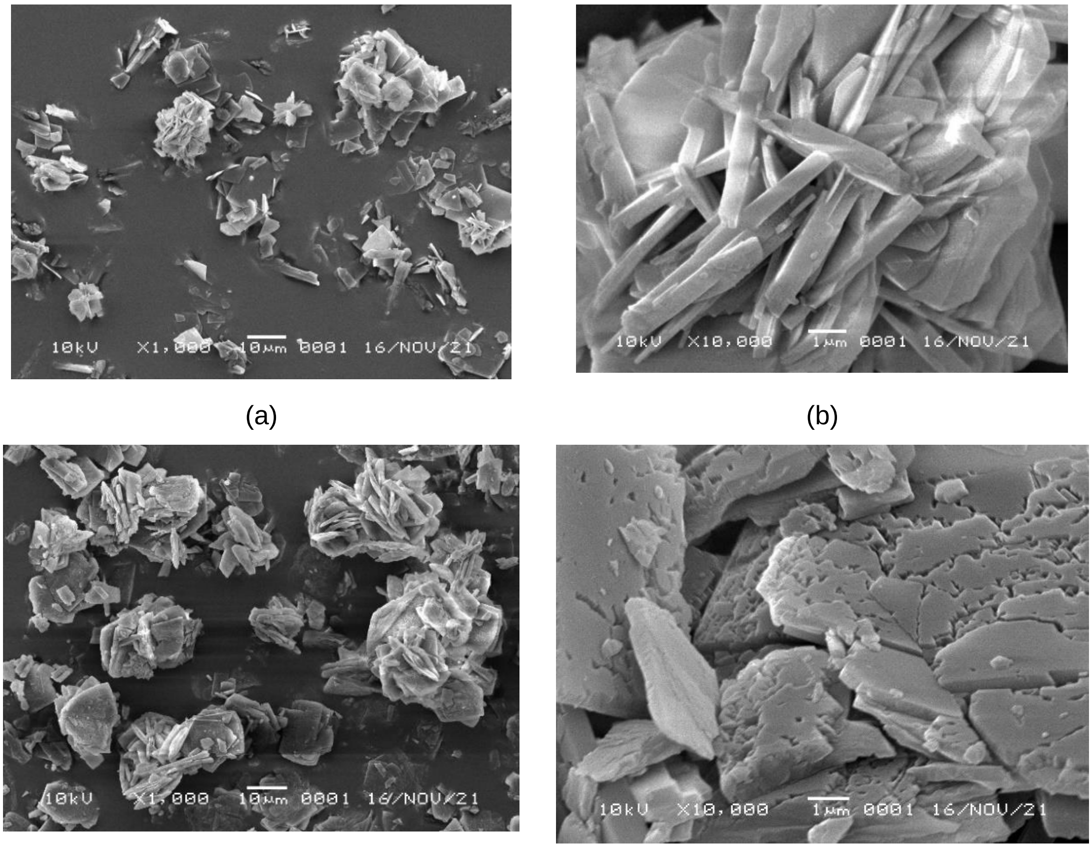


Figure 6. Comparison of FTIR analysis of C-4-methoxyphenyl calix[4] resorcin arene before (black) and after (red) being used as an inhibitor of $CaCO_3$ crust.

The graph presented in Figure 6 illustrates the discrepancy between C-4-methoxyphenyl calix[4]resorcinarene before (depicted in black) and following (shown in red) its application as a $CaCO_3$ crust inhibitor. This dissimilarity is notably discerned through the altered spectrum peak positions, involving shifts from their initial positions at 1144 cm^{-1} to 1166 cm^{-1} and 1381 cm^{-1} to 1379 cm^{-1}. These modified spectrum peak positions manifest the interaction between Ca^{2+} ions and the methoxy group within the

C-4-methoxyphenyl calix[4]resorcinarene inhibitor. The binding of Ca^{2+} ions by methoxy groups, characterized by negative charges and a surplus of electrons, prevents the binding of Ca^{2+} ions to CO^{2-} ions, thereby averting the formation of the $CaCO_3$ crust.

It is vital to note that the detected IR spectrum is notably influenced by the molecular state. Even minor alterations in molecular structure and composition can trigger changes in peak distribution, especially within the fingerprint region. The absence of shifts beyond the spectrum peaks denoting the methoxy group suggests the absence of interaction between other functional groups of the C-4-methoxyphenyl calix[4]resorcinarene inhibitor, such as OH, aromatic, and CH methine bridge, with Ca^{2+} ions.



(a) (b)

(c) (d)

Figure 7. C-4-methoxyphenylcalix[4]resorcinarene before used as an inhibitor, at (a) 1000× and (b) 10,000× magnifications C-4-methoxyphenylcalix[4]resorcinarene after used as an inhibitor, at (c) 1000× and (d) 10,000× magnifications.

4. SEM analysis of C-4-methoxyphenyl-calix[4]resorcinarene before and after being used as an inhibitor of calcium carbonate ($CaCO_3$) crust

SEM analysis of C-4-methoxyphenylcalix[4]resorcinarene before its use as a $CaCO_3$ scale inhibitor depicted the presence of aggregates resembling crystalline formations. This is evident in Figure 7a at a magnification of 1000x. However, at a higher magnification of 10,000x (Figure 7b), the morphology of C-4-

methoxyphenyl-calix[4]resorcinarene before its application as a $CaCO_3$ scale inhibitor exhibited a configuration akin to stacked square glass structures featuring a smooth surface. In contrast, SEM analysis of C-4-methoxyphenylcalix[4]resorcinarene after its usage as a $CaCO_3$ scale inhibitor displayed the presence of larger agglomerates resembling crystalline formations at 1000x magnification (Figure 7c).

These agglomerates were notably more sizable than those observed in Figure 7a. At an enhanced magnification of 10,000x (Figure 7d), the inhibitor exhibited a morphology characterized by an irregular surface with discernible augmented layering and pore-like appearances. This variance is attributed to the attachment of Ca^{2+} ions to the inhibitor's surface. This phenomenon indicates a notable reduction in the concentration of Ca^{2+} ions within the solution, leading to the effective inhibition of $CaCO_3$ crust formation.

CONCLUSION

This study conclusively demonstrated the efficacy of the compound C-4-methoxyphenyl-calix[4]resorcinarene in effectively restraining the growth rate of the $CaCO_3$ scale. The concentration and contact time variables significantly influenced the extent of crust deposition formed. A higher concentration of the inhibitor, C-4-methoxyphenyl-calix[4]resorcinarene, corresponded to a more pronounced reduction in the $CaCO_3$ scale. Similarly, the contact time variable revealed that longer interaction durations yielded more significant decreases in scale formation. The findings notably revealed that, at an inhibitor concentration of 10 ppm, the most effective reduction in scale occurred at a contact time of 20 minutes. Conversely, for a higher inhibitor concentration of 20 ppm, the optimal reduction in scale was observed at an interaction time of 40 minutes.FTIR analysis exhibited distinct functional group characteristics for C-4-methoxyphenyl calyx [4]resorcinarene before and after its utilization as an inhibitor. Notably, the methoxy group emerged as the dominant functional group that binds with Ca^{2+} ions. Morphological assessment through SEM of C-4-methoxyphenyl-calix[4]resorcinarene similarly demonstrated observable alterations after its application as an inhibitor.

ACKNOWLEDGMENT

The authors thank LPPM UNS for funding this research through a grant under contract number 228/UN27.22/PT.01.03/2023.

REFERENCES

[1] Suharso and Buhani, *Penanggulangan Kerak,* Yogyakarta: Graha Ilmu, 2015, ISBN: 9786022625094.

[2] M. Syahri and B. Sugiharto, “Scale Treatment pada Pipa Distribusi Crude Oil Secara Kimiawi,” *Prosiding Seminar Nasional Teknoin*, 2008.

[3] Y. Usmany, W.A. Putranto, A.P. Bayuseno, and S. Muryanto, “Crystallization of calcium carbonate ($CaCO_3$) in a flowing system: Influence of Cu^{2+} additives on induction time and crystalline phase transformation,” *AIP Conference Proceedings*, vol. 172, 2016, doi: 10.1063/1.4945547.

[4] A. Bhatia, “Cooling Water Problems and Solutions,” *Continuing Education and Development*. 2003.

[5] A. S. Braga and Y. Filion, “The interplay of suspended sediment concentration, particle size, and fluid velocity on the rapid deposition of suspended iron oxide particles in PVC drinking water pipes,” *Water Research X*, vol.15, pp. 100143, 2022, doi: 10.1016/j.wroa.2022.100143.

[6] M. Morita and O. Umezawa, “A Model of Scale Formation on Inner Carbon Steel Pipe Walls for Transporting Hot Spring Water,” *Materials Transactions*, vol.57, no. 9, pp. 1652-1659, 2016, doi: 10.2320/matertrans.M2016105.

[7] M. Mpelwa and S. F. Tang, “State of the art of synthetic threshold scale inhibitors for mineral scaling in the petroleum industry: a review,” *Pet. Sci*., vol. 16, pp. 830-849, 2019, doi: 10.1007/s12182-019-0299-5.

[8] Suharso, Buhani, and T. Suhartati, “Inhibition of calcium carbonate ($CaCO_3$) scale formation by calix[4]resorcinarene compounds,” *Desalination and Water Treatment,* vol. 68, pp. 32-39, 2017, doi: 10.5004/dwt.2017.20311.

[9] Suharso, Buhani, and L. Aprilia, “Influence of Calix[4]arene Derived Compound on Calcium Sulphate Scale Formation,” *Asian Journal of Chemistry*, vol. 26, no. 18, pp. 6155-6158, 2014, doi: 10.14233/ajchem.2014.16899.

[10] S. B. Utomo, Jumina, D. Siswanta, Mustofa, and N. Kumar, “Synthesis of Thiomethylated Calix[4]resorcinarene Based on Fennel Oil via Chloromethylation,” *Indo. J. Chem.*, vol. 11, no.1, pp.1-8, 2011, doi: 10.22146/ijc.21411.

[11] S. B. Utomo, A. N. C. Saputro, and Y. Rinanto, “Functionalization of C-4-methoxyphenylcalix[4]resorcinarene with several ammonium compounds,” *IOP Conf. Series: Material Science and Engineering*, vol. 107, pp. 012042, 2016, doi:10.1088/1757-899X/107/1/012042.

[12] S. B. Utomo, Jumina, D. Siswanta, and Mustofa, “Kinetics and Equilibrium Model of Pb(II) and Cd(II) Adsorption onto Tetrakis-Thiomethyl-C-4-Methoxyphenylcalix[4]resorcinarene,” *Indo. J. Chem*., vol. 12, no. 1. pp. 49-56, 2012, doi: 10.22146/ijc.21371.

[13] P. Santoso, C. Anwar, Jumina, D. Siswanta, Suharso, and Ohto, K., “Synthesis of a Novel Calix[4]resorcinarene-Chitosan Hybrid,” *Orient. J. Chem.*, vol. 34, no. 1, pp. 30-37, 2018, doi: 10.13005/ojc/340103.

[14] S. B. Utomo and Y. S. Anggun, “Sintesis C-4-karboksifenil-kaliks[4]resorsinarena dan Studi Adsorpsinya terhadap Ion Logam Ag(I),” *Seminar Nasional Kimia dan Pendidikan Kimia XII (SN-KPK XII)*, P.Kimia PMIPA FKIP UNS, Surakarta 205-213, 2021.

[15] S. B. Utomo, M. Fujiyanti, W. P. Lestari, and S. Mulyani, “Antibacterial Activity Test of the C-4-methoxyphenylcalix[4]resorcinarene Compound Modified by HexadecyltrimethylammoniumBromide against *Staphylococcus aureus* and *Escherichia coli* Bacteria,” *Jurnal Kimia dan Pendidikan Kimia (JKPK)*, vol. 3, no. 3, pp. 201-209, 2018, doi: 10.20961/jkpk.v3i3.22742.

[16] S. B. Utomo, A. Y. Solihah, and M. I. Fadilah, “The Exploration of C-4-methoxyphenyl-5,11,17,23-tetracarboxylcalix[4]resorcinarene as

Antibacterial Agent," *Mor. J. Chem.*, vol. 10, no. 2, pp. 269-278, 2022, doi:10.48317/IMIST.PRSM/morjchem-v10i2.32641.

[17] X. Cao, X. Liu, J. Zhu, L. Wang, S. Liu, and G. Yang, "Characterization of phosphorus sorption on the sediments of Yangtze River Estuary and its adjacent areas," *Marine Pollution Bulletin*, vol. 114, pp. 277-284, 2017, doi: 10.1016/j.marpolbul.2016.09.026.

[18] M. Handayani & E Sulistiyono, "Uji Persamaan Langmuir dan Freundlich Pada Penyerapan Limbah Chrom (Vi) Oleh Zeolit," *Prosiding Seminar Nasional Sains dan Teknologi Nuklir PTNBR – BATAN Bandung*, 2009.

[19] P. Mulyono, & Wibisono, "Kinetika Adsorpsi Amoniak dalam Air dengan Karbon Aktif," *Media Teknik*, No.2. pp. 36-42, ISSN: 0216-3012, 2007.

[20] Suharso, Buhani, & Aprilia, L, "Pengaruh Senyawa Turunan Kaliksarena dalam Menghambat Pembentukan Kerak Kalsium Karbonat ($CaCO_3$)," *Prosiding Semirata FMIPA Unila*, vol. 1, no. 1, pp 495–503, 2013.