



## Characterization of Clove Bud and Orange Peel Extracts for the Dissolution of Calcium Carbonate Precipitate

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**ABSTRACT**

This research strives to showcase that green chemistry could be leveraged in enhancing flow assurance performance of fluids during industrial activities of fluids transportation. In oil and gas as well as water purification industries, precipitation of dissolved salts caused the formation of scales; these block fluids transportation pathways and reduce the efficiency of these processes. Two natural products extracts; aqueous extract from clove (*Syzygium aromaticum*) buds and methanolic extract from orange fruit (*Citrus sinensis*) peels were used to dissolve CaCO<sub>3</sub> that was used as scale. The proximate analysis of the extracts showed that orange peels extract was more alkaline as it contained the higher amounts of alkaloids while clove bud extract was more acidic as it contained less. Gas Chromatographic mass spectrophotometric (GC-MS) and Fourier Transform Infrared (FTIR) analyses were used to deduce the chemical components present in these extracts and the results showed that there were variations in their composition and also in the composition of commercial antiscalants that were reviewed from other works. The commercial antiscalants were said to be produced from synthetic organic monomers with multipolymer components detected in the analytical instrument and multipolymer components were also detected in the plant extracts. From the Scanning Electron Microscopy (SEM) Instrument analysis, clove bud aqueous extract performed better than the orange peel methanolic extract, as the pore sizes of calcium carbonate was reduced by 13.0 and 2.5 times respectively during dissolution.

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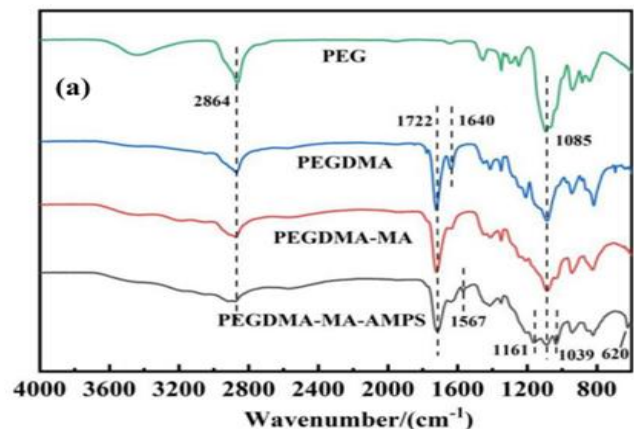
## 1. INTRODUCTION

Scale formation has always been a pervasive problem usually encountered in oil and gas industry. Scale could be formed when injected water is not compatible with formation water leading to the precipitation of insoluble salts [1]. Calcium carbonate is the most commonly formed scale. Scales accumulate in oilfield pipes causing deleterious effects spanning from reduction in pipe diameter, high cost of maintenance, production losses, corrosion of pipelines and energy wastage amongst others [2-3]. Scale removal and mitigation had deployed the use of both natural and synthetic approaches but due to environmental impacts and high cost of synthetic antiscalants, some plants are used as potential antiscalants. Many plants found useful applications in various fields ranging from medical to industries. In medicine, they have been used therapeutically since inception of civilization [4]. They are potential anti-inflammatory agents, antimicrobial agents and antioxidants [5]. The most important phytochemicals present in plants are tannins, flavonoids, saponins, alkaloids and phenolics [6]. Industrially, these phytochemicals can be used potentially for the inhibition of corrosion, pesticides and insecticides [7]. They also find useful application in the synthesis of azo dyes, in textiles, plastics and biological staining [8]. Clove and orange are some of the plants whose usefulness cannot be over emphasized. The plant, clove (*Syzygium aromaticum*), belongs to the family of Myrtaceae. It is mostly found in countries like South China, Madagascar, India, Sri Lanka and Indonesia. Its oil is commonly used for seasoning pastries, sauces and condiments. In medicine, it is for the preparation of gums and teeth. Reports have it that clove extracts contain considerable amounts of alkaloids, amino acids and carbohydrates. The major bioactive component found in clove buds is eugenol with molecular formula,  $C_{10}H_{12}O_2$ . The bud has concentration of phenolic compounds such as hydrocinnamic acid,  $C_9H_8O_3$  and hydroxybenzoic acid  $C_7H_6O_3$  [9].

The orange fruit (*Citrus sinensis*) is one of the most commonly cultivated fruit trees in various countries of the world for its taste and natural value, which is peeled, cut, eaten whole or processed. The

major components of orange peels are alpha-pinene, sabinene, myrcene and limonene. Limonene gives orange fruit its familiar aroma, hence, it is used in perfumed household cleaner for its fragrance [10]. Orange peels are rich in nutrients and contain some phytochemicals which can be effectively used for drug production and food supplements [11].

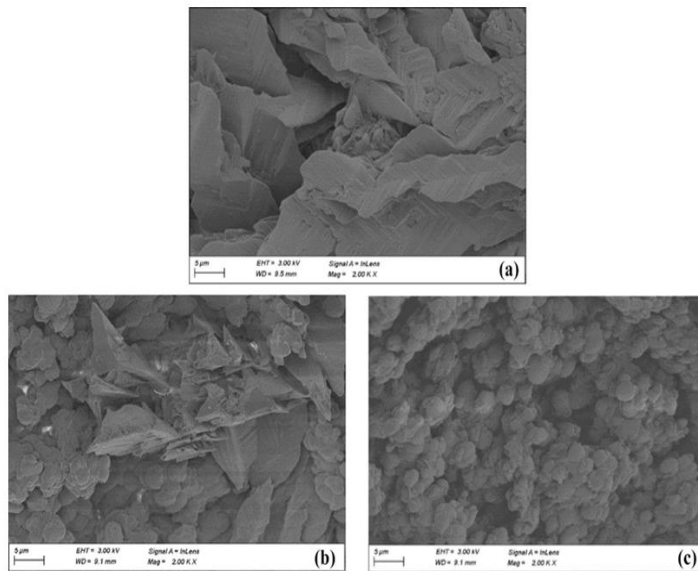
Fourier Transform Infrared (FTIR) can characterize and identify functional groups present in an unknown plant extract [12] and the Gas Chromatographic-Mass Spectrometry (GC-MS) uses both qualitative and quantitative means to identify plant's components. Ren *et al.*, (2022) [13], produced two synthetic multipolymer antiscalants; PEGDMA-MA and PEGMA-MA-AMPS from maleic anhydride, polyethene glycol monomer and 2-acrylamide-2-methylpropyl Sodium hypophosphite. Characterization of the monomers two synthesized antiscalants with FTIR is shown in Fig. 1



**Figure 1:** FTIR of PEGDMA-MA and PEGMA-MA-AMPS copolymers as well as monomer; polyethene glycol (PEG) [13].

The  $1085\text{cm}^{-1}$  bond peak for  $-\text{CH}_2\text{OCH}_2-$  stretching vibration was pronounced for the monomer and its first transition stage product (polyethene glycol maleic anhydride copolymer) as well as the second transition product (PEGDMA-MA polymer); but not pronounced for the PEGMA-MA-AMPS copolymer.  $3434\text{cm}^{-1}$  bond stretching for  $-\text{OH}$  stretching vibration was only observed for the unreacted monomer (Polyethene glycol), while  $1722\text{cm}^{-1}$   $-\text{C}=\text{O}-$  stretching vibration was observed for all substances except the starting material

polyethylene glycol. The PEGMA-MA-AMPS copolymer did not show the presence of  $2864\text{ cm}^{-1}$  bond stretching for  $-\text{CH}_2-$  synthetic bending vibration as others; rather it singly displayed  $620\text{ cm}^{-1}$  bond stretching for  $-\text{C}-\text{S}-$  as well as  $1161$  and  $1039\text{ cm}^{-1}$  asymmetric stretching vibration and  $1567\text{ cm}^{-1}$  for  $-\text{N}-\text{H}-$  bending vibration. Also, the Scanning Electron Microscopic (SEM) analysis carried out on the untreated  $\text{CaCO}_3$  and  $\text{CaCO}_3$  treated with the two copolymer antiscalant are as shown in Figure 2. This showed that, using the same condition, the untreated  $\text{CaCO}_3$  had a pore size of  $5\mu\text{m}$ , similar to the  $\text{CaCO}_3$  treated with the two synthesized antiscalants. It was observed that the two synthetic multipolymer antiscalants have more of acidic properties than basic.



**Figure 2:** SEM image of calcium carbonate in the absence of scale inhibitor (a), in the presence of PEGDMA-MA (b) and in the presence of PEGMA-MA-AMPS (c) [13].

Gupta and Soti (2021), carried out similar studies using SEM analysis to investigate the removal of scale from reverse osmosis (RO) plants, used for the treatment of RO membrane during community water treatment in India.

Gas Chromatography-Mass Spectrometry (GC-MS) has been utilized to detect the synthetic antiscalants' composition; though the displays in the GC-MS Chromatogram and mass spectra depend on the compositions of the specific commercial

antiscalant. The components that have been displayed in some commercial antiscalants include; phosphonates in the form of amino trimethylene phosphonic (ATMP) acid, diethylene triamine penta methylene phosphonic (DTPMP) acid and hydroxyethylidene diphosphonic acid; polyacrylates in the form of polyacrylic acid (PAA) and polycarboxylates in the form of polycarboxylic acid (PCA) as well as their derivatives. The displays in the instrument showed unique retention time and peaks for these components; ATMP, DTPMP and HEDP showed retention time of 10-15 minutes, 20-25 minutes and 15-20 minutes respectively, while the peaks at  $m/z$  were observed at (209,152 and 107), (425, 297 and 197) and (237, 159 and 107) respectively [14].

This study aimed at using phytochemical screening, GC-MS and FTIR to analyse and characterize components of clove buds aqueous-extract and orange peels methanol-extract for dissolution of calcium carbonate precipitate; in order to address scaling issues. The contribution from this work will prove if synthetic antiscalants could be substituted with naturally occurring substances.

## 2. MATERIALS AND METHOD

### 2.1. Sample Collection and Preparation

The clove buds and orange fruits were obtained and processed for this study. The buds were sun-dried to constant weight for one week and were pulverized. The clove bud powder was sieved using  $460\mu\text{m}$  sieve [15]. The orange fruits were washed thoroughly, peeled and sliced into pieces and the pieces of peels were oven dried to constant drying weight using aluminium foil for 48 hours at  $50^\circ\text{C}$  temperature and were pulverized. The powdered peels were sieved using a  $250\mu\text{m}$  sieve [16].

### 2.2. Solvent Extraction

Twenty grams (20g) of the clove bud powder was extracted using 200 ml of distilled water in a

water bath for 2hrs at 80 °C and was filtered using grade 42 Whatman filter paper. Ten grams (10g) of orange peel powder was extracted for 30 mins at 25°C with 20 % methanol and was left to stand for 24 hrs and this mixture was filtered [16]. The percentage (%) yield of extract is given in equation 2.1:

$$\text{Percentage (\%)} \text{ yield} = \frac{W_2}{W_1} \times 100 \% \quad (2.1)$$

Where  $W_2$  = weight of clove buds extracted (g),  
 $W_1$  = weight of powdered clove buds (g) before extraction. For clove bud,  $W_1 = 32.5\text{g}$

Percentage (%) yield of orange peel extract was also gotten using equation 2.1.

where  $W_2$  = weight of orange peels extracted (g),  
 $W_1$  = weight of powdered orange peels (g) before extraction. For orange peels,  $W_1 = 48.5\text{g}$

The extracts were stored in a refrigerator in an airtight container at 4°C awaiting usage.

## 2.3 Phytochemical analysis

### 2.3.1 Tannin Content

Thirty-seven cubic centimeters (37 cm<sup>3</sup>) of distilled water was used to dissolve 50g of sodium tungstate. This forms Folin-Denis reagent. Ten grams (10g) of phosphomolybdic acid and 25 cm<sup>3</sup> of orthophosphoric acid were added to this reagent. This mixture was refluxed for 2 hours, cooled and diluted to 500 cm<sup>3</sup> with distilled water. To a conical flask, 1g of each sample was added to 100 cm<sup>3</sup> of distilled water and this was boiled gently for 1 hour on a heating mantle and filtered using Grade 42 (125 nm) Whatman filter paper in a 100cm<sup>3</sup> volumetric flask. Five-centimeter cube (5.0 cm<sup>3</sup>) of Folin-Denis reagent and 10 cm<sup>3</sup> of saturated Na<sub>2</sub>CO<sub>3</sub> solution were added to 50 cm<sup>3</sup> of distilled water and 10cm<sup>3</sup>

of diluted extracts (aliquot volume) after being pipetted into a 100cm<sup>3</sup> conical flask in order to develop the colour. The solution was kept standing for 30 minutes at a temperature of 25°C in a water bath after thorough swirling. Optical density was measured at 700 nm and compared on a standard tannic acid curve using spectrum Lab 23A spectrophotometer. Different concentrations (0.2–1.0mg/cm<sup>3</sup>) of the standard tannic acid solution were pipetted into five different test tubes to which 5 cm<sup>3</sup> Folin-Denis reagent and 10 cm<sup>3</sup> saturated Na<sub>2</sub>CO<sub>3</sub> solution were added and made up to the 100 cm<sup>3</sup> mark with distilled water. This solution was kept standing in a water bath at 25°C for 30 minutes. At 700 nm, optical density was ascertained with the aid of a Spectrum Lab 23A spectrophotometer [17-19].

The percentage tannin content was calculated using equation 2.2:

$$\% \text{ Tannin} = \frac{100}{w} \times \frac{A_u}{A_s} \times C \times \frac{V_f}{1000} \times D \quad (2.2)$$

Where  $w$  = weight of the analyzed sample,  $A_u$  = Test sample absorbance,  $A_s$  = Absorbance of the standard solution in mg/ml,  $V_f$  = Total volume of extract and  $D$  = Dilution factor.

### 2.3.2 Alkaloid Content

Using electronic balance, the weight of empty filter paper ( $W_1$ ) was first determined. Two-hundred-centimeter cube (200 cm<sup>3</sup>) of 10% acetic acid in ethanol was added to 2.50g of each sample in a 250 cm<sup>3</sup> beaker and this was kept standing for 4 hours. The extracts were concentrated to one-quarter of the original volume in water bath and 15 drops of concentrated ammonium hydroxide was added dropwise to the extracts until the precipitation was complete immediately after filtration. After 3 hours of mixture sedimentation, the supernatant was discarded and the precipitates were washed with 20

cm<sup>3</sup> of 0.1M of ammonium hydroxide and then filtered using 12.5 cm Gem filter paper. After drying the residue in an oven, the weight of the precipitate and filter paper (W<sub>2</sub>) was determined using electronic weighing balance model B-218 and the percentage of alkaloid was obtained mathematically using equation 2.3

$$\% \text{ Alkaloid} = \frac{W_2 - W_1}{W} \times 100 \% \quad (2.3)$$

Where W = weight of the analyzed sample, W<sub>1</sub> = weight of the filter paper (empty) and W<sub>2</sub> = weight of filter paper and alkaloid precipitate.

### 2.3.3. Flavonoid Content

To determine the flavonoid content, the weight of empty crucible (W<sub>1</sub>) was first determined with the aid of electronic balance and 50 cm<sup>3</sup> of 80 % aqueous methanol was added to 2.50g of the sample in a 250 cm<sup>3</sup> beaker. This was covered and allowed to stand at room temperature for 24 hours. After the supernatant was discarded, the residue was re-extracted trice with the same volume of ethanol. Whole solution of each sample was filtered using Grade 42 (125 nm) Whatman filter paper. The filtrate of each sample was later transferred into a crucible and evaporated to dryness using a water bath and was cooled. A desiccator was used to dry the content in the crucible and weighed until constant weight (W<sub>2</sub>) was obtained [18]. The percentage of flavonoid was calculated using equation 2.4

$$\% \text{ Flavonoid} = \frac{W_2 - W_1}{W} \times 100 \% \quad (2.4)$$

Where W = weight of the sample analyzed, W<sub>1</sub> = weight of the crucible (empty) and W<sub>2</sub> = weight of crucible and flavonoid precipitate.

### 2.3.4. Saponin Content

An empty evaporating dish was weighed (W<sub>1</sub>) in order to ascertain its weight. Hundred cubic centimeters (100cm<sup>3</sup>) of 20 % aqueous ethanol was added to 5 grams of each sample in a 250cm<sup>3</sup> conical flask. The mixture was heated for 4 hours with continuous stirring at a temperature of 55°C over a water bath. The residue of the mixture was re-extracted with another 100 cm<sup>3</sup> of 20 % aqueous ethanol after filtration and heated at a constant temperature of 55°C with constant stirring for 4 hours. The combined extract was evaporated to 40 cm<sup>3</sup> at 90°C. Afterwards, 20 cm<sup>3</sup> of diethyl ether was added to the concentrate in a 250 cm<sup>3</sup> separator funnel and agitated vigorously from which the aqueous layer was recovered and discarding the ether layer. Sixty cubic centimeters (60 cm<sup>3</sup>) of n-butanol was added and extracted twice with 10 cm<sup>3</sup> of 5% sodium chloride. After the sodium chloride layer was discarded, the remaining solution was heated for 30 minutes in a water bath, after which the solution was transferred into a crucible and was dried to a constant weight (W<sub>2</sub>) in an oven [18-20]. The saponin content was calculated as a percentage using equation 2.5 and the phytochemical results, presented in Fig. 3.

$$\% \text{ Saponin} = \frac{W_2 - W_1}{W} \times 100 \% \quad (2.5)$$

Where W = weight of the analyzed sample, W<sub>1</sub> = weight of the evaporating dish (empty), W<sub>2</sub> = weight of dish and saponin extract.

### 2.2.5. Dissolution of Calcium Carbonate

The CaCO<sub>3</sub> dissolution efficiency (%) was calculated using equation 2.6:

$$\frac{M_1 - M_2}{M_1} \times 100 \% \quad \text{-----} \quad (2.6)$$

Where M<sub>1</sub> = Initial mass of CaCO<sub>3</sub> precipitate before dissolution (2g), M<sub>2</sub> = mass of the precipitate after dissolution (g)

## 2.4 Gas Chromatographic-Mass Spectroscopy Analysis

The Gas Chromatographic-Mass Spectroscopy analysis was done using the (Agilent 7890A, USA) gas chromatograph which was powered with ChemStation software and interfaced with a detector, Agilent 5975C Mass Spectrometry. HP-5 MS UI (cross-linked 5% methyl phenyl silox), capillary column (30 m x 0.25 mm) columns and film thickness of 0.25 $\mu$ m were used. At a rate of 6°C/min, the oven temperature was increased from 40 – 200 °C. This was continued at 200 – 280 °C at rate 30°C/min and was post run for 10 mins at 280 °C. Helium was the carrier gas with a flow rate of 1mL/min. The injector and detector temperatures were 250°C. GC-MS analysis was done by injecting 1 $\mu$ L of each antiscalants sample (in 0.1% absolute methanol) using scan mode and split less. The external standard used was quinaldine. The chemical constituents of each antiscalants sample were identified by comparing the results of the reference retention time and the chromatogram using Wiley mass spectra library (Wiley W9N11). The chromatogram peak area was used to calculate the extracts' chemical components percentage [21].

The GC-MS results of volatile organic compounds present in clove buds and orange peels are presented in Tables 1 and 2.

## 2.5 Fourier Transform Infrared Analysis

Agilent technology CARY 630 FTIR, USA, was used to perform the FTIR analyses on the buds and orange peels using. The machine was turned on and allowed to get started and warmed up. This lasted for about 10 – 15 mins. The computer attached to the machine was also turned on.

'MicroLab PC Window' was double clicked and was waited for, to open after initialization from the computer. Then, the 'start' icon was clicked to initiate the sampling operation i.e for absorbance or transmittance. Organic solvent was used to clean the crystal 'while clicking next' icon in order to check the crystal and collecting background. About 10 – 15mg samples were placed, closed and pressed to make a pellet on top of the crystal and the 'next' icon was clicked. For proper sampling, sample alignment check was done for Blue line from Red to the Green region and the sample identity was put for coding. After this, the 'next' icon was clicked for sampling. To pick the peaks, the computer was right clicked and peaks were selected for labeling by dragging to obtain the wavenumbers as well as the absorbance or transmittance. Fourier Transform Infrared (FTIR) of orange peels and clove buds were taken from 4000 – 650  $\text{cm}^{-1}$  range with sample scans of 32, 16 background scans and 8 Resolution. The values of transmittance were used to display FTIR spectra of orange peels and clove buds [22]. The FTIR results of the orange peels and clove buds are presented in Figures 4 and 5 respectively.

## 2.6. Scanning Electron Microscopy Analysis

SEM model Phenom ProX by PhenomWorld Eindhoven from the Netherlands was used to perform the SEM analysis. Double adhesive which was on a sample stub coated with sputter coater by quorum technologies model Q150R with 5 nm of gold was used to place each sample. Thereafter, it was taken to the SEM machine where it was viewed through NavCam for focusing and little adjustment. The samples transferred to SEM mode were focused while brightness contrasting was automatically adjusted. Thereafter, the morphologies of different magnification were stored in a USB stick ready for use. The pore sizes and magnification are related by equation 2.7 [23-25].

$$\text{Actual pore size} = \frac{\text{Measured pore size}}{\text{Magnification}} \quad (2.7)$$

Pore size is usually measured in  $\mu\text{m}$ , cm or nm).

### 3. RESULTS AND DISCUSSION

#### 3.1. RESULTS

##### 3.1.1. Percentage yield of extracts

The percentage yield clove buds and orange peels extracts are shown as follows:

$$\text{For clove buds, } \frac{20}{32.5} \times 100\%$$

$$\text{Yield} = 6.20\%$$

$$\text{For orange peels, } \frac{10}{48.5} \times 100\%$$

$$\text{Yield} = 20.61\%$$

Phytochemical results of the clove buds and orange peels shown In Fig. 3, is indicative of the fact that the extracts contained mostly tannin, alkaloids, flavonoid and saponin. The clove buds have greater percentage of all the analyzed components except alkaloid. Most of the phytochemicals analyzed have more acidic properties than alkaline; alkaloid is more identified with the pH value greater than 7 and it is prominent in the orange peels extract; while the clove buds are identified with the phytochemicals that are more of acidic in nature. The peaks from the GC-MS of most commercial antiscalants are observed to contain fractions of acidic compounds. It could be deduced that clove bud extracts may have more potency to dissolve calcium carbonates than orange peel extract.

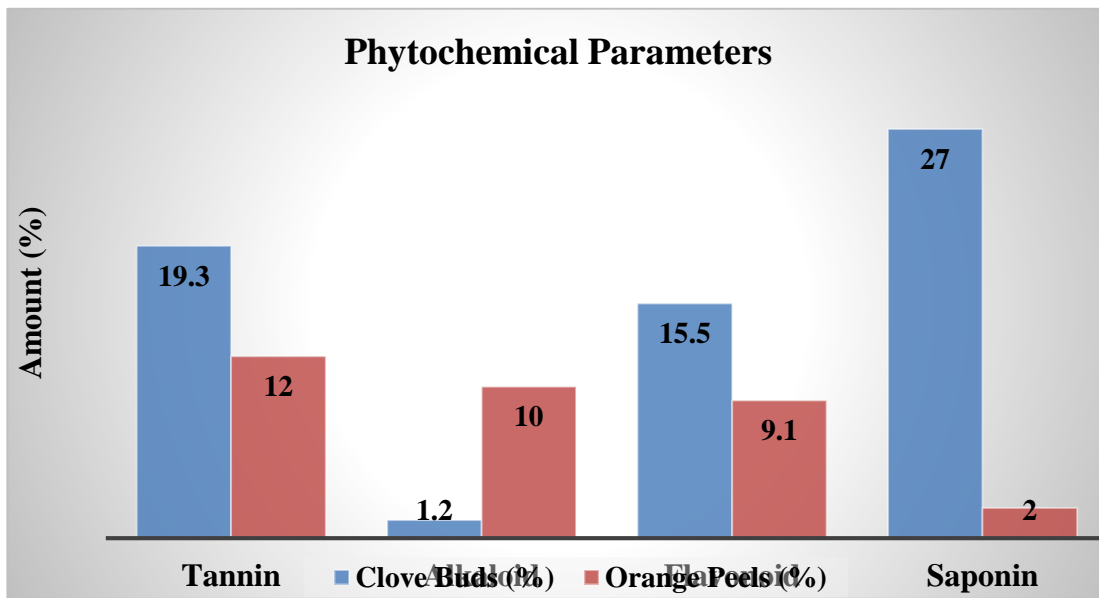


Figure 3: Phytochemical analyses of orange peels and clove bud extracts

**Table 1: GC-MS analysed chemical compounds in methanolic extract of clove buds**

S/No.	Compound Present	Molecular Weight	Molecular Formular	Chemical Abstract Services Value	Retention Time (mins)	Probability (%)
1.	4,5-Dihydro[1,2,5]oxadiazolo[3,3-f]Cinnolin, -3-oxide	190	C <sub>8</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>	25786-90-2	2.906	96
2.	2-MethylBenzo[b]thiophene	148	C <sub>9</sub> H <sub>8</sub> S	1195-14-8	3.033	79.4
3.	1,2-[Methylenedioxy]-4-propenylbenzene	162	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	120-58-1	3.368	69.9
4.	5,6-Dimethyl-2-benzimidalinone	162	C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O	2033-30-9	5.104	95.8
5.	4,6DimethylBenzene-1,3-disulfonamide	264	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	294-46-6	5.745	90.8
6.	3,8-Dichloro-11H-dibenzo[c,f][1,2]diazepin-11-ol	278	C <sub>13</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> O	23469-56-9	6.506	96.6
7.	8Phenylisoquinoline	205	C <sub>15</sub> H <sub>11</sub> N	70125-67-6	16.717	91.2
8.	2-Methyl-4,6-di[2-hydroxyphenyl]pyrimidine	278	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>		17.011	95
9.	9,10-Dihydro-9-Phenanathrene carbonitrile	205	C <sub>15</sub> H <sub>11</sub> N	56666-55-8	18.079	86.5
10	Benzyl nitrile (Benzyl cyanide)	117	C <sub>8</sub> H <sub>7</sub> N	140-29-4	19.146	69.5

The GC-MS analysis of clove buds on Table 1 showed the presence of 1,2-[Methylenedioxy]-4-propenylbenzene, 5,6-Dimethyl-2-benzimidalinone, 4,6-DimethylBenzene-1,3-disulfonamide, 2-MethylBenzo[b]thiophene, 9,10-Dihydro-9-Phenanathrene carbonitrile, 3,8-Dichloro-11H-dibenzo[c,f][1,2]diazepin-11-ol, 8Phenylisoquinoline, 2-Methyl-4,6-di[2-hydroxyphenyl]pyrimidine, Benzyl nitrile (Benzyl cyanide) and 4,5-Dihydro[1,2,5] oxadiazolo[3,3-f]Cinnolin, -3-oxide. The GC-MS analysis of orange peels on Table 2 showed the presence of 4-Azidobenzoic acid, 6-Bromo-2-Phenyl-1H-

benzo[de] isoquinoline-1,3 (2H)-dione, 4-Iodophenoxy acetic acid, 2-Chloro-1-[(2chloroethyl) disulfanyl] propane, 6-Bromo-2-(4-bromophenyl)imidazo[1,2-a] pyridine, 4-Chloro-6-[2,2,2trifluoroethoxy]-1,5 naphthridine-1-N-oxide, 4,4-Bisazido Stilbene, 3,5-Dibromo-4-hydroxybenzaldehyde. 2-Cinnamylidene-6-methoxycoumaran-3-one, 4-[(E)-2-Phenylethenyl]benzonitrile, 3-[(E)-2-Phenylethenyl]benzonitrile, (2Z)-2,3-Diphenyl-2-propenenitrile, 3-Methoxy-2-phenyl-4quinoline carboxylic acid. The mass per charge numbers (m/z) on the peaks of the two extracts were

different and same with the molecular fractions obtained in the instrument. The same variation was observed for fractions of organic antiscalants from the work of Verma & Yaagoob, (2024) [14], this means that GC-MS as an analytical tool is most

useful for detecting the presence of certain constituents in a known antiscalant and not necessary to compare the composition of the different antiscalants.

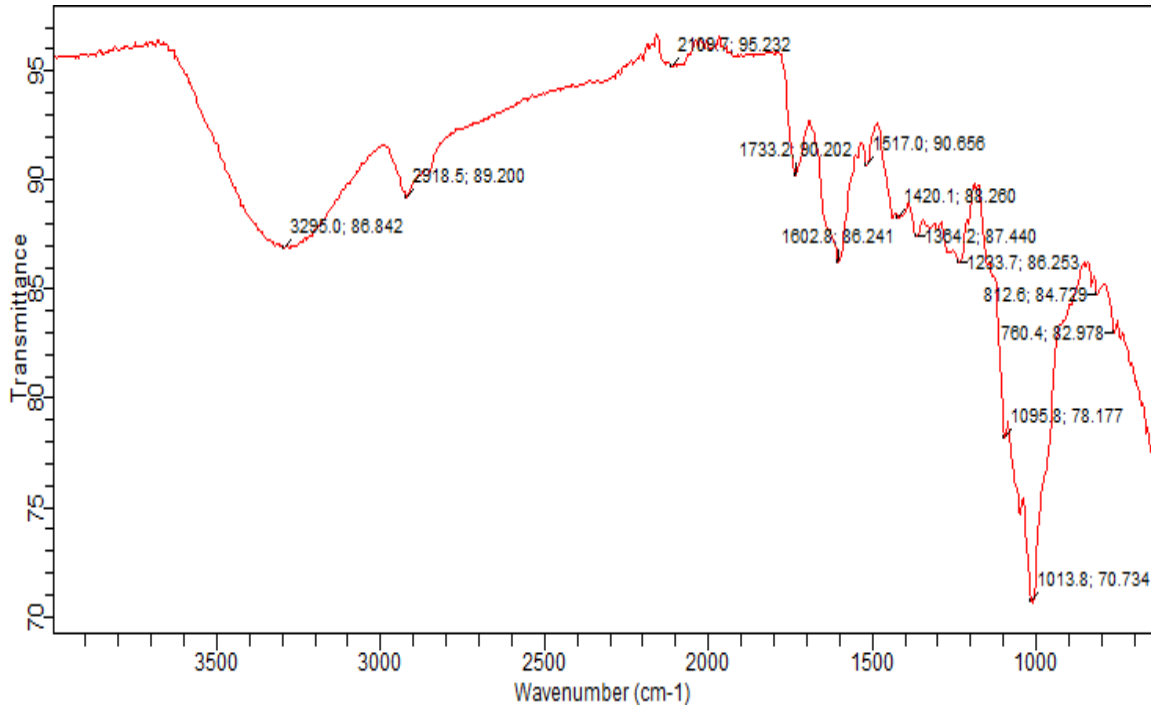
**Table 2:** GC-MS analysed chemical compounds in methanolic extract of orange peels

S/No	Compound Present	Mol. Weight	Mol. Formular	hemical bstract Services alue	etention ime (mins)	'robability (%)
1	·Azidobenzoic acid	163	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>	6427-66-3	3.708	96.4
2	4-Bisazido Stilbene	262	C <sub>14</sub> H <sub>10</sub> N <sub>6</sub>	10193-62-1	4.430	98.3
3	·Bromo-2-Phenyl-1H-enzo[de] isoquinoline-1,3(H) –dione	351	C <sub>18</sub> H <sub>10</sub> BrNO <sub>2</sub>	331-92-1	5.104	94.4
4	·Iodophenoxy acetic acid	278	C <sub>8</sub> H <sub>7</sub> IO <sub>3</sub>	1878-94-0	5.733	96.1
5	sulphur (iv) oxide	64	SO <sub>2</sub>	7446-09-5	7.833	94.0
6	·Bromo-2-(4-momophenyl)imidazo[1,2-pyridine	350	C <sub>13</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>2</sub>	38224-37-2	11.445	98.2
7	·Chloro-1-[(2chloroethyl) sulfanyl] propane	278	C <sub>5</sub> H <sub>10</sub> Cl <sub>2</sub> S <sub>2</sub>	65271-02-5	12.183	98.7
8	·Chloro-6-yl,2,2trifluoroethoxy]-1,5aphthridine-1-N-oxide	278	C <sub>10</sub> H <sub>6</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	214-32-3	12.760	97.2
9	5-Dibromo-4-hydroxybenzaldehyde	278	C <sub>7</sub> H <sub>4</sub> Br <sub>2</sub> O <sub>2</sub>	2973-77-5	14.496	97.9
10	Cinnamylidene-methoxycoumaran-3-one	278	C <sub>18</sub> H <sub>14</sub> O <sub>3</sub>	77765-15-2	17.583	98.0
11	·[(E)-2-phenylethenyl]benzotrile	205	C <sub>15</sub> H <sub>11</sub> N	1552-58-5	18.183	65.9
12	·[(E)-2-phenylethenyl]benzotrile	205	C <sub>15</sub> H <sub>11</sub> N	14064-35-8	19.054	66.0
13	(Z)-2,3-Diphenyl-2-openenitrile	205	C <sub>15</sub> H <sub>11</sub> N	16610-80-3	19.319	67.7
14	·Methoxy-2-phenyl-4-ainoline carboxylic acid	279	C <sub>17</sub> H <sub>13</sub> NO <sub>3</sub>	41957-64-6	19.521	98.0

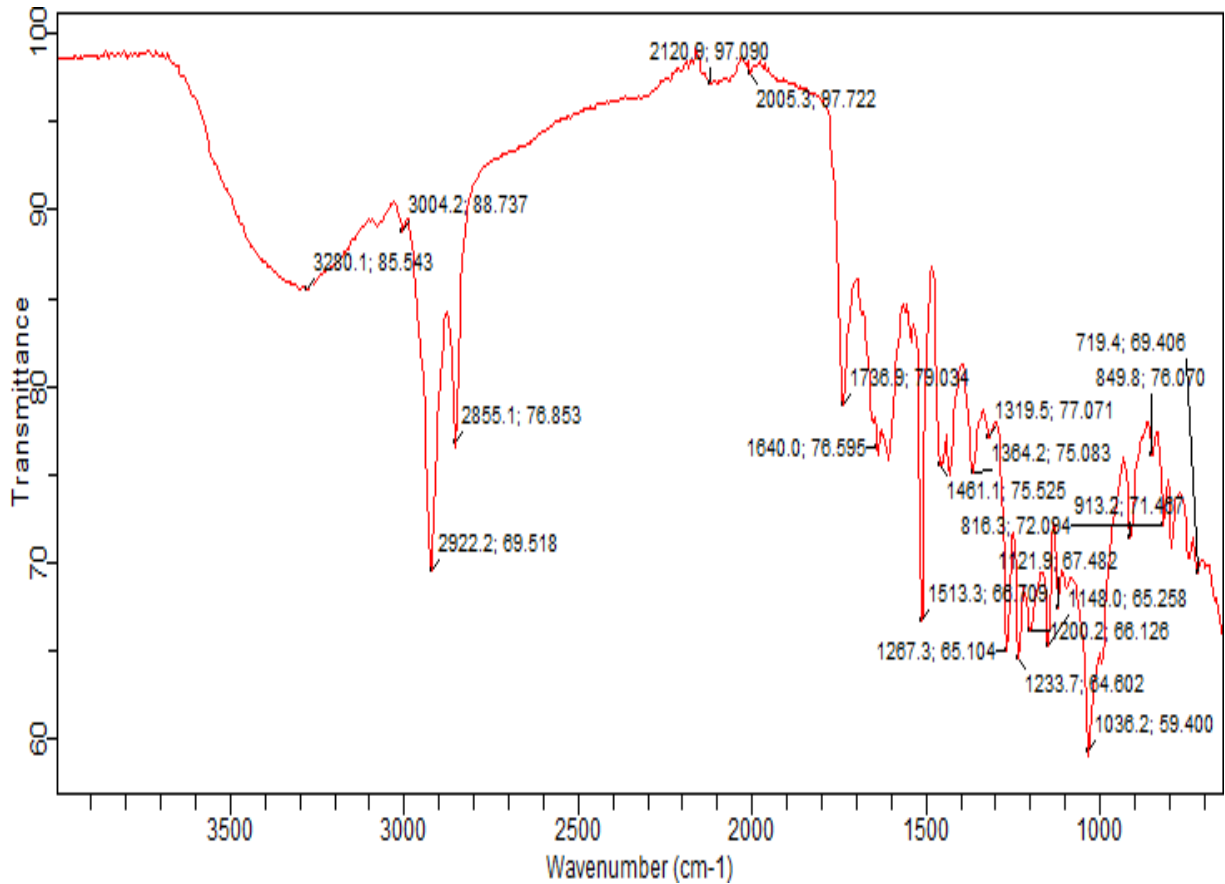
The FTIR spectrum for orange peels extract is shown in Fig. 4, the peaks are between  $1420 - 760 \text{ cm}^{-1}$  and a sharp peak at  $1013 \text{ cm}^{-1}$  in the spectrum. These peaks correspond to the out-of-plane bending for C-H [26]. Peaks at  $1517 \text{ cm}^{-1}$  and  $1602 \text{ cm}^{-1}$  depict the aromatic ring of phenolic compounds [27]. A peak at  $1733 \text{ cm}^{-1}$  shows the presence of carbonyl compounds such as ketones, carboxyl functional group, aldehydes or esters [28]. A peak at  $2918 \text{ cm}^{-1}$  suggests the C-C stretching of aromatic compounds. The FTIR spectrum for the clove buds extract is shown in Fig. 5. The peak at  $1461 \text{ cm}^{-1}$  and a sharp peak at  $1513 \text{ cm}^{-1}$  indicate the presence of aromatic rings of phenolic [27], while between  $1364 \text{ cm}^{-1}$  and  $1148 \text{ cm}^{-1}$  showed the out-of-plane bending of C-H [26]. A sharp peak at  $1036 \text{ cm}^{-1}$  suggests the C-O stretching modes. The peak at  $913 \text{ cm}^{-1}$ , is indicative of the vinyl terminals ( $-\text{CH}=\text{CH}_2$ ). Peaks between  $816 \text{ cm}^{-1}$  and  $719 \text{ cm}^{-1}$  suggests the aromatic C-H bending. A peak at  $1640 \text{ cm}^{-1}$  corresponds to amide or carboxylate functional group. Also, a peak at  $1736 \text{ cm}^{-1}$  shows the presence of carbonyl compounds like ketones, aldehydes, esters or carboxyl functional groups [28]. Peaks between  $2120 \text{ cm}^{-1}$  and  $2005 \text{ cm}^{-1}$  correspond to the absorption band of  $\text{C}\equiv\text{C}$ . Two sharp peaks at  $2855 \text{ cm}^{-1}$  indicates the long chain linear aliphatic compounds and the second peak at  $2922 \text{ cm}^{-1}$  is indicative of the C-H symmetric and C-H asymmetric stretching [29]. The peak at  $3280 \text{ cm}^{-1}$

indicates hydrogen bond. The band confirms the presence of hydrate ( $\text{H}_2\text{O}$ ), hydroxyl (OH), ammonium or amino [30]. This corresponds to the work of Adewale *et al.*, (2018) [31] who carried out FTIR analysis to determine the presence of secondary metabolites and functional groups present in sweet orange peels extract. The result showed the presence of carbonyl, hydroxyl, amine, aliphatic and organic hydrocarbon functional groups. These functional groups could make the extract to be potential antiscalant for calcium carbonate. Also, Ahamad *et al.*, (2022) [32] used FTIR adulteration to characterize clove buds. The FTIR resultant of the adulterated binary mixtures indicated different peaks at  $2852.72$  and  $2924.09 \text{ cm}^{-1}$  (for  $-\text{C}-\text{H} \text{ sp}^3$  and  $-\text{C}-\text{H} \text{ sp}^2$  stretching); equivalent to the observation in Fig. 5 for the clove bud extract.

In Fig. 1, the FTIR for the parent material or monomer PEGD and the first and second transition products, PEGDMA and PGDMA-MA (commercial organic antiscalants) are more related to that of the clove bud extract in Fig. 5 than orange peel extract in Fig. 4. The FTIR of the antiscalant PGDMA-MA-AMPS varied from its transitioned compounds and natural antiscalants with  $-\text{C}-\text{S}-$  bond stretching vibration peak of  $620 \text{ cm}^{-1}$  and  $1161 \text{ cm}^{-1}$  as well as  $1039 \text{ cm}^{-1}$  bond stretching for symmetric and asymmetric stretching vibration peak of  $-\text{S}=\text{O}-$ .

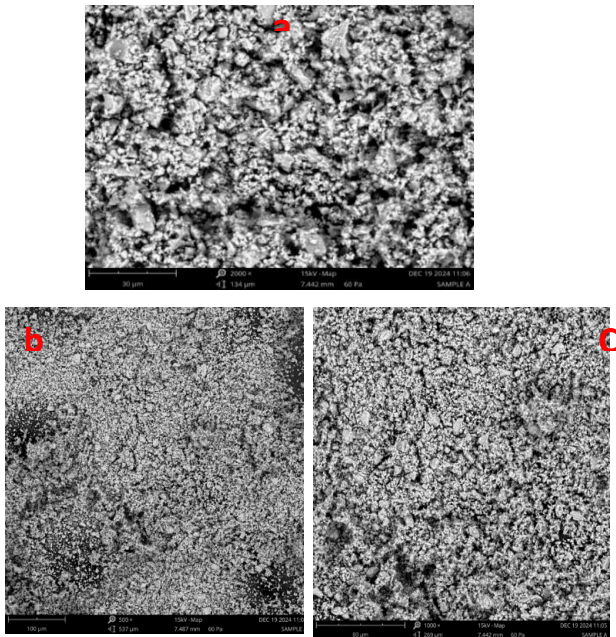


**Figure 4:** FTIR spectrum of orange peels methanol extract



**Figure 5:** FTIR spectrum of clove buds aqueous extract

Furthermore, changes in the morphology of the precipitate were seen from SEM images in Figure 6. The SEM image of  $\text{CaCO}_3$  precipitate in the absence of antiscalant (a) had measured pore size of  $100\ \mu\text{m}$  and magnification of 500x, giving an actual pore size of  $0.2\ \mu\text{m}$  ( $200\ \text{nm}$ ). The SEM image of the precipitate in the presence of clove bud aqueous extract (b) had measured pore size of  $30\ \mu\text{m}$  and magnification of 2000x, giving an actual pore size of  $0.015\ \mu\text{m}$  ( $15\ \text{nm}$ ), while the SEM image of the precipitate in the presence of orange peel methanolic extract (c) had measured pore size of  $80\ \mu\text{m}$  and a magnification of 1000x, giving the actual pore size of  $0.08\ \mu\text{m}$  ( $80\ \text{nm}$ ). Clove bud extract reduced the size of the precipitate from  $30\ \mu\text{m}$  to  $0.015\ \mu\text{m}$  ( $15\ \text{nm}$ ) while the orange peel extract reduced it from  $80\ \mu\text{m}$  to  $0.08\ \mu\text{m}$  ( $80\ \text{nm}$ ). These values were obtained using equation 2.7 [23-25]. From this analysis, the clove bud aqueous extract performed better than the orange peel methanol extract since the pore sizes of calcium carbonate was reduced by 13.0 and 2.5 times respectively.



**Figure 6:** SEM Morphology of untreated  $\text{CaCO}_3$  (a);  $\text{CaCO}_3$  treated with clove buds extract (b) and ( $\text{CaCO}_3$  treated with orange peels extract (c)

#### 4. CONCLUSION

Comprehensive analyses of clove buds and orange peels extracts revealed the presence of phytochemicals such as tannins, alkaloids, flavonoid and saponin; the results of the GC-MS showed Polycyclic Aromatic Hydrocarbons (PAHs) and FTIR analysis showed the presence of compounds having the amino, hydroxyl, carboxyl, aldehyde, ketone and phenyl functionalities. Generally, Clove buds extract dissolved calcium carbonate better than orange peels. It can therefore, be concluded that 20g of clove buds aqueous extract which gave yield of 6.20 % and 10g of orange peels methanol extracts which gave a yield of 20.61 % were able to change the morphology of  $\text{CaCO}_3$  precipitate. So, these extracts have the potentials of being utilized as antiscalants, the efficiency of these extracts were better than those of some commercial antiscalants reviewed in this study [33].

**Declaration of Conflict of Interest:** The authors declare no conflict of interest.

**Data Availability Statement:** Data are available upon request from the first author or corresponding authors.

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