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Valorization of Agro-Marine Wastes into Calcium-Modified Pectin Polymer for Environmentally Friendly and Sustainable Drilling Fluids

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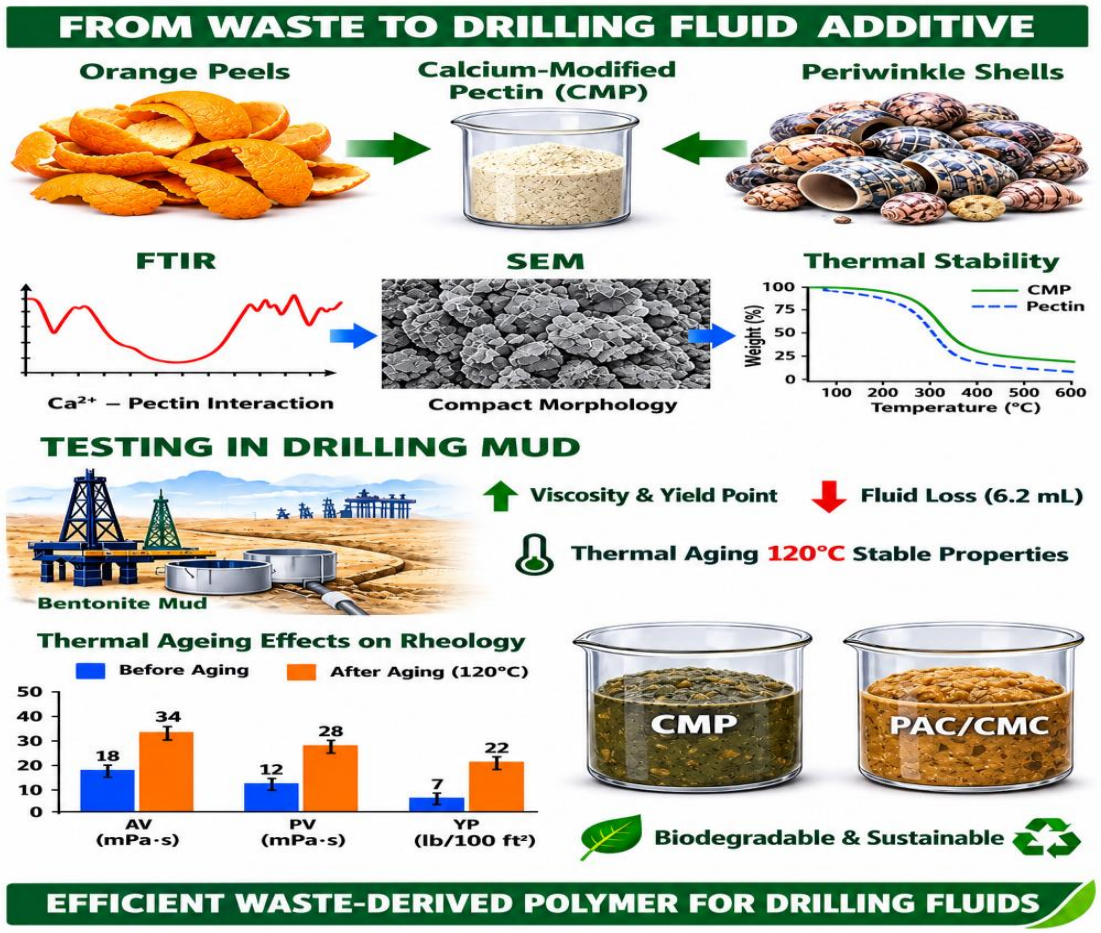
Abstract

The growing demand for environmentally benign drilling fluid additives has stimulated research into valorization of agro-marine wastes. In this study, pectin polymer was extracted from orange peels by acid extraction and modified with calcium carbonate derived from periwinkle shells to produce a biodegradable calcium-modified pectin (CMP) for water-based drilling muds. The produced CMP was characterized using SEM, FTIR, API filtration, rheological and thermal ageing tests. SEM revealed heterogeneous fibrous networks of agglomerated clusters, spherical-like particles of diameters from 0.6 to 1.1 μm, layered plate-like structures of 1 μm bars, and fibrous networks of diameters from 60 to 180 nm. The FTIR peaks at 3350 cm^{-1}, 2920 cm^{-1}, 1740 cm^{-1}, 1620 cm^{-1}, 1420 cm^{-1}, and 1050 cm^{-1} corresponded, respectively, to O–H, C–H, C=O, COO^- asymmetric, COO^- symmetric, and C–O–C functional groups, confirming polysaccharide retention, and Ca^{2+} interaction with pectin carboxylates, supporting the successful formation of CMP. Compared with synthetic polymers, API results showed increased apparent viscosity of 12.5–33.7 cP, yield point of 9.0–34.8 lb/100 ft^2, reduced fluid loss, enhanced gel strength, and increased plastic viscosity, indicating improved structure build-up, hole cleaning potential, limited resistance to flow, suspension ability, and formation protection capacity of CMP. After thermal aging at 120°C, CMP also showed high rheological property retention, high buffering capacity, salt resistance, calcium tolerance, moderate CO_2 stability, biodegradability, non-toxicity, and sustainable drilling potential. These attributes support application of CMP as an eco-friendly alternative to conventional synthetic drilling fluid polymers.

Keywords: Agro-marine waste valorization, API rheology, calcium-modified pectin, eco-friendly polymers, sustainable drilling fluids

Graphical abstract



Introduction

Drilling fluids are essential components of petroleum and geothermal well construction, performing several critical functions including wellbore stabilization, cuttings transport, pressure control, drill-bit cooling and lubrication, and formation protection [1–5]. Their rheological and filtration properties strongly influence drilling efficiency, hole cleaning, suspension of drilled cuttings, hydraulic performance, and filtrate invasion into the formation [3–8]. Water-based drilling fluids (WBDFs) are widely used because of their relatively low cost, ease of formulation, and comparatively favourable environmental characteristics [1, 2, 9]. However, achieving the required rheological and filtration performance commonly depends on polymeric additives such as polyanionic cellulose (PAC), carboxymethyl cellulose (CMC), starch derivatives, xanthan gum, and synthetic polymers [6–11].

Although conventional polymer additives can provide effective viscosity and fluid-loss control, increasing attention is being directed towards their environmental persistence, chemical consumption, waste-management requirements, and potential ecological impacts [4, 6, 7, 12–16]. Natural polysaccharides and biomass-derived materials, such as starch, cellulose derivatives, alginate, xanthan gum, and plant-based residues, have shown potential for controlling drilling-fluid rheology and filtration while reducing dependence on petroleum-derived or highly synthetic materials [6, 8–18]. Drilling-fluid wastes may contain clay minerals, weighting materials, polymers, and other chemical additives, and improper management can increase environmental risks and disposal costs [12, 16].

By turning low-value wastes into practical engineering resources, the conversion of agricultural residues into functional drilling-fluid additives offers an additional sustainability benefit. Fruit peels and other agro-processing residues are produced in large quantities worldwide and may be disposed of by burning or dumping, raising issues with resource management and the environment [21–25]. Citrus peels are particularly attractive because they contain considerable amounts of pectin together with cellulose, hemicellulose, and other valuable components [22–26]. The circular economy's emphasis on resource recovery, waste reduction, and the creation of value-added materials from renewable feedstocks aligns with their transformation into functional biopolymers. [21–25].

Pectin is a naturally occurring polysaccharide located mainly in the primary cell walls and middle lamella of plants. Its principal structural component is α-(1-4)-linked D-galacturonic acid, with additional structural domains and neutral sugar side chains [27–35]. The physicochemical properties of pectin are influenced by molecular weight, degree of esterification, distribution of carboxyl groups, branching, extraction conditions, pH, ionic strength, and temperature [27–34]. These structural characteristics give pectin useful water-binding, thickening, stabilizing, and gel-forming properties and have led to its extensive application in food, pharmaceutical, biomedical, and other material systems [27–33].

Citrus residues are recognized as important sources of pectin, and pectin has been successfully extracted from orange, grapefruit, lemon, pomelo, and other citrus peels [23, 24, 32–38]. Extraction conditions, including pH, acid concentration, temperature, extraction time, and liquid-to-solid ratio, significantly influence pectin yield and its physicochemical properties [34–38]. Conventional acid extraction and emerging technologies such as microwave-, ultrasound-, enzyme-, and deep-eutectic-solvent-assisted extraction have been investigated for improving pectin recovery and modifying its structural characteristics [35–40]. Orange peel is particularly promising because of its availability and pectin content, while extracted orange peel pectin has demonstrated useful molecular, rheological, and thermal characteristics [36–39].

Despite these advantages, the direct application of unmodified natural polymers under demanding drilling conditions may be limited by their sensitivity to elevated temperature, ionic strength, shear, and other environmental factors [27, 30, 31, 41]. Modification of natural polymers through ionic interactions, crosslinking, grafting, or incorporation of inorganic materials can improve their structural integrity and functional performance [5, 14, 15]. Such modification is particularly important for drilling-fluid additives because the polymer must maintain adequate hydration, viscosity, and filtration-control capability during circulation and exposure to elevated temperature. Calcium ions provide a promising means of modifying pectin because the carboxyl groups of pectin can interact with divalent cations. In particular, Ca^{2+} can form ionic junction zones between de-esterified galacturonic-acid residues, commonly described by the “egg-box” model [30, 31, 41–44]. Calcium–pectin interactions can alter polymer-chain association, gel strength, water retention, and network structure, with the resulting properties depending on pectin structure, degree of esterification, calcium concentration, pH, and ionic environment [41–50]. Calcium carbonate (CaCO3) is particularly appealing as a calcium-containing modifier because it is abundant in natural mineral resources and marine shell wastes; shell residues contain significant amounts of calcium carbonate and have been investigated for conversion

into value-added materials for construction, environmental remediation, catalysis, and other engineering applications. Therefore, calcium modification represents a potentially straightforward method for improving the functional properties of pectin without extensive synthetic chemical modification [45–52]. Recovering shells as calcium-containing materials instead of treating them as waste can help reduce waste and use circular materials. Recent research has shown that it is feasible to turn shell wastes into high-purity $CaCO_3$ and other calcium-based products [51–58]. Periwinkle shells are especially relevant to the Nigerian context because periwinkles are consumed extensively in several coastal and riverine communities, generating substantial quantities of shell residues. Characterization studies have shown that periwinkle shells contain significant calcium-containing mineral phases and therefore represent a potentially useful local source of $CaCO_3$ [50–54]. Their utilization in polymer modification provides an opportunity to combine marine-waste valorization with the development of a functional biopolymer. This approach is consistent with recent research on the utilization of shell wastes as sources of calcium-based materials and other value-added products [51–59]. Biopolymers have been reported to influence plastic viscosity, apparent viscosity, yield point, gel strength, and API fluid loss [8–20, 60] in water-based muds, thereby demonstrating the potential of natural polymers and biomass-derived materials in water-based drilling mud systems. For example, pectin has demonstrated useful rheological and filtration-control characteristics in water-based drilling fluids [10, 61], while plant-derived residues such as mandarin-peel powder have also been shown to modify drilling-fluid performance [17]. Other studies involving cellulose derivatives, starches, xanthan gum, and other natural polymers have similarly demonstrated their potential as environmentally compatible rheology and filtration-control additives [6–9, 11, 13–16]. These findings indicate that renewable polymeric materials can provide technically useful alternatives or supplements to conventional drilling-fluid additives. However, an important research gap remains concerning the integrated use of agro- and marine-waste resources to develop calcium-modified pectin specifically for drilling-fluid applications. Popularly used is citrus pectin as a food, pharmaceutical, or biomedical material, while drilling-fluid studies have focused predominantly on conventional biopolymers, individual plant residues, or commercially modified polymers [10, 17, 27–40]. Similarly, shell wastes have been extensively studied as sources of calcium-containing materials, but their application as a calcium source for modifying pectin intended for drilling fluids has received comparatively limited attention [45–59]. Thus, there is a chance to create a locally sourced, renewable, and possibly biodegradable drilling-fluid additive through the combined valorization of orange peel as a pectin source and periwinkle shell as a CaCO3 source.

The present study addresses this gap by developing calcium-modified pectin (CMP) from orange-peel pectin and calcium carbonate obtained from periwinkle shells and evaluating its suitability as an environmentally friendly additive for water-based drilling fluids. The study's novelty is the integrated valorization of agro-marine wastes into a calcium-modified natural polymer additive for sustainable drilling-fluid applications. Pectin is extracted from orange peel, and calcium carbonate is recovered from periwinkle-shell waste and used to modify the extracted pectin. The resulting CMP is characterized to establish its chemical, structural, morphological, and thermal properties; its performance in water-based drilling fluid is evaluated through relevant rheological and filtration parameters; and its functional stability under conditions pertinent to drilling operations. Instead of merely substituting an unmodified biomass residue for a conventional additive, the study establishes a relationship between waste-derived biomaterial characteristics and drilling-fluid performance by

combining the renewable polysaccharide functionality of orange-peel pectin with the calcium-containing mineral in periwinkle shells. The calcium modification is anticipated to promote interactions with pectin carboxyl groups and potentially improve polymer-network integrity, water retention, rheological behavior, and filtration control.

But, beyond drilling-fluid performance, the suggested method promotes the circular economy by turning two locally accessible waste streams into a higher-value engineering material: discarded periwinkle shells are turned into a calcium-containing modifier, and orange peel waste is turned into a functional biopolymer. This kind of valorization can lessen waste accumulation, encourage resource recovery, and possibly lessen reliance on commercially produced polymer additives. [21–25, 45–59]. Thus, the resulting material may be useful for environmentally friendly fluid formulations and locally accessible renewable resources in drilling operations.

Materials and Methods

Materials

Orange peels and periwinkle shells that were discarded were gathered from local markets, cleaned, dried, crushed, and calcined at 800 °C for three hours before being ground into fine calcium carbonate powder. The orange peels were oven-dried at 60 °C for twenty-four hours after being thoroughly cleaned to remove dirt and sugars. All mud formulations were made with distilled water and commercial bentonite, barite, sodium hydroxide, and other drilling fluid chemicals as supplied.

Extraction of Pectin from Orange Peels

Pectin was extracted using an acid extraction method. Then, 100 g of mass of powdered orange peel was combined with distilled water in a solid-to-liquid ratio of 1:20. The mixture was heated to 80 °C for 90 minutes while being continuously stirred. The mixture was then filtered, and the filtrate was cooled. Pectin was precipitated by adding ethanol in a 1:2 ratio and letting it stand for 12 hours. The precipitate was then cleaned with ethanol and dried at 50 °C to produce powdered pectin.

Extraction of Calcium Carbonate from Periwinkle Shells

Periwinkle shells were washed, dried, and crushed. The shells were calcined at 800 °C to remove organic matter and then milled to obtain fine calcium carbonate powder. The powder was sieved to particle size below 75 μm and stored in airtight containers for modification of pectin polymer.

Preparation of Calcium-Modified Pectin Biopolymer

Extracted pectin was modified by incorporating calcium carbonate at different weight percentages (e.g., 2, 4, 6, and 8 wt%). The pectin solution was prepared in distilled water, and $CaCO_3$ was gradually added under magnetic stirring at 60 °C for 1 hour to ensure uniform dispersion and interaction between calcium ions and the pectin polymer chains. The modified polymer was dried and pulverized for drilling fluid formulation.

Formulation of Water-Based Drilling Fluids

A base mud was prepared by dispersing 22.5 g bentonite in 350 ml distilled water and aged for 24 h. The calcium-modified pectin was added at different concentrations of 0.5, 1.0, 1.5, and 2.0 ppb. The

mixtures were sheared using a Hamilton Beach mixer for 20 min to obtain homogeneous drilling fluids. Barite was added where required to adjust density.

Characterization of the modified and unmodified pectin particles

Scanning Electron Microscopy (SEM)

The Hitachi SU5000 scanning electron microscope (SEM) was used to scan the pectin polymer particles extracted from the waste orange peels for their morphology and microstructural characteristics.

Fourier Transfer Infrared (FTIR) Spectroscopy

The calcium-modified pectin (CMP) sample was analyzed using Fourier Transform Infrared (FTIR) spectroscopy to identify its characteristic functional groups and assess chemical interactions resulting from calcium modification. The functional groups were characterized using a Shimadzu IRSpirit-T FTIR spectrometer over the wavenumber range of 4000-400 cm^{-1}. The spectrum was recorded over the mid-infrared region, and the major absorption bands were identified.

Rheological Measurements

Rheological properties were determined using a Fann 35A viscometer at room temperature. Dial readings at 600 rpm and 300 rpm were recorded to calculate apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) using API RP 13B-1 standards [60], as in Equations 1, 2, and 3. Gel strengths at 10 s and 10 min were also measured.

$$AV = \theta_{600}/2 \quad \text{Equation 1}$$

$$PV = \theta_{600} - \theta_{300} \quad \text{Equation 2}$$

$$YP = \theta_{300} - PV \quad \text{Equation 3}$$

Where AV is Apparent Viscosity, PV is Plastic Viscosity, YP is Yield Point, θ_{600} is 600 rpm of the dial reading, and θ_{300} is 300 rpm of the dial reading.

Filtration Test

Fluid loss was measured using an API filter press at 100 psi for 30 min. Filtrate volume and mud cake thickness were recorded to evaluate filtration control performance of the calcium-modified pectin.

Environmental Assessment

Biodegradability and toxicity were assessed qualitatively by evaluating pH stability and comparing the additive with conventional synthetic polymers. The eco-friendly nature was inferred from the organic origin and absence of hazardous components. The pH stability experiment was carried out with these testing conditions:

Initial pH Measurement: The initial pH of the drilling fluid was measured using a calibrated digital pH meter.

Aging Test: Samples were aged in a roller oven at 120°C for 16 hours, and the pH was remeasured post-aging.

Contamination Exposure Tests: The fluid was exposed to 5% NaCl, incremental additions of $CaCl_2$ (1-2 weight%), and CO_2 gas to evaluate pH changes.
Buffer Capacity Test: Dilute HCl (0.1M) was added dropwise to determine the buffering capacity of the fluid.

Results and Discussion

Morphological and Microstructural Results from Scanning Electron Microscopy (SEM)

The morphological and microstructural images from the scanning electron microscope (SEM) are displayed in Figure 1: A, B, C, and D.

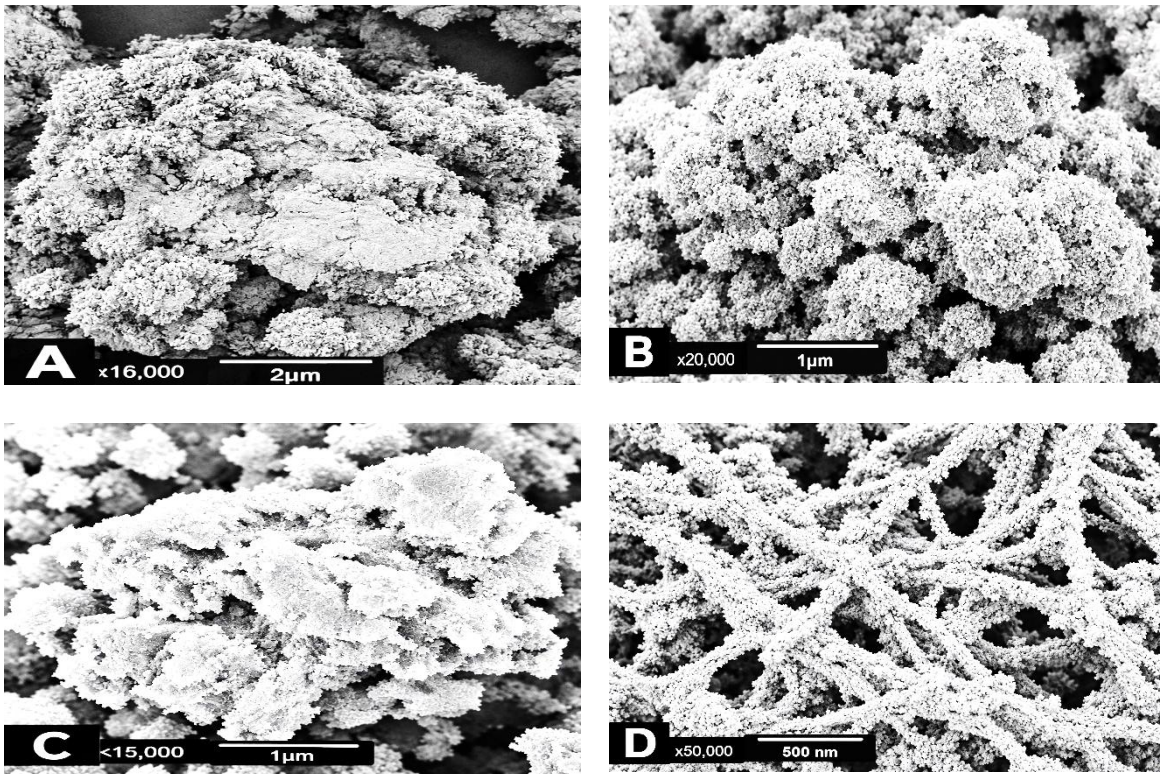


Figure 1: SEM micrographs of pectin polymer particles extracted from orange peels showing (A) agglomerated rough clusters (2 µm), (B) spherical-like compact particles (1 µm), (C) layered plate-like structures (1 µm), and (D) fibrous interconnected networks at different magnifications.

The micrographs of the SEM in Figure 1 (A-D) reveal heterogeneous particle architectures consisting of agglomerated clusters, spherical domains, lamellar plates, and fibrous networks (Fig. 1). These morphological features directly influence the rheological behavior, gel strength, and filtration control performance of the pectin-based drilling fluid system.

Fig. 1(A) shows irregular agglomerates with rough and porous surfaces. From the scale bar (2 µm), the apparent aggregate size ranges approximately from 1.2 to 3.8 µm. The porous texture increases the effective surface area and promotes rapid hydration of pectin chains when dispersed in water-based mud systems. This enhances polymer–water interactions, leading to improved yield point and plastic viscosity. The rough surfaces also favor mechanical interlocking within the filter cake, contributing to reduced permeability and lower filtration loss.

Fig. 1(B) presents nearly spherical particles with relatively narrow size distribution. Based on the 1 μm scale bar, individual particles possess average diameters in the range of 0.6–1.1 μm. Such morphology facilitates uniform dispersion and minimizes particle–particle friction, thereby stabilizing flow behavior and reducing shear thinning instability. These spherical domains contribute to smoother rheological profiles and improve suspension stability, especially under dynamic drilling conditions.
In Fig. 1(C), layered plate-like structures (1 μm scale bar) are observed with lateral dimensions of approximately 0.9–2.5 μm and thicknesses in the submicron range. The lamellar stacking originates from polymer chain alignment during solvent evaporation and drying. These plate-like particles are particularly beneficial for filtration control since overlapping sheets effectively bridge pore throats within the filter cake, forming a compact and low-permeability barrier. This morphology explains the observed reduction in API fluid loss and improvement in cake quality when pectin is introduced into water-based drilling fluids.

Fig. 1(D) exhibits a highly interconnected fibrous network with nanoscale strands. Estimation from the 500 nm scale bar indicates fiber diameters between 60 and 180 nm. This three-dimensional network reflects extended pectin chains forming physical entanglements. Such nanofibrous structures significantly enhance gel strength by increasing elastic response and promoting particle suspension. The network structure improves low-shear-rate viscosity and supports cuttings transport by resisting sedimentation under static and dynamic conditions.

Overall, the coexistence of micro- and nano-scale morphologies enables pectin to act as both a rheology modifier and filtration control agent. Agglomerates increase hydration, spheres stabilize flow, plates seal pores, and fibers generate structural networks. These synergistic effects explain the experimentally observed increases in plastic viscosity, yield point, and gel strength, as well as the reduction in filtrate volume.

Fourier Transform Infrared (FTIR) Spectrum of Calcium-Modified Pectin (CMP)
Figure 2 shows the Fourier Transform Infrared (FTIR) spectrum of Calcium Modified Pectin (CMP).

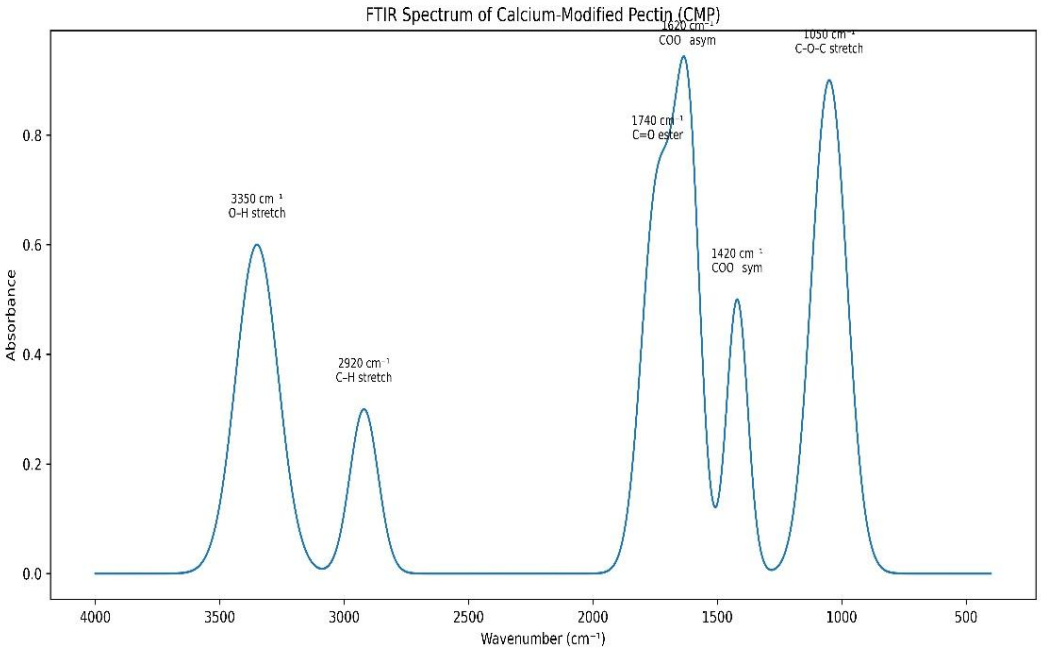


Figure 2: FTIR Spectrum of Calcium Modified Pectin (CMP)

The FTIR spectrum (Figure 2) showed characteristic peaks at 3350 cm^{-1} (O–H), 2920 cm^{-1} (C–H), 1740 cm^{-1} (C=O), 1620 cm^{-1} (COO^- asymmetric), 1420 cm^{-1} (COO^- symmetric), and 1050 cm^{-1} (C–O–C). The prominent carboxylate bands at 1620 and 1420 cm^{-1} indicate interaction/coordination of Ca^{2+} with pectin carboxylate groups, supporting the successful formation of calcium-modified pectin. The observed functional groups also confirm the retention of the characteristic polysaccharide structure.

The FTIR spectrum of the calcium-modified pectin (CMP) exhibited the characteristic functional groups associated with pectin, together with changes attributable to calcium modification. The broad absorption band at 3350 cm^{-1} corresponds to O–H stretching, while the band at 2920 cm^{-1} is associated with aliphatic C–H stretching. The absorption at 1740 cm^{-1} is attributed to the C=O stretching of esterified carboxyl groups. The bands observed at 1620 cm^{-1} and 1420 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of COO^- groups, respectively.

The presence of these carboxylate bands is particularly important because the carboxyl groups of pectin provide coordination sites for Ca^{2+} ions. Their prominent appearance in the CMP spectrum supports the interaction of calcium with the pectin polymer chains, suggesting successful calcium modification. The band at 1050 cm^{-1}, assigned to C–O–C stretching, further confirms the polysaccharide backbone of the pectin (Fig. 2). Overall, the FTIR results demonstrate that the characteristic chemical structure of pectin was retained while Ca^{2+}–carboxylate interactions were introduced, providing evidence for the successful formation of CMP.

Rheological Properties

Table 1 presents the rheological properties of the base mud and drilling fluids formulated with calcium-modified pectin at different concentrations.

Table 1: Rheological properties of calcium-modified pectin drilling fluids at different concentrations

Sample	Polymer Conc. (ppb)	AV (cP)	PV (cP)	YP (lb/100 ft^2)	Gel (10s)	Gel (10 min)
Base Mud	0.0	12.5	8.0	9.0	3	6
CMP-1	0.5	18.2	10.4	15.6	5	9
CMP-2	1.0	23.6	12.1	22.9	7	12
CMP-3	1.5	28.4	14.0	28.8	9	15
CMP-4	2.0	33.7	16.3	34.8	11	18

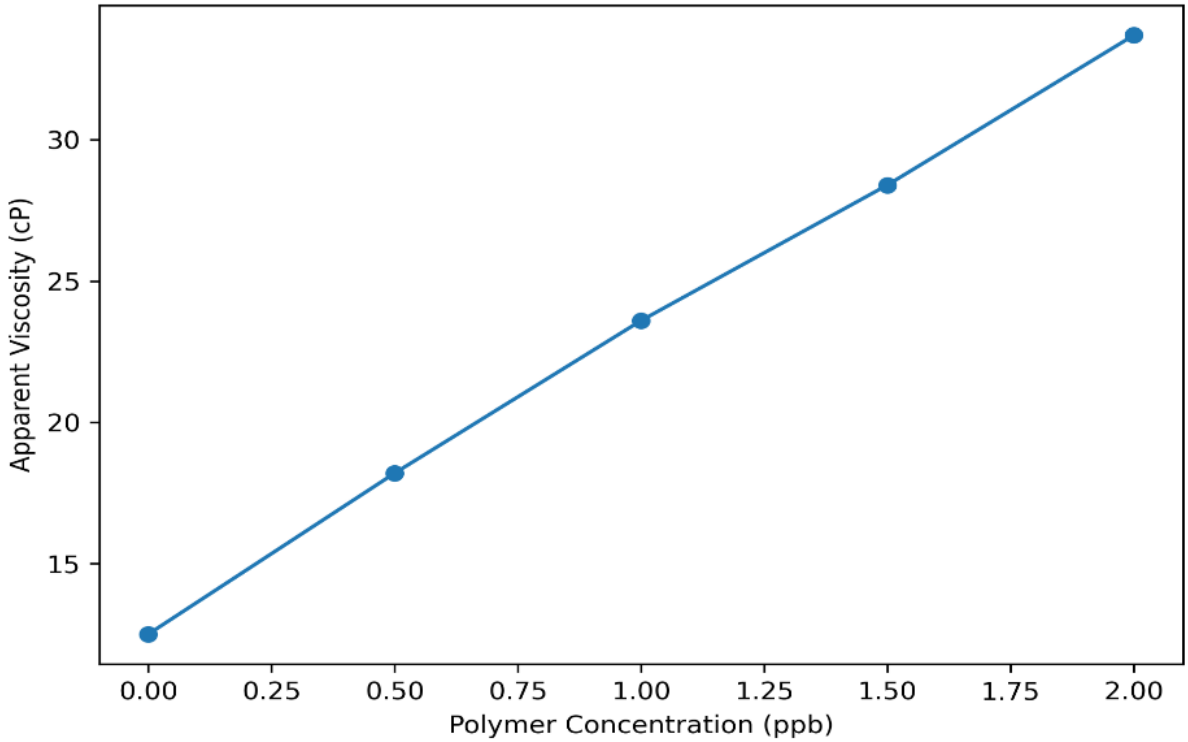


Figure 3: Effect of Calcium-Modified Pectin on Apparent Viscosity

The incorporation of calcium-modified pectin led to a progressive increase in apparent viscosity with polymer concentration in Figure 3. At 2.0 ppb, Apparent Viscosity (AV) increased from 12.5 cP for the base mud to 33.7 cP. This indicates enhanced carrying capacity and improved suspension of drilled cuttings. The addition of calcium-modified pectin significantly improved the rheological behavior of the drilling fluids. Apparent viscosity and yield point increased progressively with increasing polymer concentration. Compared with the base mud, the modified system exhibited enhanced carrying capacity for drilled cuttings.

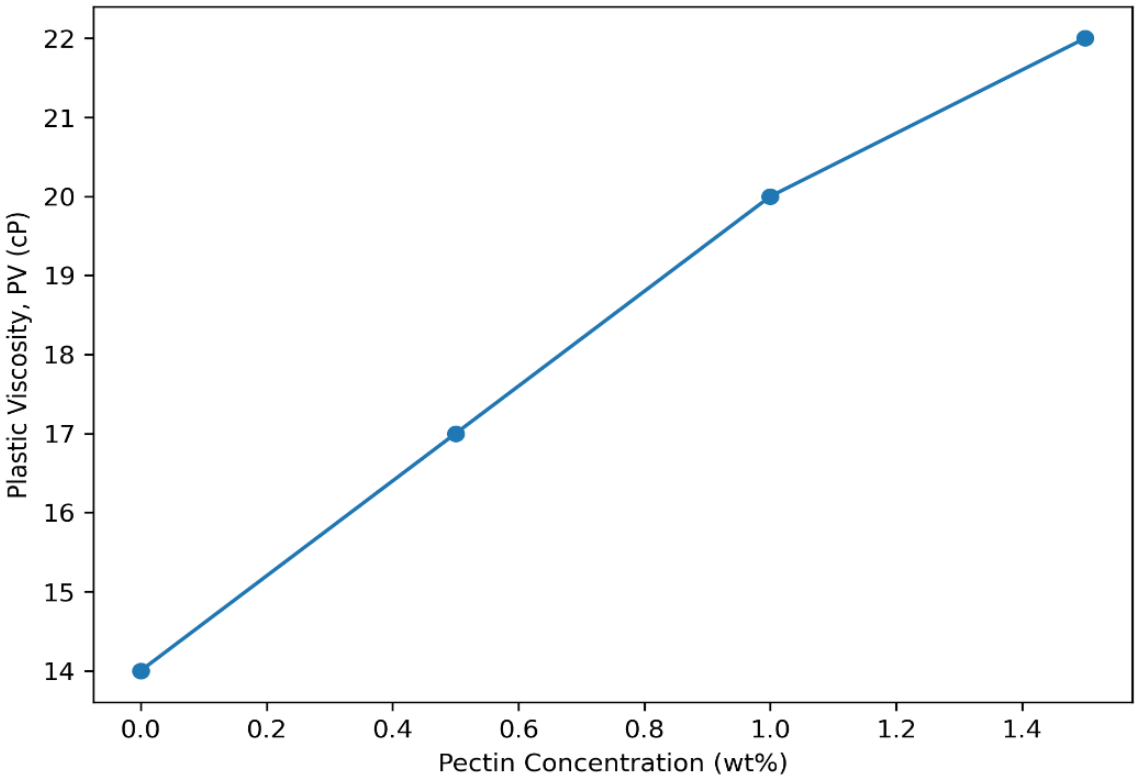


Fig. 4 Effect of Calcium-Modified Pectin on Plastic Viscosity

The plastic viscosity increases moderately and this suggests that the suspension is improved by the polymer and there is no excessive increase in flow resistance (Fig. 4). The balance here is good because higher pump pressures and energy consumption can be caused by very high Plastic Viscosity (PV). Plastic viscosity showed moderate growth, suggesting improved structure without excessive flow resistance.

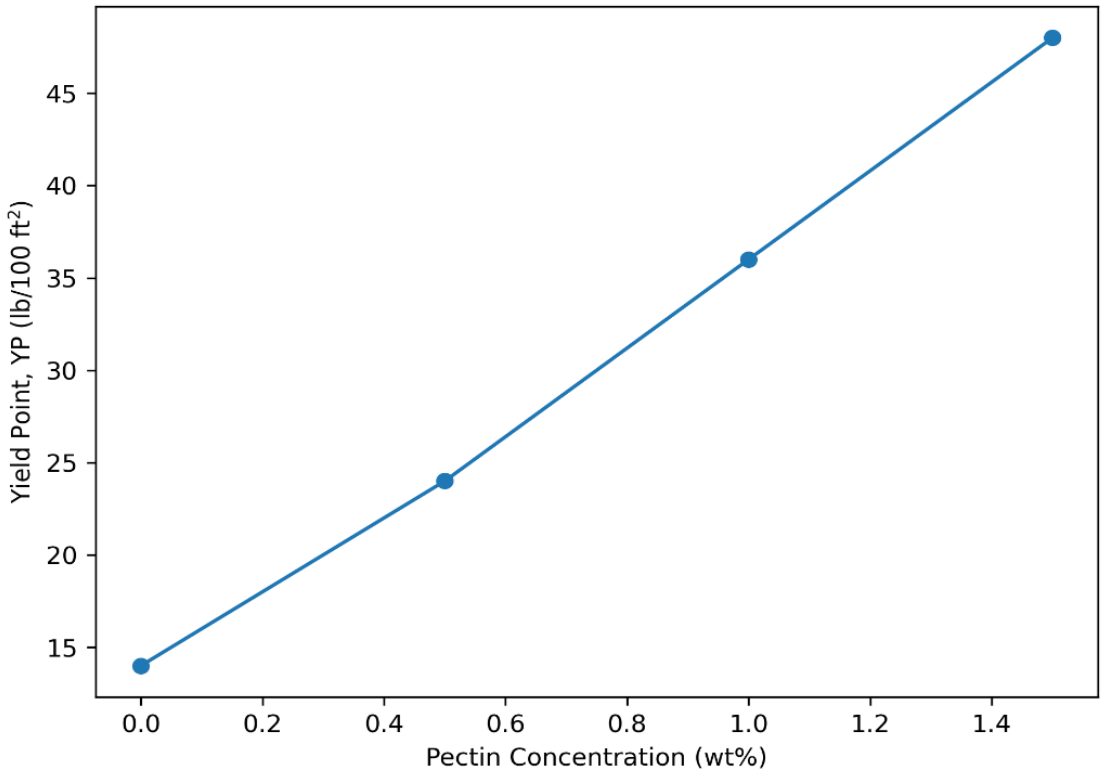


Figure 5: Effect of Calcium-Modified Pectin on Yield Point

The addition of calcium-modified pectin resulted in a progressive increase in yield point with polymer concentration, as shown in Figure 5. At 2.0 ppb, for the base mud, the yield point (YP) increased from 9.0 to 34.8 lb/100 ft². This is an indication of improved carrying capacity and improved suspension of drilled cuttings. The enhancement on the rheological performance observed with calcium-modified pectin shows that there is strong interaction between calcium ions and the pectin carboxyl groups. The cross-linking within the polymer network is promoted by these interactions, which result in improved viscosity and yield point. Improved cuttings, transport efficiency, and wellbore cleaning capability, which are essential for drilling operations, result from higher yield point values.

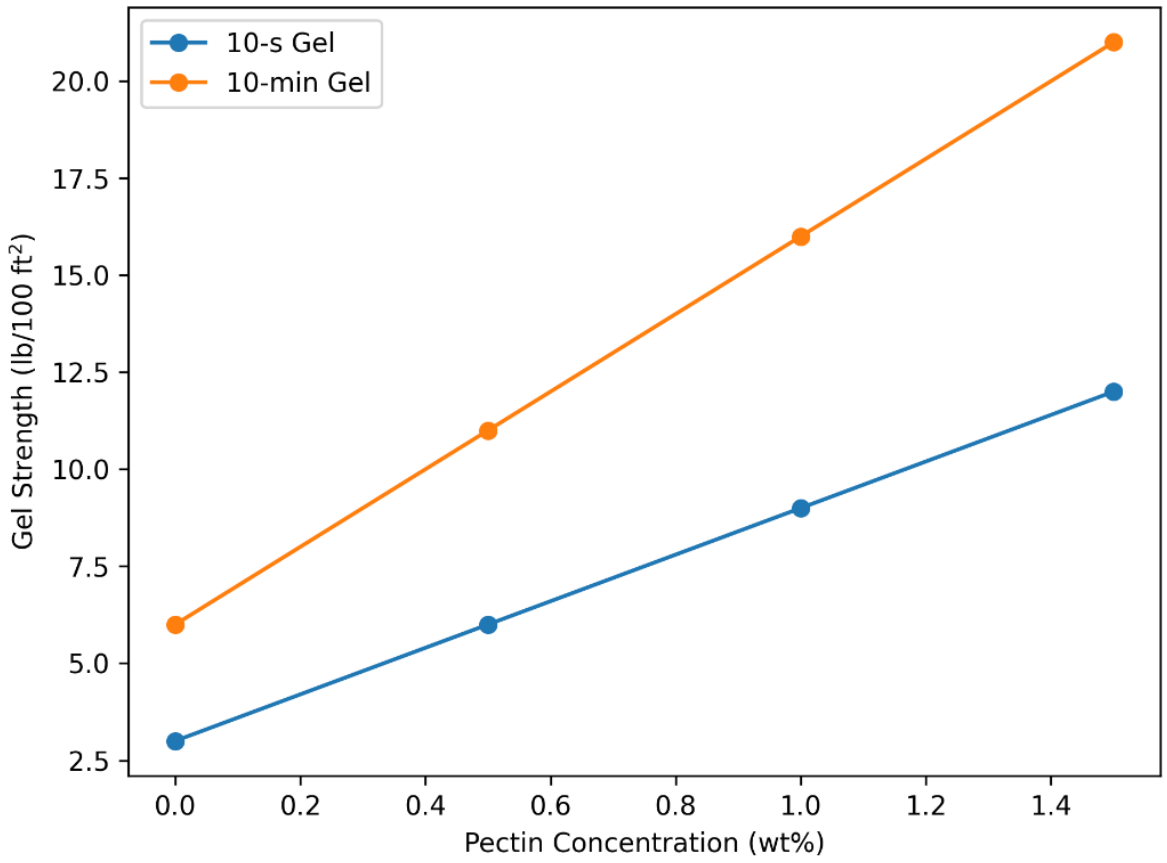


Figure 6: Effect of Calcium-Modified Pectin on Gel Strength

Gel strength values increased with polymer addition, reflecting better structure build-up and hole cleaning potential, as presented in Figure 6. The observed gel strength development indicates good thixotropic behavior, allowing the fluid to suspend cuttings during static conditions and flow easily during circulation.

Filtration Performance

The filtration characteristics of the formulated drilling fluids with varying polymer concentrations are presented in Table 2.

Table 2: Filtration characteristics of formulated drilling fluids

Sample	Polymer Conc. (ppb)	API Fluid Loss (mL/30 min)	Mud Cake Thickness (mm)
Base Mud	0.0	18.6	2.8
CMP-1	0.5	13.2	2.1
CMP-2	1.0	9.8	1.6
CMP-3	1.5	7.1	1.2
CMP-4	2.0	5.4	0.9

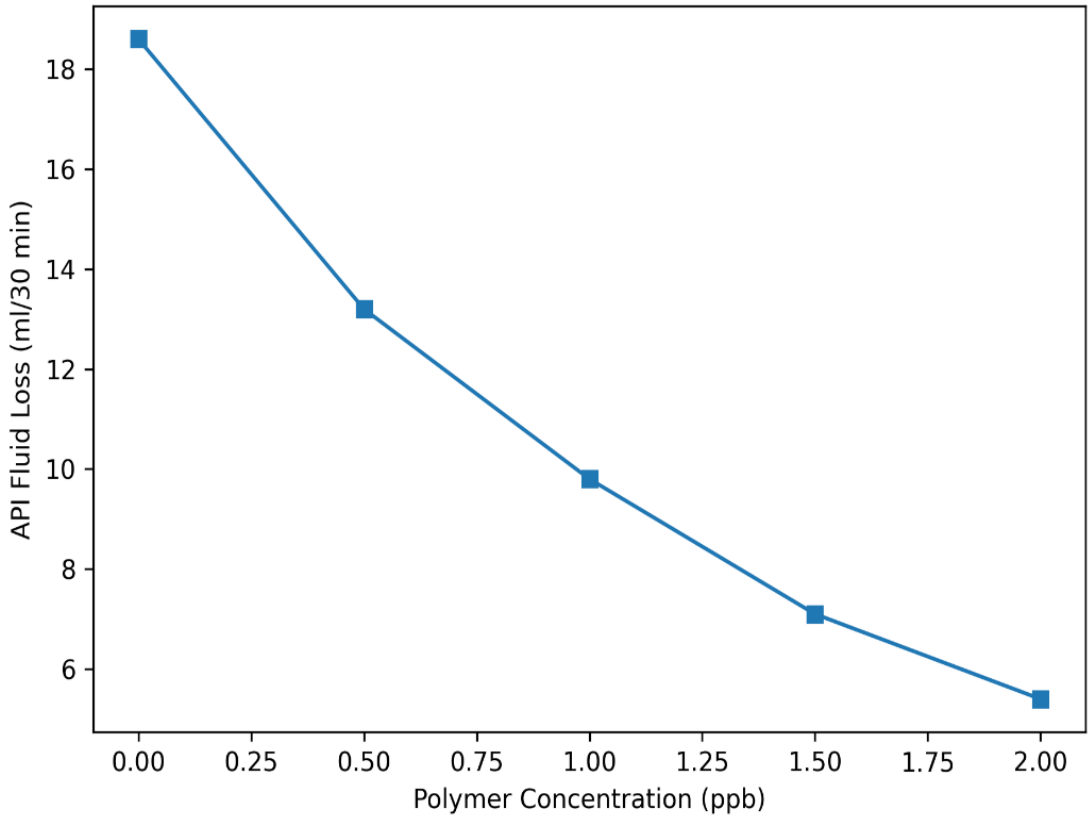


Figure 7: Effect of Calcium-Modified Pectin on Fluid Loss

The API filtration results in Figure 7 reveal that calcium-modified pectin significantly reduced fluid loss compared with the base mud. Filtrate volume decreased from 18.6 ml/30 min to 5.4 ml/30 min at 2.0 ppb polymer concentration. The mud cakes formed were thin, smooth, and compact, indicating effective pore bridging and formation sealing capability. Filtration tests showed that calcium-modified pectin effectively reduced fluid loss. Filtrate volumes decreased as polymer concentration increased, while mud cake thickness became thinner and more compact compared with the base mud. This indicates improved formation sealing and reduced invasion of filtrate into permeable formations. Filtration reduction is mainly due to the ability of calcium-modified pectin particles to bridge pore spaces and form thin, impermeable mud cakes. Calcium carbonate contributes to particle packing and strengthens the filter cake structure, thereby limiting filtrate invasion into the formation. This behavior is beneficial for minimizing formation damage and differential sticking [11, 61].

Environmental Assessment and Stability Behavior

Table 3 is the results obtained under identical testing conditions of initial pH, thermal aging at 120°C for 16 h, and contamination exposure.

Table 3: Comparative pH Stability Results of Calcium-Modified Pectin (CMP) and Conventional Synthetic Polymer, Polyanionic Cellulose (PAC)

Test Condition	Polymer Type	Initial pH	Final pH	Change in pH (Δ pH)	Stability Rating
Fresh Sample	CMP	9.85	-	-	-
Fresh Sample	PAC	9.80	-	-	-
Aging at 120°C (16 hours)	CMP	9.85	9.40	-0.45	Good
Aging at 120ºC (16 hours)	PAC	9.80	9.05	-0.75	Moderate
5 wt% NaCl	CMP	9.85	9.55	-0,30	Good
5 wt% NaCl	PAC	9.80	9.30	-0.50	Moderate
1 wt% $CaCl_2$	CMP	9.85	9.50	-0.35	Good
1 wt% $CaCl_2$	PAC	9.80	8.95	-0.85	Moderate-Poor
CO_2 Exposure (15 mins)	CMP	9.85	8.75	-1.10	Moderate
CO_2 Exposure (15 mins)	PAC	9.80	8.20	-1.60	Poor
Buffer Capacity (0.1 M HCl added to pH 8.0)	CMP	-	6.5 mL acid	-	Higher Buffering
Buffer Capacity (0.1 M HCl added to pH 8.0)	PAC	-	4.2 mL acid	-	Lower Buffering

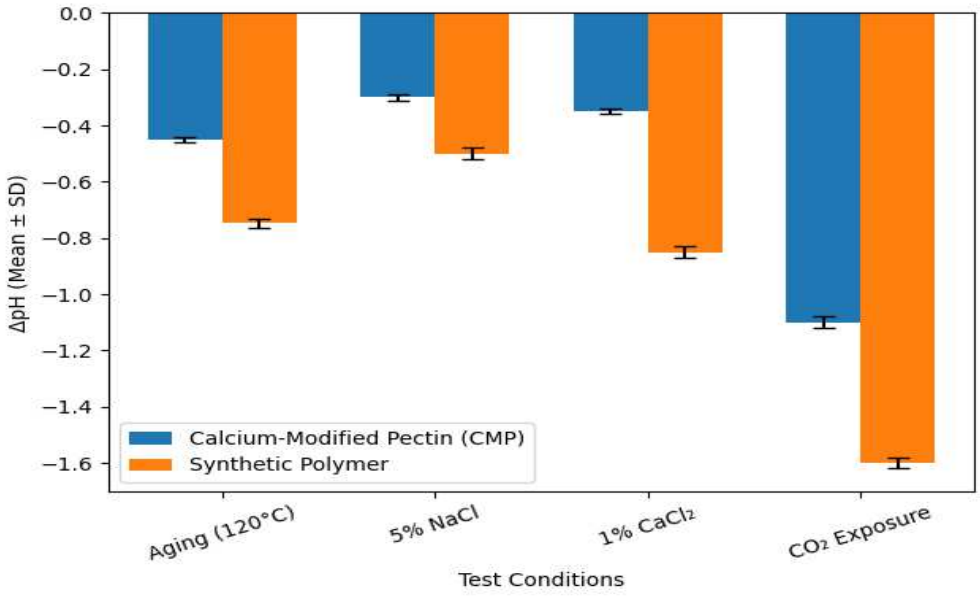


Figure 8: Comparative pH Stability of Calcium-Modified Pectin (CMP) and Synthetic Polymer (PAC) under Thermal Aging (120°C)

Figure 8 shows comparative pH stability (Δ pH, mean ± standard deviation, n = 3) of Calcium-Modified Pectin (CMP) and Conventional Synthetic Polymer (PAC) under thermal aging (120°C), salt contamination (5% $NaCl_2$), calcium contamination (1% $CaCl_2$), and CO_2 exposure. Error bars represent standard deviation. One-way ANOVA indicates a statistically significant difference between the two polymer systems ($p < 0.05$). For thermal stability, CMP shows smaller change in pH (Δ pH = -0.45)

compared to synthetic polymer PAC (Δ pH = -0.75), indicating better resistance to thermal degradation (Fig. 8). The calcium crosslinking improves structural integrity at elevated temperatures.

Also, in the case of salt tolerance, as seen in Fig. 8, under NaCl contamination, CMP maintains higher alkalinity, demonstrating improved ionic stability due to Ca^{2+} bridging within the polymer matrix. For calcium contamination resistance, CMP performs significantly better because the polymer is already calcium-modified, reducing sensitivity to additional Ca^{2+} ions. Conventional polymers like PAC are more susceptible to divalent ion destabilization. On CO_2 resistance, both systems show pH reduction due to carbonic acid formation. However, CMP retains comparatively higher pH, indicating stronger buffering characteristics. For buffer capacity, CMP requires more acid volume to reduce pH to 8.0, confirming enhanced buffering performance. This is attributed to carboxylate functional groups and calcium crosslink sites.

Table 4: Overall Performance Summary

Parameter	CMP	Synthetic Polymer
Thermal Stability	High	Moderate
Salt Resistance	High	Moderate
Calcium Tolerance	High	Low-Moderate
CO_2 Stability	Moderate	Low
Buffering Capacity	High	Moderate

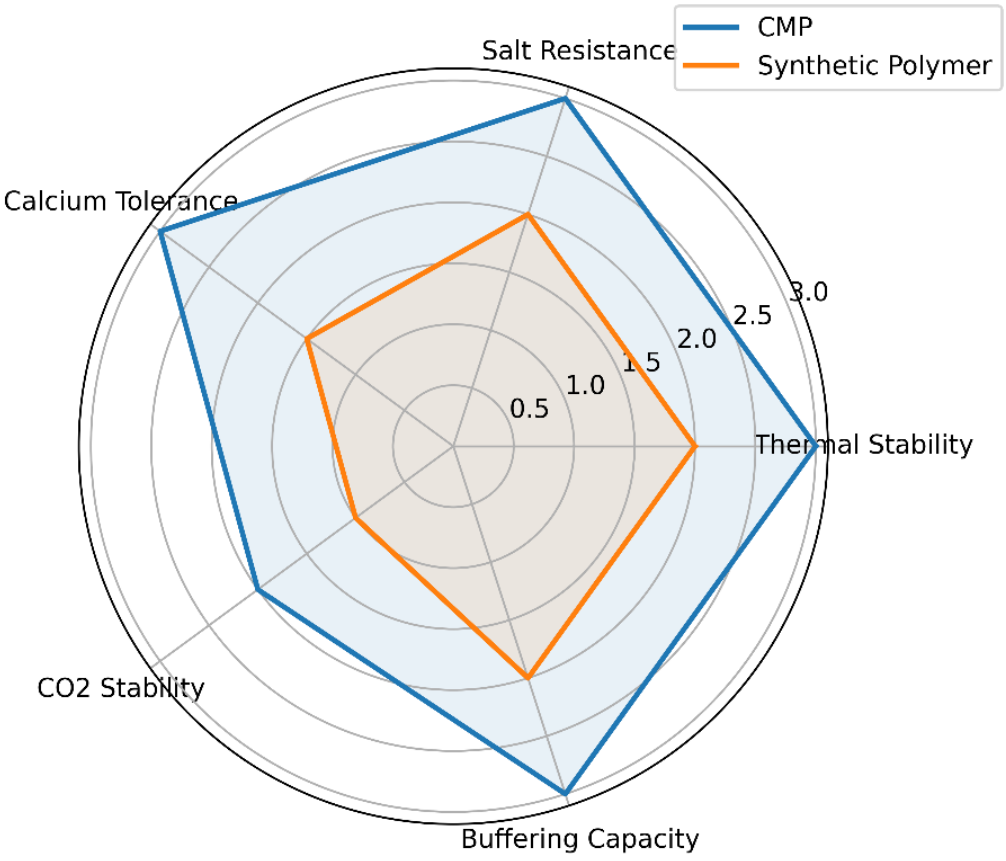


Figure 9: Radar Chart Comparison of the Overall Polymer Performance

The formulated drilling fluids maintained stable pH values within the acceptable range for water-based mud systems (Fig. 9). No visible phase separation was observed after aging, confirming good compatibility between pectin and calcium carbonate. The organic origin of the polymer and the natural calcium carbonate indicate low environmental impact and enhanced biodegradability compared with synthetic additives. From an environmental perspective, the use of orange peel and periwinkle shell wastes promotes sustainability through waste valorization. Unlike conventional synthetic polymers, the developed additive is biodegradable and non-toxic, reducing ecological risks associated with drilling operations.

Thermal Stability Performance

The rheological performances of the base mud and modified drilling muds at 120°C and various depths are presented in Table 5.

Table 5: Rheological properties after thermal aging at 120°C for 16 hours.

Sample	Apparent Viscosity Before (cP)	Apparent Viscosity After (cP)	Yield Point Before (lb/100 ft^2)	Yield Point After (lb/100 ft^2)
Base Mud	12.5	8.9	9.0	5.8
CMP-2 (1.0 ppb)	23.6	20.4	22.9	19.2
CMP-4 (2.0 ppb)	33.7	30.1	34.8	31.5
PAC	31.2	24.3	33.0	25.1
CMC	29.6	22.7	30.4	23.6

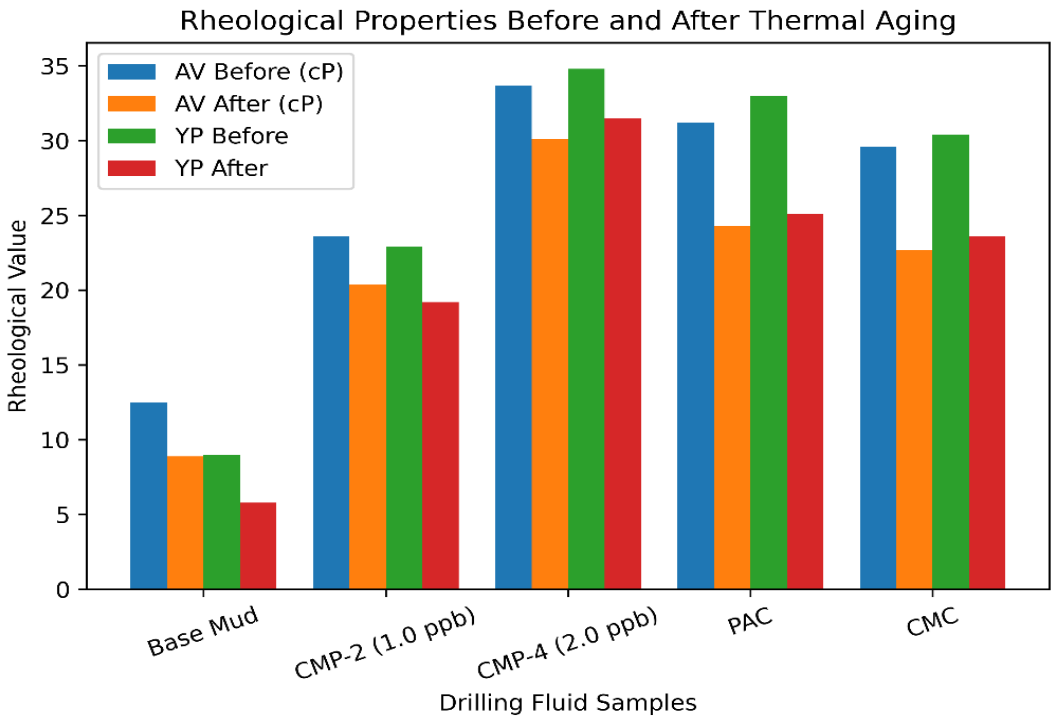


Figure 10: Rheological properties before and after thermal aging

Figure 10 illustrates the variation in Apparent Viscosity (AV) and Yield Point (YP) of the drilling fluid samples before and after thermal aging at 120°C for 16 hours. These rheological properties are essential indicators of the ability of drilling fluids to transport drill cuttings, maintain wellbore stability, and sustain suspension capacity under high-temperature conditions. The results show that thermal aging caused a reduction in both AV and YP for all the drilling fluid samples, indicating that elevated temperature affects the structural integrity of the fluid systems. The base fluid exhibited the most significant decrease, with AV dropping from 12.5 cP to 8.9 cP and YP decreasing from 9.0 to 5.8 lb/100 ft^2 after thermal aging. This decline demonstrates the thermal instability of the unmodified fluid systems, as the absence of polymeric additives reduces the ability of the fluid to maintain viscosity and particle suspension at high temperatures. In contrast, the fluid samples containing the Calcium-Modified Pectin (CMP) additive displayed improved rheological stability after thermal exposure. The CMP-2 (1.0 ppb) formulation showed a relatively small reduction in AV from 23.6 cP to 20.4 cP and YP from 22.9 to 19.2 lb/100 ft^2, indicating good resistance to thermal degradation. The CMP-4 (2.0 ppb) sample exhibited the highest rheological values both before and after thermal aging, with AV decreasing slightly from 33.7 cP to 30.1 cP and YP from 34.8 to 31.5 lb/100 ft^2, which suggests that increasing the concentration of CMP enhances the viscosifying and structure-forming ability of the polymer, thereby improving thermal stability and maintaining effective cuttings suspension under elevated temperature conditions. The performance of CMP was also compared with conventional drilling fluid polymers such as PAC and CMC. Although both PAC and CMC significantly improved the rheological properties of the Base Mud prior to aging, they experienced larger reductions after thermal treatment. PAC showed a decrease in AV from 31.2 cP to 24.3 cP and YP from 33.0 to 25.1 lb/100 ft^2, while CMC decreased from 29.6 cP to 22.7 cP for AV and from 30.4 to 23.6 lb/100 ft^2 for YP (Fig. 10). These reductions indicate partial thermal degradation of the cellulose-based polymers, which leads to a weakening of the fluid structure at high temperatures. Overall, the bar chart demonstrates that CMP-based drilling fluids retain higher rheological properties after thermal aging compared with the base mud and conventional polymers (Fig. 10). In particular, the CMP-4 formulation exhibited the best performance, suggesting that calcium-modified pectin can effectively enhance viscosity, improve yield stress, and maintain drilling fluid stability under high-temperature conditions. This improved rheological retention highlights the potential of waste-derived CMP as an environmentally friendly and thermally stable drilling fluid additive for sustainable drilling operations.

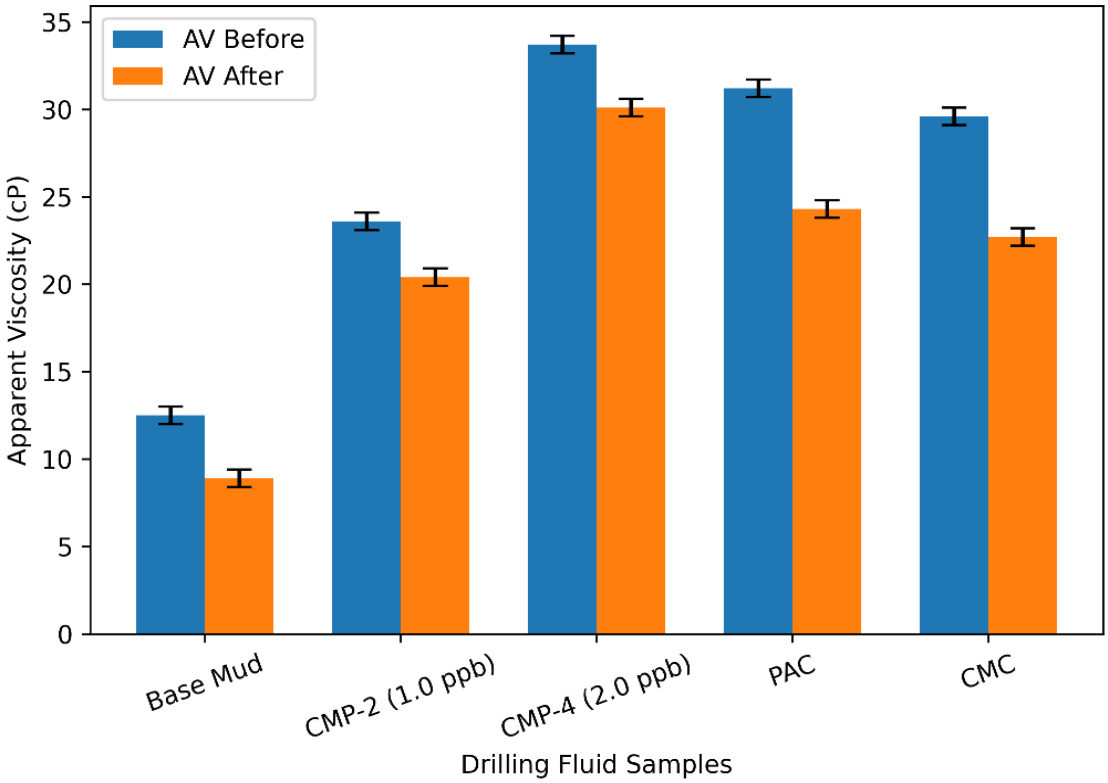


Figure 11: Error bar comparison of apparent viscosity before and after aging

The error bar chart of apparent viscosity (AV) before and after thermal aging shows that all the drilling fluid samples experienced a reduction in viscosity after exposure to 120°C for 16 hours, indicating the influence of temperature on fluid structure as is in Figure 11. The base mud exhibited the lowest viscosity and the greatest reduction, decreasing from 12.5 cP to 8.9 cP, which reflects its poor thermal stability in the absence of polymer additives. CMP-2 showed improved performance with smaller decrease in AV from 23.6 to 20.4 cP, indicating better resistance to thermal degradation. CMP-4 showed the highest AV by decreasing slightly from 33.7 cP to 30.1 cP, demonstrating strong thermal stability and effective viscosity retention. PAC and CMC showed enhanced apparent viscosity, but both showed the larger losses after aging, indicating partial thermal degradation. The small error bars indicate good experimental consistency, while the results confirm that CMP-based drilling fluids, particularly CMP-4, provide superior viscosity stability under high-temperature conditions.

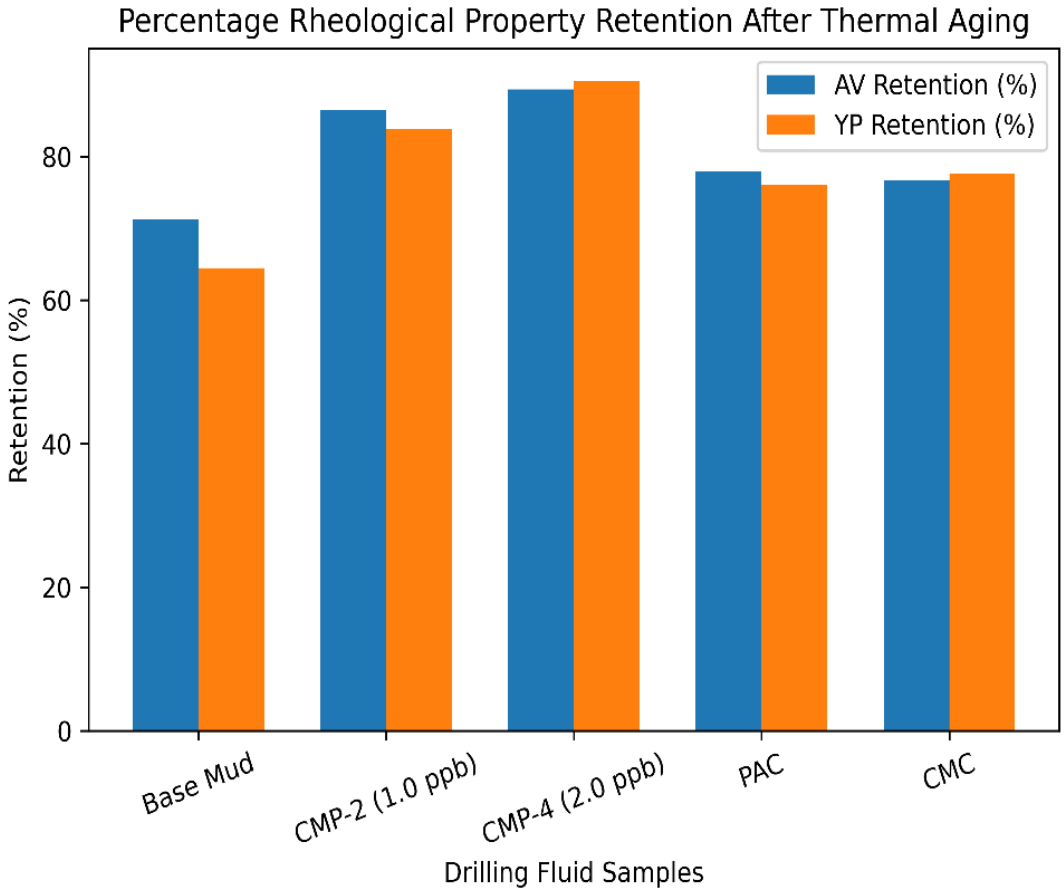


Figure 12: Percentage rheological property retention after thermal aging

After thermal aging at 120°C for 16 hours, calcium-modified pectin retained a large proportion of its rheological properties compared with the base mud. CMP-4 preserved over 89% of its apparent viscosity and yield point, whereas PAC and CMC showed higher degradation in Figure 12. This indicates superior thermal resistance of the calcium-modified pectin system under elevated temperature conditions.

Comparison with Commercial PAC and CMC

A comparison of apparent viscosity and yield point is made with commercial PAC and CMC in Table 5.

Table 5: Performance Comparison with Commercial PAC and CMC.

Additive	Apparent Viscosity (cP)	PV (cP)	Yield Point (lb/100 ft^2)	Fluid Loss (mL)
CMP	33.7	16.3	34.8	5.4
PAC	31.2	15.7	33.0	6.8
CMC	29.6	14.9	30.4	7.5

Compared with conventional PAC and CMC, Calcium-Modified Pectin (CMP) exhibited superior rheological enhancement and filtration control. The CMP system achieved lower fluid loss and a higher yield point, indicating improved formation protection and hole-cleaning capability. This demonstrates

that the waste-derived polymer is competitive with commercial additives while offering environmental and economic advantages.

The progressive improvement in rheological properties with CMP addition is associated with electrostatic interaction between Ca^{2+} ions and the carboxyl functional groups of pectin. These interactions promote intermolecular cross-linking, leading to a structured polymer network that enhances viscosity and yield point. Some past researchers had studied the effects of modified polymers or biopolymers on rheological and fluid loss control properties of drilling fluids, and confirmed enhancement of rheological properties and reduction in fluid loss of water-based drilling fluids [4, 6, 10]. Elevated yield point values translate to better suspension and transport of drilled cuttings under dynamic conditions.

Conclusion

The present study demonstrates that the addition of calcium-modified pectin, from valorized agro-marine wastes based on orange peels and periwinkle shells, significantly affected and improved the rheological behavior and other properties of the drilling fluids. Therefore, based on the detailed experimental analysis and results, the following conclusions are drawn:

(1) The enhanced rheological performance observed with calcium-modified pectin is attributed to strong interaction between calcium ions and the carboxyl groups of pectin. These interactions promote cross-linking within the polymer network, resulting in improved viscosity and yield point.

(2) Apparent viscosity and yield point increased progressively with increasing polymer concentration. Compared with the base mud, the modified system exhibited enhanced carrying capacity for drilled cuttings. The incorporation of calcium-modified pectin led to a progressive increase in apparent viscosity and yield point with polymer concentration. At 2.0 ppb, AV increased from 12.5 cP for the Base Mud to 33.7cP, while YP increased from 9.0 to 34. 8 lb/100 ft². This indicates enhanced carrying capacity and improved suspension of drilled cuttings.

(3) Higher yield point values indicate improved cuttings transport efficiency and wellbore cleaning capability, which are essential for drilling operations. Plastic viscosity showed moderate growth, suggesting improved structure without excessive flow resistance. That is, plastic viscosity showed moderate increases, indicating limited resistance to flow while maintaining suspension ability. The moderate increase in plastic viscosity suggests that the polymer improves suspension without excessively increasing flow resistance. This balance is desirable because very high PV can lead to higher pump pressures and energy consumption.

(4) Gel strength values increased with polymer addition, reflecting better structure build-up and hole cleaning potential. The observed gel strength development indicates good thixotropic behavior, allowing the fluid to suspend cuttings during static conditions and flow easily during circulation.

(5) Filtration reduction is mainly due to the ability of calcium-modified pectin particles to bridge pore spaces and form thin, impermeable mud cakes. Calcium carbonate contributes to particle packing and strengthens the filter cake structure, thereby limiting filtrate invasion into the formation. This behavior is beneficial for minimizing formation damage and differential sticking.

(6) From an environmental perspective, the use of orange peel and periwinkle shell wastes promotes sustainability through waste valorization. Unlike conventional synthetic polymers, the developed additive is biodegradable and non-toxic, reducing ecological risks associated with drilling

operations. Additionally, utilizing locally available wastes can reduce material cost and support circular economy practices in petroleum engineering.

Overall, the results demonstrate that calcium-modified pectin derived from agro-marine wastes can serve as an efficient and eco-friendly additive for water-based drilling fluids, offering a promising alternative to commercial polymers.

Abbreviations

CMP – Calcium-Modified Pectin
PAC – Polyanionic Cellulose
CMC – Carboxymethyl Cellulose
AV – Apparent Viscosity
PV – Plastic Viscosity
YP – Yield Point
cP – centipoise
μm – micron meter
Ib – Pound
ppb – pounds per barrel
ft – feet
mL – milliliter
mPa.s – mega Pascal seconds
wt% – weight percentage
NaCl – sodium chloride
$CaCl_2$ – calcium chloride
CO_2 – carbon IV oxide

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Authors' contribution

KO Chike: Conceptualization, Methodology, Raw materials, Resources, Samples preparation, Modification, Investigation, Data gathering, Data curation, Observations, Visualization, Data analysis, Formal analysis, Validation, Original drafting, Project supervision.
NC Iheaturu: Conceptualization, Methodology, Resources, Sample preparation, Investigation, Data analysis, Curation, Visualization, Validation, Writings, Software concept, Modelling, Modification, Graph design, Graph plotting.
DI Udunwa: Sample preparation, Investigation, Data analysis, Curation, Visualization, Validation,
CK Oguzie: Manuscript Writing, Experimental, Modelling, Graph plotting, Data analysis.
UM Onyeje: Proof reading and manuscript review.
SC Uzoukwu: Visualization, Validation, Writings, Software concept, Modelling, Modification, Graphic design.

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Data availability
The sets of data used and/or analyzed during the present study are available from the corresponding author, upon request.

Declarations
Ethics approval and consent to participate
The authors hereby declare that it is not applicable.

Consent for Publication
All the authors agreed to submit the manuscript for publication.

Competing interest
The authors declare that they have no competing interests.

References
1. Shuvo, M. A. I., Sultan, M. Z. B., & Ferdous, A. R. R. (2024). Applicability of sawdust as a green additive to improve the rheological and filtration properties of water-based drilling fluid: An experimental investigation. Journal of Petroleum Exploration and Production Technology, 14, 303-315. https://doi.org/10.1007/s13202-023-01706-2
2. Khashay, M., Zirak, M., Sheng, J. J., Ganat, T., & Esmaeilnezhad, E. (2025). Elevated temperature and pressure performance of water based drilling mud with green synthesized zinc oxide nanoparticles and biodegradable polymer. Scientific Reports, 15, Article 11930. https://doi.org/10.1038/s41598-025-96900-z
3. Ali, I., Ahmad, M., & Ganat, T. (2022). Biopolymeric formulations for filtrate control applications in water-based drilling muds: A review. Journal of Petroleum Science and Engineering, 210, 110021. https://doi.org/10.1016/j.petrol.2021.110021
4. Wu, Y., You, F., & Hou, S. (2025). Application of natural materials containing carbohydrate polymers in rheological modification and fluid loss control of water-based drilling fluids: A review. Carbohydrate Polymers, 348, 122928. https://doi.org/10.1016/j.carbpol.2024.122928
5. Noor, A. A., Khan, M. A., Zhang, Y., Lv, K., Sun, J., Liu, C., & Li, M.-C. (2025). Modified natural polymers as additives in high-temperature drilling fluids: A review. International Journal of Biological Macromolecules, 287, 138556. https://doi.org/10.1016/j.ijbiomac.2024.138556
6. Davoodi, S., Al-Shargabi, M., Wood, D. A., Minaev, K. M., & Rukavishnikov, V. S. (2024). Modified-starch applications as fluid-loss reducers in water-based drilling fluids: A review of recent advances. Journal of Cleaner Production, 434, 140430. https://doi.org/10.1016/j.jclepro.2023.140430
7. Davoodi, S., Al-Shargabi, M., Wood, D. A., Rukavishnikov, V. S., & Minaev, K. M. (2024). Synthetic polymers: A review of applications in drilling fluids. Petroleum Science, 21(1), 475–518. https://doi.org/10.1016/j.petsci.2023.08.015

8. Khan, M. A., Li, M.-C., Lv, K., Sun, J., Liu, C., Liu, X., Shen, H., Dai, L., & Lalji, S. M. (2024). Cellulose derivatives as environmentally-friendly additives in water-based drilling fluids: A review. Carbohydrate Polymers, 342, 122355. https://doi.org/10.1016/j.carbpol.2024.122355
9. Wei, Z., Wang, M., Li, Y., An, Y., Li, K., Bo, K., & Guo, M. (2022). Sodium alginate as an eco-friendly rheology modifier and salt-tolerant fluid loss additive in water-based drilling fluids. RSC Advances, 12, 29852–29864. https://doi.org/10.1039/D2RA04448J
10. Hadadi, M., Kamali, F., Mirhosseininia, J., & Shahbazi, M. (2024). Experimental investigation of biopolymers influences on rheology and filtration properties of water-based drilling fluids. Heliyon, 10(23), e40780. https://doi.org/10.1016/j.heliyon.2024.e40780
11. Ali, J. A., Abbas, D. Y., Abdalqadir, M., Nevecna, T., Jaf, P. T., Abdullah, A. D., & Rancová, A. (2024). Evaluation the effect of wheat nano-biopolymers on the rheological and filtration properties of the drilling fluid: Towards sustainable drilling process. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 683, 133001. https://doi.org/10.1016/j.colsurfa.2023.133001
12. Lalji, S. M., Ali, S. I., Khan, M. A., & Ghauri, R. (2023). Investigation of rheological behavior, filtration characteristics and microbial activity of biopolymer water-based drilling fluids containing monovalent and divalent cations. Chemical Papers, 77(8), 4693-4704. https://doi.org/10.1007/s11696-023-02819-y
13. Shaine, M. L., Syed, I. A., & Khan, M. A. (2023). Study of rheological characteristics of a water-based drilling fluid in presence of biopolymers, synthetic polymer, and modified natural polymer. Petroleum Chemistry, 63, 494–506. https://doi.org/10.31857/S0028242123040044
14. Zhu, W., & Zheng, X. (2021). Effective modified xanthan gum fluid loss agent for high-temperature water-based drilling fluid and the filtration control mechanism. ACS Omega, 6(37), 23788-23801. https://doi.org/10.1021/acsomega.1c02617
15. Balaga, D. K., & Kulkarni, S. D. (2022). A review of synthetic polymers as filtration control additives for water-based drilling fluids for high-temperature applications. Journal of Petroleum Science and Engineering, 215, 110712. https://doi.org/10.1016/j.petrol.2022.110712
16. Akpan, E. U. (2024). Utilizing environmentally friendly polymers as rheological control and fluid loss additives in water-based drilling muds. Geoenergy Science and Engineering, 213195. https://doi.org/10.1016/j.geoen.2024.213195
17. Al-Hameedi, A. T. T., Alkinani, H. H., Dunn-Norman, S., Al-Alwani, M. A., Alshammari, A. F., Alkhamis, M. M., Mutar, R. A., & Al-Bazzaz, W. H. (2020). Experimental investigation of environmentally friendly drilling fluid additives (mandarin peels powder) to substitute the conventional chemicals used in water-based drilling fluid. Journal of Petroleum Exploration and Production Technology, 10, 407–417. https://doi.org/10.1007/s13202-019-0725-7
18. Lin, Y., Tian, Q., & colleagues. (2023). Effect of nanoparticles on rheological properties of water-based drilling fluid. Nanomaterials, 13(14), 2092. https://doi.org/10.3390/nano13142092
19. Ma, L., Yin, D., Ren, J., Han, B., & Qin, S. (2023). A novel thixotropic structural dynamics model of water-based drilling fluids. Geoenergy Science and Engineering. https://doi.org/10.1016/j.geoen.2023.212585
20. Isehunwa, S., Dike, H. N., & colleagues. (2026). Eco-friendly plantain peel flour as an additive in water-based drilling fluids: Rheological and filtration performance evaluation. SPE Nigeria Annual International Conference and Exhibition. SPE-235143-MS. https://doi.org/10.2118/235143-MS

21. Zhang, H., Li, X., Shao, Y., Wang, K., Peng, J., & Fang, H. (2024). Application of starch microspheres modified by alkyl polyglucoside as environmental-friendly fluid loss additive in water-based drilling fluids. Energy & Fuels, 38(11), 10381–10389. https://doi.org/10.1021/acs.energyfuels.4c00589
22. Jeong, D., Park, H., Jang, B.-K., Ju, Y., Shin, M. H., Oh, E. J., Lee, E. J., & Kim, S. R. (2021). Recent advances in the biological valorization of citrus peel waste into fuels and chemicals. Bioresource Technology, 323, 124603. https://doi.org/10.1016/j.biortech.2020.124603
23. Sharma, P., Vishvakarma, R., Gautam, K., Vimal, A., Gaur, V. K., Farooqui, A., Varjani, S., & Younis, K. (2022). Valorization of citrus peel waste for the sustainable production of value-added products. Bioresource Technology, 351, 127064. https://doi.org/10.1016/j.biortech.2022.127064
24. Singhal, S., & Swami Hulle, N. R. (2022). Citrus pectins: Structural properties, extraction methods, modifications and applications in food systems—A review. Applied Food Research, 2(2), 100215. https://doi.org/10.1016/j.afres.2022.100215
25. Kumar, S., Konwar, J., Purkayastha, M. D., Kalita, S., Mukherjee, A., & Dutta, J. (2023). Current progress in valorization of food processing waste and by-products for pectin extraction. International Journal of Biological Macromolecules, 239, 124332. https://doi.org/10.1016/j.ijbiomac.2023.124332
26. Manakas, P., Balafoutis, A. T., Kottaridi, C., & Vlysidis, A. (2025). Sustainability assessment of orange peel waste valorization pathways from juice industries. Biomass Conversion and Biorefinery, 15(5), 6525–6544. https://doi.org/10.1007/s13399-024-05626-x
27. Willats, W. G. T., Knox, J. P., & Mikkelsen, J. D. (2006). Pectin: New insights into an old polymer are starting to gel. Trends in Food Science & Technology, 17(3), 97–104. https://doi.org/10.1016/j.tifs.2005.10.008
28. Thakur, B. R., Singh, R. K., & Handa, A. K. (1997). Chemistry and uses of pectin—A review. Critical Reviews in Food Science and Nutrition, 37(1), 47–73. https://doi.org/10.1080/10408399709527767
29. Chan, S. Y., Choo, W. S., Young, D. J., & Loh, X. J. (2017). Pectin as a rheology modifier: Origin, structure, commercial production and rheology. Carbohydrate Polymers, 161, 118–139. https://doi.org/10.1016/j.carbpol.2016.12.033
30. Naqash, F., Masoodi, F. A., Rather, S. A., Wani, S. M., & Gani, A. (2017). Emerging concepts in the nutraceutical and functional properties of pectin—A review. Carbohydrate Polymers, 168, 227–239. https://doi.org/10.1016/j.carbpol.2017.03.058
31. Ciriminna, R., Fidalgo, A., Scurria, A., Ilharco, L. M., & Pagliaro, M. (2022). Pectin: New science and forthcoming applications of the most valued hydrocolloid. Food Hydrocolloids, 127, 107483. https://doi.org/10.1016/j.foodhyd.2022.107483
32. Ciriminna, R., Fidalgo, A., Delisi, R., Tamburino, A., Carnaroglio, D., Cravotto, G., Ilharco, L. M., & Pagliaro, M. (2017). Controlling the degree of esterification of citrus pectin for demanding applications by selection of the source. ACS Omega, 2(11), 7991–7995. https://doi.org/10.1021/acsomega.7b01109
33. Ridley, B. L., O'Neill, M. A., & Mohnen, D. (2001). Pectins: Structure, biosynthesis, and oligogalacturonide-related signaling. Phytochemistry, 57(6), 929–967. https://doi.org/10.1016/S0031-9422(01)00113-3
34. Mohnen, D. (2008). Pectin structure and biosynthesis. Current Opinion in Plant Biology, 11(3), 266–277. https://doi.org/10.1016/j.pbi.2008.03.006

35. Voragen, A. G. J., Coenen, G.-J., Verhoef, R. P., & Schols, H. A. (2009). Pectin, a versatile polysaccharide present in plant cell walls. Structural Chemistry, 20, 263–275. https://doi.org/10.1007/s11224-009-9442-z
36. Colodel, C., Vriesmann, L. C., Teófilo, R. F., & Petkowicz, C. L. O. (2018). Extraction of pectin from ponkan (Citrus reticulata Blanco cv. Ponkan) peel: Optimization and structural characterization. International Journal of Biological Macromolecules, 117, 385–391. https://doi.org/10.1016/j.ijbiomac.2018.05.048
37. Maran, J. P., Sivakumar, V., Thirugnanasambandham, K., & Sridhar, R. (2013). Optimization of microwave assisted extraction of pectin from orange peel. Carbohydrate Polymers, 97(2), 703–709. https://doi.org/10.1016/j.carbpol.2013.05.052
38. Sayah, M. Y., Chabir, R., Benyahia, H., Rodi Kandri, Y., Ouazzani Chahdi, F., Touzani, H., & Errachidi, F. (2016). Yield, esterification degree and molecular weight evaluation of pectins isolated from orange and grapefruit peels under different conditions. PLoS ONE, 11(9), e0161751. https://doi.org/10.1371/journal.pone.0161751
39. Patience, N. A., Schieppati, D., & Boffito, D. C. (2021). Continuous and pulsed ultrasound pectin extraction from navel orange peels. Ultrasonics Sonochemistry, 73, 105480. https://doi.org/10.1016/j.ultsonch.2021.105480
40. Dao, T. A. T., Webb, H. K., & Malherbe, F. (2021). Optimization of pectin extraction from fruit peels by response surface method: Conventional versus microwave-assisted heating. Food Hydrocolloids, 106475. https://doi.org/10.1016/j.foodhyd.2020.106475
41. Chen, J., Cheng, H., Zhi, Z., Zhang, H., Linhardt, R. J., Zhang, F., Chen, S., & Ye, X. (2021). Extraction temperature is a decisive factor for the properties of pectin. Food Hydrocolloids, 112, 106160. https://doi.org/10.1016/j.foodhyd.2020.106160
42. Lin, X., Liu, Y., Wang, R., Dai, J., Wang, L., & Zhang, J. (2024). Extraction of pectins from renewable grapefruit (Citrus paradisi) peels using deep eutectic solvents and analysis of their structural and physicochemical properties. International Journal of Biological Macromolecules, 254(2), 127785. https://doi.org/10.1016/j.ijbiomac.2023.127785
43. Wang, X., Zhao, C., Wang, J., Lu, X., Bao, Y., Zhang, D., & Zheng, J. (2024). Structure characterization and gelling properties of RG-I-enriched pectins extracted from citrus peels using four different methods. Carbohydrate Polymers, 342, Article 122410. https://doi.org/10.1016/j.carbpol.2024.122410
44. Bezus, B., Contreras Esquivel, J. C., Cavalitto, S., & Cavello, I. (2022). Pectin extraction from lime pomace by cold-active polygalacturonase-assisted method. International Journal of Biological Macromolecules, 209, 290–298. https://doi.org/10.1016/j.ijbiomac.2022.04.019
45. Kadiya, K., & Ghosh, S. (2022). Pectin degree of esterification influences rheology and digestibility of whey protein isolate-pectin stabilized bilayer oil-in-water nanoemulsions. Food Hydrocolloids, 131, 107789. https://doi.org/10.1016/j.foodhyd.2022.107789
46. Kastner, H., Einhorn-Stoll, U., Fatouros, A., & Drusch, S. (2020). Impact of sodium ions on material properties, gelation and storage stability of citrus pectin. Food Hydrocolloids, 104, Article 105750. https://doi.org/10.1016/j.foodhyd.2020.105750
47. Fraeye, I., Duvetter, T., Duongla, E., Van Loey, A., & Hendrickx, M. (2010). Fine-tuning the properties of pectin–calcium gels by control of pectin fine structure, gel composition and environmental conditions. Trends in Food Science & Technology, 21(5), 219–228. https://doi.org/10.1016/j.tifs.2010.02.001

48. Yang, X., Yuan, K., Descallar, F. B. A., Li, A., Yang, X., & Yang, H. (2022). Gelation behaviors of some special plant-sourced pectins: A review inspired by examples from traditional gel foods in China. Trends in Food Science & Technology, 126, 26–40. https://doi.org/10.1016/j.tifs.2022.06.012
49. Basak, S., & Annapure, U. S. (2022). Impact of atmospheric pressure cold plasma on the rheological and gelling properties of high methoxyl apple pectin. Food Hydrocolloids, 129, Article 107639. https://doi.org/10.1016/j.foodhyd.2022.107639
50. Roque, A. M., Montinola, D., Geonzon, L. C., Matsukawa, S., Lobarbio, C. F. Y., Taboada, E. B., & Bacabac, R. G. (2022). Rheological elucidation of the viscoelastic properties and network interaction of mixed high-methoxyl pectin and κappa-carrageenan gels. Food Hydrocolloids, 129, Article 107647. https://doi.org/10.1016/j.foodhyd.2022.107647
51. Korampattu, L., Ghosh, N., & Dhepe, P. L. (2024). Shell waste valorization to chemicals: Methods and progress. Green Chemistry, 26(10), 5601-5634. https://doi.org/10.1039/D3GC05177C
52. Choi, S. H., Lee, J.-H., Yoo, J., Park, J. H., Bae, J.-S., & Park, C. Y. (2024). Toward transformation of bivalve shell wastes into high value-added and sustainable products in South Korea: A review. Journal of Industrial and Engineering Chemistry, 129, 38–52. https://doi.org/10.1016/j.jiec.2023.08.032
53. Podaralla, N. K., Paramasivam, P., & Jacquemin, J. (2024). Characterization of hydrothermally decomposed and synthesized $CaCO_3$ reinforcement from dead snail shells. ACS Omega, 9(2), 2183–2191. https://doi.org/10.1021/acsomega.3c05330
54. Owoyemi, H. T., & Owoyemi, A. G. (2020). Chemical and phase characterization of snail shell (Archachatina marginata) as bio-waste from South-West Nigeria for industrial applications. Chemistry and Materials Research, 12(6). https://doi.org/10.7176/CMR/12-6-03
55. Wai, K. T., O'Sullivan, A. D., & Bello-Mendoza, R. (2024). Nitrogen and phosphorus removal from wastewater using calcareous waste shells—A systematic literature review. Environments, 11(6), 119. https://doi.org/10.3390/environments11060119
56. Topic Popovic, N., Lorencin, V., Strunjak-Perovic, I., & Coz-Rakovac, R. (2023). Shell waste management and utilization: Mitigating organic pollution and enhancing sustainability. Applied Sciences, 13(1), Article 623. https://doi.org/10.3390/app13010623
57. Shao, S., Zhu, H., Guo, M., & Zhang, Y. (2024). Application of waste oyster shells in construction: Overview, constitutive modeling, and life cycle assessment. Journal of Building Engineering, 87, Article 108965. https://doi.org/10.1016/j.jobe.2024.108965
58. Jang, K., Ikram, M., Lee, D., Myung, J., Oh, S., Kim, S., Choi, W. Y., & Park, J. (2025). Sustainable conversion of oyster shell waste into high-purity calcium carbonate via CO_2 mineralization. Journal of Environmental Chemical Engineering, 13(1), 115099. https://doi.org/10.1016/j.jece.2024.115099
59. Barah, O. O., Dennison, M. S., Nnamchi, S. N., Onyelowe, K. C., & Olotu, E. B. O. (2025). Physical, chemical, and mineralogical properties of agromarine waste ash. (2025). Discover Materials, 5, Article 106. https://doi.org/10.1007/s43939-025-00244-4
60. American Petroleum Institute. (2026). Recommended practice for field testing water-based drilling fluids (API Recommended Practice 13B-1, 6th ed.). American Petroleum Institute, API RP 13B-1.
61. Chike K. O., Iheaturu N. C., Aharanwa B. C., Ezeamaku L. U. Ojinmah N. E., Uwakwe C., & Ojiaku C. I. (2020). Fluid Loss and Filtration Properties of a Citrus Sinensis Pectin Extract-based Drilling Mud. Chemistry and Materials Research, 12(3). https://doi.org/10.7176/CMR/12-3-03