**Green Synthesis of Nano-Particles and their Effects on the Rheological Properties of Non-Damaging Drilling Fluids – A Practical Approach**

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**ABSTRACT**

Due to their unique physical traits and behaviors, nanoparticles (NPs) are regarded as crucial nano-materials for a variety of industrial and academic applications. NPs are currently in significant demand for application in the oil sectors. The addition of NPs to drilling fluid can significantly improve its rheological characteristics. This research explores the potential application of green nanoparticles synthesized from copper (Cu) and magnesium (Mg) using Aloe-Vera and orange peel extracts in non-damaging drilling fluids. The incorporation of copper and magnesium green nanoparticles into non-damaging drilling fluids showed promising results. The nanoparticles enhanced the fluid's lubricity, reducing friction between the drill bit and the wellbore, thereby minimizing wear and tear on drilling equipment. Furthermore, the nanoparticles exhibited excellent inhibitive properties, preventing clay swelling and shale hydration, which are common issues in drilling operations. Experimental investigations involve conducting laboratory tests to evaluate the performance of green nanoparticle-based drilling fluids. Rheological measurements and fluid loss tests conducted to determine the nanoparticles' effect on drilling fluid properties and their ability to minimize formation damage.

The findings of this study help to clarify the potential advantages and restrictions of drilling fluids based on green nanoparticles. The results can help drilling fluid engineers and operators create effective and environmentally friendly fluid systems that will minimize formation damage, boost well productivity, and maximize hydrocarbon recovery in this basin with significant geological significance.

**Keywords**: drilling fluids, green nanoparticles, non-damaging, formation damage, hydrocarbon recovery, formation damage, lubricity.

1. **INTRODUCTION**

Small, invisible to the human eye particles called nanoparticles (NPs) range in size from 1 to 100 nanometers. Compared to larger materials, nanoparticles have very diverse physical and chemical characteristics. Their high surface area for interaction with the surrounding medium increases the stability of shales by bridging its pore throats, reduces filtrate loss, forms a thin, non-erodible and impermeable mud-cake around the well bore to prevent clay swelling, spurt loss and loss circulation, prevents pipe sticking by forming a thin film covering over the drill pipe, and also improves wellbore stability (Abdolhamid Sameni, et al. 2015).

Nanoparticles can be synthesized from top to bottom or bottom to top. Methods of Nano-particle synthesis may include either Chemical Reduction or Biological reduction. However, in each of the methods Precursor, Reducer and a Capping Agent are essential to the synthesis of nanoparticle. Chemical reduction entails three key steps: using reducing agents to reduce metallic salts, stabilizing ionic complexes, and using a capping agent to regulate size. The most frequent biological reducers are plant extracts, yeasts, fungus, bacteria, enzymes, etc., whereas in biological reduction, a biological source is used as a reducer. Since the reducer itself serves as a capping agent, this technique does not require the use of a capping agent. The term "Green Nanoparticles" refers to the source of the NP synthesis media, which is typically based on plants or algae. This reduces the need for inorganic chemicals and lowers the environmental costs of mining inorganic ores for NP synthesis.

Specialized chemicals known as non-damaging drilling fluids are employed in the drilling sector to hasten the extraction of oil, gas, and other resources from underground formations. They are also referred to as non-damaging muds or drilling fluids. By reducing formation damage during drilling, non-damaging drilling fluid (NDDF) offers a way to boost crude oil or hydrocarbon production (Talukdar et al., 2014). In order to minimize formation damage, this type of drilling fluid is specifically employed while drilling horizontal wells in the production zone of development wells. The development and utilization of non-damaging drilling fluids are driven by the industry's growing emphasis on environmentally sustainable practices and the need to maximize production while minimizing formation damage. By using these specialized fluids, drilling operations can be conducted with reduced environmental impact and improved long-term reservoir productivity.

This chapter explores the application of copper and magnesium-based green nanoparticles derived from Aloe Vera and orange peel extract in non-damaging drilling fluids. As the drilling industry seeks more environmentally sustainable solutions, the utilization of eco-friendly additives has gained significant attention. These nanoparticles offer promising potential for enhancing the performance of drilling fluids while minimizing their impact on the subsurface. In this report, investigation of the synthesis, characterization, and application of copper and magnesium-based green nanoparticles derived from Aloe Vera and orange peel extract in non-damaging drilling fluids has been done. The objective is to evaluate the performance of these nanoparticles as environmentally friendly additives and their impact on drilling fluid properties, wellbore stability, and formation damage prevention.

The chapter will delve into the synthesis methods employed to produce the nanoparticles and provide an in-depth analysis of their physicochemical properties. Additionally, the chapter will examine the effects of incorporating these nanoparticles into non-damaging drilling fluids through laboratory experiments, including filtration rate analysis, compatibility with formation rocks, lubricity enhancement, and overall drilling performance improvements.

1. **EXPERIMENTAL ANALYSIS**

**2.1 Materials used**

|  |  |
| --- | --- |
| **Chemicals**  | **Apparatus** |
| Methanol | Soxhlet setup |
| Copper sulphate pentahydrate | Rotary vacuum evaporator |
| Magnesium sulphate hepta-hydrate | Magnetic stirrer |
| Distilled water | Weighing balance |
| XC Polymer | Nano-particle size analyzer |
| CMC | Cuvette  |
| Calcium Carbonate | Desiccator |
| NaCl, KClFormaldehyde | Fann VG ViscometerFilter PressMarsh FunnelMud BalanceHamilton Beach Homogenizer |

Table 1 – Materials Used

**2.2. Methods employed**

**2.2.1. Synthesis of Green Nano-particles**

For the fabrication of nanoparticles, a number of chemical and physical preparation techniques are available, such as radiation, chemical precipitation, photochemical methods, electrochemical, and Langmuir-Blodgett techniques. However, these techniques are frequently very expensive and not environmentally friendly because they use toxic, combustible, and hazardous chemicals that could pose a risk to the environment and biological systems and require a lot of energy (Awwad et al. These nanoparticles synthesis have the disadvantages of poor production rate, structural particle deformation, and prevention of particle growth. The development of green, sustainable nanoparticle preparation techniques that do not rely on hazardous organic chemicals is currently becoming more and more important.

**BIOLOGICAL METHOD**

Extracts from biological agents, such as bacteria and plants, can be used in biological methods to create metal nanoparticles as a reducing or protecting agent. Amino acids, vitamins, proteins, enzymes, and polysaccharides—all chemically complicated but environmentally friendly—as well as other combinations of biomolecules with reducing potential can be identified in these extracts (Moghaddam 2010). An example is the room-temperature synthesis of single-crystalline copper and magnesium nanoparticles using an extract of the unicellular green alga Chlorella vulgaris. In our experiment, it was proposed that proteins in the extract serve the twin functions of size and shape (as a capping agent) and Cu2+ and Mg2+ reduction. These Nanoparticles were biosynthesized using a bottom-up strategy.

**THE BOTTOM UP APPROACH**

It involves downsizing material components to the atomic scale, followed by a self-assembly process that creates nanostructures. The physical forces acting at the nanoscale combine fundamental elements to create more substantial, stable structures during self-assembly. Examples of typical processes include the creation of quantum dots during epitaxial growth, the synthesis of nanoparticles from colloidal dispersion, physical and chemical vapor deposition, etc.

In bottom up method, Nano-structures are built by the direct manipulation of atoms or molecules. Bottom up methods involve atom by atom, molecule by molecule or cluster by cluster manipulation for synthesis of Nano structures. In these methods, the starting material is either in liquid state or gaseous state. These techniques include chemical synthesis, self-assembly and position assembly. The molecular recognition (Self-assembly) concept serves as the foundation for the bottom-up method. Self-assembly is the process of creating more and more items that are similar to oneself. The idea of self-assembly is to gather precursors in random positions and orientations and supply energy to allow them to sample configuration of the space. The hugeness of this space suggests that a convergent pathway is inherent in the process in order to allow it to be completed in reasonable time.

**REDUCER PREPARATION**

The aloe-vera leaves were obtained from the fields, sorted and the dry ones were separated. The oranges were obtained from the market and were peeled. The fresh aloe-vera leaves and orange peel were cleaned, chopped into pieces of approximately 2cm size and loaded into the thimble of the Soxhlet extractor.

**PRECURSOR PREPARATION**

500ml of 0.1M of both Magnesium Sulphate and Copper Sulphate were prepared as precursors.

**PREPARATION OF NANO-PARTICLES**

Copper and Magnesium nano-fluid were prepared in a 1:2 ratio of reducer-precursor . The prepared nano fluid was first filtered with Membrane Filtration method using membrane pore size of 0.45µm (450nm) then again filtered with Syringe Filtration method using membrane pore size of 0.2µm (200nm).

**2.2.2. Characterization of Green nano-particles**

**PARTICLE SIZE ANALYSIS**

To determine the size of individual particles and the size distribution range for a specific sample, a nano particle size analyzer is utilized. Nano particle size analyzers are used by the pharmaceutical industry since a particle's size and shape might alter how a drug interacts with the body. Light scattering, laser diffraction, photon correlation spectroscopy, sedimentation, and other techniques are just a few of the methods that nano particle size analyzers can detect particles. The first three methods work by observing how light or lasers are shifted as a result of the particles, while sedimentation measures how quickly the particles settle to the bottom of the sample to assess particle size. The capability to treat wet and/or dry dispersions is one quality to look for in nano particle size analyzers.

**ULTRAVIOLET SPECTROPHOTOMETRY**

In contrast to a reference or blank sample, the amount of distinct wavelengths of UV or visible light that are absorbed by or transmitted through a sample can be determined using the analytical technique known as UV-Vis spectroscopy. This feature, which is influenced by the sample composition and might reveal what is in the sample and in what concentration, is.

Various sizes of Cu particles' optical absorption spectra are also described; these spectra contain the Plasmon band in the 560–580 nm range and a UV band peak between 222–360 nm, becoming flatter with increasing particle size. Hengleiin (2000). Dry dispersions; the particle size range that can be measured; whether it can determine shape in addition to size; and whether it can measure concentration, zeta potential, and aggregation. Magnesium absorption is measured at a wavelength of approximately 285.2 nm, and reported to exhibit a broad absorption peak in between 260-330 nm (Almontasser, et al., 2019).

**2.2.3. Green nano-particles in drilling fluids**

**FORMULATION OF NON-DAMAGING DRILLING FLUID**

Non-damaging drilling fluids, also known as non-invasive or environmentally friendly drilling fluids, are specially designed fluid systems used in drilling operations to minimize damage to the formation and the environment. Unlike traditional drilling fluids that may contain harmful additives, non-damaging drilling fluids are formulated with environmentally friendly components that reduce the risk of contaminating groundwater and ecosystems. These fluids aim to balance the requirements of efficient drilling and wellbore stability while mitigating the negative impacts associated with drilling activities. Non-damaging drilling fluids offer benefits such as improved wellbore stability, reduced formation damage, and enhanced environmental sustainability, making them a preferred choice for modern drilling operations.

In order to prevent formation damage, NDDFs are typically utilized in the pay zone parts of development wells and more specifically during horizontal drilling. To prevent formation damage and environmental contamination, NDDF does not use non-degradable compositional fine solids like clay, barite, etc. Therefore, the XC-Polymer is employed in NDDF rather than non-degradable clays to give the aforementioned qualities in drilling fluid to carry out the aforementioned duties (Talukdar, Gogoi, 2015). In this research, Xanthan Gum is used as a biopolymer viscosifier, CMC as fluid loss control agent, Calcium Carbonate is used as Weighing and bridging material, Sodium Chloride and Potassium Chloride used as clay swelling inhibitor and Formaldehyde is used as biocide.

**Materials -**

* Base Fluid – Distilled Water
* Xanthan Gum (0.5%)
* Caboxymethyl Cellulose (CMC) (1.5%)
* Calcium Carbonate (10%)
* Sodium Chloride, Potassium Chloride (3%)
* Formaldehyde (0.02%)

**2.2.3.1. Study of Density behavior**

A Mud Balance device was used to calculate the density of the mud both before and after the nanoparticles were added. The Mud Balance offers a straightforward, useful tool for precisely determining fluid density.

It is one of the most sensitive and precise field devices available for figuring out the specific gravity, often known as density, of drilling fluids.

This Mud Balance's noteworthy benefit is that the accuracy of measurements is not significantly impacted by the sample's temperature. The balance is shielded from damage while being transported and is supported securely when in use by a high impact plastic case.

The Mud Balance is made with a readably graduated beam with four scales.

Specific gravity, pounds per cubic foot, pounds per square inch, and pounds per gallon

**2.2.3.2. Rheological analysis**

The changes in the rheology of the drilling fluid before and after the addition of nano-fluid were determined in many stages. The apparent viscosity was determined using a Marsh Funnel viscometer, the absolute viscosity was determined using a Fann VG Viscometer, and the filtrate loss and spurt losses were determined using the filter press.

1. **RESULTS & DISCUSSIONS**

**3.1. Synthesis of Green Nano-particles**

**Cu Nano-particles bio-synthesis**

|  |  |
| --- | --- |
| **Precursor** | CuSO4.5H20 |
| **Reducer** | Aloe-Vera extract and Orange peel extract |
| **Capping agent** | Not required |
| **RPM** | 1200 |
| **Temperature** | 25 degree Celsius  |

**Magnesium Nano-particles bio-synthesis**

|  |  |
| --- | --- |
| **Precursor** | MgSO4.7H20 |
| **Reducer** | Aloe-Vera extract and Orange peel extract |
| **Capping agent** | Not required |
| **RPM** | 1200 |
| **Temperature** | 25 degree Celsius  |

Biological reduction does not involve the use of a capping agent, because the reducers have phytochemicals that act as natural capping agents.

**3.2. Characterization of Green nano-particles**

**Summary of results from Particle Size Analyzer**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Type**  | **Effective diameter** | **Poly Dispersity** | **Baseline Index** | **Elapsed Time** |
| **CuSO4 + Aloe-Vera** | 3637.9 nm | 0.372 | 0.0/95.35% | 00:03:00 |
| **CuSO4 + Orange peel** | 805.2 nm | 0.321 | 0.0/91.01% | 00:03:00 |
| **MgSO4 + Aloe-Vera** | 1426.3 nm | 0.011 | 00/94.98% | 00:03:00 |
| **MgSO4 + Orange Peel** | 417.1 nm | 0.065 | 8.5/99.26% | 00:03:00 |

Table 2 – Particle size analysis of various Nano-particles

**N.B** From the table, it was observed that only (MgSO4 + Orange Peel) and (CuSO4 + Orange peel) came in the nano-range, and hence only those two nano-particles were considered for further experimentation on non-damaging drilling fluids.

**3.4**. **GREEN NANO-PARTICLES IN DRILLING FLUIDS**

**3.4.1. Study of Density behavior**

|  |  |  |
| --- | --- | --- |
| **Concentration (%)** | **Density for MgSO4 (g/cm3)** | **Density for CuSO4 (g/cm3)** |
| 0 | 1.03 | 1.03 |
| 2 | 0.99 | 0.8583 |
| 4 | 1.02 | 0.8883 |
| 6 | 1.03 | 0.9063 |

Table 3 – Concentration vs. Density

Fig. 1 Concentration vs. Density

**3.4.2. Rheological analysis**

|  |  |  |
| --- | --- | --- |
| **Concentration (%)** | **Effective Viscosity for MgSO4** | **Effective Viscosity for CuSO4** |
| 0 | 88.4 | 88.4 |
| 2 | 9.2862 | 66.9474 |
| 4 | 7.6194 | 49.7448 |
| 6 | 5.4384 | 47.5 |

Table 4 – Concentration vs. Effective Viscosity

Fig. 2 Concentration vs. Effective Viscosity

|  |  |  |
| --- | --- | --- |
| **Concentration (%)** | **Filtrate volume MgSO4 (ml)** | **Filtrate Volume for CuSO4 (ml)** |
| 0 | 11 | 11 |
| 2 | 7 | 9 |
| 4 | 5 | 8 |
| 6 | 3 | 6 |

Table 5 – Concentration vs. Filtrate Volume

Fig. 3 Concentration vs. Filtrate Volume

|  |  |  |
| --- | --- | --- |
| **Concentration (%)** | **Spurt Loss MgSO4 (ml)** | **Spurt Loss for CuSO4 (ml)** |
| 0 | 3 | 3 |
| 2 | 2 | 2.5 |
| 4 | 1.5 | 2 |
| 6 | 1 | 1.5 |

Table 6 – Concentration vs. Spurt Loss

Fig. 4 Concentration vs. Spurt Loss

From the experiments performed, it has been observed that the addition of nano-particles in increasing concentration keeps reducing the viscosity of the drilling fluid reduces the spurt loss and also the filtrate volume. Therefore, the nano particles can be effectively used as thinning agents as well as filtration control agents in the NDDF.

Moreover, we observe that the increase in concentration of the nano-particles in the NDDF reduces the density at first, but it starts increasing as it goes past an optimum concentration. We find that the optimum concentration of nano-particles in the NDDF is around 2.5% v/v.

Typically, the viscosity of plastic will increase with mud weight. However, if the plastic viscosity trend is rising while the mud weight remains constant, it indicates that the drill solid content of the mud system is rising. Higher plastic viscosity will be the result of any increase in the solid content of the drilling mud, such as drill solid, lost circulation material, etc.

The negative effects of increased plastic viscosity are numerous. It raises the surge and swab pressures, lowers ROP, raises the possibility of differential sticking, and raises the equivalent circulating density.

The nano-particles can be used effectively in such situations to decrease the viscosity of the NDDF.

1. **Conclusion**

The successful utilization of copper (Cu) and magnesium (Mg) green nanoparticles in Non-Damaging Drilling Fluid (NDDF) have proven to be highly effective in reducing its viscosity, filtration and density. By incorporating these environmentally friendly nanoparticles, the viscosity, filtrate volume and density of NDDF has been significantly decreased, resulting in improved flow characteristics and enhanced drilling performance. The results of the experimental findings highlights that the characterization study done using UV-Vis technique summed up the fact that the Cu & Mg NP synthesized is compatible for use as it was found to be stable, uniform and within nano size to validate the results. The application of Cu and Mg green nanoparticles represents a promising solution for addressing viscosity-related challenges in NDDF formulations, offering potential advantages in terms of wellbore stability, cuttings transport, and overall drilling efficiency, although the Magnesium nano-particle yielded a significantly better result than the Copper nano-particle.

In conclusion, the utilization of copper and magnesium green nanoparticles synthesized from aloe-vera and orange peel extracts in non-damaging drilling fluids presents a promising solution for improving drilling efficiency while minimizing environmental and health risks. The distinct characteristics of the nanoparticles aid in improved wellbore stability and decreased formation damage. To analyze the nanoparticles' efficacy in actual drilling operations, optimize their dosage, and assess their long-term stability, more study and field trials are required.

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