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

Spandan Priyam, Joseph Kirembeka, Gayatri Sharma, Pradip Borgohain, Borkha Mech

Department of Petroleum Technology, Dibrugarh University

**ABSTRACT**

Nanoparticles (NPs) are known as important nano-materials for a broad range of commercial and research applications owing to their physical characteristics and properties. Currently, the demand for NPs for use in oil industries is very high. The use of NPs in Drilling Fluid can drastically enhance its rheological properties. 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 results of this research contribute to the understanding of the potential benefits and limitations associated with green nanoparticle-based drilling fluids. The findings can provide valuable insights for drilling fluid engineers and operators in designing environmentally friendly and effective drilling fluid systems, thereby reducing formation damage, improving well productivity, and optimizing hydrocarbon recovery in this geologically significant basin.

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

1. **INTRODUCTION**

Nanoparticles (NPs) are small particle that ranges between 1 to 100 nano-metres in size, undetectable by the naked human eye. Nanoparticles exhibit significantly different physical and chemical properties to their larger material counterparts. 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 consists of three essential stages, namely: reduction of metallic salts by reducing agents, stabilization of the ionic complexes, and controlling of the size by the capping agent. Whereas, in Biological reduction, a biological source as a reducer is employed (most common biological reducers are plant extracts, yeasts, fungi, bacteria, enzymes, etc.). This process, does not involve the use of a capping agent as the reducer itself acts as a capping agent. The name Green Nanoparticles is representative of the source of the NP synthesis media, usually plant / algae based to reduce the use of inorganic chemicals and mitigate the environmental costs associated with mining of inorganic ores for NP synthesis application.

Non-damaging drilling fluids, also known as non-damaging muds or drilling fluids, are specialized substances used in the drilling industry to facilitate the extraction of oil, gas, and other resources from underground formations. Non-damaging drilling fluid (NDDF) provides a method to increase crude oil or hydrocarbon production by controlling formation damage during the drilling process (Talukdar et al, 2014). This kind of drilling fluid is generally used for drilling production zone of development wells; it is specifically used in horizontal well drilling to reduce the formation damage.

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**

The materials used for the experimental analysis along with the apparatus are shown below in Table 1.

|  |  |
| --- | --- |
| **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, KCl  Formaldehyde | Fann VG Viscometer  Filter Press  Marsh Funnel  Mud Balance  Hamilton Beach Homogenizer |

Table 1 – Materials Used

**2.2. Methods employed**

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

There are a variety of chemical and physical preparation methods available for the fabrication of nanoparticles including radiation, chemical precipitation, photochemical methods, electrochemical, and Langmuir–Blodgett techniques, but these methods are often extremely expensive and non-environmental friendly due to the use of toxic, combustible, and hazardous chemicals, which may pose potential environmental and biological risk and high energy requirement (Awwad et al. 2013). The drawbacks of low production rate, structural particle deformation, and inhibition of particle growth are also encountered in these nanoparticles synthesis. Currently, there is a growing need to develop green sustainable preparation method of nanoparticles that get rid of using harmful organic chemical substances.

* + - 1. ***Biological method***

Through biological method, extracts from biological agents such as microbes and plants can be employed either as reducing or protective agent for the fabrication of metal nanoparticles. In these extracts, various combinations of biomolecules which have the reducing potential can be found such as amino acids, vitamins, proteins, enzymes, and polysaccharides that are environmental friendly, yet chemically complex (Moghaddam 2010). For instance, the unicellular green algae Chlorella vulgaris extract was utilized to synthesize single-crystalline copper and magnesium Nano-particles at room temperature. Proteins in the extract were suggested to perform dual function of Cu2+ and Mg2+reduction and size and shape (capping agent) in our project. The bottom up approach was employed for the biosynthesis of these Nanoparticles.

* + - 1. ***The Bottom Up Approach***

It includes the miniaturization of materials components to atomic level with further self-assembly process leading to the formation of Nano structures. During self-assembly, the physical forces operating at Nano scale combine basic units into larger stable structures. Typical examples are quantum dot formation during epitaxial growth and formation of nanoparticles from colloidal dispersion, physical vapor deposition, 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. Bottom-up approach is based on the principle of molecular recognition (Self-assembly). Self-assembly means growing more and more things of one’s kind from them. 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.

* + - 1. ***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.

* + - 1. ***Precursor Preparation***

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

* + - 1. ***Preparation of Nanoparticles***

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**

***2.2.2.1. Particle Size Analysis***

A nano particle size analyzer is used to determine the size of individual particles as well as a size distribution range for a given sample. The pharmaceutical industry uses nano particle size analyzers because the size and shape of a particle can affect how a medication works in the body. Nano particle size analyzers can measure particles in many ways, including light scattering, laser diffraction, photon correlation spectroscopy, and sedimentation. The first three methods work by watching how light or lasers are shifted due to the particles and sedimentation determines particle size by measuring how fast the particles fall to the bottom of the sample. Some features to look for in nano particle size analyzers include the ability to process wet and/or dry dispersions; the particle size range that can be measured; whether it can determine shape as well as size; and whether it can measure concentration, zeta potential, and aggregation.

***2.2.2.2. Ultraviolet Spectrophotometry***

UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample. This property is influenced by the sample composition, potentially providing information on what is in the sample and at what concentration.

The optical absorption spectrum of Cu particles of different size is also reported; it contains the Plasmon band in the 560−580 nm region and a UV band peak between at 222-360 nm and becomes flatter with increasing particle size. (Henglein, 2000). Magnesium absorption is measured at a wavelength of around 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**

***2.2.3.1. 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.

NDDFs are mostly used in pay zone sections of development wells and specifically in horizontal drilling to avoid formation damage. Non degradable compositional fine solid like clay, barite, etc. are not used in NDDF to counter the formation damage as well as environmental pollution. So, to provide the above mentioned properties in drilling fluid to perform the above mentioned functions, the XC-Polymer (with some assistant constituents) is used in NDDF instead of the non-degradable clays (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.The composition of materials and chemicals used are as follows -

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

***2.2.3.2. Density behavior analysis***

The density of the mud before and after the addition of the nano-particles was determined by using a Mud Balance apparatus. The Mud Balance provides a simple, practical method for accurate determination of fluid density.

It is one of the most sensitive and accurate field instruments available for determining the density or weight-per-unit-volume (specific gravity) of drilling fluids.

An outstanding advantage of this Mud Balance is that the temperature of the sample does not materially affect the accuracy of readings. A high impact plastic case protects the balance during transport and provides a secure base in its working position.

The Mud Balance is constructed with an easy-to-read beam graduated into four scales

* Pounds per gallon
* Specific gravity
* Pounds per cubic foot
* Pounds per square inch per 1,000 feet of depth

***2.2.3.3. Rheological property 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**

***3.2.1. Summary of results from Particle Size Analyzer***

The particle size analysis of various nano-particles synthesized are shown in Table 2.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **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

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. Density behavior analysis**

The density behavior of drilling fluid with the addition of various concentrations of nano-particles are analyzed in Table 3 and Fig 1.

|  |  |  |
| --- | --- | --- |
| **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 property analysis**

The rheological property analysis of formulated green nanofluids is shown in Table 4 and Fig 2. Table 5 & 6 and Figure 3 & 4 respectively shows the filtrate and spurt loss bahaviour.

|  |  |  |
| --- | --- | --- |
| **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.

Normally, the higher the mud weight, the higher plastic viscosity will be. However, if there is an increasing trend of plastic viscosity with constant mud weight, it means that there is an increase in drill solid content in a mud system. Any increase in solid content in drilling mud such as drill solid, lost circulation material, etc., will result in higher plastic viscosity.

An increase in Plastic Viscosity has a lot of disadvantages. It increases the Equivalent Circulating Density, increases the surge and swab pressures, reduces ROP and increases the chances of differential sticking.

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 nanoparticles' unique properties contribute to better wellbore stability and reduced formation damage. Further research and field trials are necessary to optimize the nanoparticles' dosage, evaluate their long-term stability, and assess their performance in real drilling operations.

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