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Impact of Nanoparticles on Clay Sedimentation in Liquids

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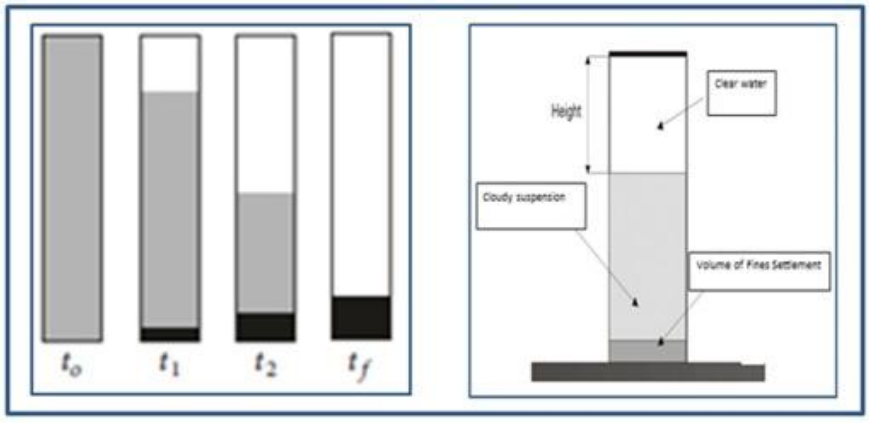
ABSTRACT

Clay sedimentation in colloids is a natural phenomenon that can be accelerated or retarded with additives. This is important in drilling operations where clay suspension in drilling muds is desired for effective functionality. Current studies have indicated that nanoparticles can improve rheological properties of drilling fluids but not much is known about their impact on clay sedimentation. Hence, this work investigates the effect of eight kinds of nanoparticles on clay sedimentation in the absence and presence of crude oil. A small fraction of these nanoparticles were dispersed in distilled water, brine of 30g/l salinity, ethanol and diesel containing clays, and the volume of settled particles under gravity were plotted against time. Linear graphs and parabolic shaped graphs within the short periods of observation indicate slow and accelerated sedimentations respectively. Results show that aluminum oxide and zinc oxide nanoparticles speed up clay sedimentation while nanoparticles of magnesium, zirconium, nickel, iron, tin and silicon oxides retard clay sedimentation rate in liquids, rendering these six kinds of nanoparticles potential clay stabilizers. In the absence of nanoparticles it was observed that clay sedimentation in water is slower than in ethanol and diesel and the presence of crude oil further slows down sedimentation. But in the presence of nanoparticles, the effect of crude oil on clay sedimentation is inconclusive, necessitating further studies.

Keywords: Water, brine, ethanol, diesel, dispersing fluid, suspension.

Graphical abstract



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1. Introduction

Clay minerals are important raw materials in various industries and they are encountered and studied in earth science. In engineering, clays that are mixed with liquids or suspended in fluids are used in chemical, civil, environmental and petroleum engineering. Suspension of clay in liquids such as water and oil is of particular interest to environmental and petroleum engineers. Clay sedimentation in flood waters, aquatic and marine environments such as rivers and oceans are studied by environmental scientists, oceanographers and geologists. During drilling of oil and gas wells, clay sedimentation is not desired, it is avoided; in fact, the ability of drilling muds to suspend clay particles in fluids is one of the characteristics of a good mud hence, additives are sometimes used to improve clay stability in drilling muds. Some additives that can be introduced into drilling fluids to enhance suspension of clay particles are nanoparticles. It is therefore imperative to identify nanoparticles that can initiate and maintain particle suspension in fluids such as in polar and non-polar liquids. The dispersing fluid no doubt can affect the performance of the nanoparticles, necessitating that such study be conducted with several kinds of fluids. Hence in this study, the effect of different nanoparticles on clay suspension in water, ethanol and diesel is conducted in the absence and presence of crude oil.

Some experimental investigations have studied the effect of nanoparticles on drilling fluids. A study has shown that adding 1g of Al_2O_3 and Fe_2O_3 nanoparticles can improve rheological, swelling, filtration and lubrication properties of drilling fluids [1, 2]. It has been observed that Al_2O_3 nanoparticles can improve some drilling fluid properties [3 - 7]. However, the stability of Al_2O_3 nanoparticles has posed a challenge [8], leading to further studies where using sodium dodecylbenzenesulfonate (SDBS) to improve the stability of Al_2O_3 nanoparticles was investigated. It is reported that 1% SDBS gives the highest stability amongst other concentrations studied [9]. ZnO nanoparticles is another kind of nanoparticle that has been studied in relation to improving drilling fluid properties and experimental results have been positive [10 - 15]. The interaction of gold nanoparticles with Montmorillonite clay in aquatic environments and uses of other nanoparticles in drilling fluids have been reviewed [16, 17].

Laboratory studies of water based drilling fluids containing Fe_3O_4 and SiO_2 nanoparticles has shown that these two kinds of nanoparticles have the potential to improve filter cakes at low pressure and temperature conditions, and at high pressure and temperature conditions. They also have the ability to maintain optimal rheological properties in mitigating drilling problems [18]. Uses of nano-silica to stabilize drilling fluids at high temperature and high pressure conditions and to inhibit clay swelling have been studied. The use of Fe_3O_4 nanoparticle to stabilize suspensions of bentonite particles in drilling muds have been reported [19 – 23] however, it is necessary to also investigate the ability of other nanoparticles in performing same tasks.

In crude oil refining, clays are used at different stages for different functions. Acid modified wax is treated with clay to remove reaction products and traces of acid sludge by adsorption on clay particles. The clay is later separated from the wax, of which clay sedimentation rate plays a role in the process. Clay treatment is also used to improve petroleum product colouration. Clay and lime treatment of acid-refined gasoline removes traces of asphaltic materials and other compounds, improving product colour, odour and stability. When used clays are required to be separated from liquids, fast sedimentation is desired. Thus, there are industrial processes that require fast sedimentation of clay in liquids to enhance separation while others require continuous clay particle suspension in liquids such as during oil well drilling operations. Since some nanoparticles can enhance or retard clay sedimentation in liquids, it is imperative to identify nanoparticles that can function as clay stabilizers and destabilizers in liquids in order to optimize industrial processes.

The use of nanoparticles in various industries for specific functions on consumer products have been studied. But the study of nanoparticles with regard to clay sedimentation is just emerging probably because much attention has been given to product improvement than process optimization. The effect of nanoparticles on production processes is important as this can reduce cost of production, speed up reactions, slow down undesired reactions and enhance productivity. In this work, the impact of nanoparticles on clay sedimentation in liquids is studied in order to identify nanoparticles that can promote clay stability and instability in liquids. This is important because clays are used in various industrial processes including well drilling operations and oil refining in the petroleum industry.

2. Materials and Methods

2.1. Materials

The primary materials deployed in this work are clay minerals, nanoparticles and four liquids used as suspending mediums for particles of clay and nanoparticles. The aim of the experimental study is to identify nanoparticles that can retard and accelerate the rate of clay sedimentation in distilled water, brine of 30g/l salinity, ethanol of 98% and diesel, thus, enhance or decelerate particle dispersion and suspension in liquids. The eight kinds of nanoparticles used are Aluminum oxide (Al_2O_3), Magnesium oxide (MgO), Zinc oxide (ZnO), Iron oxide (Fe_2O_3), Nickel oxide (Ni_2O_3), Tin oxide (SnO_2), Zirconium oxide (ZrO_2) and Silane treated Silicon oxide (SiO_2). These nanoparticles were selected based on a study of their compound properties in the powder form, and on literature reports of their performances in various practical work. The nanoparticles were procured from Skyspring Nanomaterials, Inc., Houston, Texas, USA and their sizes and surface areas are presented in Table 1. Each of the nanoparticles was dispersed in the four liquids at the concentration of 3g/l because studies have shown that very small concentrations are enough to initiate change in solutions, processes and reactions.

Table 1. Particle Size and Surface Area of Nanoparticles

S\No.	Type of Nanoparticles	Particle Size (m)	Surface Area (m^2/g)
1.	Aluminium Oxide	40	~ 60
2.	Magnesium Oxide	20	~ 50
3.	Iron Oxide	20-40	40-60
4.	Nickel Oxide	100	6
5.	Tin Oxide	50-70	10-30
6.	Zinc Oxide	10-30	90
7.	Zirconium Oxide	20-30	35
8.	Silane Treated Silicon Oxide	10-30	> 400

The three types of clay selected for this work are the frequently used and encountered clays in the petroleum industry and they are Montmorillonite, Kaolinite and Illite, purchased from Clay Mineral Society, USA. Montmorillonite is a swelling clay which is sometimes encountered in the formation during drilling operations. Aside from being used in drilling of oil and gas wells, it is also used as a catalyst in crude oil refining. In other industries, Montmorillonite is used in construction, cosmetics, medicine and pharmacology. Kaolinite is the migratory clay that causes fines migration in petroleum reservoir formations. It is a raw material in pottery, cosmetics, paint and brick making. It is also used in medicine and in wastewater treatment as an adsorbent. Illite is a non-expanding clay that is commonly found in sedimentary rocks. It is used as an additive in drilling muds and as a filler in the paper and paint industry, it is also used in agriculture.

Montmorillonite, Kaolinite and Illite were mixed together in the ratio of 2:2:1 respectively and a concentration of 10g/l was dispersed in each of the four liquids used in the experiments. The crude oil used has a density of 0.9114g/cc at 27^oC, viscosity of 53.28cp and API gravity of 22.44^o.

2.2. Methods

Clay in the different liquids formed a colloid and 20ml of the colloid, 4ml of nano-fluid and 4ml of crude oil (when the presence of crude oil is required) were mixed together, thoroughly stirred and poured into a calibrated cylinder. The volume of settled particles of clay and nanoparticles was recorded against time within 20minutes observation period and the results were graphically plotted. Each experiment was conducted at least twice and average results were used for the graphical plots. When discrepancies between two sets of results are large, a third experiment is conducted, but only very few cases of such occurred during the experimental work. Note that in quick sedimentation, the graphs take the shape of a parabola or quadratic equation graph opening downward, while slow sedimentation of particles gives a linear equation graph within the short period of observation.

For the first few minutes of observation, the fluid column of colloid is uniform but with time, two layers of fluid can be seen and after a while, a third layer at the bottom of the fluid appears. The volume of this third layer contains settled clay

particles and this is the layer that is plotted against time. This volume of settled particles increases to a peak and then gradually starts shrinking due to compaction. At this point, the second layer gradually disappears because all the particles in it have descended into the third layer, leaving the column with only two layers; a particle free layer at the top and a layer of settled particles at the bottom as illustrated in Fig. 1.

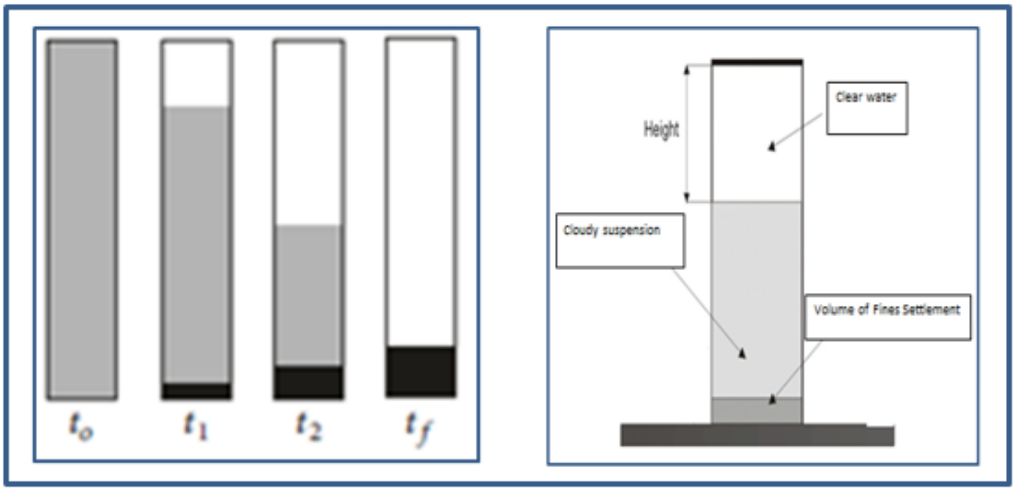

Fig. 1. Illustration of the Particle Settling Process

3. Results and Discussion

All experimental results are presented in Figs. 2 to 5; they are grouped into four and each group has the control experiments as the first set of results where there are no nanoparticles. Results of the influence of nanoparticles are presented below the control experiments in order to make comparisons easy. Note that cases of nanoparticles with similar patterns of results have been grouped together and each set of result for distilled water, brine, ethanol and diesel comprise of two graphs. The graphical results in blue color are those conducted in the absence of crude oil while those in red color are those conducted in the presence of crude oil. For the graphical plots, the x-axis is time in minutes as all experiments were conducted under 20minutes while the y-axis is volume of settled clays recorded in ml.

The control experiments in Fig. 2 show that clay sedimentation is faster in organic liquids (ethanol and diesel) than in water. Clays therefore seem to be more stable in water than in organic liquids. The presence of crude oil in water tends to further retard the rate of clay sedimentation as observed from results of the control experiments. Presented also in Fig. 2 are results of Al_2O_3 and ZnO nanoparticles and it is clear that these nanoparticles exhibit the same trend in clay sedimentation. Both Al_2O_3 and ZnO nanoparticles speed up clay sedimentation which is not desirable for drilling fluids, but may be required for other industrial processes such as separation of clay from a liquid. It is therefore necessary for other clay stabilizing additives to be introduced if Al_2O_3 and ZnO nanoparticles are used in significant quantities in drilling fluids. The effect of crude oil on the performance of the nanoparticles is not consistent and clear for these cases.

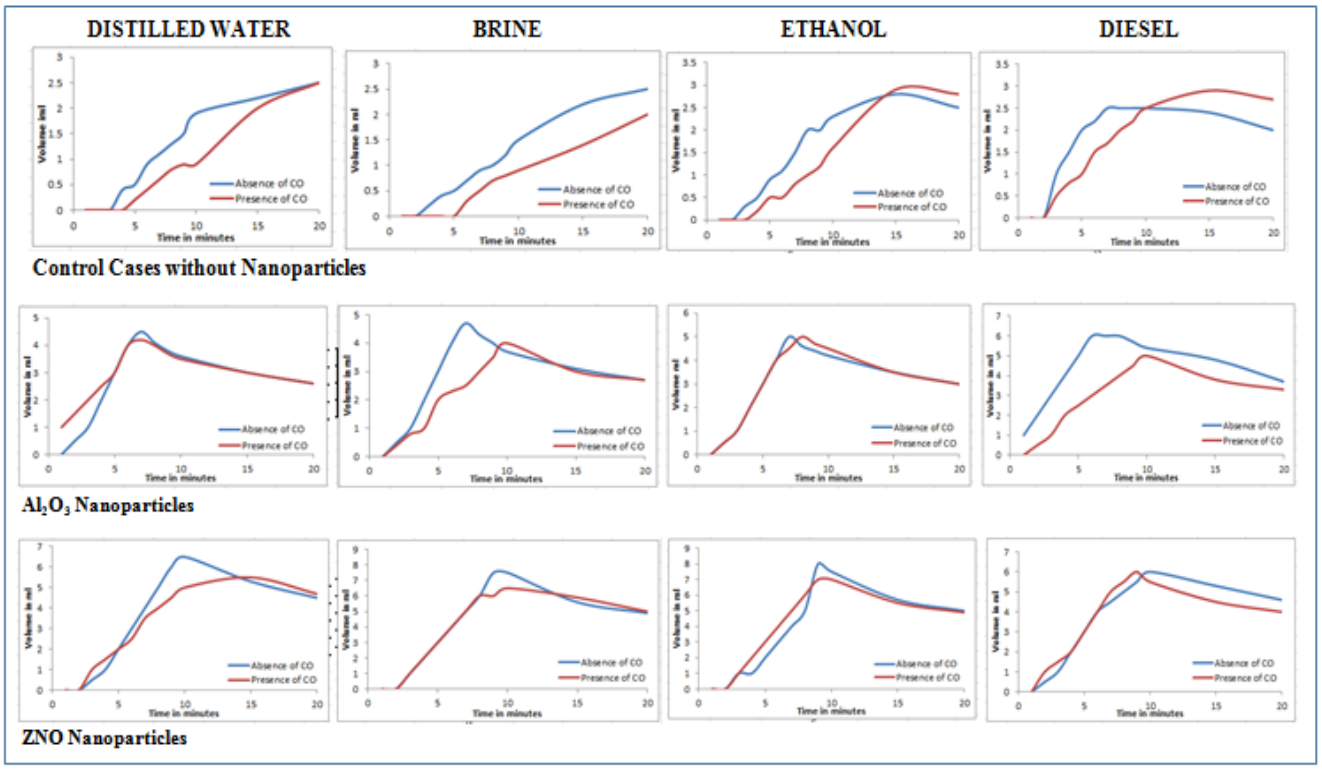

Fig. 2. Trend of Clay Sedimentation under the Influence of Al_2O_3 and ZnO Nanoparticles

Fig. 3 shows results of clay sedimentation trend under the influence SnO and SiO_2 nanoparticles which are similar. However, the effect of crude oil tends to be in the opposite direction at least for brine, ethanol and diesel. Generally, it is observed that the presence of SnO and SiO_2 nanoparticles in liquids slow down clay sedimentation. Particles in distilled water tend to settle faster than in other liquid mediums.

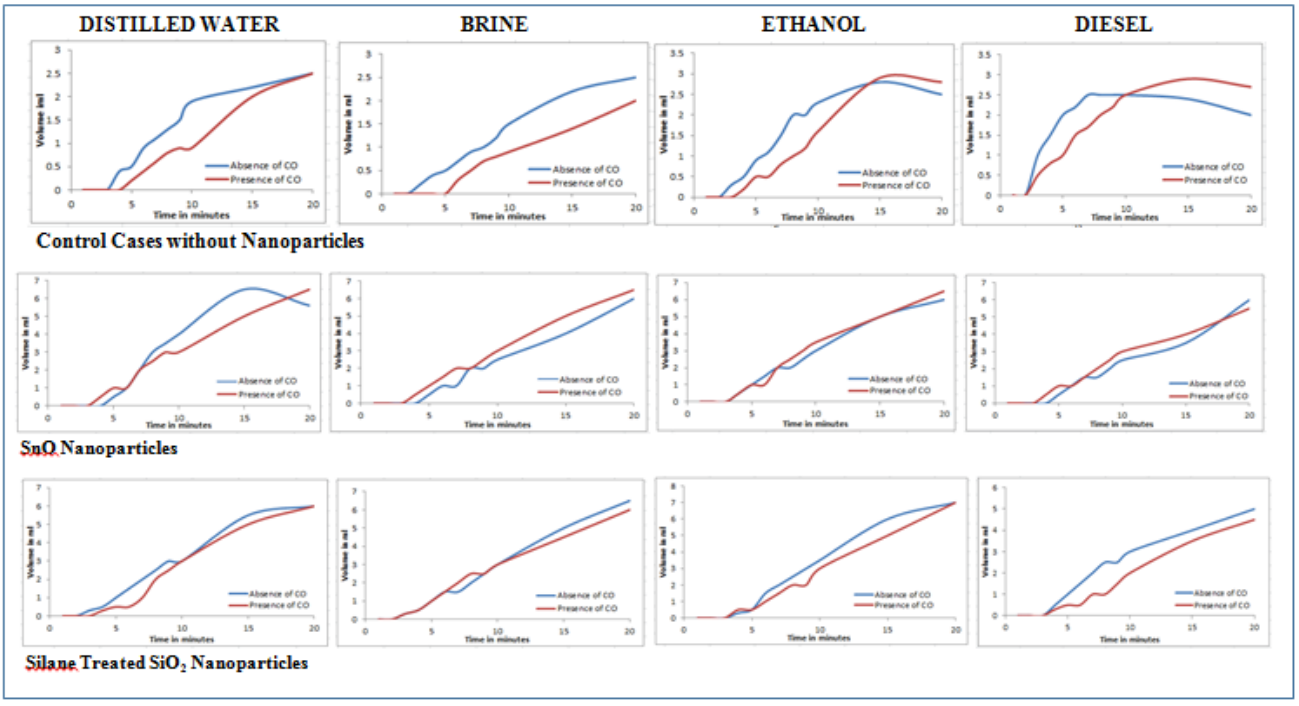

Fig. 3. Trend of Clay Sedimentation under the Influence of SnO and SiO_2 Nanoparticles

Fig. 4 shows clay sedimentation trends in the presence of Fe_2O_3 and NiO_2 nanoparticles. Both kinds of nanoparticles are potential good clay stabilizers in fluids, and crude oil seems to have very minimal effect in distilled water and brine than in ethanol.

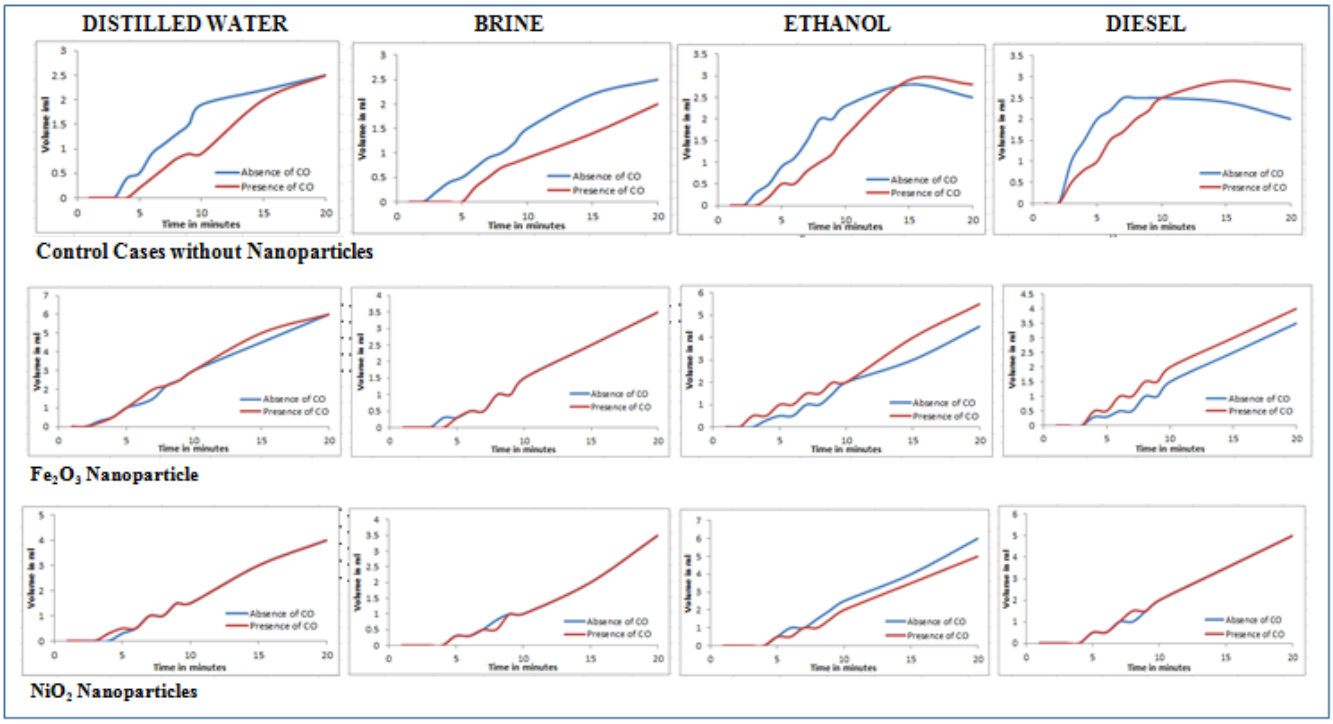

Fig. 4. Trend of Clay Sedimentation under the Influence of Fe_2O_3 and NiO_2 Nanoparticles

Results of the effect of MgO and ZrO_2 nanoparticles on clay sedimentation are presented in Fig. 5. The effect of crude oil on the performance of the nanoparticles is opposite at least for distilled water and diesel. MgO and ZrO_2 nanoparticles retard the rate of clay sedimentation, thus they are prospective good clay stabilizers in fluids.

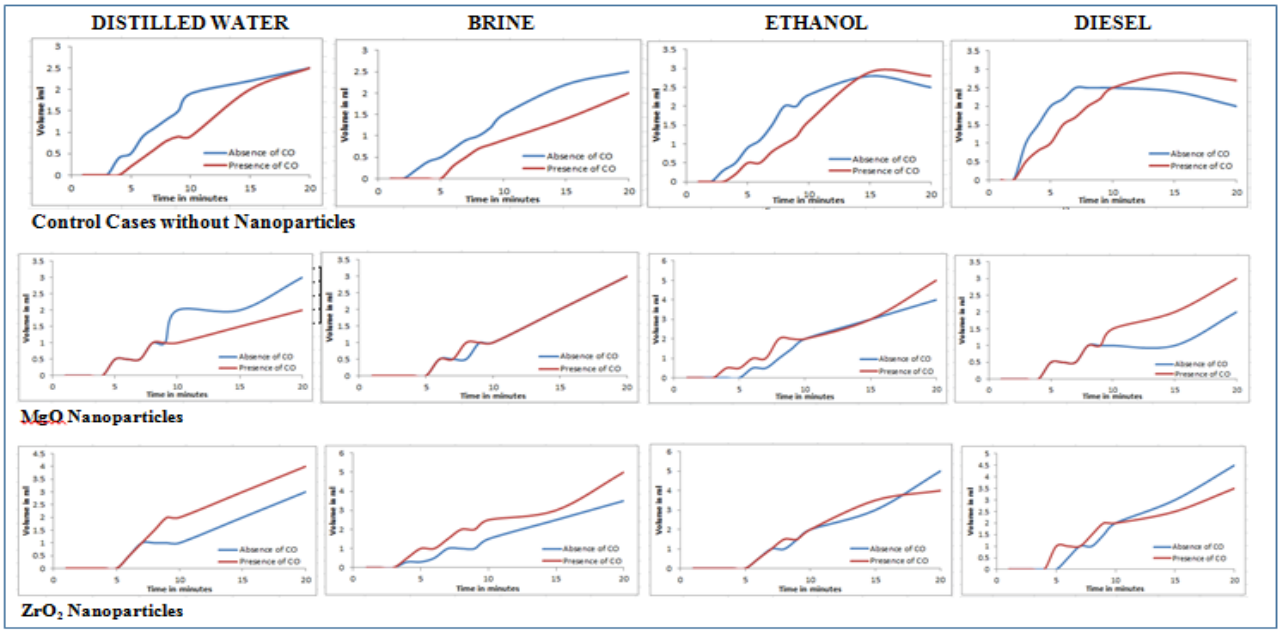

Fig. 5. Trend of Clay Sedimentation under the Influence of MgO and ZrO_2 Nanoparticles

Potential clay stabilizers in liquids therefore includes MgO, ZrO_2, NiO_2, Fe_2O_3, SnO and SiO_2 nanoparticles, while poor clay stabilizers in liquids include Al_2O_3 and ZnO nanoparticles. However, the most effective nanoparticle that suspends clay

in liquids for a long time, delaying clay sedimentation is yet to be determined, in fact, this constitutes an area for further research. While the presence of crude oil slows down clay sedimentation in the control experiments, it is observed that its effect in the presence of nanoparticles is not consistent. An aspect of this work that can be explored further is mathematically modeling clay sedimentation in different fluids in the absence and presence of nanoparticles.

Certain chemical properties of these nanoparticles must have been responsible for their effect on clay sedimentation. These properties might be the zeta potential, electric charges, chemical reactions or prevalent electrostatic forces. Nevertheless, note that Al_2O_3 and ZnO nanoparticles destabilized clay particles in solution (Fig. 2), causing early sedimentation, and same is observed for SnO_2 nanoparticles at least in distilled water (Fig. 3). Interestingly, Al_2O_3, ZnO and SnO_2 are all amphoteric oxides. SiO_2 nanoparticles which behaved almost like SnO in distilled water (Fig. 3) is a weak acid that has some amphoteric oxide characteristics. Hence, certain amphoteric oxide properties of these compounds might have contributed to trigger quick clay sedimentation in liquids.

The effect of crude oil on clay sedimentation especially in the presence nanoparticles is inconclusive and slightly complex. This is because in some cases, clay sedimentation is delayed, in other cases, it does not have any effect on sedimentation, while in some cases clay sedimentation is enhanced. The reason for this inconsistency requires further work, however, it has been reported that the presence of organic compounds in liquids can promote clay sedimentation [24]. Crude oil is an organic substance thus, its presence can trigger early clay sedimentation or other effects.

4. Conclusion

In the absence of nanoparticles, clay sedimentation in organic fluids such as ethanol and diesel is faster than in distilled water and brine. In the absence of nanoparticles, crude oil slows down clay sedimentation, but in the presence of nanoparticles, the effect of crude oil on clay sedimentation is not consistent. Al_2O_3 and ZnO nanoparticles accelerate clay sedimentation in distilled water, brine, ethanol and diesel. MgO, ZrO_2, NiO_2, Fe_2O_3, SnO and SiO_2 nanoparticles retard the rate of clay sedimentation in liquids, rendering these nanoparticles potential clay stabilizers in fluids. MgO, ZrO_2, NiO_2, Fe_2O_3, SnO and SiO_2 nanoparticles have potentials to serve as good clay stabilizers in fluids but further studies are required to determine the most effective ones.

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Ethical Statement

This study does not contain any studies with human or animal subjects performed by any of the authors.

Conflict of Interest

The authors declare that they have no conflict of interest.

Data Availability Statement

Not applicable.

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