Environmental, Health and safety Assessment of Nanoparticle Application in Drilling mud – Review

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Abstract

The rapid increase in the use of engineered nanoparticles in different industrial applications makes risk assessment on human health, ecosystem and the environment necessary. Health, safety and environmental (HSE) risks of a technology are an inseparable part of which it threatens all exposed employees. There has been an increase and public interest in nanotechnology because of its applications in several areas including, processing and engineering industries e.g., oil and gas, electronics, cosmetic, biomedical, agriculture, medicine and public health. The increased use of nanomaterials in various sectors has raised concerns about their impact on health and safety, as well as the environment. As nanomaterials become commonly and widely used in every sector, environmental and personal exposure to nanomaterials is therefore unavoidable and this has led researchers to gain interest in nanotoxicity. Based on this, this paper reviews the application of nanotechnology in drilling engineering, with a focus on drilling fluids and environmental concerns regarding their disposal after use. Meanwhile, combined with the risks of nanotechnology toxicity to both humans, the ecosystem and the environment, this paper expounds the challenges of nanotechnology in oil and gas, the cost of nanoparticle mud fluids, fate and behaviour of nanoparticles, and then puts forward future recommendations for safe disposal of ENPs in drilling fluids and other industrial applications.

Keywords

Nomenclature

WBMs	Water based muds
OBMs	Oil based muds
DI	Deionised water
ROS	Reaction oxygen species
NNI	National Nanotechnology Initiative
HPHT	Hight pressure/High temperature
NOM	Naturally present Organic material
ENPs	Engineered nanoparticles
NPs	Nanoparticles
API	American Petroleum Institute
YP	Yield point
PV	Plastic viscosity

1. Introduction

Engineered nanoparticle environmental risk assessments would require an exhaustive analysis and characterization of nanomaterials and their aggregates. Therefore, the quantitative and analytical procedures to establish environmental concentrations and allow both effect and exposure analysis and assessments is required [1]. With increased search of oil and gas in unfriendly environments situated in regions with elevated pressure and temperature, the petroleum industry has found its self-lacking in the aspects of creating smart drilling fluid systems capable of performing well in such environments. Mud fluid also commonly known as a drilling mud fluid plays a vital role in the drilling operation. Not only does it serve as a drilling string and bit lubricant, but it is also used throughout the drilling operation and well construction. Unlike the need to fulfil the technical requirements, of avoiding caving in and sloughing of the well, it is vital to take into consideration the environmental aspect.

Mud fluids are designed to work together with mud additives in order to achieve the required characteristics. The discovery of nanotechnology from other branches of science such as aerospace, medical and electronics led the petroleum industry to pick interest in the same. The meaning of nanotechnology according to the National Nanotechnology Initiative (NNI) is the engineering, science and technology performed at the nano size of about 1 to 100 nm [2]. There have been great expectations due to the emerging of this technology in the petroleum industry. It's in recent years that the idea of using nanomaterials to design smart drilling muds to improve

the rheological properties has taken forefront. Properties of nanoparticles such as their very ultrafine size and high surface area to volume ratio, ease to modify etc have allowed engineers to modify drilling fluids rheology by changing the composition, charge, reactivity, type, or size distribution of nanoparticles that suit designing of stable drilling fluid systems. The emerging challenges and changes in operating environments, such as harsh conditions of high pressure and high temperature (HPHT), have resulted in the failure of conventional muds and poor performance.

Although the use of nanomaterials in drilling fluids is still investigated, the issue of toxicity cannot be neglected. The future release of drilling fluid wastes containing nanoparticles may cause negative impacts to the ecological system such as the marine organisms. Therefore, a precautionary measure on the amount of release or usage which might affect the chain should be put in place. Aitken et al. [3, 4] stated that because of the increased present and future investments, nanoparticles used for industrial applications, consumer products might end up entering the environment. A risk assessment of engineered nanoparticles (ENPs) introduced from different applications is needed for guaranteeing sustainable development of nanotechnology [5]. ENPs are different from the majority of conventional chemicals in regards of their size distribution, surface charge, sharp, degree of dispersion and composition, etc. This makes it difficult to determine their concentration. With limited information available in regard to determining the toxicity of nanoparticles, different authors have stated that indeed nanomaterials are toxic to humans and environment.

According to Buzea et al. [6], animals and human studies proved that inhaled nanoparticles are difficult to rinse off than large particles in the lungs hence resulting to lung damage. Nanoparticles besides that can move through the circulatory and nervous systems to many organs and tissues including the brain. Also, Jackson et al [7] stated that nanomaterials target the organs in fish such as the liver, gut, gills and brain and are trapped by the mucus layer in the gills causing death. The investigations conducted by rainbow trout juveniles, single walled carbon nanotubes (SWCNT) of concentration beginning from 0.1 mg/L were reported to have caused respiratory toxicity [7, 8]. It is important to access therefore the potential effects that may be caused by the introduction and application of nanoparticles based on similar findings as such.

From the studies done by Bob el al. [9], they observed from their experiment that the amount of particles and pollutants is increased when the concentration increases. They stated that in

both esters-based mud (EBM) and water-based mud (WBM), the application of multi wall carbon nanotubes (MWCNT) and nanosilica resulted to a lower percentage of fish surviving compared to mud without nanoparticles implying that nanoparticles resulted and led to the mortality rate increase. This proved the clogging of the breathing structures in the fish by the nanoparticles which resulted to the fish suffering from oxygen stress caused by the mud content and nanoparticle additives. MWCNT has the tendency to aggregate due to its hydrophobicity i.e., it repels water and forms droplets which in return are harmful to living cells. Many authors have concluded that carbon nanotubes in general are very toxic [6]. The tendency of reactivity of nanoparticles towards other pollutants from mud content is increased by the high surface to volume ratio of nanoparticles [6].

Abdul. [10] also observed from his research that although the highest percentage of mortality was from MWCNT, nano silica too contributed to a higher mortality of fish when compared with the mud fluid without nanoparticles. This showed that nanoparticles acted as a carrier of harmful substances. According to Zhang et al. [11], this was due to the high surface area of silica nanoparticles leading to an increased adsorption capability therefore allowing particles to participate as possible toxic carrier in two ways either by carrying the toxic molecules and depositing them to the organisms or by non – toxic combinations by entering the organisms and accumulating in the interfacial area.

Chapter 1 presents an introduction of the review, nanotechnology including the emerging challenges of engineered nanoparticles. Chapter 2 presents the economic assessment of nanoparticle including the cost of nanomaterials in drilling fluids. It also presents the technical assessment of nanoparticles in drilling fluids such as the effects of nanoparticles on the rheology of drilling fluids and stability of the wellbore. This chapter also presents the challenges of drilling fluid waste and advancements in drilling technology. The chapter also presents nanoparticle drilling fluid cost calculation. The fate and behaviour of nanomaterials when released into the environment are discussed in Chapter 3. Chapter 4 discusses the toxicity of nanoparticles to human. Chapter 6 presents the challenges of nanotechnology in the oil and gas industry. Chapter 7 presents the recommendations on how nanoparticles can be safely handled. Chapter 8 presents the summery and Chapter 9 present the conclusion

2. Economic and Technical assessment of Nanomaterials in drilling fluids

The global nanomaterials market was estimated to be worth $7.3 billion [12], in 2016 with drilling fluid applications accounting for only a small portion of that total. In 2022, the revenue

of the nanomaterials market, which includes chemicals, polymers, metal oxides, and minerals, is expected to be around US$16.8 billion. Analysts have predicted that the global nanomaterials market will likely grow at a 13.1% annual rate from 2020 to 2027 [13]. Others predict that the global nanomaterials market will reach $15.9 billion by 2025 [14]. Fig.1 below shows the historical growth and forecasts for the global nanomaterials markets.
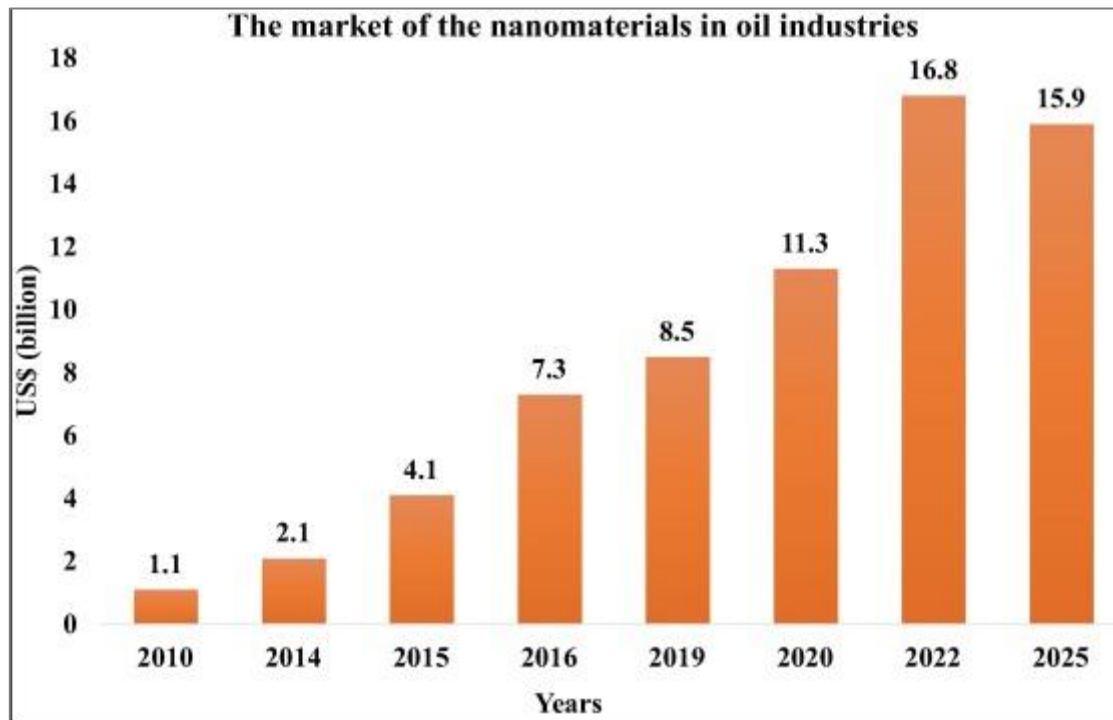

Figure 1. Global nanomaterial market [12, 13]

Increased nanotechnology research and development (R & D) has been vividly seen by the sums of money invested in nanotechnology research and development. The National Nanotechnology Initiative (NNI) alone received nearly $27 billion, including the proposed budget for 2019, compared to a cumulative total of $25 billion since the NNI's inception [15, 16]. The NNI cumulative investment by 2021 inclusive reached $31 billion and the cumulative investment for 2022 reached over $38 billion [17, 18]. NanoMech a leading company in manufacturing nanoparticles received $10 million investment from Saudi Aramco Energy ventures (SAEV) [19]. Another example is the huge investment of $350 million by Massachusetts Institute of Technology (MIT) for the state-of-the-art nanoscale research centre named "MIT. nano" [20]. The UK Engineering and Physical Science Research Council (EPSRC) invested $36 million in graphene and carbon nanotechnology research to UK universities and currently, a total of $84 million is being invested for projects with nanotechnology applications in energy and manufacturing [21]. This demonstrates that there is

a great deal of interest in the potential of nanotechnology in various industries, as evidenced by the large investments. Nanotechnology has widely been received and used in the petroleum industry in many applications such as in drilling muds to enhance performance. The use of nanomaterials in drilling fluid has been discovered to have both technical and economic impacts. The selection of any drilling fluid for a specific well is influenced by three critical factors: cost, technical competence, and environmental compatibility. Before beginning any drilling operation, the cost of drilling fluid must be considered. A drilling fluid may be technically viable and environmentally friendly, but it might not be used in drilling operations if it is not economically feasible. The advantages of nanoparticles in the oil and gas industry are now well known. However, their unit and cumulative costs, as well as their availability has impacted on their usage, particularly in drilling applications, as well as deciding on which specific NP to use to achieve specific goals is still a challenge [22-24]. Nanoparticles are more expensive than many of the basic drilling mud additives. However, nanoparticles continue to provide a cost-effective alternative to replacing oil-based and diesel drilling fluids while also reducing the environmental footprint [25, 26].

Davoodi et al. [27], investigated the effects of silica nanoparticles and graphene nanoparticles on the filtration and rheological properties of the drilling mud under normal reservoir conditions. This allowed them to compare the technical and economic properties of NP-enhanced and standard drilling fluids. The cost of drilling fluid components is specified in Table 1

Table 1. Unit cost of key additives used in drilling fluids [27]

Drilling Fluid components	Unit Costs, 4/Kg (2021)
Soda ash	0.3
Caustic soda	0.9
HT starch	1.2
XC polymer	1.5
KCI	0.1
NaCl	0.0
CaCO$_3$	0.4
PAC-LV	1.7
SNPs	100.0
GNPs	200.0

The financial impact analysis provided demonstrated that the introduction of nanoparticles significantly increased the overall cost where drilling fluids with silica nanoparticles and graphene nanoparticles as mud fluid additives even at low concentrations $1kg/m^3$ was two to four times more than the base mud fluids and/or industrial fluids with low viscosity polyanionic cellulose additives. As a result, despite the property enhancements that nanoparticles have on drilling fluids, the cost of nanoparticles still remains the primary impediment to their adoption by the commercial drilling sector [27]. Another factor is that existing macro-molecular commercial additives, which are currently in widespread use to control fluid losses and improve drilling-fluid rheology, are significantly less expensive than NP. Many of those materials can provide, at least in part, the benefits provided by NP. Because of the current cost of producing NPs on a large scale, their use in drilling fluids is primarily limited to laboratory and pilot-scale testing [12]. The cost of widely used NPs in drilling muds are compared in Fig. 2.
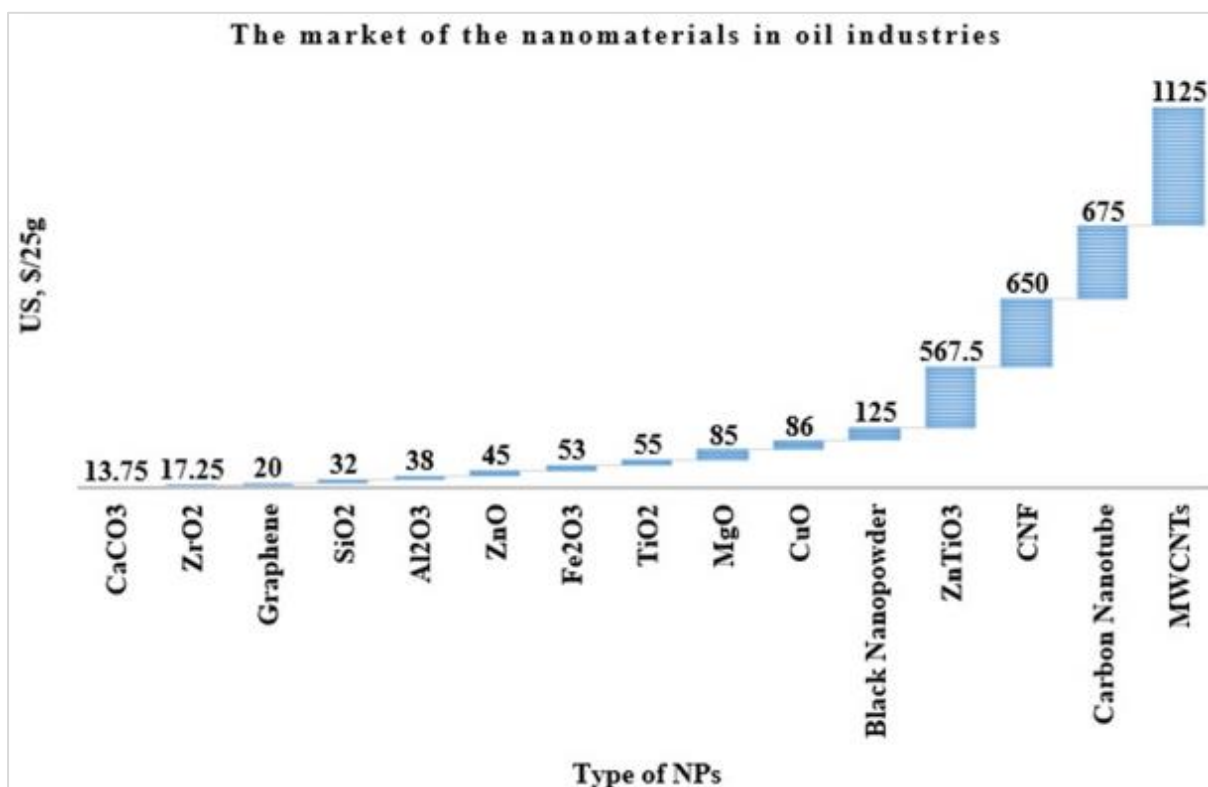

Figure 2. Unit costs of nanoparticles used in drilling fluids [28]

Nevertheless, there is some potential for developing less expensive NPs as drilling fluid additives. Gilsonite, for example, is a naturally occurring bitumen/asphalt that forms minable deposits near the Earth's surface. It may provide a relatively inexpensive source of nanomaterial. At room temperature,

the introduction of hydrophilic Gilsonite (HGN) NP to water-based drilling mud has been found to reduce differential sticking [29]. HGN, in general, provides a low-cost, viable multifunctional additive suitable for use in water-based drilling muds. It has the potential to improve the rheology and lubricity of those muds, lowering the risk of differential sticking under HPHT conditions. Gilsonite mines can be found all over the world, providing easy access to low-cost HGN. As a result, the commercial cost of HGN production is expected to be lower than that of silica and Titanium dioxide nanoparticle synthesis [29].

Nanomaterials are expected to produce game-changing fluid properties with a very low concentration of nanomaterial (1% in the fluid system) due to their large surface area and the dominance of surface, van der Waals, molecular, and atomic forces which are all physical forces [30]. The extremely high surface-area/volume ratio of nanoparticles can provide several other technical advantages for safe and cost-effective drilling operations. The large surface area/volume ratio of nano-based mud additive, for example, is expected to improve the thermal conductivity of nano-based fluids. As a result, the better cooling conductivity of drilling mud will provide efficient cooling of the drill bit, resulting in a significant increase in the bit's operating life cycle. Due to the extremely small sizes of nanoparticles, the abrasive action of nano-sized particles on downhole equipment is reduced due to their low kinetic energy impact hence leading to less wear and tear of equipment [30].

In 2009, one of the earliest studies on wellbore stability using nanoparticles in drilling fluids was published by Sensoy et al. [31]. This study looked into the possibility of reducing permeability by plugging shale pore throats with nanoparticles. Thus, a pressure transmission test was used to evaluate the permeability reduction of Atoka and Gulf of Mexico shale using nanosilica with different sizes of 5 and 20 nm and concentrations of 10-40 wt.%. When compared to using common brine, fluid penetration into the formation was reduced by up to 98%. Furthermore, 20 nm N.P. contributed better shale sealing performance than 5 nm N.P. It was demonstrated that N.P. can reduce shale permeability and thus prevent water filtration loss.

Further research on the effects of nanoparticle type and size on wellbore stability was conducted in 2012. For instance, Ji et al., [32] and (Riley et al., [33] evaluated the performance of nanosilica on Manco's shale samples. In this study, the use of nanosilica resulted in a significant reduction in permeability of up to 98%. Furthermore, higher nanoparticle concentrations resulted in better plugging efficiency.

Laponite nanoparticles were used in a WBDF for wellbore stabilisation and mechanism analysis by Huang et al.,[34]. The findings of this study revealed that laponite N.P. can fill clay

interlayer spaces via attraction and repulsion forces, resulting in reduced shale permeability and increased wellbore stability. Furthermore, laponite N.P. has low free water contents and excellent shear-thinning properties, allowing a nanofilm to form on the shale's surface to limit water invasion. Hoxha et al.,.[35] studied the mechanisms that explain shale stability through N.P using modified nanosilica based on surface charge at different pH values. They used Derjaguin-Landau-Verwey-Overbeek (DLVO) curves to investigate the interaction of NP and shale. Based on the findings, they proposed that DLVO forces, such as van der Waals attraction and electrostatic repellency, should be considered when evaluating the interaction between nanoparticles and shale surfaces. They highlighted that the main mechanism involved was the intermolecular (or interparticle) interactions between nanoparticle and the interactions with charged shale surfaces, which resulted in the pressure transmission test being reduced by plugging pore throats. When plugging occurred, the near-wellbore pore pressure elevation decreased and effective stress decreased, resulting in wellbore stability. Furthermore, when using Mancos' shale, it was discovered that 20 nm modified nanosilica has better shale plugging capability than 5 nm particles. Finally, they suggested a maximum nanoparticle concentration of 5 wt.% taking into account the cost and logistical difficulties.

Martin et al. [36] investigated synthesised modified silica in water based to enhance the rheological properties under HPHT wellbore conditions. Formulations containing 0.5 wt.% silica with the highest absolute zeta potential value of 35.4 mV and 37.1 mV exhibited stable rheological and filtration properties at temperature of 232 °C. They used a cationic surfactant to functionalise the surface of silica nanoparticles. Based on the findings, they suggested that electrostatic repulsive and attractive forces on the surfaces of silica and bentonite played a major role in stabilising the mud system under elevated conditions. The performance of modified silica was due to the face-to-face electrostatic attraction between (modified silica and bentonite) and the edge-to-face (positive edge bentonite - negative face bentonite) seen in Figure 3 (b). This configuration traps modified silica between the clay particles forming clusters known as heterocoagulated formation hence leading to rheology and filtration property enhancement.

Figure 3. Repulsion and attraction between bentonite particles and (a) unmodified (b) modified nano silica [37]

Riley et al. [38] investigated silica nanoparticles in water-based mud to enhance inhibition of shale materials and compared it with a synthetic based mud that is commonly used for wellbore stability in shale formations. A formulation containing 3.0 wt.% silica reduced permeability by 20.1% more than the sample without silica nanoparticles, demonstrating its ability to plug and seal micro-pores and micro-fractures. Liu et al. [39] carried out a study using novel latex and aluminium complexes with diameters ranging from 80 to 345 nm as potential shale stabilisers. They discovered that superior shale stability resulted from reduced pressure transmission and improved membrane efficiency caused by bridging and sealing micro and nano scale pore throats.

According to Zhang et al [40], they reported that studying nanoparticles in an oil-based mud fluid had similar results as testing in a water-based mud and helped to improve shale stability by plugging micro-pores and micro-fracks. A field test was also carried out using the NP-based OBF, and it was discovered that even after being run for 30 days, the mud still demonstrated good overall performance, and borehole instability was significantly reduced, with problems such as hole collapse and stuck pipe not occurring.

Nasser et al., [41] stated that nano fluids are good to use in new oil production techniques and in solving extreme drilling operation challenges such as found in HPHT formations. According to Abdo et al. [42], they stated that using nanofluids enabled the exploration of unconventional and deep-lying reserves with high temperatures and pressures that would not have been explored if conventional additives had been used instead. Furthermore, unproductive time was

reduced as a result of the elimination of potential problems and challenges, resulting in significant cost savings. [43].

Drilling mud is costly, and any excessive increase in filtrate loss will lead to corresponding costs. More so, filtrate loss in the formation reduces the productivity of the well as it leads to skin factor increase as a result of formation damage [44]. Nanoparticles, unlike bulk materials, can invade ultratiny pore spaces of nanoscale, forming physical adsorption bridges and effectively plugging pore spaces. The hydrostatic pressure forces nanoparticles into formation pores thereby plugging the nanopore spaces. This compaction also reduces the filter cake's permeability leading to less filtrate loss due to reduced porosity. This, in turn, improves wellbore stability and drilling operations [30, 45]. According to the evidence presented above, drilling fluids containing nanoparticles can improve mud rheology and plug pores, forming compact plugged layers and preventing water invasion into formations.

Designing stable drilling fluids successfully saves the petroleum industry a lot of money. During drilling, formation porosity and permeability control the flow of fluids in the formation. But other factors like drilling fluid hydrostatic pressure and other fluid pressures surrounding the wellbore play a vital role. Since fluid flows from a raised pressure direction to a low pressure, the main aim of the drilling mud is to sustain and maintain a high hydrostatic pressure than that of the formation in order to stop a kick and blowout. That means, preventing filtrate loss is a good option than remedying treatments to reduce the associated risks and costs.

The entire cost of drilling a well mostly depends on the drilling operation [25]. Therefore, a successful drilling fluid design safeguards the efficiency of the drilling program which amounts to 80% of the entire total drilling budget [46, 47]. Nanoparticles have been used in the petroleum industry to address the issues above especially with high pressure and high temperature (HPHT) well drilling operations. Though success has been registered with the application of nanoparticles in drilling mud systems, nanoparticles are still very expensive when used in drilling operations hence a cheap replacement is still needed.

Table 2. Current studies investigating the addition of nanoparticle impact on the rheological properties of drilling muds

Author (s)	Nanoparticle type	NP size (nm)	optimization	Optimum concentration of NPs	Drilling mud type	LPLT	HPHT	Reference
Huang et al.	Laponite	25	According to the findings of this study, laponite N.P may fill clay interlayer spaces via attraction and repulsion forces, resulting in decreased shale permeability and increased wellbore stability. Furthermore, laponite NPs have low free water contents and excellent shear-thinning properties, allowing a nanofilm to form on the shale's surface to limit water invasion.	0.1, 1.0 and 2.0 wt.%	WBM- 4 wt.% bentonite	o	o	[34]
Hoxha et al.	Modified silica	20	Improved wellbore stability. Based on the findings, they proposed that DLVO forces, such as van der Waals attraction and electrostatic repellency, should be considered when assessing the interaction between NPs and shale surfaces. They highlighted that the primary mechanism involved was intermolecular (or interparticle) interactions between nanoparticles and interactions with charged shale surfaces, which resulted in the pressure transmission test being reduced by plugging pore throats. When plugging occurred, the near-wellbore pore pressure elevation decreased and	5 wt.%	WBM -bentonite	o	o	[35]

			effective stress decreased, resulting in wellbore stability.					
Martin et al.	Silica	67.54	Improved the filtration characteristics. Modified silica performed better than unmodified silica as the volume of filtrate loss was less compared to other mud samples especially muds with a higher value of zeta potential (35.4 mV and 37.1 mV). The performance of modified silica was due to the face-to-face electrostatic attraction between (modified silica and bentonite) and the edge-to-face (positive edge bentonite - negative face bentonite). This configuration traps modified silica between the clay particles forming clusters known as heterocoagulated formation. This formed structure holds and retains the fluid within the formation hence reducing the filtrate volume loss	0.5 wt.%	WBM – 22.5 g bentonite	o	o	[36]
Mahmoud et al..	Fe_2O_3	50	Improved filter-cake and filtration properties at HPHT conditions which might be because of a better packing of the solid particles during the filter-cake generation leading to a less-porous structure.	0.3 - 0.5 wt.%	WBM-7 wt. % bentonite	o	o	[48]

Barry et al.	FeO$_3$ – clay Hybrid	3 and 30	Increased the rheological properties and reduced filtration loss due to the restructured mode of clay platelet interaction attributed to a modification in surface charge. Improvement in rheological properties was due to the electrostatic repulsive and attractive forces in the drilling mud formulation	0.5 wt.%	WBM-5 wt. % bentonite	o 14%	o 37% and 47%	[49]
William et al.	CuO and ZnO	50	Enhanced electrical and thermal properties at HP/HT conditions when NPs were increased from 0.1 – 0.5 wt.%. The increased thermal conductivity of nano-drilling fluids is due to the nanoparticles' high specific surface area.	0.1 - 0.5 wt.%	0.4 wt.% XG in water	o	o	[50]
Al-Yasiri et al.	Graphite-alumina (Gr-Al$_2$O$_3$) hybrid NP	80 and 400	Decreased filtrate loss. At 0.8 wt.% Gr-Al$_2$O$_3$ concentration in WBDF, thermal conductivity was improved by 10% at room temperature. The electrical conductivity was also improved by 8.4% and zeta potential was increased 13% by addition of 0.8 wt.% Gr-Al$_2$O$_3$. The presence of nanoparticle sizes increases the particle's surface area per unit volume. Because heat transfer is a function of surface area, it ultimately improves the nanoparticles' ability to transfer heat to the base fluid.	0 – 0.8 wt.%	WBM – 20 g sodium bentonite	o	o	[51]
Saboori et al.	CuO	4	There was significant decrease in fluid loss with addition of CuO/PAM nanocomposite. The addition of NPs decreased the thickness of mud cake.	Acrylamide monomer/CuO:10/1 1-10 g	WBM- 10 g bentonite	o	o	[52]

			Thermal conductivity was enhanced with addition of CuO/PAM nanocomposite.					
Mahmoud et al.	SiO_2	50	Improved and stabilised rheology, improved filtration properties and reduced mud cake thickness.	0.5 wt.%	WBM- 7 wt.% bentonite, WBM - bentonite	o	o	[53]
Parizad et al.	TiO_2	10 and 15	Enhanced mud properties, improved thermal and electrical conductivity and improved filtration properties.	0.35 – 0.9 wt.%	WBM – 4wt.% bentonite	o	o	[54]
Medhi et al.	ZnO	40 - 50	There was consistency in rheological properties with addition of ZnO. Addition of 1 wt.% led to greater fluid loss control capabilities.	0.8 – 1 wt.%	NDDF and ZnO NDDF – 20 wt.%	o	o	[55]
Ali et al.	SiO_2/KCl/xanthan nanocomposite	500 nm -1 µm	Adding 0.4 wt.% NP increased the rheological properties. Filtrate loss and mud cake thickness were reduced using NP at 0.4 wt.%. Shale swelling was reduced by 41 and 52 % by adding 0.4 wt.% of SiO_2/KCl/xanthan nanocomposites.	0.05 – 0.4 wt.%	WBM – 20 g bentonite	o	o	[56]
Jia et al.	Polymer grafted silica nanocomposites	20	2 wt.% of copolymers led to higher YP and low PV. Filtration loss was reduced after aging at a high temperature of 260 $^\circ$C	0.5 – 2.0 wt.%	WBM – bentonite	o	o	[57]
Sajjadian et al.	TiO2, ZnO, untreated and	40, 50 and 40	Rheology of WBDF improved by addition of 0.143 wt.% of f-MWCNTs.	0.143 wt.%	WBM – 15 g bentonite	o	o	[58]

Author	Material	Size	Description	Concentration	Base fluid			Ref.
	functionalised MWCNT		F-MWCNTs resulted in the reduction in drilling fluid filtrate loss volume.					
Ahasan et al.	ZnO	27.82	Nanoparticles were more effective in improving the rheology at concentrations of 0.1 and 1.0 wt.% compared to a higher concentration of 2.0 wt.%. Mud cake thickness reduced with addition of 1.0 wt.% ZnO equivalent to 55% decrease compared to the conventional drilling mud.	0.1 – 1.0 wt.%	WBM – 10 g bentonite	o	-	[59]
Beg et al.	TiO$_2$	250	At both LPLT and HPHT conditions, WBDF containing 1 wt.% led to a decrease in filtrate loss compared to the WBDF containing 0.5 wt.%.	1 wt.%	WBDF – 4 wt.% bentonite	o	o	[60]
Keshavarz Moraveji et al.	SiO$_2$	12, 22, 54	Adding NPs to glycol drilling fluid improved the rheology of the mud. This improvement is directly related to NP size and concentration. The filtration properties of the NP mud were better than the glycol mud. NPs improved the thermal stability of the mud. Adding silica NPs to glycol mud improve shale stability.	2.5 wt.%	NP- WBDF and Glycol-based mud– 20 g bentonite	o	-	[61]
Rana et al.	Glucopyranose modified graphene (Glu-Gr)	2 µm	Glu-Gr in WBM improved the rheological properties of the mud fluid and exhibited high thermal stability after hot rolling. Glu-Gr in WBM displayed reduced filtrate loss and exhibited high dispersion recovery rate as compared to the base fluid.	0.85 wt.%	WBM - bentonite	o	-	[62]

						@ LPLT	@ HPHT	
Zhang et al.	Calcium carbonate NP (CaCO$_3$) NPs	10 - 40	Improved rheological properties when 1 wt.% NPs were added but when NP concentration increased to 2 wt.%, rheology decreased because of dispersion efficiency. The API filtration loss was reduced by the addition of NPs in the mud system and the thickness of the mud cake was reduced.	1 wt.%	WBM - bentonite	o	o	[63]
Rezaei et al.	Iron oxide NP Fe$_3$O$_4$	15- 20	Iron oxide NPs enhanced the rheological properties and filtration properties especially in salt free conditions than in salty formations. NP mud exhibited greater cutting carrying capabilities than the conventional drilling mud suggesting that they might be used in to enhance cutting transport.		WBM – bentonite 28 g	o	-	[64]

Note: *o means enhancement; @ LPLT- Low Pressure-Low Temperature: @HPHT- High Pressure-High Temperature

2.1.Drilling fluids waste

Oil and gas industrial operational exploration discharges of spent drilling fluid, produced water, accumulated drill cuttings from oil and gas, accidental spillage, or improperly disposed drilling wastes have serious negative effects on humans and the environment. To meet the stringent environmental standards for waste disposal, the oil and gas industry faces various technological challenges to ensure a clean and safe environment. Oil and gas industry generates a large amount of spent drilling fluid, produced water, and drill cuttings, which are very different in every drilling operation in terms of composition and characterisation. When oil and gas drilling fluids and cuttings are deposited on the ground, the liquid fraction of the chemicals begin to permeate through the ground, eventually destroying the organisms in the ground and polluting the groundwater [65]. As a result, compliance with net zero discharge requirements for oil-based drilling fluids (OBFs) and water-based fluids containing toxic additives and associated drill cuttings has become a major challenge in the industry. Due to the European Union (EU) Waste Framework Directive (WFD), new regulations for waste recycling in Eu member states, including the United Kingdom have been implemented with the goal of preventing and reducing waste landfilling [66, 67].

Different environmental organisations and government agencies developed a guideline in 1970 that is now used in various processing industries, including the oil and gas industry [65] . It follows that drilling is one of the most chemically intensive operation in the oilfield and has a substantial source of chemical exposure and subsequent health effects [68, 69]. OBFs containing drill-cutting discharge in offshore-drilling are not permitted in most areas in oil-based drilling operations. A large number of pollutants are introduced into drilling fluids during the drilling operation, posing a significant challenge in terms of solid waste handling in process operations. Those drill cuttings and spent drilling fluids are processed and shipped to shore for disposal [70]. For onshore operations, pit burial is the common method used for drill cuttings management. The process involves drill cuttings being temporarily stored in earthen pits for both offsite and onsite operation before disposal to the land or subsurface [71]. Therefore, the sources, toxicity and characterisation of drilling wastes, and environmentally the additives present in the drilling wastes should be known in order to provide support for designing an effective waste treatment plan. The variations in drilling fluid composition and geological structure produce a complex mixture of drilling fluid wastes that cannot be classified into any traditional drilling fluid waste profile. For example, in OBFs, base oil can be of various types, and the additives used in OBFs can be very complex, such as surfactants, organophilic clays,

nanoparticles and viscosifiers. The toxicity of such a mixture may be difficult to assess, and when the spent mud is discharged, it may pollute the environment [69, 72]. Hudgins et al. [73] presented chemical discharge quantities and concentrations in the North Sea exploration and production activities. The data was from ten operating companies and six chemical suppliers Fig 4. It was also discovered that the weighting agents, salinity, and bentonitic chemicals accounted for approximately 90% of the total WBM discharge. It can be concluded that approximately 53% of chemicals used in drilling operations are discharged as wastes, contributing to the pollution burden in the environment [73, 74].
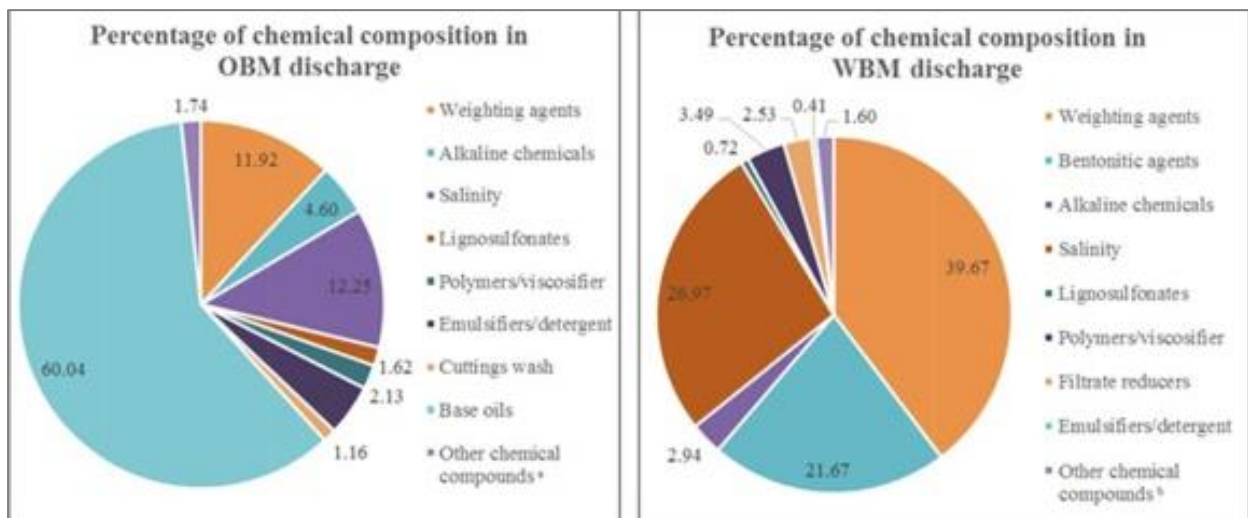
Figure 4. Percentage of individual chemical constituents present in OBM and WBM discharge [73].

2.2.Drilling technologies

The industry recognises that developing oil and gas fields from a small number of pads reduces the surface footprint and environmental impact while increasing the overall economic efficiency of upstream projects [75]. Because of the active development of shale formations, multi-well pad drilling technology has seen an emergence in recent years. Modern drilling technologies have been introduced in conjunction with nano additives to reduce the impact of localization of wells or precision for example pad drilling, steerable drilling.

2.2.1. Pad drilling

Recent years have seen a rebirth in multi-well pad drilling technology due to the active development of shale deposits **[75].** Combining wells into pads has long been recognised as a technique of developing oil and gas fields with difficult surface conditions feasible. The industry has recognized that developing oil and gas fields from a small number of pads reduces

the surface footprint and environmental effect while increasing the overall economic efficiency of upstream projects [76]. Many researchers have reported how effective well pad is.

Pad drilling techniques have enabled rig operators to drill groups of wells more efficiently because improved rig mobility reduces the time required to move from one well location to the next while also reducing the overall surface footprint. Drilling rigs can be moved metres rather than kilometres to complete additional wells. Rigs are frequently placed on tracks or pads to allow for easier mobility around surface locations, shortening the time between drilling activities and reducing labour required during movements.

By consolidating wellheads on a single site reduces the environmental impact of facility construction and pipeline gathering systems across an area in comparison to the increased production. Pad drilling also allows the operators to drill multiple wells in less time than they would with just one well per site. Wells can be drilled next to each other to maximise exposure to the target formation, increasing total production. [75].

Parallel execution of jobs is another approach to increasing efficiency in well pad development. Implementation of drill-drill, complete-complete, and drill-complete procedures at the same time by handling simultaneous (done within a cluster of wells) and concurrent (done inside different clusters of wells) operations is another direction for higher efficiency in well pad development which allows parallel execution of jobs **[77].** Furthermore, an industrial application of technology to stimulate multiple pay zones of multiple wells on the same well pad while drilling additional wells resulted in time savings, improved production rates, and reduced environmental impact [78]. From the above-mentioned research among other effects

The studies mentioned above, among other effects, show that well pad drilling speeds up the construction of oil and gas fields, however the benefits of the technology are not limited to the development stage only but continue to manifest themselves in day-to-day operations. Although multi-well pad drilling is a well-established and widely used technology, it appears that there is a significant void in modern information and literature about well pad configurations with an unequal number of wells. It was only recently demonstrated that well pad designs with an unequal number of wells in groups further improves economic performance of well pad drilling projects and are cost effective than those with an equal number of wells [79, 80].

2.2.2. Rotary Steerable systems

Directional drilling has transformed oil and gas production by allowing operators to explore previously inaccessible geologically challenging reservoirs. Rotary steerable systems (RSS), which can provide continuous rotation, constant steering, and smoother boreholes, are a technology that has expanded the operations envelope in the growing number of horizontal and deviated wells. RSS technology is entering its fourth decade. The first RSS tools were commercialized in the 1990s, after being developed in the late 1980s and early 1990s. Their success was spurred in part by early extended-reach horizontal wells and the need for directional drilling technology capable of drilling those wells. These rotary steerable tools are classified into two distinct design categories whereby:

Point-the-bit: Point-the-bit rotary steerable tools use a variety of methods to tilt the drill bit, resulting in an off-axis direction and side force for steering. One common method is to bend an internal drive shaft located within a non-rotating housing [81]

Push-the-bit: By extending external steering pads against the borehole wall, push-the-bit rotary steerable tools generate a side force at the bit. The application of side force from steering pads mounted on a rotating housing is the most common indication [81]. As the rotary steerable service industry matured, evolved, and responded to changing market demands, more opportunities for push-the-bit designs emerged than for point-the-bit rotary designs. This shift has been driven largely by the unconventional horizontal well market, which has created a demand for systems that can steer sometimes complex and extended reach trajectories with increasing reliability and consistency in performance and results [81]. Only 21% of RSS wells are pure point the bit, while 72% are push the bit [82].

The RSS market has evolved and expanded over time. RSS technology, which was a niche product in the 1990s, accounted for more than 60% of the US directional drilling market by 2017, and the majority of the worldwide directional drilling market was addressed by RSS technology beginning in 2016 [82]. The RSS tool is designed to enhance drilling performance while maintaining wellbore integrity. With the development of the new RSS tools, came with more advantages.

To change the trajectory of the well, conventional directional drilling techniques require the use of bent housing downhole motors that are oriented in the borehole and "slid" along the borehole without rotating the drillstring. To achieve the desired three-dimensional wellbore trajectory, periods of "slide" drilling are interspersed with periods of rotary drilling [82, 83].

Conventional directional drilling methods use bent housing downhole motors that are aligned in the borehole and "slid" along the borehole without rotating the drill string to attain a change in the well's trajectory. To achieve the desired three-dimensional wellbore trajectory, periods of "slide" drilling are interspersed with intervals of rotary drilling. Technology that allows for full three-dimensional directional drilling control while drilling with continuous drillstring rotation from the surface. No "slide" drilling is required. This has led to immediate benefits listed below. These include significant time savings as a result of ROP improvements, continuous effective hole cleaning, and drilling a hole with less "tortuosity [83]. Other advantages brought by using RSS are.

Easy to repair: The RSS tool was designed in a highly modular form for simple disassembly and assembly to allow repair almost anywhere in the world. All parts that are expected to be subject to significant wear and erosion are assembled into one valve/motor/actuator (VMA) assembly that can be removed as a single piece from the outside of the tool [82].

Efficient: The entire tool can be tested on the bench without the need for a flow loop or other special installation. This eliminates the need for a specialized facility, enables repair and maintenance to be delegated to locations around the world, and allows for quick turnaround and optimum tool utilization. This, in turn, is a critical factor in assuring that the economics of RSS drilling align with the new market paradigm.

Simplicity: The RSS tool is reliable, cost effective, simple, and easy to train peoples to use for both rig floor operations or for repair and maintenance. Push the bit design has been found to be simpler and more cost effective for the reasons stated above

Logging while drilling (LWD) Imaging: Wellbore quality is essential during an oil and gas asset's assessment, drilling, completion, and production operations. The RSS tool is designed to enhance drilling performance while ensuring wellbore integrity by correctly sharing time between off and steering modes. The ability to assess the integrity of the wellbore proactively allows the resulting wellbore integrity to be tested, providing significant technical and operational advantages [82].

Safety*:* Fewer trips in and out of the hole of the drillstring should be required when drilling with rotary steerable systems. Fixed cutter bits are commonly used in these systems where Tricone bits were previously used for directional control. Furthermore, continuous rotation at high rotary speeds results in extremely efficient hole cleaning, eliminating the need for numerous short trips [83].

Environmental: Drilling with rotary steerable assemblies produces a hole that is more in-gauge than drilling with steerable motor systems. This fundamental advantage results in less drilled cuttings waste and less drilling fluid loss. Furthermore, because the cuttings are fresher as a result of continuous hole cleaning, they are easier to clean, and less drilling fluid is lost. When an in-gauge hole is drilled, the environmental impact and waste disposal costs are both reduced. Where "skip & ship" or cuttings re-injection systems are used, the constant stream of cuttings combined with reduced waste volumes from the use of rotary steerable systems is a recognised benefit. The significant benefits of using rotary steerable technology have been adopted by the industry, as evidenced by the industry's continued exponential growing demand. [83].

2.2. Nanoparticle drilling fluid cost simple calculations

Many technological processes can increase efficiency through controlling liquid thermophysical parameters by altering hydrodynamics and by means of nano additives. Based on what is now known about nanofluids, it is assumed that the properties of nanofluids vary depending on the concentration of nanoparticles in the fluid. This is due to the presence of intermolecular forces, and as nanoparticle concentration increases, it causes other effects in the dispersion such as agglomeration, flocculation, increased or decreased friction, surface charge, and so on. These effects affect the properties nanofluids. Therefore, it is important to systematise and analyse the data thoroughly [84] as the improper selection of additive concentration can lead to the system incurring extra operational costs due to failures during operations. Additive properties could then be compared to those of distilled water to ascertain the costs. Different commonly used nanofluids were compared basing on their costs whose additive concentration varied. According to Hsieh et al. [85], the properties of nano fluids such as density (ρ), Kg/m^3, which is needed to ascertain their unit price in solution were presented basing on the data in the literature. Unit price of the nanofluid solution C_{Nano} was assumed to be fully a dependant of the unit cost of the nanoparticles purchase $c_{u, EUR}/1$ g, and the unit mass of those particles m = ρ V. From equation (1), C_{other} represents the variable addition costs due to the preparation of the solution. Those costs can vary considerably due to the system's operational conditions and the means of condition stabilisation. Sarsam et al. [86] noted that systems that rely on surfactants are the cheapest and least energy-consuming systems. Whoever, at high pressure and temperature, the latter are not applicable. Also, purchase and operational costs are generated by the use of mechanical stirrers and ultrasonic cleaner. Further in the analysis, the term C_{other} is disregarded. The nanofluid preparation total unit cost C_T is

given as equation (2), which also puts in consideration the unit purchase price of the base liquid C_{Base}.

$$C_{Nano} = \frac{C_u \rho V}{0.001} + C_{other}, \frac{EUR}{dm^3} \tag{1}$$

$$C_T = C_{Nano} + C_{Base}, \frac{EUR}{dm^3} \tag{2}$$

Were C_{Nano} is the nanofluid unit price, C_u is the purchased nanoparticle unit cost in EUR/g, ρ is the liquid density, V is the volume, C_{other} represents the extra additional costs, C_T is the total unit costs, and C_{Base} represents the base liquid unit price. It should be noted that the purchase costs per unit of nanoparticles and the base liquid (i.e., deionised water) were based on the observed market prices. Table 3 presents the results of the calculations. The concentration of nanoparticles of specific size changes the price of preparation of 1 m^3 of nanofluid. The thermophysical data availability from the literature was used to determine the choice of nanoparticles. Gross prices contained 23% VAT rate [87].

Table 3. Gross total unit costs of nanofluid prepared with different nanoparticle concentrations [87].

No	Nanofluid	Nanoparticle size (nm)	Nanofluid gross costs, EUR		Concent-ration, vol, %	Market net unit price of material, EUR
			of 1 dm^3, EUR	of 1 m^3, EUR		
1	Pure DI	-	0.07	70.76	-	54.49
2	TiO$_2$	4 - 8	3.03	3034.21	0.04	10 g ~ 60.47
			5.26	5256.76	0.07	
				7479.37	0.1	
3	Al$_2$O$_3$	<50	1.4	1403.74	0.04	10 g ~ 27.21
			2.4	2404.91	0.07	
			3.4	3403.21	0.1	
4	SiO$_2$	10 - 25	1.19	1186.35	0.04	50 g ~ 113.93
			2.02	2024.47	0.07	
			2.86	2862.58	0.1	
5	Ag	<100 nm	223.47	223,473.09	0.04	1 g ~ 455.81
			391.01	391,010.53	0.07	
			558.54	558,542.26	0.1	

3. Nanomaterials fate and behaviour in the environment

Scientific analysis of the fate and potential environmental implications of drilling mud discharged into the marine environment can help to make informed decisions and reduce environmental damage. Therefore, offshore petroleum operators, regulators, government agencies, the fishing sector, and environmentalists would all benefit from a quantitative methodology for predicting the possible implications of discharged drilling mud fines.[88]. There are basically two primary drilling fluid types used in drilling operations such as, water muds (WBMs) and nonaqueous drilling fluids (NADFs) [89]. Adverse effects may be caused on the aquatic biological systems due to toxic chemicals being discharged into the environment and their degree of effect will depend on their concentration and dosage, the type and exposure duration of chemicals [90].

With the increasing rates of nanomaterial production, their effect to the ecosystem health and release in the environment is becoming a concern needing address [91, 92]. For that reason, the need to first understand the fate and behaviour of produced nanomaterials is a must. Produced nanomaterials end up entering the atmosphere through deliberate and accidental releases such as air pollution and the disposal of solid or liquid waste from manufacturing facilities and processes. Disposed nanomaterials will be deposited on land and water surface. Those emitted on land will potentially contaminate the soil and move into the ground and surface waters. Particles in accidental spillages, direct discharges, solid wastes and wastewater flow can be carried to marine environments by rainwater or wind runoff. The largest releases into the atmosphere are spillages related to the transport of processed nanomaterials from the manufacturing facilities to other locations.[93].

Ecological studies on the behaviour of engineered nanoparticles (ENPs) is based on many investigations from geosciences that has studied the behaviour of naturally occurring nanomaterials in the environment [94]. Even though natural nanoparticles are diffusely and randomly structured within the environment, industrially manufactured nanoparticle powders or suspensions contain pure nanomaterials of very uniform fine size, shape and structure. These types of materials have special properties like the photo catalytic activity of nano-TiO_2 or carbon nanotubes (CNTs) with high tensile strength which makes them better candidates for making novel products and applications [95]. On the other hand, these special characteristics make it so unpredictable to determine their fate and behaviour in the environment [94].

Inhalation exposure due to the nano size of ENP will potentially occur to airborne particles consisting of nanoparticles of size ranging from a few nanometres to micrometres in diameter. Nanomaterials can aggregate into bigger particles or longer fibre chains that can change their properties and affect the way they behave inside and outside environments as well as their potential exposure and entry into the human body [91, 92, 96]. Due to nanomaterial small diameter and high surface area, high surface activity and also degrading into smaller particles after deposition, they can position themselves in the breathing system and cause nanostructure influenced toxicity. Particles developed from nanomaterial degradation can in the same way exhibit serious potential risks if they have a nanostructure dependent biological activity. Nanoparticles have high deposition efficiencies in the lungs of healthy individuals and even higher efficiencies in individuals with asthma [97]. Stahlhofen et al. [97] also stated that the 20 nm particle deposition was 2.7 times greater than 100 nm particles and 4.3 times greater than 200 nm particles. From the study of Kreyling et al. [98], the authors observed higher deposition efficiencies in asthma patients than healthy patients because of the clearance ability decrease. They indicated that 50 and 100 nm particles had less than 25 percent clearance in the first 24 hours after inhalation.

Table 4. Dangers of using nanoparticles

Nanomaterials	Possible effects	Reference
Carbon, silver and gold nanoparticles	They spread to various organs and tissues including the central nervous system	Oberdorster et al. [99] Oberdorster et al. [100] Semmler et al. [101]
Quantum dots, carbon and TiO_2 nanoparticles	Penetrate the skin	Mortensen et al. [102] Zhang et al. [103] Baroli et al. [104] Rouse et al. [105]
Carbon, silica nanoparticles	Fibrosis, granulomas and pulmonary inflammation	Oberdorster et al. [100] Warheit et al. [106] Chou et al. [107] Lam et al. [92]

By deliberate (intentional) or accidental (nonintentional) means, the outer skin may be exposed to nanoscale solid particles [102, 104, 105, 108]. The human skin has 10 µm deep, hard layers of dead keratinized cell that is impermeable for particles, water- soluble components and ionic compounds. Intentional exposure of the skin to nanomaterials is through creams, application of lotions, detergents and socks containing silver nanomaterials. Nonintentional exposure may

be during nanomaterial manufacturing or combustion [93]. Every design involving any new material requires that risks to health and the environment the design is associated to addresses the use and disposal of the products. This will help protect the employees who create them, those using them and will also protect the ecosystem [93]. The following summarises the current state in regard to the fate and behaviour of ENPs in the environment, air, water and soil.

Water: Nanoparticles distributed in water always act like colloids. Particles or droplets that are well distributed in a medium are referred to as colloid. They are always unstable as they stick to one another because of the attractive forces (electrostatic) or repel each other because of the repulsive forces. Water bodies contain dissolved materials including nanomaterials. The fate and behaviour of nanomaterials in water is determined by pH, salinity and the existence of organic material. Naturally present Organic material (NOM) can result to decomposition of C_{60} fullerenes and their aggregates hence altering the size and shape of the particle [109]. Certain MWCNT in water can be stabilized by a NOM such as humic acid thus preventing their settlement [110]. Special surface changes can be used to produce carbon nanotubes (CNT) so that they do not aggregate. It's always difficult to present justified statements about the fate and behaviour of CNT in the environment because it is very polymorphic. The influence of the surrounding environment on behaviour of nanomaterials such as metal or metal oxides has to be investigated especially in presence of NOM [93].

Air: Nanoparticles migrate from higher concentration zones to lower concentration when they enter the atmosphere. Air currents travel vast distances from their original source distributing the particles rapidly. Nanomaterials appear to accumulate into larger structures hence making detecting them in the air difficult as simple size distribution measurements hardly distinguishes agglomerates from natural particles. The particle diameter determines the rate at which particles in the air are deposited in the water, on the ground or onto plants. Nanoparticles deposit much slower from the air in comparison to larger particles due to their smaller diameter [93].

Soil and sediment: Unfortunately, there is extensive research on the mobility of natural colloids in the groundwater and soil leading to assumptions about nanomaterial behaviour. Nanomaterials in sediments and in the soil bind themselves to solids [111]. Possibly, the potential toxicity and bioavailability of nanomaterial for soil organisms depends on whether they bind on naturally present Organic material. The bioavailability of Nano silver in complex

media like soil is lower than that of water because the reactive silver ions bind on the components in the soil [93].

4. Environmental, Health and Safety assessment of using nanoparticles

Environment risk assessments of ENP need thorough characterisation of the nanoparticles and their aggregates. To allow both impact and exposure assessments and to determine environmental concentrations, further quantitative analytical methods are required [1]. From the National Nanotechnology Initiative (USA), thousands of tonnes of silica, ceria and alumina in tons in the form of ultrafine abrasive particle blends are used annually in slurries including nanoparticles [112]. The Carbon Nanotechnology Research Institute (Japan) within the next five years plans to increase its annual output to 120 tonnes [112]. Because nanomaterials are becoming part of our everyday lives, exposure of nanomaterials to the environment is becoming unavoidable and as a result, research in nanotoxicity has gained attentions. If their use increases, the number of exposed populations to nanoparticles will constantly keep growing. Even though there have been visible advantages regarding to the ability of nano size materials, there is still unanswered questions regarding to how the day-to-day use of nanoparticles impacts the environment. The main issues to be resolved before fabrication of nanomaterial is their toxicity to the environment and to humans. There has been a lot of discussions about the new properties of nanomaterials and how they could result to serious biological effects with the capability of causing toxicity. Therefore, it will be better that nanotoxicology research uncovers and understands how the environment is influenced by nanomaterials so as to avoid undesirable properties [93]. Because of their nanoscale, engineered nanomaterials inhalation exposure can occur to airborne particles.

According to Karkare [113], the effect of nanomaterials on the health, safety and environment (HSE) can be classified into two types of nanostructures such as, fixed nanoparticles and free nanoparticles. Nanoscale particles incorporated into a material, device and substance are called fixed nanoparticles. Individual nanoparticles present at any point of production for use are free nanoparticles. The health and safety issue are on free nanoparticles which appear in powder form or in liquids containing nanoparticles. The particles can be released into the atmosphere and come into contact with humans. In oil and gas industry, free nanoparticles are the likely nanoparticles to be pumped in the wellbore and reservoir with drilling, waterflooding, EOR or completion fluids. These nanoparticles possess the ability to penetrate the human body either by being ingested or absorbed through the skin. These nanoparticles in the body become very

mobile and might interact with the cells in the body. The possible dangers to this are that they will affect the cells that ingest and kill foreign bodies and will interact with biological processes in the body. Nanomaterials as you expose them to tissues and fluids in the body will absorb onto their surface some of the macromolecules they meet because they possess a broad surface area, this can affect the regulatory mechanisms of enzymes and other proteins in the body. According to Nabhani et al. [114], SWCNT have been found to have severe health effects on lung cells in rats.

Apart from the atmosphere and aqueous ecosystems, the soil may be the main sink for nanoparticles [115, 116]. According to Boxall et al. [117], nanoparticles released into the soil may be degraded by biotic and abiotic processes, sorbed into soil particles, or transported to groundwater through runoff, drain flow and leaching. According to Hanna et al. [118], marine and estuarine sediments are the endpoint for most nanoparticles due to enhanced sedimentation and aggregation. Heavily used ZnO, CuO, NiO nanoparticles were tested for toxicity on the estuarine amphipod and results found that Zn dissolved greater than other NPs in sediment pore water samples at a high dissolution rate of zinc oxide nanoparticles. Investigations suggested that sediments with zinc oxide nanoparticles might be hazardous to aquatic organisms [119, 120]. ZnO nanoparticles have been found to possibly penetrate the soil through accidental and intentional release. Some nanoparticles have been found to affect and influence crop yield and development, circulate in plant tissues, including edible parts [121, 122].

Until now, all concerned agencies such as The food and drug Administration in the US or the Health and Consumer Protection Directorate of the European Union, Environmental Protection Agency, National centre for nanoscience and technology in China, National institute for nanotechnology in Canada and the United nations educational, science and cultural organization (UNESCO) and UNESCO's member states have recognised the potential for new risks associated with nanomaterials but have not currently released any special regulations in relation to handling, labelling or regarding to their production [123]. The present risk management techniques are not capable of evaluating the risks connected with nanoparticles because they are based on exposure presented in mass instead of quantity or surface area [123]. In most cases, the Material Safety Data Sheet does not distinguish between bulk and nanoscale materials. Furthermore, existing risk assessment methods are unsuitable for the hazards associated with nanoparticles because they are based on mass exposure rather than quantity or surface area [123]. There is also, an inadequacy of devices to perform routine identification and measurement of nanoparticles in water, air or soil. It is therefore necessary to carry out

research on nanotoxicity in order to form the basis for international and government legislations. This is so because there is less data on toxicology of nanomaterials. Better practices for safe management and disposal of nanomaterials for laboratory and industrial use have been suggested at the moment such as for, nano dispersions in liquid media, nanomaterial comprising of pressurised aerosols and for single walled carbon nanotubes powder [124, 125]. These include using personal protective equipment, environmentally friendly nanomaterials, avoiding skin contact, waste minimization, transport and disposal of nanoparticles as dangerous chemical wastes, the use of specialised containments and planned procedures on accidental release of nanoparticles [113].

5. Toxicity of nanoparticles

Nanoparticles for industrial use are classified based on their relative toxicity and potential risks to human/animal health, ecosystems, and wider environmental impacts. Their toxicity levels range from low to high. To classify them in terms of toxicity, a color-coding system is used [126]. The price ranges and potential toxicity values range from very low to very high, and the comparison table has been colour coded for easier evaluation of the results. Green, light yellow, and orange represent materials with low or moderate toxicity-cost combinations, whereas pink and red represent materials with both high risk and high cost as shown in Table 5. Nine of the NPs listed are classified as low/very-low toxicity, three as moderate toxicity, and ten as high/very-high toxicity. There are materials that are low in cost but high in toxicity, materials that are low to moderate in toxicity but very expensive, and materials that are both expensive and highly toxic.

Table 5. Nanomaterials' average price versus risk [127]

		Average Price Range				
		Very low (0-10 €/gr)	Low (11-50 €/gr)	Moderate (51-150 €/gr)	High (151-500 €/gr)	Very high (501+ €/gr)
Toxicity	Very Low	Titanium Carbonitride	Aluminium, Calcium Carbonate			
	Low	Cerium oxide, Boron Nitride, Magnesium Oxide	Hafnium Oxide, Indium Oxide, Silicon Carbide	Carbon Nanotubes, multiwalled (normal and charged, water soluble)	Carbon Nanotubes, double-walled, Iron Oxide	Carbon Nanotubes, single-walled
	Moderate		Graphene			
	High	Black Nanopowder, Titanium Boride, Aluminium Nitride				Gallium Antimonide
	Very High		Titanium Oxide	Copper Oxide		Gallium Arsenide

Toxicity and exposure to humans and the environment are the most pressing near-term issues related to nanotechnology. This is more of a health and safety issue than an ethical one, but because of nanotechnology's perceived novelty, there are increased concerns that it may pose new types of hazards or exposure risks, and thus new questions about how to deal with them. Research has proved that the physiochemical properties of substances can influence their biological functions. These properties include particle size, surface charge, surface area, shape etc. The main reason why nanotechnology has been attracting attentions is the unique properties that objects exhibit when they are formed at nano scale. These distinct properties of nanosized materials in comparison to their natural-existing form are both useful in the creation of high-quality products and dangerous when in contact with the body or spread in the environment [114]. Even though anything can be toxic when used in excess, the arising questions is, how toxic are nanoparticles at the potential concentration at which they might be applied for use? Nanomaterial toxic effects would be related to the type of nanoscale, shape coating and base material [93]. Because nanoparticles have such properties, they acquire new characteristics compared to larger form of the same substance they are formed of. Nanosized particles, for example, have a high potential to enter the body when in the form of aerosols or in contact with the skin [123]. When inhaled, they may deposit in the respiratory system,

causing pulmonary inflammation and lung tumours, which is unlikely to happen with larger particles, or they may be absorbed in the blood and move to other parts of the body [114].

Nabhani et al. [114] discussed the two major nanoparticles that may pose a significant health risk. The PTFE (poly tetra fluoro ethylene) and the other one being carbon nano tube (CNT).

PTFE fumes produced are extremely toxic to the lungs, causing pulmonary edema and death in laboratory rats and it has been reported that the same problems have occurred in workers exposed to great dose of PTFE fumes [114]. Single wall carbon nanotubes (SWNTs) show adverse health effects in rats like granuloma in lung that was not noticed for ultrafine carbon black despite the fact they are all carbon-based materials. Research showed that rats displayed pulmonary inflammation, oxidative stress and interstitial fibrosis. For multi walled carbon nanotubes (MWCNTs) both types, ground and unground, pulmonary inflammation and fibrosis in rats was reported and it was noticed that MWCNTs could be dispersed greater in lung and cause fibrotic lesions in the lungs [114]. This agrees with Gkika el al [127] work who concluded that MWCNT are very toxic.

Even with the commercial and technological advances of nanomaterials in many processes, and with their importance and benefits, they are still toxic, expensive to maintain and produce hence their application has been limited [128]. Their small size with a very large surface area will eventually render them harmful to the oil and gas industry as they can easily be absorbed through the skin and damage human organs if exposed to during use and development [129]. According to Arnot et al. [130], nanomaterials are very small and can accumulate in individual cells and penetrate the cell wall easily. Nanosilica and metallic oxide nanoparticles are the most commonly investigated nanomaterials in the oil and gas industry as they have different effects on the environment and on humans [131]. Prakash et al. [131] stated that the main implication of aluminium oxide is that it can oxidize cells and stop breathing, hence causing death to any exposed organisms. Valdiglesias et al. [132] stated that zinc oxide can release reactive oxygen that may damage the cell membrane thus altering the cell and DNA. Furthermore, previous studies concluded that zinc oxide nanoparticles may cytotoxicity and genotoxicity by releasing Zn^{2+} ions. Deng et al [133] after studying the cytotoxicity of ZnO nanoparticles in mouse neural stem cells at various levels (cell viability, apoptosis, and necrosis), researchers discovered that Zn^{2+} ions dissolved in the culture medium or inside cells were primarily responsible for ZnO nanoparticle toxicity. Fukui et al [134] also discovered that cytotoxicity was due to the increased levels of Zn^{+2} ions in vitro, in ZnO NP-treated human lung carcinoma cells, and in

vivo, in rat lung cells after intratracheal instillation of ZnO NPs. Furthermore, increases in intracellular levels of Zn+2 ions released by ZnO NPs were linked to high levels of Reaction oxygen species (ROS) and, as a result, cell death [134], agreeing with the positive findings of Valdiglesias et al [132] on apoptosis and oxidative DNA damage.

Furthermore, titanium oxide can contribute to the development of Reaction oxygen species (ROS), plasma membrane leakage, calcium influx in the cell by causing the interaction on the surface of the cells [135, 136]. Investigations by Xiong et al. [135] uncovered the effect of TiO2 nanoparticle size on potential toxicity, the cytotoxicity of various-sized TiO2 nanoparticles with and without photoactivation. The phototoxicity of TiO2 nanoparticles was found to be related to their size. This was consistent with the fact that tiny particles had a larger surface area per unit mass than larger particles. As a result, it was concluded that the increased cytotoxicity caused by smaller particles is due to their larger surface area and thus a greater number of surface exposed TiO2 molecules. Moreso, the observations indicated that cell membrane damage, ROS generation caused were proportional to the surface area of nanoparticles.

Alarifi et al [137] investigated the cytotoxicity and genotoxicity of copper oxide nanoparticles in human skin cells. Because nanoparticles are primarily absorbed through the skin and inhaled, the apoptotic and genotoxic potential of CuO NPs (50nm) in human skin epidermal cells, as well as the underlying mechanism by which CuO NPs exert their toxicity to the cells, were investigated. From the findings, CuO NPs were found to get internalized into the human skin epidermal cells or adhere to the cell membrane depending on their size. Larger particles (>500 nm) remained outside the cells while smaller particles (30 to 100 nm) were internalized into the cytoplasm, vesicles, and nucleus. They concluded that CuO NPs had cytotoxic and genotoxic effects on human skin epidermal cells. The mode of cell death was apoptosis which was facilitated by the ROS-induced mitochondrial pathway [137].

Johnston et al [138] identified the attributes most likely to drive the toxicity of carbon nanotubes (CNTs). Metal content, CNT length, tendency to aggregate/agglomerate and surface chemistry are some of the factors that influence CNT toxicity. CNTs can cause an oxidative reaction, which can lead to inflammatory, genotoxic, and cytotoxic effects. CNTs may also have varying environmental health effects depending on the product's life cycle in the environment. Nanoparticulate impurities, such as catalytic trace metals that remain on the surface of CNTs even after several post-purification treatments, can have an impact on CNT toxicity. Post-purification techniques can change the length, purity, degree of aggregation, wall structure, and surface functionalization of CNTs [139].

The long-term exposure to nanosilica can cause death of cell bodies and these implications of nanoparticles have reduced their application and use in the oil and gas industry [140, 141]. A growing body of evidence suggests that amorphous silica nanoparticles (SiO2-NP) can cause toxic effects and inflammation in lung cells because of their distinct physiochemical profile and nanometre size McCarthy et al. [140]. Inflammatory and cytotoxic effects in cells induced by SiO_2 have resulted from an increase in reactive oxygen species (ROS) followed by enhanced gene expression in size, time and concentration. The research showed that SiO_2 -NP could affect the human lung submucosal cells. The research discovered that SiO2 -NP are highly toxic to lung cell in comparison to larger sized SiO2- NP of the same composite material and that the mechanism of toxicity was largely dependent on ROS production and oxidative stress [140].

Table 6. List of how toxic nanoparticles are to human cells

Nanomaterials	Composition	Mechanism of toxicity	References
Metallic	Silver	Silver nanoparticle accumulation displays toxicity through oxidation. The particles lead to degradation of the antioxidant cells in the body. The Reaction oxygen species (ROS) generated in silver nanoparticles is higher compared to bulk silver.	Yildirimer et al. [142] Bahadar et el.[143] Khalili et al. [144]
	Gold	Larger gold nanoparticles have a larger exposed surface area for oxidation and are cytotoxic than smaller ones. Cationic side chains stabilizers and surface-coated ligands used with gold nanoparticles enhance the cytotoxic effects. They present a higher surface activity due to the higher surface area to volume ratio.	Yildirimer et al. [142] Khalili et al. [144] Yah. [145]
Metallic oxide	Copper oxide (CuO)	Copper oxide nanoparticles decrease reactions in cells and increases the rate of cell damage in the epidermal cells (layers that make up the skin) of human.	Alarifi et al [137]
	Aluminium oxide (Al_2O_3)	Aluminium oxide nanoparticles have the capacity to oxidize cells and restrict breathing and permeability of the cells resulting to cell death.	Arul et al. [146] Srikanth et al [147]
	Zinc oxide (ZnO)	The cause the reduction of cellular viability by generating reactive oxygen species and facilitates the breakdown of cell membrane. They alter the cell cycle and produces DNA damage.	Valdiglesias et al. [132]

	Titanium oxide (TiO$_2$)	These nanoparticles interact with different biomolecules in the body via surface-to-surface interaction. This causes ROS generation, the leakage of the plasma membrane which then damages the cells.	Xiong et al. [135] Ghosh et al. [136]
Non metallic	Carbon nanotubes	Multiwalled carbon nanotubes cause the release of cytokines. They lead to generation of ROS in different cell line.	Murphy et al [148] Johnston et al [138] Clift et al [149]
	Silica	Silica nanoparticles causes cell death with long term exposure and lethal dose applied. They also affect the immune system functionality. It also activates reactive oxygen species which also damage the cells in the body.	McCarthy et al. [140] Murugadoss et al [141]

6. Nanotechnology challenges in the oil and gas industry

One challenge that is highlighted among others regarding to the application of nanotechnology in the oil and gas industry relates to the nanomaterial development. It is expensive to produce nanomaterials and nanoparticles for use in the industry on a large-scale due to the traditional methods of synthesis used. The non-standardized approach of nanomaterial production is the main factor that has led to the expensive nature of nanoparticles [150] therefore, a cheap and inexpensive procedure is needed for the development of nanoparticles for field applications in the petroleum industry. New and efficient methods of nanoparticle production are evolving as technology advances. The use of domestically manufactured products and resources to provide solutions to the problems faced in the industry has been promoted by laws such as the local content act. This has resulted in expanded research into the possible use of agricultural waste in the synthesis of nanoparticles.

Though there is an increased interest in the study of utilizing nanomaterials, there are a few problems that still need to be addressed. The challenges come from the raised questions such as; What are the health, safety and environment implications of nanoparticles? Is the performance of nanoparticles on a large scale (field conditions) comparable to the small scale (lab conditions) or similar? Would it be financially attainable and feasible to utilize nanoparticles instead of ordinary materials? Can nanoparticles be easily and economically produced? A summarised description of these questions and challenges will be highlighted in this section.

In respect to the effect of nanoparticles on health, safety and environment, NPs can be hazardous and can lead to severe health problems [114] as they have a greater potential of being breathed in or even absorbed by the skin [123] due to their properties in terms of nano size and surface-to - area ratio. Because of the above-mentioned concerns, standards, regulations, working guidelines and recommended practices are being put in place by the governing agencies such as the local and international Environmental Protection Agencies (EPA), American society for Testing and Materials (ASTM) and the International Organization (ISO) to reduce and prevent risks associated with handling nanoparticles.

With respect to using nanoparticles effectively in large quantities in the field instead of the laboratory, stronger cooperation between researchers and oil companies is required to approve their success through pilot testing.

With the issue of economic viability of nanoparticles versus ordinary materials, the reason resulting to this question is to do with the higher cost of creating certain nanoparticles compared to traditional materials. According to Kim et al., the higher production cost is essentially due to the relatively higher cost of production and higher embodied energy needed for nanoparticle development compared to bulk products per unit mass [151]. Different nanotechnologies in the oil and gas industry have been proposed based on laboratory tests. Reported results have shown in the literature that nanoparticles have the potential of improving the tested parameters.

7. Recommendations

According to the findings of this review, there is lack of well-explained health, safety, and environmental guidelines and protocols for the safe handling, disposal, and delivery of nanoparticles. Therefore, to minimise the challenges addressed in the review, it is proposed that joint efforts in the areas below are needed by the industry.

It would be of advantage for oilfield engineers and scientists to work together with their colleagues in other sectors where an impact has been made by nanotechnology. There have been significant nanotechnology advances within the pharmaceutical, medical, chemical processing industries and material science, therefore it is possible that solutions in the oil and gas processes and operations may be sought in these sectors. This type of collaboration could yield a lot of low-hanging fruit for oilfield applications. There are three main approaches to risk and exposure

It must be highlighted that inhalation exposure by absorption through the mucosal lining of the trachea is one of the greatest concerns with regards to the effects of particulate nanomaterials

on occupational safety and health. Therefore, Nanoparticles must be handled in a non-airborne form, such as in solution. It is recommended that respiratory air filters N100 or N95 be used. Nanoparticle exposure is frequently caused by the use of insufficient personal protection equipment (PPE). Therefore, protective clothing such as that required in a wet-chemistry laboratory would be appropriate and could include but not limited to:

- Closed-toed shoes made of a low permeable material,
- long pants without cuffs, a long-sleeved shirt,
- Gauntlet-type gloves or extended sleeves nitrile gloves
- Laboratory coats and chemical splash goggles [152, 153].

It is also recommended that written operating procedures be developed, as well as adequate operational training and that regular and timely inspections of process, manufacturing, operational and exposure control equipment and ancillary systems (such as ventilation and filtration equipment) are regular and timely preventative and corrective maintenance and repair of such equipment [154].

There are currently no specific exposure limits for airborne exposures to engineered nanoparticles (except 0.1 mg/m^3 for ultrafine TiO_2 particles), though occupational exposure limits and guidelines exist for bigger particles of similar chemical composition. It would therefore be prudent to consider both the current exposure limits and guidelines and the increase in surface area of the nanoparticles relative to that of the particles for which the exposure limits or guidelines were developed when determining the effectiveness of controls or the need for respirators [155]. The P-100, FFP and P3 cartridge-type respirators have been found to provide a higher level of protection than others [156-158]

Moreso, the issue of exposure by ingestion within the workplace can be avoided following good personal hygiene simple safety practice rules such as not wearing personal protective clothing outside work areas and handwashing with soap and water before and after breaks and at the end of the workday. This should prevent any oral uptake.

More so, nanotechnology research and development for oil and gas processes and applications is still in the laboratory stage and design stage. Therefore, to speed up field testing of nanotechnology, service companies, oil companies service companies and researchers need to collaborate. National oil companies can play an important role in this by piloting nanotechnology in their oilfields at a lower cost than international oil companies.

Also, the issue of cost needs to be addressed. Nanoparticle application in the oilfield will involve large quantities, it will be advantageous to investigate cheaper naturally available nanomaterials. Using unwanted industrial nanoparticles e.g., fly-ash or any other source may be beneficial especially if they can perform in oilfield operations

Lastly, research should focus and prioritise secure deployment and recovery of nanomaterials in oilfield operations to minimise their impact on health, safety and environment (HSE). Introducing manufacturing best practises would be extremely beneficial, especially in the absence of government regulations.

8. Summery

An extensive review of recent nanoparticle investigations in the oil and gas industry and other sectors has revealed that nanotechnology has recently emerged as an appealing topic of research, with many studies showing very promising results in terms of performance and effectiveness. The distinct properties of nanoparticles are responsible for these promising results. Despite the high potential of using nanoparticles, there are some issues to consider, such as their economic feasibility and impact on HSE. Engineered nanomaterials will present unusual new risks but there is little information on how this risk can be identified, assessed and controlled especially in the engineering sector. The science sector is far ahead in addressing these challenges of nanomaterials risks to health and the environment; therefore, industries such as oil and gas should ensure that these challenges are addressed as soon as possible. To address key challenges, we propose a collaborative effort in the following areas: closer collaboration with other industries to facilitate cross-industry nanotechnology applications, increased collaboration between academia, service providers, and oil companies to expedite field pilots, research into less expensive nanoparticle sources, such as natural or industrial waste nanoparticles, as well as research into the safe deployment and recovery of nanoparticles in the oilfield to reduce the impact on HSE.

9. Conclusion

An extensive review of recent nanoparticle investigations has revealed that nanotechnology has emerged as an appealing topic for research, and many studies have shown promising results in terms of their effectiveness and performance. Despite the high potential of using nanoparticles, there are some questions to address, such as their economic feasibility and

impact on HSE. Based on a thorough review of the literature, the following conclusions were reached:

- Before using nanomaterials in any oil and gas application, environmental effects must be considered, especially in cases of heavy metals that are likely to cause environmental hazards and can also affect and harm humans and aquatic creatures.
- These nanomaterials would cause long-term diseases that would manifest in the body years after being penetrated in human organs, and because this science is still being developed on an industrial scale, more information about their hazard to the body needed
- These particles can easily spread throughout the environment and remain in the air, soil, or water for an extended period of time, in addition to their high ability to penetrate the body skin and cause new types of diseases.
- Good occupational hygiene practises and prior knowledge of hazardous substance handling provide a solid foundation for working safely with nanomaterials. However, where existing knowledge falls short, new research is required to fill the gaps.
- Nanomaterials should be considered hazardous materials until more information becomes available.
- Nanomaterials were found to improve drilling mud properties and exhibited stable rheological profiles under extreme temperatures and pressures. Whoever, there is limited availability of commercial cost data for NP additives for drilling fluids. Research has shown that NPs are more expensive than many of the basic drilling-fluid additives.
- Lastly, many types of nanoparticles may turn out to be of limited toxicity in the future due to advancements in technology but until then, precautions should be used until more is known.

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