International Conference & Exhibition on Oil Field Chemicals & Treatments
Mumbai, India, July, 2019

Nanoparticles for Enhanced Oil Recovery: A comprehensive review

Mohit Kalra, Rajneesh Kashyap, Arti Kashyap
Indian Institute of Technology Mandi, Kamand, Mandi, HP 175005, India

Abstract

Despite the enormous impact of enhanced oil recovery (EOR), oil reserves all over the world are in a phase of diminishing production. Although Tertiary Stage EOR is extremely effective, some oil is still bypassed. The reason is that surface forces responsible for holding oil inside the rock surface are not being altered by the application of existing technologies. Materials nanosized are showing a significant role in EOR techniques and is a promising approach to increase crude oil production, as is revealed by the scientific literature in the domain. It is also an interesting fact that in different operational conditions and parameters, the performance of nanoparticles also varies and some are more effective than others, which leads to various levels of recovery in the EOR process. In the present study, we intend to summarize a report having an up-to-date status on nanotechnology-assisted EOR mechanisms where nanoparticles are used as nano-catalysts, nano emulsions, and nanoparticles assisted EOR mechanisms to destabilize the oil layer on carbonate surface. Afterward, the study focuses on various applications of nanoparticles on EOR. The nanoparticles of various types, have been considered in the EOR process are reviewed with regards to their associated properties, their functioning, and also their advantages, and disadvantages. We then focus upon the parameters and guidelines that affect the performance of nanoparticles in EOR process, and also the recommendations for propitious oil recovery are highlighted. Laboratory experimental as well as computational simulations both are considered as an adequate approach to gain more microscopic insights into the oil displacement process to classify the suitability of nanomaterials. The purpose of this review article is to put forward the vast knowledge and competence expertise associated with experimental and computational nanotechnology applications in the EOR process.

1. Introduction

The demand for energy is rising as a result of population growth and the rate of industrial development worldwide. One source of renewable energy is crude oil. Figure 1 depicts the production rate as a function of the various stages of recovery over time. However, the oil and gas resources now available are at a diminishing stage [1]. The ultimate recoverable oil reserves should be enhanced in order to fulfill the steadily rising demand for oil and maintain a sustainable oil supply. This might be done by using enhanced/improved oil recovery (EOR/IOR) techniques to maximize oil recovery from present mature oil fields by reducing the trapped oil remaining in the reservoirs in addition to replacing the produced oil with fresh reserves from new discoveries. EOR/IOR techniques uses already-developed oil reservoir's machinery, infrastructure, and equipment, requiring no additional technology. [1].

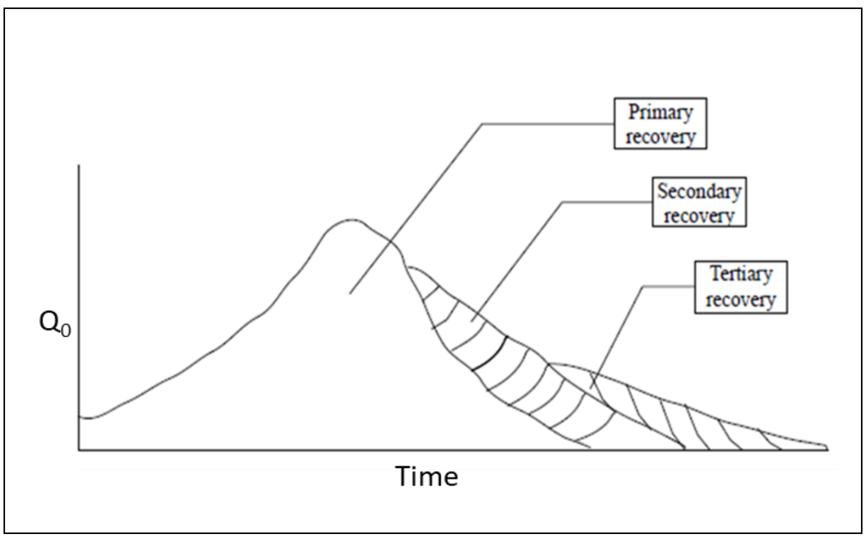

Figure 1. Recovery stages of a reservoir with time [2].

Research activities and trends have changed throughout the past few decades across a variety of fields, moving from the "Macro-domain" to the "Microdomain" and "Nano-domain" and, most likely, the "Pico-domain" and "Femto-domain" in the years ahead. Due to the growing desire to scale down technological advancements, study has increased in a number of disciplines including microfluidics, nanoscience and nanotechnology, and nanofluidics. Nanoparticles are designed to have at least one dimension that ranges from 1 to 100 nm. Nanoparticles are special because of their size-dependent characteristics, which are the result of their high surface-to-volume ratio. Consequently, this allows surface atoms or molecules to significantly affect its characteristics [3,4]. These approaches are expected to play a significant role in the future oil supply because they are not only more environmentally friendly but also more energy efficient. As per various studies, Nanoparticles and nanotechnology have been recommended as constructive for EOR operation for the reason that nanoparticles are able to penetrate the pore throat, i.e. a compact pore space at a particular point where two grain boundaries meet and this leads to the significant change in the reservoir properties to intensify the process of oil recovery. Computational Nanotechnology is also gaining enormous interest as an efficient method of achieving EOR. The interfacial tension reduction and wettability alteration have been put forward as the driving mechanisms. Computation, in this area, has come up with new means of strengthening rheological properties of the fluids at both ambient as well as elevated temperatures and the detrimental effects commence above certain nanoparticle concentrations.

These theoretical studies i.e. the atomic scale simulations uses classical molecular dynamics (MD) as their basis by making use of model potentials, concentrating predominantly on wettability and the adsorption of organic molecules in water [5-8]. By applying classical MD, it is comparatively a challenging task to investigate the underlying mechanism behind wettability alteration due to the reason that there exist many fundamental difficulties in constructing a complex model potential, specifically, when in a system many parameters are taken into account for properly describing the interactions between solvated nanoparticles, calcite surface, and the water. As an illustration, it was found that using classical MD simulations, the results obtained on preferential adsorption positions of Na+ and Cl- ions were contradictory [9]. DFT is considered as the best method to achieve the parameter-free and quantum mechanical characterization results in a complicated system having brine/calcite/oil interfaces. In the past few years, DFT studies [9] have made a remarkable progress, for studying the mechanism of ion substitution, binding energies of the organic compounds and water molecules on a calcite surface are employed and wettability is considered as the indicator, water is treated at various different levels of approximation. A real indicator for the wettability alteration is macroscopic contact angle measurement, this represents the adhesion properties at the interface of the liquid and the solid surface. It is of great significance when the effect of added ions in a liquid are studied.

In this paper, we report a comprehensive review which is divided into four main sections (2,3,4 and 5). In section 2, we have briefly summarized the applications of nanotechnology in petroleum industry. In section 3, the review study is based on various nanoparticles and focuses on the effect of nanoparticle type and governing parameters in EOR process. In section 4 we discussed parameter affecting nano EOR. Finally, in Section 5 we discussed the challenges for nano-EOR and outlook for future research. The pedagogical design of this review article is intentional, and the motive is to a resource for beginners seeking to conduct computations for understanding the interaction energies for EOR.

2. Use of Nanotechnology for EOR in petroleum sector

"Nano-EOR" is the term used for describing applications of nanoparticles in Enhanced Oil Recovery (EOR) processes. Many research groups claim that by making use of Nanotechnology the petroleum industry can be revolutionized in various aspects such as both upstream and downstream operations comprising of exploration process, drilling operation, production procedure, and EOR techniques, and refinery processes as well [10-15]. Therefore, in order to supplement the existing oil recovery processes, nanotechnology has come out as an embryonic alternative for oil recovery techniques and also provides wide ranging materials which can be employed for petroleum industry. Nanosized materials in numerous forms such as complex fluids, solid composites, and functionalized nanoparticle fluids amalgamation are requisite for this new technological advancement. Over the past few decades, research activities in the field of application of nanotechnology in petroleum industry is growing rapidly. As shown in the Figure 2, number of research articles issued in this field, it can be observed that even in the downturn of oil industry, numerous research activities have been conducted.

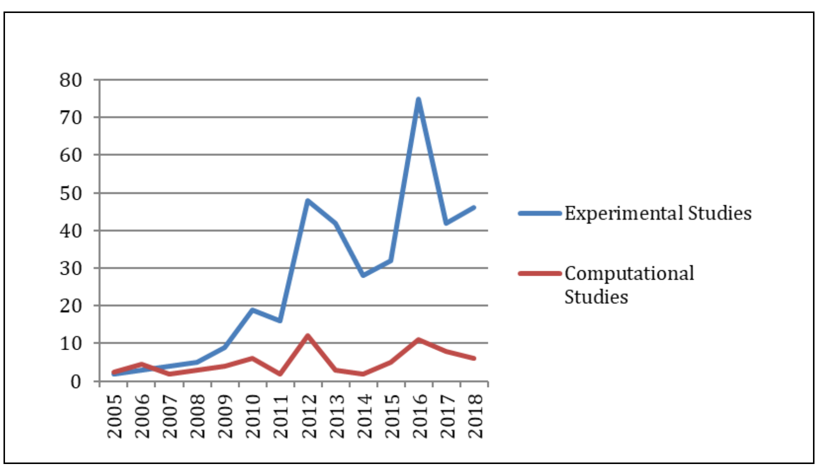

Figure 2. Research on nanotechnology application in the petroleum industry.

3. Different types of Nanoparticles used in EOR

In order to meet the continuously increasing oil demand and keep sustainable oil supply, the ultimate recoverable oil reserves should be increased [12]. This could be achieved by replacing the produced oil by new reserves from new discoveries as well as applying enhanced/improved oil recovery (EOR/IOR) methods to maximize oil recovery from current mature oil fields by minimizing the trapped oil left behind in the reservoirs. It is a well-known fact that finding new hydrocarbon source is onerous since most of the oil reservoirs have recovery efficiency of about 30% to 40% and rest of the oil is non-reproducible which leads to the necessity of developing novel technologies for EOR process [16]. Nanoparticles (NPs), as a part of nanotechnology, have size typically less than 100 nm in one dimension [17]. They are well known for their size and their capabilities such as (1) to significantly modify or alter optical, electrical and magnetic properties of any material; (2) their stability is good, due to the fact that their surface forces are more propellant than gravity; (3) ability of modify the shape and size of NPs while manufacturing process along with flexibility; (4) it is easy to tailor the surface chemical properties of NPs to hydrophobic or hydrophilic; and (5) silica nanoparticles are most often employed in the EOR process, where silicon oxide is used 99.8%, it is found in abundance in sandstone and is also environmental friendly [18]. There exist three categories of nanoparticles which are applied in EOR process are nanofluid, nano emulsion and nano-foam.

According to the definition, nanofluid are colloidal suspensions having nanoparticles dispersed in them. Whereas nano emulsion is known as two phase dispersion of two immiscible liquids which can either be a water in oil (W/O) emulsion or oil in water (O/W) emulsion which stabilizes with the help of nanoparticles, this is also called Pickering emulsion. In the case of nanofoam, the gas bubbles in a liquid are stabilized with the help of nanoparticles.

For nanoparticles in EOR applications, as compared to nanofluid flooding, nano-forms and nano emulsions are used more often. And for these two categories, i.e. for nanoforms and nano emulsions, the effect of different types of functionalized nanoparticles is synergized with, in-situ and ex-situ surface-activated nanoparticles and surfactants. The most prevalent nanoparticles for such applications are silica-based, since its surface hydroxyl groups can be modified to either hydrophobic or hydrophilic, which leads to the formation of W/O or O/W emulsions, respectively. In the past few decades, a lot of experimental studies have been conducted on nano-EOR considering nanofluid flooding [19]. For EOR, different nanomaterials exhibit distinctive properties which results in effective changes in porous media and the fluids. Review work done by Agista, M. N. et al. [19] has been mostly summarized here. In the following section, results of different research studies will be discussed for various nanomaterials that have been studied for EOR.

3.1 Silica-Based

Silica-based nanoparticles are topmost used materials for studying in EOR applications due to the fact that they are easy to synthesis, have widely known physico-chemical properties, and can also be tailored to distinguishing properties such as hydrophilicity and hydrophobicity [13,20]. They fall under the category of non-toxic inorganic materials and are also available in abundance. Their production cost is also comparatively lower as compared to other NPs. There have been numerous tailored silica nanoparticles and on the basis of their wettability behavior, can be classified into three major types [21]: neutral-wet polysilicon (NWP), lipophilic polysilicon (HLP) and lipophobic and hydrophilic polysilicon (LHP). It is a proven fact that Silica -based nanoparticles can alter the wettability of a porous media on adsorption. Also, the silica nanoparticles show excellent thermal properties as confirmed by infrared spectroscopy, scanning electron microscopy and x-ray diffraction and precluding the instances of lack of thermal stability where it is used in high temperature applications [22,23]. Caetano Rodrigues Miranda et al. [24] used neutral silica nanoparticle and carried out theoretical studies to inspect the application of neutral silica nanoparticles on adding various functional groups such as (PEG, EG, hydroxide, sulfonic acid) in the presence of aqueous NaCl, along with oil and 1% solution of oil/brine. They tried to study the impact on stability and interface mobility at temperature 300K and pressure 0.1 MPa. There results indicated that NaCl is a more suitable candidate as compared to NP-H, for the enhanced oil recovery applications in wells i.e. to alter the wettability of surface which will further lead to increase in the oil recovery. The results of the simulations further demonstrated that polar groups in the oil having electronegative atoms such as nitrogen or oxygen were more inclined to get adsorbed on the silica nanopores, this lead the polar groups to accumulate on the pore wall and interface which ensued the decrease in the displacement velocity. Onyekonwu and Ogolo [25] worked on computational studies to study the effect of oil and nanoparticles to migrate nanofluids into silica nanopores. All the three types of silica nanoparticles i.e. LHP, HLP, and NWP were dispersed in different solvents such as (ethanol, alcohol and water). Both HLP and NWP silica nanoparticles which were dispersed in ethanol were successful to alter the wettability of water-wet surface and behaved as surfactants in order to reduce the by reducing the oil-water interfacial tension.

Kazem Sepehrinia et al. [26] worked on simulation to study the effect of functionalized silica nanoparticles as wettability modifiers. The functional groups trifluoromethyl and pentafluoroethyl were assigned as hydro and oleophobic sites. It was observed that, as the number or length of fluorocarbon groups on nanoparticles increased, this lead to increase in the diffusion coefficient i.e. adsorption of nanoparticles on mineral surface increased. This makes fluorinated silica nanoparticles a suitable candidate for enhanced gas recovery. A molecular scale study to investigate the impact of silica nanoparticles on oil adsorption over the calcite surface was done by Salehzadeh et al [27]. The concentration of nanoparticles is 7000 ppm homogeneously dispersed in distilled whereas for oil phase, a mixture of heptane and decane in molar ratio of ½ is taken. The results indicated that in the presence of silica nanoparticles there was a considerable about of decrease in the binding energy calculation of oil-calcite surface, the value decreased from 5224 kcal/mol to 3278 kcal/mol. Also, the average distance between oil and calcite surface increased and ultimately there was an increase in the oil recovery.

Hendraningrat et al. [28] conducted experimental studies by taking LHP silica nanoparticles and conducted coreflood experiment on berea sandstone by varying the concentrations of nanoparticles ranging from 0.01wt% to 0.1 wt % by dispersing them in 3.0 wt% NaCl solution. It was found out that as the concentration of nanoparticles increased, the contact angle decreased but on further increasing the concentration the pore throat of low permeable berea core plug got blocked. According to [29], for oil recovery over a carbonate surface, the silica nanoparticles mixed with brine solution lead to extra recovery of oil by 39% to 61%.

For chemical EOR techniques, silica nanoparticles injected in a polymer was studied by Maghzi et al. [30]. In this experimental study, the silica nanoparticles were injected in polyacrylamide polymer solution in glass micromodel. The motive was to examine the behavior of polyacrylamide solution in the presence of silica nanoparticles. On adding silica nanoparticles by 0.1 wt % into the polymer solution, pseudo-plasticity of the polymer solution increased at low shear rate and this lead to an overall increase in the viscosity of the solution, therefore, overall oil recovery increased by 10%. Similarly, Sharma et al. [31] also worked on silica nanoparticle by dispersing them in a polymer solution and surfactant. Here, it was discovered that silica nanoparticle have the ability to reduce the interfacial tension and also stabilize the formed emulsion, i.e. Pickering emulsion. The overall oil recovery increased by 21%.

In case of conventional polymer or surfactant-polymer flooding, the oil recovery rate decreases on increasing the temperature. Whereas, in the presence of nanoparticles, the nanofluids remain stable in high temperature operations. In the case of CO_2 flooding for EOR, various issues such as poor sweep efficiency, channeling and viscous fingering are often encountered. Therefore, to overcome these issues, Hamed et al. [32] put hydrophobic silica nanoparticles of various sizes and concentrations in CO_2-water foam and tried to studied its impact. It was found out that, when the concentration of nanoparticles was less, the nanoparticles having large size contributed in stability of foam; whereas, as the concentration increased, nanoparticles with small size contributed.

3.2 Copper oxide

In this experimental study, the silica nanoparticles were injected in polyacrylamide polymer solution in glass micromodel. The motive was to examine the behavior of polyacrylamide solution in the presence of silica nanoparticles. On adding silica nanoparticles by 0.1 wt % into the polymer solution, pseudo-plasticity of the polymer solution increased at low shear rate and this lead to an overall increase in the viscosity of the solution, therefore, overall oil recovery increased by 10%. In this a very few research studies have been done so far consider copper oxide for its applications in the EOR process. One of the main findings regarding the potentiality of CuO nanoparticles for EOR applications was conducted by Shah et al. [33], on the Berea Sandstone, the effect of CuO nanoparticles was studied CO_2 gas injection. The results indicated that an average of CuO nanoparticles ranging from 23-40 nm could reduce the viscosity of oil and density and viscosity of the injected gas increased. In addition, for the CO_2 EOR process when 1% CuO nanoparticles were injected with Poly-Di-Methyl-Siloxane (PDMS) polymer solution, there was a considerable in nanofluid viscosity of about 104 times. For this reaction,

Therefore, it was concluded that application CuO nanoparticles are efficient for the EOR process. Further, the oil viscosity was found to be the lowest when 1% CuO nanoparticles were taken with PDMS and 30 mol% CO_2 at the temperature of 122°F. The recovered oil was increased by 71%. Thereafter, Shah tried increase the concentration of CuO nanoparticles to 3% wt. But the results showed However, the negative results showed that on increasing the concentration of nanoparticles from 1% wt to 3% wt the oil viscosity also increased.

3.3 Aluminum Oxide

There exist various methods to synthesize Aluminum oxide (Al_2O_3) nanoparticles such as modified plasma arc method [34], flame spray pyrolysis [35], and mechanochemical synthesis [36]. Giraldo et al. [37] studied the effect of adsorption of Al_2O_3 nanoparticles to alter the wettability of mineral surface. In an anionic surfactant, the Al_2O_3 nanoparticles were dispersed, and the concentration was varied from 0.01 to 1.00 weight percentage, it was observed that Al_2O_3 nanoparticles in the presence of anionic surfactant could successfully alter the wettability, the residual water saturation increased from 0.07 to 0.23, modifying the surface from strong-oil wet to strong water-wet. Ogolo et al. [38] did a comparative study on the application of various metal oxide nanoparticles and concluded that the Al_2O_3 nanoparticles having an average particle size of 40 nm showed the maximum recovery rate of 12.5%. Zaid et al. [39] considered the two different kinds of Al_2O_3 nanoparticles (one made by sol-gel process and one commercial) and dispersed them in sodium dodecyl sulfate, an aqueous surfactant. Both kinds of Al_2O_3 nanoparticles could increase the efficiency in producing the remnant oil by 53.5%. There was an interesting finding that commercially available Al_2O_3 -RM (commercial) was more successful and could achieve 63% more oil than Al_2O_3 prepared by sol-gel process inspite of the fact that Al_2O_3 prepared by sol-gel process yielded lower interfacial tension (IFT) with smaller size. Thus, by this it can be deduced that only with low IFT the oil recovery rate does not increase and a few other factors such as fluid rheology, sweep efficiency, etc. are also important.

Hendraningrat et al. [40,41] did a comparative study to examine the potential of three different types of nanoparticles i.e. silica, aluminum and titana on Berea core plug via two-phase core flooding process. In order to prevent the agglomeration of nanoparticles, Polyvinylpyrrolidone (PVP) dispersant stabilizer was also added. The experimental results indicated that there was an increase in the oil recovery for titana and aluminium and not for silica nanoparticles, particularly in the case of water-wet system, due to the fact that both the metal oxides could adsorb in the pore surface more easily as compared to silica . Also, inspite of the fact that titania could produce a larger contact angle reduction, of about 54 degrees at oil-water and rock interface,still the oil recovery rate was higher for alumina.

As shown in the Figure 3, on dispersing Al_2O_3 nanoparticles in an anionic surfactant and varying their concentration from 0.01 to 1.00 wt %, it was observed that both Al_2O_3 nanoparticles and the surfactant solution altered the rock surface wettability from strong oil-wet to strong water wet, the residual water saturation Swr changed from 0.07 to 0.23. One more comparative experimental study was done using iron oxide, alumina and silica. Here also the alumina proved to be better than both iron oxide and silica in maximizing the oil recovery. Alomair et al. [42] worked on combination of alumina and silica nanoparticles where the the concentration of silica nanoparticles was kept as 0.05 wt %. The results indicated that maximum amount of oil was recovered. They recommended usage of mixture of alumina and silica nanoparticles when the reservoir has high temperature, high pressure and salinity and also to control asphaltene formation.

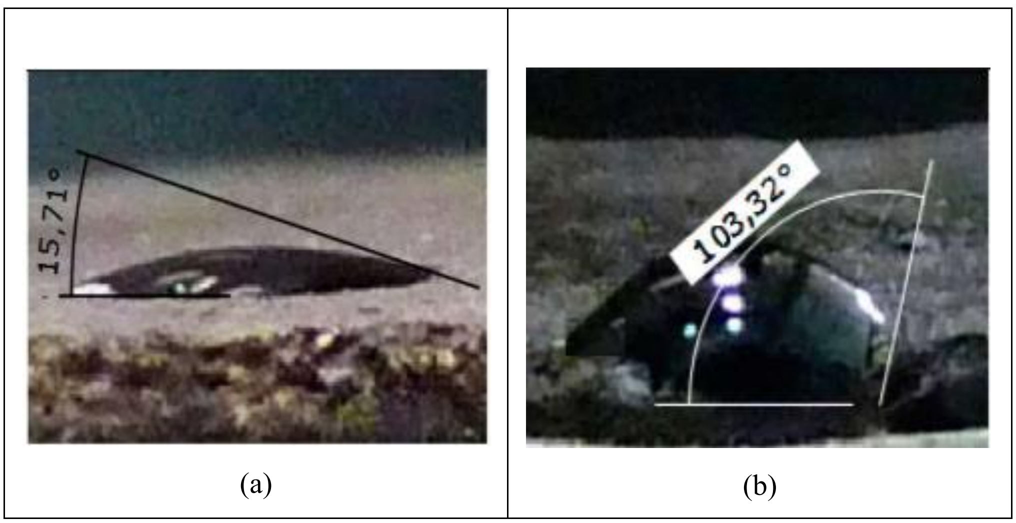

Figure 3. Experimental Results of Oil-air contact angle on the rock surface (a) before and (b) after treatment with Al_2O_3 nanoparticles of size 100 ppm. [19].

3.4 Iron Oxide

Due to that fact iron oxide (Fe_2O_3/Fe_3O_4) nanoparticles show unique electrical and magnetic properties, they have been used as sensors for oil and gas pipelines. However, for the increase in oil recovery, only a few studies are available. The concept of Ferrofluids (Fe_3O_4) in enhanced oil recovery i.e. oil recovery using magnetic nanoparticles was introduced by Shekhawat et al. [43]. The mechanism on which the magnetic recovery works is that initially the magnetic nanoparticles are injected and are pushed towards reservoir by making use of repelling magnetic force created by downhole tools. Afterwards, an inward magnetic force is put into operation towards to borehole to attract and finally recover the magnetic nanoparticles soaked with oil. Haroun et al. [44] did a relative study on various metal oxide nanoparticles such as Fe_3O_4, NiO and CuO over carbonate surface. The recovery rate for iron oxide nanoparticles was far lesser than the other two i.e. iron oxide reached only 57% whereas other nanoparticles achieved upto 85%.

Whereas, according to a few researchers, the nanoparticles dispersed in water can enhance the oil recovery by 24% [45]. It was also discovered that viscosity of the displacing fluid can be improved by using iron oxide nanoparticles, which can further lead to increase in the sweep efficiency. According to the studies conducted by Joonaki et al. [46] iron oxides nanoparticles could only recover 17% of the extra oil whereas both Al_2O_3 and SiO_2 nanoparticles could increase the recovered oil by 20%.

3.5 Nickel Oxide

Nickel oxide (NiO/Ni_2O_3) nanoparticles, also known as hydrophilic metal oxide nanoparticles are potential candidates for EOR applications. On comparing the results of NiO with different metal oxides i.e. Al_2O_3 and ZrO_2, NiO is inferior for EOR applications, but still it has capability to alter wettability and also to increase viscosity. According to Ogolo et al. [45], in the presence of diesel and brine, nickel oxide nanoparticles showed positive results of enhancing the oil recovery by altering wettability of rock surface and also enhancing the oil viscosity of brine. Nwidee et al. [47] worked on NiO and ZrO_2 nanoparticles for EOR process on a fractured limestone core surface. It was found out that ZrO_2 showed good results, but still NiO was considered as a potential candidate for EOR because on increasing its concentration, salinity and injection time, the water contact angle reduced.

3.6 Titanium Oxide

The applicability of titanium oxide (TiO_2) nanoparticles for enhancing the oil recovery process has been proved by many researchers. According to Ehtesabi et al. [48] if TiO_2 nanoparticles in the presence of water are used for enhancing oil recovery over a sandstone core plug, it was found out that there was a major increase in the recovery of extra oil ranging between 49% to 80%, reason being uniform adsorption lead to alteration in wettability, it was also proved by SEM. According to an experimental study, if the concentration of TiO_2 nanoparticles is kept low ranging from 0.01 and 0.05 wt %, it was found out that in such a case only wettability of the surface changed from oil-wet to water-wet and there was no change on interfacial tension and viscosity. Hendraningrat et al. [49] worked on Al_2O_3 and, Cheraghian et al. [50] studied the capabilities of TiO_2 nanoparticles which shows that titanium is a potential candidate for EOR.

3.7 Zinc Oxide

Numerous studies have been conducted in past a few decades on Zinc oxide (ZnO) to alter wettability and increase the oil recovery in EOR process. Zaid et al. [51] did a comparative study considering ZnO and Al_2O_3 and it was proved that ZnO showed better performance than Al_2O_3 i.e. using ZnO the recovery rate increased by 72% whereas for Al_2O_3 it was 53% and the IFT values were also low in the case of ZnO. It was also found that when large sized ZnO nanoparticles were used. The recovery increased by 145% than the smaller sized particles. Similarly, Tajmiri et al. [52] studied the impact of ZnO nanoparticles, a concentration of 0.2 wt % ZnO nanoparticles was taken over carbonate and sandstone core samples. For both the core plugs, the oil recovery increased, for carbonate the value increased by 8.89% and for sandstone the increment was upto 20.68%. By using ZnO nanoparticles, both viscosity of heavy oil and wettability of the grain surface can be altered. Latiff et al. [53] studied the combined effect of electromagnetic (EM) along with ZnO nanofluid injection for a glass micromodel saturated with heavy oil.

Whereas, according to Ogolo et al. [54] it was discovered that when ZnO was dispersed in brine and water, the ZnO nanoparticles agglomerated into large particles and this caused permeability reduction, this further blocked pore throats of the core. Since stability is one of the key factors for a successful EOR application, Adil et al. [55] studied the effect on stability of ZnO NPs dispersed in water and used various anionic surfactants which acted as stabilizers along with varying concentrations of nanoparticles. It was found that 0.025 wt% of sodium dodecyl benzenesulfonate (SDBS) was required to stabilize 0.1 wt % ZnO nanoparticles, and the particles showed highest stability at 95˚C and the viscosity enhanced upto 11%. Various factors which affect the mobility of ZnO nanofluid are, surfactant, ultrasonication, and pH.

4. Parameters Affecting Nano-EOR

4.1 Nanoparticle Size

In the chemical - enhanced oil recovery processes, pore plugging and entrapment of chemicals in the porous media are major challenges, this leads to reduction in the formation permeability and also an increase in the the injection cost. SiO_2, Al_2O_3 and TiO_2 nanoparticles, having size in the range of 1 nm–100 nm, have size smaller than the size of pore and throat sizes can easily pass through a porous media and not getting trapped. This leads to the efficient increase in the EOR process on injecting nanofluids. Also, the ultra-small size of NPs has an added advantage that they can easily penetrate those pores in which traditional fluids get stuck.

Therefore, the nanoparticles due to their small size contact more swept zones, and increase the macroscopic sweep efficiency. Moreover, charge density and size of nanoparticles are the two factors having a notable contribution on the disjoining pressure. If two nanoparticles have similar masses, in that case, the nanoparticles having smaller size will have higher particle density and will lead to more reduction in the contact angle in between fluid and the rock surface. Therefore, the nanoparticles with higher particle density show a remarkable increase the structural disjoining pressure. In the case of slightly hydrophilic surfaces, the nanoparticles having small size tend to stretch on a surface more easily as compared to bigger sized nanoparticles. According to Hendraningrat et al. [56], smaller particles have proved not only to increase the considerable amount of oil recovery, but also improve the displacement efficiency. Several other experiments concluded that smaller particles would lead to higher ultimate oil recovery. According to Kondiparty et al. [57] if the size of nanoparticles is reduced, there will be an increase in the disjoining pressure, his results showed that on decreasing the nanoparticles size from 30 nm to 18.5 nm, there was an considerable increase in structural disjoining pressure of about 4.3 times. The size of nanoparticles neither should be somewhat like not too big to avoid log jamming and and not too small to avoid mechanical entrapment. Therefore, in comparison to bigger sized nanoparticles, small sized nanoparticles lead to more oil recovery. Surface energy also plays a significant role in influencing the stability of a nanofluid, if the surface energy is high, it can lead to adsorption and agglomeration of the nanoparticles and affecting the overall stability of nanofluids. Also, the size of nanoparticles have an effect on surface coating properties. Therefore, we recommend that the nanoparticles should have an optimum size.

4.2 Nanoparticle Concentration

The amount of nanoparticles taken or injected in the fluid is one of the main factors to determine efficiency of the EOR process. Chengara et al [58], found that as the concentration of nanoparticles increases, it leads to increase in the disjoining pressure, which further increases the repulsive forces. Increase in the concentration also leads to increase in the viscosity of nanofluid which further increases the displacement efficiency and due to the nanoparticles get adsorbed on the grain boundaries. On increasing the concentration of injected nanoparticles, interfacial tension in between reservoir and fluids can also be reduced. With higher concentration of nanoparticles, wettability alteration also increases. Therefore, it is advantageous to have a high concentration of nanoparticles for enhancing oil recovery. However, beyond a certain limit the, on further increasing the concentration, the pore throat may get blocked and oil recovery may turndown. An optimum amount of concentration of nanoparticles will reduce interfacial tension, enhance the displacement efficiency and will also improve wettability alteration. Hendraningrat et al. [59] studied the effect of silica nanoparticles on porosity and permeability of Berea core, it was found out that on injecting about 0.5 wt % of the silica nanoparticles was decreased by around 2%. However, there exist various factors on which the optimal concentration depends such as type of nanoparticle, environmental conditions around reservoir and porosity and permeability of the rock surface.

4.3 Salinity

The salinity of the of the dispersed nanoparticles in the displacing surfactant or fluid has a major impact on the overall stability of the formed dispersion. Salinity leads to decrease in the zeta potential, which finally leads to agglomeration . High salinity also leads to an increase in the ionic strength and decreases the electrostatic repulsion and due to this, there exist Van der waals forces in between the particles. In most of the cases, rock surfaces are charged and in a high saline environment, the particle-particle interaction will be more as compared to interaction between particle and surface. Therefore, in such an environment, stability of the nanoparticles should be maintained, this can be attained by surface modification, using ionic surfactants, or by both.

Worthen et al. [60] found out that in a highly saline environment, nanoparticles can be stabilized by attaching low molecular ligands to their surface. The stability of nanoparticles originates from steric hindrance. On the other hand, by using high-stability silica NPs, according to Hendraningrat et al. [61] by injecting silica nanoparticles in a highly saline nanofluid, the wettability of the rock could be altered and made more water-wet. Due to the fact that, in a highly saline environment, the adsorption of nanoparticles increases due to increase in physicochemical reactions. Kanj et al. [62] discovered that salinity of a surfactant does not affect the mobility of nanoparticles but it increases their adsorption on the reservoir surface. Therefore, salinity increases the adsorption, which leads to increase in the recovery of extra oil. However, stability of nanoparticles is lost in a saline environment. Therefore, ionic surfactants, surface modifications, and favorable amount of salinity level must be maintained to avert agglomeration and maximize the oil recovery.

4.4 Reservoir Temperature

Temperature has a significant impact on the efficient EOR process. The temperature of the reservoir is always more than that on the surface, therefore, nanofluids should be operating at high temperatures also. Caldelas et al. [63], studied the dependence of nanoparticle retention on temperature and concluded that for adsorption or desorption, nanoparticles show a very weak dependence on temperature. According to Hendraningrat et al. [56], the temperature has an important contribution to oil recovery because at high temperatures the reservoir fluids are reorganized at the molecular level, and due to this the contact angle between fluids minimizes.

Yet, the temperature dependence on the EOR process is a complex process since various variables are involved in it. According to PM Mcelfresh increase in the temperature lowers the zeta potential of the nanoparticles in the fluid. This leads to instability and agglomeration of nanoparticles and ultimately the oil recovery process becomes ineffective. Also, according to Hendraningrat [56], high temperature leads to a decrease in the interfacial tension because as the temperature increases, the interaction between molecules becomes weak, Brownian motion in between particles increases, and viscosity also is reduced. As per our survey, both reservoir and nanofluids are temperature dependent and the effectiveness of temperature for EOR cannot be ascertained. A few more studies should be carried out to understand the overall mechanism.

4.5 Rock Wettability

By making a rock reservoir more water-wet, the EOR process can be made more efficient. Morrow [64] concluded that for efficient oil recovery, capillary imbibition and water wetness are favored. However, in a few cases, it has also been reported that neutral wettability and an oil-wet reservoir can lead to an increase in the oil recovery. Therefore, wettability greatly affects the mobility of oil, it affects the displacement and distribution of oil and a few other reservoir fluids present in the matrix. For nano-EOR, the initial wettability determines the magnitude of wettability that can be altered. In an experimental study, using silica NPs, the maximum increase in the oil recovery was possible from an intermediate-wet core.

In an intermediate-wet condition, oil and brine are in the equilibrium state, which reduces the possibility of a disconnected and trapped oil phase in the matrix [56]. According to Li et al. [65] wettability has a major impact on the adsorption of nanoparticles. As compared to oil-wet media, the neutral or water-wet cores show higher adsorption of nanoparticles. In the case of an oil wet media, the adsorption and desorption areas are close and, therefore more prone to desorption. In such a case, the impact of nanoparticles on oil-wet rock surfaces is negligible. More efforts are needed to study known and unknown parameters that are responsible for nano-EOR. To have a deep understanding of both mechanisms and parameters can lead to the successful implementation of real-world applications of nanotechnology-assisted EOR processes.

5. Challenges for Nano-EOR

One of the main barriers to the petroleum industry's use of nanotechnology is the production of nanoparticles. For usage in this industry, nanomaterials must be created in more quantities, which is far more expensive than using conventional synthesis techniques[66]. The production of nanoparticles is an expensive procedure that has the potential to contaminate due to the unconventional methods utilized in its production. However, any form of pollution and heavy metals [67] from industries is also one of the most deadly because it pollutes the environment, destroys biological chains, and produces vast amounts of hazardous waste [68]. Employing traditional physio-chemical procedures to produce nanoparticles on a wide scale is challenging from an environmental and economic point of view. Green nanotechnology will therefore be able to offer a low-cost alternative for their synthesis and uses in the petroleum industry. Makarov et al. [69], studied the mechanism for synthesis of metal nanoparticles via biological route which comprised of three main steps i.e. activation phase, growth phase, and termination phase. The application of these materials is also hindered by the stability of nano-suspensions in challenging environments. The force of attraction between nanoparticles must be overcome by repulsive forces, also referred to as steric hindrance. Surfactants have been utilized in a few experiments to disperse and stabilize nanoparticles in various continuous media [70].

6. Conclusions

The major goal of this thorough review is to provide a summary of the current developments in EOR using nanomaterials and its mechanism. In the last two decades, there have been a considerable increase in the number of publications and patent applications that use nanomaterials for EOR. In addition to classifying and summarizing the most popular experimental and computational approaches used in the EOR process, this article also describes how they work. This review demonstrates that there is a significant need for extensive computational research to understand the principles underlying nano-EOR and identify workable solutions to the problems.

References

1. William, Jay Karen Maria, et al. "Effect of CuO and ZnO nanofluids in xanthan gum on thermal, electrical and high pressure rheology of water-based drilling fluids." Journal of Petroleum Science and Engineering 117 (2014): 15-27.
2. Jelmert, Tom Aage, et al. "Comparative study of different EOR methods." Norwegian University of Science & Technology, Norway (2010).
3. Gerogiorgis, Dimitrios I., et al. "Experimentally validated first-principles multivariate modeling for rheological study and design of complex drilling nanofluid systems." SPE/IADC drilling conference and exhibition. SPE, 2017.
4. Afolabi, Richard O., et al. "Optimizing the rheological properties of silica nano-modified bentonite mud using overlaid contour plot and estimation of maximum or upper shear stress limit." Cogent Engineering 4.1 (2017): 1287248.
5. Chai, Rukuan, et al. "Experimental and molecular dynamic simulation study on calcite-organic molecule-water interaction mechanism." Journal of Petroleum Science and Engineering 197 (2021): 108114.
6. Underwood, Thomas, et al. "Molecular dynamic simulations of montmorillonite–organic interactions under varying salinity: an insight into enhanced oil recovery." The Journal of Physical Chemistry C 119.13 (2015): 7282-7294.

7. Sedghi, Mohammad, Mohammad Piri, and Lamia Goual. "Atomistic molecular dynamics simulations of crude oil/brine displacement in calcite mesopores." Langmuir 32.14 (2016): 3375-3384.
8. Hakim, S. S., et al. "Interactions of the calcite {10.4} surface with organic compounds: structure and behaviour at mineral–organic interfaces." Scientific reports 7.1 (2017): 7592.
9. Liu, Jian, et al. "Wettability alteration and enhanced oil recovery induced by proximal adsorption of Na+, Cl−, Ca 2+, Mg 2+, and SO 4 2− ions on calcite." Physical Review Applied 10.3 (2018): 034064.
10. Mahendranath, Ananthu, A. Varkey, and Sonal Mazumder. "Application of nanotechnology in petroleum industry." International Journal of Recent Scientific Research 6.09 (2015): 6152-6157.
11. Ali, Jagar A., et al. "A state-of-the-art review of the application of nanotechnology in the oil and gas industry with a focus on drilling engineering." Journal of Petroleum Science and Engineering 191 (2020): 107118.
12. Hassani, Sedigheh Sadegh, Maryam Daraee, and Zahra Sobat. "Advanced development in upstream of petroleum industry using nanotechnology." Chinese Journal of Chemical Engineering 28.6 (2020): 1483-1491.
13. Cheraghian, Goshtasp, and Luky Hendraningrat. "A review on applications of nanotechnology in the enhanced oil recovery part B: effects of nanoparticles on flooding." International Nano Letters 6.1 (2016): 1-10.
14. Pourafshary, P., et al. "Priority assessment of investment in development of nanotechnology in upstream petroleum industry." SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition. SPE, 2009.
15. He, L. I. U., J. I. N. Xu, and D. I. N. G. Bin. "Application of nanotechnology in petroleum exploration and development." Petroleum Exploration and development 43.6 (2016): 1107-1115.
16. Hammershaimb, E. C., V. A. Kuuskraa, and George Stosur. "Recovery efficiency of enhanced oil recovery methods: a review of significant field tests." SPE Annual Technical Conference and Exhibition, SPE, 1983.

17. Aziz, Hassan, and Saleem Qadir Tunio. "Enhancing oil recovery using nanoparticles—A review." Advances in Natural Sciences: Nanoscience and Nanotechnology 10.3 (2019): 033001.
18. Youssif, Magda I., et al. "Silica nanofluid flooding for enhanced oil recovery in sandstone rocks." Egyptian Journal of Petroleum 27.1 (2018): 105-110.
19. Agista, Madhan Nur, Kun Guo, and Zhixin Yu. "A state-of-the-art review of nanoparticles application in petroleum with a focus on enhanced oil recovery." Applied Sciences 8.6 (2018): 871.
20. Cheraghian, Goshtasp, and Luky Hendraningrat. "A review on applications of nanotechnology in the enhanced oil recovery part A: effects of nanoparticles on interfacial tension." International Nano Letters 6 (2016): 129-138.
21. Hendraningrat, Luky, Li Shidong, and Ole Torsœter. "A glass micromodel experimental study of hydrophilic nanoparticles retention for EOR project." SPE Russian Petroleum Technology Conference, SPE, 2012.
22. Ruiz-Cañas, María C., et al. "New nanohybrid based on hydrolyzed polyacrylamide and silica nanoparticles: Morphological, structural and thermal properties." Polymers 12.5 (2020): 1152.
23. Agi, Augustine, et al. "Synthesis and application of rice husk silica nanoparticles for chemical enhanced oil recovery." Journal of Materials Research and Technology 9.6 (2020): 13054-13066.
24. Miranda, Caetano Rodrigues, Lucas Stori de Lara, and Bruno Costa Tonetto. "Stability and mobility of functionalized silica nanoparticles for enhanced oil recovery applications." SPE international oilfield nanotechnology conference and exhibition. OnePetro, 2012.
25. Onyekonwu, Mike O., and Naomi A. Ogolo. "Investigating the use of nanoparticles in enhancing oil recovery." Nigeria Annual international conference and exhibition. OnePetro, 2010.
26. Sepehrinia, Kazem, and Aliasghar Mohammadi. "Wettability alteration properties of fluorinated silica nanoparticles in liquid-loaded pores: An atomistic simulation." Applied Surface Science 371 (2016): 349-359.

27. Salehzadeh, Jamal, Zahra Tohidi, and Arezou Jafari. "Molecular dynamics study of oil adsorption on the rock surface in presence of silica nanoparticles." AIP Conference Proceedings. Vol. 1920. No. 1. AIP Publishing, 2018.
28. Hendraningrat, Luky, Shidong Li, and Ole Torsæter. "Effect of some parameters influencing enhanced oil recovery process using silica nanoparticles: an experimental investigation." SPE Reservoir Characterization and Simulation Conference and Exhibition. OnePetro, 2013.
29. Jafarnezhad, Mahtab, Mohammad Samipour Giri, and Mostafa Alizadeh. "Impact of SnO2 nanoparticles on enhanced oil recovery from carbonate media." Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 39.1 (2017): 121-128.
30. Maghzi, Ali, et al. "Pore-scale monitoring of wettability alteration by silica nanoparticles during polymer flooding to heavy oil in a five-spot glass micromodel." Transport in porous media 87 (2011): 653-664.
31. Sharma, Tushar, G. Suresh Kumar, and Jitendra S. Sangwai. "Comparative effectiveness of production performance of Pickering emulsion stabilized by nanoparticle–surfactant–polymerover surfactant–polymer (SP) flooding for enhanced oil recoveryfor Brownfield reservoir." Journal of Petroleum Science and Engineering 129 (2015): 221-232.
32. Farhadi, Hamed, et al. "Experimental study of nanoparticle-surfactant-stabilized CO2 foam: Stability and mobility control." Chemical Engineering Research and Design 111 (2016): 449-460.
33. Shah, Rusheet D. "Application of nanoparticle saturated injectant gases for EOR of heavy oils." SPE Annual Technical Conference and Exhibition. SPE, 2009.
34. Chang, Ho, and Yu-Chun Chang. "Fabrication of Al2O3 nanofluid by a plasma arc nanoparticles synthesis system." Journal of Materials Processing Technology 207.1-3 (2008): 193-199.
35. Hafshejani, Laleh Divband, et al. "Synthesis and characterization of Al2O3 nanoparticles by flame spray pyrolysis (FSP)—Role of Fe ions in the precursor." Powder Technology 298 (2016): 42-49.
36. Tsuzuki, Takuya, and Paul G. McCormick. "Mechanochemical synthesis of nanoparticles." Journal of materials science 39 (2004): 5143-5146.

37. Giraldo, Juliana, et al. "Wettability alteration of sandstone cores by alumina-based nanofluids." Energy & Fuels 27.7 (2013): 3659-3665.
38. Ogolo, N. A., O. A. Olafuyi, and M. O. Onyekonwu. "Enhanced oil recovery using nanoparticles." SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition. SPE, 2012.
39. Zaid, Hasnah Mohd, Noorhana Yahya, and Noor Rasyada Ahmad Latiff. "The effect of nanoparticles crystallite size on the recovery efficiency in dielectric nanofluid flooding." Journal of Nano Research 21 (2013): 103-108.
40. Hendraningrat, Luky, and Ole Torsaeter. "Unlocking the potential of metal oxides nanoparticles to enhance the oil recovery." Offshore Technology Conference Asia. OTC, 2014.
41. Hendraningrat, Luky, and Ole Torsæter. "Metal oxide-based nanoparticles: revealing their potential to enhance oil recovery in different wettability systems." Applied Nanoscience 5 (2015): 181-199.
42. Alomair, Osamah A., Khaled M. Matar, and Yousef H. Alsaeed. "Experimental study of enhanced-heavy-oil recovery in Berea sandstone cores by use of nanofluids applications." SPE Reservoir Evaluation & Engineering 18.03 (2015): 387-399.
43. Shekhawat, Dushyant Singh, et al. "Magnetic recovery-injecting newly designed magnetic fracturing fluid with applied magnetic field for EOR." SPE Asia pacific hydraulic fracturing conference. SPE, 2016.
44. Haroun, Mohamed, et al. "Smart nano-EOR process for Abu Dhabi carbonate reservoirs." Abu Dhabi International Petroleum Exhibition and Conference. SPE, 2012.
45. Ogolo, N. A., O. A. Olafuyi, and M. O. Onyekonwu. "Enhanced oil recovery using nanoparticles." SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition. SPE, 2012.
46. Joonaki, Edris, and S. J. P. S. Ghanaatian. "The application of nanofluids for enhanced oil recovery: effects on interfacial tension and coreflooding process." Petroleum Science and Technology 32.21 (2014): 2599-2607.
47. Nwidee, Lezorgia N., et al. "Nanofluids for enhanced oil recovery processes: wettability alteration using zirconium oxide." Offshore Technology Conference Asia. OTC, 2016.

48. Ehtesabi, Hamide, et al. "Enhanced heavy oil recovery in sandstone cores using TiO2 nanofluids." Energy & Fuels 28.1 (2014): 423-430.
49. Hendraningrat, Luky, and Ole Torsaeter. "Unlocking the potential of metal oxides nanoparticles to enhance the oil recovery." Offshore Technology Conference Asia. OTC, 2014.
50. Cheraghian, Goshtasp. "Effects of titanium dioxide nanoparticles on the efficiency of surfactant flooding of heavy oil in a glass micromodel." Petroleum Science and Technology 34.3 (2016): 260-267.
51. Zaid, Hasnah Mohd, Noorhana Yahya, and Noor Rasyada Ahmad Latiff. "The effect of nanoparticles crystallite size on the recovery efficiency in dielectric nanofluid flooding." Journal of Nano Research 21 (2013): 103-108.
52. Tajmiri, Masoumeh, et al. "Wettability alteration of sandstone and carbonate rocks by using zno nanoparticles in heavy oil reservoirs." Iranian Journal of Oil and Gas Science and Technology 4.4 (2015): 50-66.
53. Latiff, Noor Rasyada Ahmad, et al. "Novel enhanced oil recovery method using dielectric zinc oxide nanoparticles activated by electromagnetic waves." 2011 National Postgraduate Conference. IEEE, 2011.
54. Onyekonwu, Mike O., and Naomi A. Ogolo. "Investigating the use of nanoparticles in enhancing oil recovery." Nigeria Annual international conference and exhibition. OnePetro, 2010.
55. Adil, Muhammad, et al. "Effect of dispersion stability on electrorheology of water-based ZnO nanofluids." Energy & Fuels 30.7 (2016): 6169-6177.
56. Hendraningrat, Luky, Shidong Li, and Ole Torsæter. "Effect of some parameters influencing enhanced oil recovery process using silica nanoparticles: an experimental investigation." SPE Reservoir Characterization and Simulation Conference and Exhibition. OnePetro, 2013.
57. Kondiparty, Kirti, et al. "Wetting and spreading of nanofluids on solid surfaces driven by the structural disjoining pressure: statics analysis and experiments." Langmuir 27.7 (2011): 3324-3335.
58. Chengara, Anoop, et al. "Spreading of nanofluids driven by the structural disjoining pressure gradient." Journal of colloid and interface science 280.1 (2004): 192-201.

59. Hendraningrat, Luky, Shidong Li, and Ole Torsæter. "A coreflood investigation of nanofluid enhanced oil recovery." Journal of Petroleum Science and Engineering 111 (2013): 128-138.
60. Worthen, Andrew J., et al. "Steric stabilization of nanoparticles with grafted low molecular weight ligands in highly concentrated brines including divalent ions." Soft Matter 12.7 (2016): 2025-2039.
61. Hendraningrat, Luky. "Unlocking the potential of hydrophilic nanoparticles as novel enhanced oil recovery method: an experimental investigation." (2015).
62. Kanj, Mazen Y., Jim J. Funk, and Zuhair Al-Yousif. "Nanofluid coreflood experiments in the ARAB-D." SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition. SPE, 2009.
63. Caldelas, Federico, et al. "Factors governing distance of nanoparticle propagation in porous media." SPE Oklahoma City Oil and Gas Symposium/Production and Operations Symposium. SPE, 2011.
64. Morrow, Norman R. "Wettability and its effect on oil recovery." Journal of petroleum technology 42.12 (1990): 1476-1484.
65. Li, Shidong. "An experimental investigation of enhanced oil recovery mechanisms in nanofluid injection process." (2016).
66. Kashyap, Rajneesh. "A review on multiscale computational studies for enhanced oil recovery using nanoparticles." arXiv preprint arXiv:2310.05800 (2023).
67. Donatus, Michael. "Removal of heavy metals from industrial effluent using Salvinia molesta." Int. J. Chemtech. Res 9 (2016): 608-613.
68. Kashyap, Rajneesh, et al. "Comparison of nitrogen, phosphorus and potassium level in two differentplant species in controlled and polluted areas of Vellore, Tamil Nadu, India." Poll Res. 35 (2) : 403-407 (2016)
69. Makarov, V. V., et al. "“Green” nanotechnologies: synthesis of metal nanoparticles using plants." Acta Naturae 6.1 (20) (2014): 35-44.
70. Sheng, James J. "Status of surfactant EOR technology." Petroleum 1.2 (2015): 97-105.