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Nanomaterials for Subsurface Application: Study of Particles Retention in Porous Media

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Abstract:	The ability to transport nanoparticles through porous media has interesting engineering applications, notably in reservoir capacity exploration and soil remediation. A series of core-flooding experiments were conducted for quantitative analysis of functionalized TiO2 nanoparticles transport through various porous medias including calcite, dolomite, silica, and limestones rocks. The adsorption of surfactants on rock surface and nanoparticles retention in pore walls were evaluated by chemical oxygen demand (COD) and UV-vis spectroscopy. By applying TiO2 nanoparticles, 49.3 and 68.0 wt.% of surfactant adsorption reduction were observed in pore walls of dolomite and silica rock, respectively. Not surprisingly, the value of nanoparticles deposition for dolomite and silica rocks was near to zero, implying that surfactant adsorption is proportional to the nanoparticles deposition. On the other hand, surfactant adsorption was increased for other types of rock in presence of nanoparticles. 5.5, 13.5 and 22.4 wt.% of nanoparticles deposition was estimated for calcite, black and red limestone, respectively. By making a connection between physicochemical rock properties and nanoparticles deposition rates, we concluded that the surface roughness of rock has a significant influence on mechanical trapping and deposition of nanoparticles in pore-throats.
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Author Comments:	Editors Journal of Applied Nanoscience Dear Editor, My co-authors and I would like to submit the revised manuscript entitled “Nanomaterials for Subsurface Application: Study of Particles Retention in Porous

	Media" for the consideration of publication in the Journal of Applied Nanoscience. We have considered the comments of the referees and addressed them all in revised manuscript. Full responses to the comments are also provided. I again confirm that the manuscript is original and unpublished and is not being considered for publication elsewhere. Should you require further information please do not hesitate to contact me. Yours sincerely Dr. Ehsan Nourafkan
Response to Reviewers:	The authors would like to extend their sincere thanks to the reviewers for their valuable and constructive comments. The manuscript has been carefully modified according to the reviewers' suggestions, and the modifications are highlighted in the revised version. A point-by-point reply is appended, where the reviewers' comments are in black color and the replies are in blue. Compared with the previous submission, the major changes are: •The abstract was rewritten and some important numbers were added to highlight the main achievements of the study. •More recent research studies have been added to the manuscript to reinforce the literature review of the revised version. • The CMC measurement and procedure for choosing surfactant/NPs concertations has been discussed in more detail. •Conducting a thorough proof-reading of the manuscript A point-by-point reply is appended, where the reviewers' comments are in black colour and the replies are in blue. ---------- Reviewer #2: The manuscript entitled "Nanomaterials for Subsurface Application: Study of Particles Retention in Porous Media" generally is interesting to the audiences of Journal of Applied Nanoscience. However, there are some flaws that need to be corrected before final acceptance. My specific comments are as follows: 1-Abstract should be rewritten. The current form is qualitative and needs to be quantitative. Response: The author thanks from reviewer for this comment. The abstract was rewritten and quantitative values were added for the surfactant adsorption and nanoparticles retention values. 2- Introduction also needs to be modified and completed by more references such as: *Transport and aggregation of Al2O3 nanoparticles through saturated limestone under high ionic strength conditions: measurements and mechanisms. Journal of nanoparticle research 16 (12), 1-12. *Influence of clay particles on Al2O3 and TiO2 nanoparticles transport and retention through limestone porous media: measurements and mechanisms. Journal of Nanoparticle Research 17 (5), 1-14. *Transport and retention of TiO2 rutile nanoparticles in saturated porous media under lowionic-strength conditions: measurements and mechanisms. Langmuir 27(9):5393-5402. Response: Thanks for the comment. The recent research relevant to the current study including those are suggested by reviewer were added to the introduction part of the revised version (paragraph 2 page 1-3). 3 -The results revealed in Table 1, in Zeta potential and contact angle sections are questionable. The Zeta potential of limestone and dolomite cannot be negative. The contact angles of limestones and dolomite also show water-wet condition. Please justify how you measure them. Response: The negative/positive value of Zeta potential of rock particles is significantly a function of pH, salinity and mineralogy of rock. The zeta potential was measurement in the neutral water and zero salinity. There are other studies that reported negative zeta potential values for limestone and dolomite in same condition such as: https://doi.org/10.2118/175568-MS https://doi.org/10.1016/0166-6622(91)80102-T The below image briefly shows the results of zeta potential measurement in this study: For the measurement of contact angle, some pieces of rocks were polished using different grades of sandpaper (including very-fine sandpaper size) to smooth the surface at last (below image): The polished and cleaned rock pieces were then washed using deionized water and dried in an oven. A water droplet (usually 1 to 10 µl) was dispensed on top of rocks

pieces using a 0.74 mm outer diameter syringe needle and contact angle was calculated using goniometer (CAM 2008, KSV instruments Ltd. Finland) right after. The procedure of the contact angle measurement was added into the revised version (page 4, paragraph 2).

Reviewer #3: The authors conducted core-flooding experiments to investigate the transport of functionalized nanoparticles through various porous media including calcite, dolomite, silica, and limestones rocks. The adsorption of surfactants on rock surface and nanoparticles retention in porous media were evaluated by chemical oxygen demand (COD) and UV-Vis spectroscopy. The work is very interesting. However, there are issues that need to be addressed before the manuscript can be recommended for acceptance.

1-Please improve your abstract. State the significant findings from this study. You can cite values where necessary.

Response: The author thanks from reviewer for this comment. The abstract was rewritten and quantitative values were added for surfactant adsorption and nanoparticles retention values.

2-Change the word "delivering" in line 20 page 2 to a more mature and convenient word. Maybe "propagation"

Response: Done. The "delivering" term was substituted by “transport”.

3-Your manuscript is lacking in recent references, you cited so many old references, there are lot of recent studies in this area. Please consult and cite more recent literature. For instance, in the statement "However, adsorption of surfactant on rock surface reduces the effectiveness of the process and makes it economically unfeasible". In page 2, line 37-39, the most recent reference you cited is in 2011. This is unacceptable in 2021. Please kindly cite recent literature. The following literature that discussed surfactant adsorption in relationship with nanoparticles are suggested for authors. You can cite them if you find them relevant.

i. Journal of Petroleum Science and Engineering Volume 149, 20 January 2017, Pages 612-622

ii. Journal of Petroleum Science and Engineering Volume 179, August 2019, Pages 841-854

iii. Journal of Petroleum Science and Engineering Volume 159, November 2017, Pages 115-134

Response: The comment of reviewer is completely right and authors thank for this comment. The old-fashioned conclusions were substituted with recent studies relevant to the topic of chemical flooding in absence and presence of NPs (including those are suggested by reviewer) (page 2). The authors hope that the revised version now meet the reviewer expectation.

5-The objective of the present study is not very clear. Clearly outline the knowledge gaps that motivate this study with clearer reference to what has been reported so far in previous studies.

Response: The chemicals & NPs flooding inside the porous media is not a novel topic. However, there are lots of unknow facts regarding the synergistic effect between NPs and chemical for improvement of flooding process by reduction of surfactant adsorption and/or NPs retention inside porous media. Particularly the studies about the effect of physical and chemical properties of pore walls (e.g. wettability, mineralogy, roughness, surface charges, surface area and pores size) on efficiency of functionalized NPs flooding for subsurface applications are very limited and inconclusive. The authors tried to highlight this gap in the last paragraph of the introduction by adding some new sentences.

6-What is the reason for the choice of Titanium (IV) oxide NPs for this study, considering their surface charges and dispersion in aqueous and surfactant solutions? Previous studies showed that silica nanoparticles are better option.

Response: This study has been done as a part of ERC research project entitled NanoEOR (https://cordis.europa.eu/project/id/648375). My colleagues in this project had lots of experience for synthesis, functionalization and characterization of TiO2 NPs for EOR application. Their result has been published in a several research papers such as:

-Ghulam Raza, Muhammad Amjad, Inder Kaur, Dongsheng Wen, Stability and Aggregation Kinetics of Titania Nanomaterials under Environmentally Realistic Conditions, Environ. Sci. Technol. 2016, 50, 16.

Zhongliang Hu, Siddeequah M. Azmi, Ghulam Raza, Paul W. J. Glover, Dongsheng Wen, Nanoparticle-Assisted Water-Flooding in Berea Sandstones, Energy Fuels 2016,

30, 4, 2791–2804.
The available experience and promising result of the previous experimental works were the main reasons for selecting the Titanium (IV) oxide NPs.
7-Did the authors measured the rock surface roughness in this study?
In Page 7, line 50-53, the authors stated that "Moreover, it seems other important factor which have effect on retention of NP is surface roughness of rock. The SEM images and BET analysis together reveal some detail about the surface roughness and topographical of different rocks".
This is a major issue in this study, firstly, the statement seems like a mere speculation with no mechanistic or experimental evidence to support the statement,
Secondly, from the reviewer experience, SEM and BET do not give adequate information regarding surface roughness. Authors are encouraged to use Atomic Force Microscopy to determine the rock surface roughness. This will give more credibility to the results of this study.
Response: The authors agree with the reviewer that the AFM result can drastically improve the quality of manuscript for justifying the NPs retention result. However, we didn't have access to the AFM in our school because it was out of service due to an electronic fault. As an alternative option the authors tried to quantify the surface roughness of the rock using optical profilometer. The below images show the result of profilometer analysis from surface of the rocks. Unfortunately, the resolution of the profilometer was not enough to provide informative information for us to use for justifying the observation.

Optical profilometer image of Silica rock.

Optical profilometer image of dolomite.
The authors believe the combination of SEM and BET results still is valuable to qualitatively justify the NPs deposition in the porous media. The SEM techniques was used for the same purposes in other studies such as:
https://doi.org/10.1038/srep14264
https://doi.org/10.1038/s41598-017-13423-y

8-In Page 8, line 50-55, "The functionalized NPs have the potential to preserve surfactant molecules from adsorption on porous media. However, the actual efficiency is depending upon the retention amount of NPs during flooding process through the porous media".
The authors should explain this statement and make it clearer, it is very fundamental to the findings from this study. Did the nanoparticles get adsorbed on the rock surfaces instead of the surfactants? Some explanations are required.
Response: The author thanks from reviewer for this comment. The statement was modified in the revised version. These modifications are incorporated in page 13 and 14 (first paragraph) of the revised version.
9-In conclusion, the authors mentioned that the optimum surfactant concentration is 25 wt%-75 wt %. It is very uneconomical to use such high concentration of surfactants. Moreover, surfactant optimum performance is at the critical micelle concentration. Was the CMCs of the surfactant determine? The authors should make this clearer please.
Response: Thanks for the comment. Basically, in ASP/SP flooding the surfactant concentration should be in the range of 0.2–1.0 wt% which was stated in several references such as:
-L.L. Schramm, Surfactants: Fundamentals and Applications in the Petroleum Industry, Chapter 6: Surfactant flooding in Enhanced oil recovery, reissue ed., Cambridge University Press, 2006.
-O. Massarweh, A. S. Abushaikha, Review article: The use of surfactants in enhanced oil recovery: A review of recent advances, Energy Reports, Volume 6, November 2020, Pages 3150-3178.
In this study, the total concentration of surfactants blend (AAS-EA) was considered equal to 0.3 wt% (i.e. 0.003 g/ml). Critical micelle concentration (CMC) of AAS was determined by surface tension measurement of surfactant solution with air and conductivity method (below image):

Conductivity measurement of surfactant solution.

The conductivity of anionic surfactant solution increased linearly with increasing surfactant concentration until it reached 2.4×10-3 g/ml, beyond which the rate of conductivity increasing was slightly reduced. This point on the graph where the slope of conductivity line was changed has been identified as the CMC. Therefore, the selected surfactant concentration for EOR process could be sensible, considering the CMC value. The CMC measurement of surfactant was added in the revised version (Fig. 5, page 9, first paragraph).
11-Please put your conclusions in bullet points to make it clearer.
Response: Done. The conclusions were put in bullet points as reviewer suggested (page 16).
12-Improve your work with more recent references to show that you are current in this line of research.
Response: Done. The answer was provided in comment number 3.

Reviewer #4: The authors conducted a comparative experiments on loss of surfactant and nanoparticlies in different porous rocks media to justify the potential of functionalized nanoparticles while flowing through porous media. Authors nicely explained the whole study and results are interesting and useful in many applications. The report looks standard and can be considerably suitable for the publication in Applied Nanoscience. However, this study contains very narrow range of study and have some flaws, therefore some considerations should be revised by the authors:
1- Last two lines of the abstract need technical and grammatical revision.
Response: The comment of reviewer is completely right and the authors thank for this comment. The abstract was rewritten and quantitative values were added for surfactant adsorption and nanoparticles retention.
2-Nanotechnology has been widely utilized for drug delivery in nanomedcine field….this statement has been mentioned without having any correlations with the rest of the statements in the introduction.
Response: Done. The text has been modified in the revised version.
3-Introduction is not in line with the research theme in context of the used surfactant and nanoparticles. It would be better to add one more paragraph to compare the novelty of work with recent published works or previous research in presence of similar surfactants and nanoparticles or functionalized nanoparticles.
Response: Done. The recent studies relevant to the current study including those are suggested by reviewer were added to the introduction part of the revised version (page 3). The authors tried to highlight the novelty of the work in the last paragraph of the introduction and to identify which gaps have been addressed in this study.
4-It would be better to discuss the science behind the particles retention in terms of particles-rock interactions, physical and chemical heterogeneity (already mentioned but not clear even no references have been referred), rock types (surface charges, pore size, fluid-rock interaction, mineralogy etc.) instead of just mentioning the different rock properties (in the second last line of the introduction).
Response: Done. The format of discussion in the revised version was completely modified which was supported with recent references. At first discussion about the retention of bare NPs in pore walls and science behind that has been provided. Then advantage of chemical flooding following by the available opportunity of chemical flooding using NPs has been explained. Finally, the gap in the literature and objective of the current study were highlighted.
5-Overall, the introduction need revision and need suitable discussion in line with the current research theme. It would be better if authors talk about the results and limitation reported so far relevant to the current studies and why this studies is now required at current situation.
Response: Thanks for the comment. The authors modified the introduction part to highlight the importance of synergistic effect between NPs and surfactant for improvement of chemical flooding process. Several recent studied were added to elucidate the state of art of this topic. A new paragraph also was added to explain the gap in the literature for the effect of rock properties on efficiency of the functionalized NPs flooding. The authors hope introduction now meets the expectation of reviewer.
Experimental Procedure:
6-At what pH the Zeta potential and hydrodynamic size of rock particle were measured? Is it same to the pH of injecting fluid(s)? Same about the salinity (it is 4% for the sample fluid). Justify the case for the nanoparticle and rock's particles.
Response: The zeta potential and hydrodynamic size of TiO2 NPs was measured in the brine (4 wt.% salinity, neutral pH) and Zeta potential of the rock’s particles was

measured in the deionized water (neutral pH). The condition of measurement was added into the revised version.
7-What was the condition of rock while measuring contact angle, whether dry and polished or saturated (with oil or water) and polished?
Response: For measurement of contact angle, some pieces of dry rocks surfaces were polished using different grades of sandpaper (including very-fine sandpaper size) to smooth the surface at last (Fig. 2 in revised version). The polished and cleaned rocks pieces were then washed with water and dried in an oven. A water droplet (usually 1 to 10 µl) was dispensed on top of rocks pieces using a 0.74 mm outer diameter syringe needle and contact angle was calculated using goniometer (CAM 2008, KSV instruments Ltd. Finland) very quick and in a couple of seconds after that. The procedure of contact angle measurement was added into the revised version (page 4, paragraph 2).
8-Why the flow rate in each three injection period is not same? Is there any effect of flow rate on particle retention; such as at high flow rate, fraction of retained nanoparticle can flow out to the porous media or less retention at higher interstitial velocity?
Response: Thanks for the comment. Basically, the core flooding tests are time consuming and due to high number of tests, we considered the rate of brine flooding (initial stage) equal to 2 ml/min. This stage is just for saturation of core sample and don't have any adverse impact on the final results. The rate of injection for chemical fluid was 0.5 ml/min (0.1 cm/min for core holder with 2.44 cm internal diameter) which is close to the field application numbers (1-1.5 m/day). The flooding rate could influence the NP's deposition rate; but study of such a parameter was beyond the scope of this study. The authors just applied the injection rate in domain of practical field applications.
9-The rock particles size range is 250-425 micron; it would be better if the particle size distribution will be added as a supplementary data. Also on the basis of rock's particle size, average pore-size should be mentioned (or a range of pore size variation, for example 25-70 micron) to justify that whether the few retention were due to the mechanical trapping or not.
Response: As the authors mentioned in the manuscript, five different types of reservoir rock were crushed, sieved using Test Sieves (Retsch) and collected in different vessels (e.g. below image).

The standard sieves size of 45, 53, 106, 150, 180, 250, 425 and 500 microns were used for particles screening. The rock particles of 250-425 µm size fraction then was selected because this fraction produced a desirable permeability value. Unfortunately, more detail for size distribution of the selected fraction size (between 250-425 µm) is not available to put in the supplementary document. The permeability was calculated based on Darcy's law by using the average pressure gradient at the both end of packed bed column during brine saturation. The authors provided the data for pressure drop and permeability calculation in the supplementary document of revised version. The calculated permeability values were in the range of 90-125 mD and so the packed porous media is well representative of conventional oil reservoir rocks.

Results and discussion:
10-Please justify the huge variation in the contact angle (29-68 degree) of different rock samples (except silica). If all the rock samples were cut and polished identically, how the surface roughness differ largely. If the rock were dry, whether the average pore size were similar so that the water droplet spreading was influenced due to different entry capillary pressure in different rock samples?
Response: Thanks for the comment. However, the authors didn't fully realize that the reviewer's comment is for the possibility of contact angle variation or the reasons behind this variation. So, we tried to address both of them. As authors provided some references in the manuscript, both surface chemistry and roughness could change the wettability of rock surface. The research studies for the effect of surface mineralogy on wettability are limited, but several studies showed that the surface rock minerals can drastically change the wettability of rocks:
M.H. Alqam, S.A. Abu-Khamsin, A.S. Sultan, T.M. Okasha, H.O. Yildiz, Effect of Rock Mineralogy and Oil Composition on Wettability Alteration and Interfacial Tension by Brine and Carbonated Water, Energy Fuels 33 (2019) 1983-1989.
-I. Mohammed, D. Al Shehri, M. Mahmoud, M. S. Kamal, O. S. Alade, Impact of Iron

Minerals in Promoting Wettability Alterations in Reservoir Formations, ACS Omega (2021) 4022-4033.
Alqam et al. showed that the contact angle for the crude oil changed from 127.9°on dolomite to 88.5°on calcite. Mohammed et al., also showed how just iron mineral influenced the wettability of rock surface. In addition to effect of minerals, the surface roughness of rock surface is different is nanoscale which may change the wettability. The objective of this research from wettability measurement is to investigate any connection between NPs deposition and rock properties such as wettability. We cannot for sure propose a mechanism or reason for the contact angle variation because it needs further investigation in a separate research.
11-The mass balance was done for calculating the deposition of NPs. Please mention whether the effluent sample was first dried and then measured the concentration or it was done without drying.
Response: The concentration of TiO2 NPs was at the outlet stream was species using UV-Vis spectroscopy (below image):

For this purpose, a series of standard TiO2 sample solution (with known concentration) was prepared and a calibration curves of TiO2 NPs concentration versus UV absorption ratio (at wavelength of 450 nm) was generated. The concentration of the TiO2 NPs in the outlet stream was specified by interpolation from calibration curve each 30 second. A sentence was added to the revised version to clarify the procedure.
12-Double check the statement in line 38-42 at page 6 about intensity and mineralogy. Do the authors have compositional analysis of minerals present in the different rocks?
Response: Thanks for the comment. The text was modified to be clear for the readers.
13-Please update the caption of Fig. 4 with the surfactant name.
Response: Done. The caption of Fig. 4 was modified as reviewer suggested.
14-Why the tracer test were not carried out before conducting the nano-fluid injection? It would be better if a brief discussion will be added about tracer test results in case of used rocks based on the previously reported research.
Response: This study has been done as a part of ERC research project entitled NanoEOR (https://cordis.europa.eu/project/id/648375). Our team had several sub-groups which worked on different projects including: NPs application for 1-EOR, 2- for reservoir characterization and 3-for drilling applications. Characterization of reservoir rocks using tracer tests (QD particles) was the research topic of another team; however, I had a minor contribution for that work. Due to the conflict of interest, it was rarely possible to do the test in this study. Many thanks for your understanding.
15-Based on the data provided in table 2 and figure 5; the surfactant are attached or grafted to the nanoparticles surface (probably electrostatically); please mention whether all the surfactant molecules were enough to cover the nanoparticle's surface or less or more? For example, if the total amount of surfactant was just equal to the required concentration to cover the complete surface of each nanoparticles, if the nanoparticle retention was zero (seems to ideal) or almost zero, why the adsorption of surfactant onto the rock's surface were not zero. Please discuss this in the context of surfactant-particle interaction and surfactant-rock interaction and which one was dominating. Also incorporate the properties of functionalized nanoparticles before the injection and after or in the effluent sample, whether are they identical?
Response: The conductivity measurement was also used to specify the amount of NPs which is required for attachment of all surfactants molecules on NPs surface. For this purpose, the conductivity of surfactant solution (0.3 wt%), deionized water and TiO2 nanofluid (500, 1000, 1500, 2000 ppm of TiO2 NPs) were measured (supplementary document). The nanofluids have been kept in a dark place immobile for 20 days for sedimentation of NPs. According to Fig. S10, the supernatants conductivity of 2000 ppm TiO2 nanofluid is close to pure TiO2 nanofluid (without surfactant) which confirms a small fraction of surfactant molecules are free inside nanofluids. Therefore 2000 ppm concentration was selected for coreflooding experiment since the higher concentration is not more efficient for surfactant delivery. The conductivity of supernatants solution shows in Fig. S10. According to the figure, the supernatants conductivity of 2000 ppm TiO2 nanofluid is close to pure TiO2 nanofluid (without surfactant) which confirms a small fraction of surfactant molecules are free inside nanofluids.
The method of grafting surfactants to NPs can be classified as covalent assembly and non-covalent adsorption. There are several types of linkage groups such as thiol, ether, phosphonate, carboxylate, sulphate, alkene and amines, which can be introduced onto oxide and graft to NPs with terminal OH groups. As we showed in our previous research, the AAS molecule makes hydrogen bonds to the oxide surface of

	TiO2 NPs via condensation that occurs between the Sulphate-OH groups to form S-O-Ti bond. A similar procedure is proposed for grafting EA molecules to surface of NPs via oxygen atom in ethoxylated group. Such a hydrogen bonds could be break during the core flooding which leads to adsorption on the surfactant on pore walls. Therefore, a degree of surfactants adsorption is observed even in the presence of NPs. However, the efficiency of chemical flooding process could increase by drastically reducing the surfactant amount (around 50%) which is interesting for EOR or soil remediation applications. Moreover, according to authors estimation (based on conductivity measurement), 5.17 wt% of surfactant molecules are free in TiO2 nanofluid before coreflooding. Therefore, the small fraction of free surfactants molecules was not removed before core flooding experiments. In fact, the total efficiency of application of NPs for surfactant delivery was calculated after injecting of TiO2 nanofluid containing a fraction of free surfactant molecules. Supplementary data: 16-Please cross check the Figs. S5 (d) and (e); they seem identical. Also mention the condition of the rock samples (dry or saturated) in the caption. Response: Thanks for the comment. The comment of reviewer is completely right and the authors apologise for the mistake. The authors reviewed the data again and modification was done in the revised version. 17-It would be better, if data that represents contact angle in presence of surfactant and nanoparticles system are added. Response: Thanks for the comment. Unfortunately, because of addressing high number of comments within one month and prioritizing the experimental tests, the authors did not find any time to measure the contact angle in presence of surfactant and NPs. The authors accept that are interesting for the readers; however, they do not have any effect on main messages of the manuscript. The authors are more than happy to provide these data in next run of comments, if the reviewer still think it is urgent to provide the data before publication. 18-Additional references are required to support some of the research statements that are just reported in the current format. https://doi.org/10.1016/j.phpro.2011.11.009 https://doi.org/10.1016/j.molliq.2020.113079 https://doi.org/10.1016/j.molliq.2020.113876 https://doi.org/10.1021/acs.energyfuels.6b00152 https://doi.org/10.1016/j.apsusc.2013.07.029 https://doi.org/10.2118/124418-MS https://doi.org/10.3390/nano8070547 https://doi.org/10.1016/j.petrol.2018.11.002 https://doi.org/10.1016/j.fuel.2018.12.122 Response: The recent studies relevant to the current study including those are suggested by reviewer were added to the introduction part of revised version (paragraph 3).

Nanomaterials for Subsurface Application: Study of Particles Retention in Porous Media

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Abstract

The ability to transport nanoparticles through porous media has interesting engineering applications, notably in reservoir capacity exploration and soil remediation. A series of core-flooding experiments were conducted for quantitative analysis of functionalized TiO_2 nanoparticles transport through various porous medias including calcite, dolomite, silica, and limestones rocks. The adsorption of surfactants on rock surface and nanoparticles retention in pore walls were evaluated by chemical oxygen demand (COD) and UV-vis spectroscopy. By applying TiO_2 nanoparticles, 49.3 and 68.0 wt.% of surfactant adsorption reduction were observed in pore walls of dolomite and silica rock, respectively. Not surprisingly, the value of nanoparticles deposition for dolomite and silica rocks was near to zero, implying that surfactant adsorption is proportional to the nanoparticles deposition. On the other hand, surfactant adsorption was increased for other types of rock in presence of nanoparticles. 5.5, 13.5 and 22.4 wt.% of nanoparticles deposition was estimated for calcite, black and red limestone, respectively. By making a connection between physicochemical rock properties and nanoparticles deposition rates, we concluded that the surface roughness of rock has a significant influence on mechanical trapping and deposition of nanoparticles in pore-throats.

Keywords: Surface Chemistry-Nanoparticles Deposition-Porous Media-Surfactant Adsorption.

Highlights

The retention of functionalized nanoparticles was evaluated in different porous media.

The functionalized nanoparticles retention was connected to the properties of rock reservoirs.

There is a synergistic effect between NPs and surfactant for chemical flooding.

1 Introduction

Nowadays, nanotechnology has become one of the promising approaches in enhanced hydrocarbon recovery, soil remediation and reservoir characterization. 0D (e.g. QDs), 1D (e.g. CNTs), 2D (e.g. Graphene oxide) and 3D NPs (e.g. silica, titanium oxides and alumina) were successfully applied for reservoir exploration (Hu et al. 2019), foam stabilizing (Yekeen et al. 2017) and enhanced oil recovery (EOR) (Luo et al. 2016; Haruna et al. 2019). Due to the relatively small size of NPs, they are much more sensitive to the physical and chemical heterogeneities present in the subsurface. Transport of bare or functionalized NPs through saturated porous media under different ionic strength conditions was a topic of several researches (Babakhani et al. 2017; Qin et al. 2020; Foroozesh and Kumar 2020). Bayat et al. (Bayat et al. 2014; Bayat, Junin, Mohsin, et al. 2015) studied the transport of bare metal oxide NPs (Al_2O_3 and TiO_2 NPs) through limestone including kaolinite, montmorillonite, and illite (clay minerals). They concluded that the recovery of NPs in effluent solution had noticeably declined in the presence of clay minerals which was attributed to the trapping of NPs in pore-throats and morphology of the clays.

The NPs flooding is more effective than water flooding for subsurface applications but much less than chemical flooding. Therefore injection of NPs along with low salinity water (LSW) or chemicals (surfactant/polymer) is suggested to alter the rheological properties of injecting fluid, reduce IFT between oil/aqueous phases and decrease the surfactant adsorption on the pore walls of porous media (Olayiwola and Dejam 2019; Venancio, Nascimento, and Pérez-Gramatges 2020). Surfactant slugs could decrease the interfacial tension (IFT) between oil and aqueous phases which results in reducing the fluid capillary force in pore scale, mobilizing more residual crude oil in pore structures. Furthermore, surfactants help maintaining NPs integrity in harsh subsurface conditions of reservoirs (Nourafkan et al. 2018; Nourafkan et al. 2019). Employing the synergistic effect between NPs and surfactant is a promising idea for the improvement of chemical flooding

efficiency (Fig. 1) (Wu et al. 2017; Neves Libório De Avila et al. 2016; Venancio, Nascimento, and Pérez-Gramatges 2020). Yekeen et al (2019) studied the amount of adsorption of different surfactants (CTAB, SDBS, Triton X-100) on Malaysia shale rock in the presence and absence of SiO_2 NPs. Maximum 49.83% and 81.33% reduction in the adsorbed surfactant on pore walls was reported at 3 wt% NaCl salinity and high temperature (80 ºC), respectively (Yekeen et al. 2019). Venancio et al., (2020) showed that surface modification of silica NPs with alkyl groups (octyl and hexadecyl) increased the surfactant (SDS) recovery after nanofluid injection in an unconsolidated porous medium. The reason was due to the additional hydrophobic interaction between NPs and surfactant tails which improved the colloidal stability of NPs as compared to bare silica NPs when dispersed in micellar solutions of SDS (Venancio, Nascimento, and Pérez-Gramatges 2020). Betancur et al., (2019) evaluated the impact of magnetic NPs on the adsorption reduction of surfactants mixture (propoxy sulfate and olefin sulfonate) in the sand pack porous media (Betancur et al. 2019).

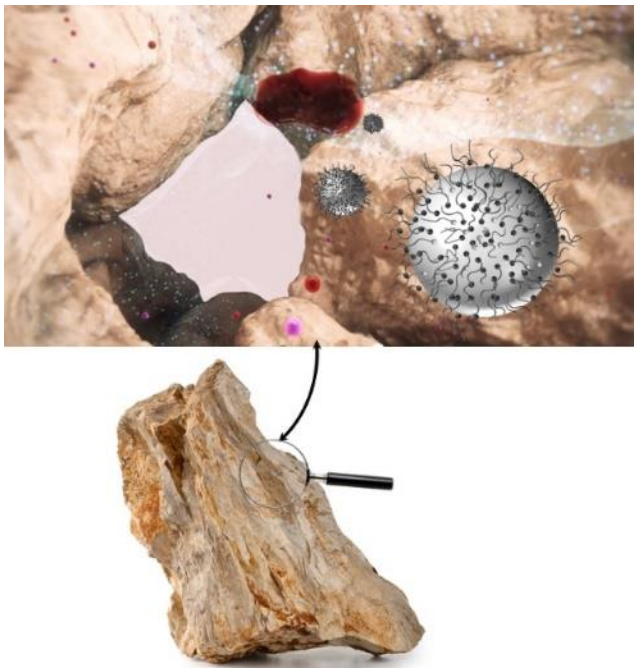


Fig. 1 Employing the synergistic effect between NPs and surfactant for chemical flooding.

Although several researches have been done for the evaluation of functionalized NPs transport through porous media, but there is no consensus among researchers regarding the effect of rock properties on the efficiency of NPs transport. It has been long recognized that the mineralogy and surface structure of rocks significantly could affect the efficiency of NPs and chemical flooding

(Arsalan, Buiting, and Nguyen 2015; Liang et al. 2020). Therefore, the effect of physicochemical properties of porous media on the retention of functionalized NPs in pore walls must be considered while designing the process. This study aims to address the gap in the literature by investigating the effect of pore wall's properties on the transport of surfactant and functionalized NPs through five different types of reservoir rocks. The main important achievement of this study is that the efficiency of chemical flooding could significantly improve by adding NPs into flooding process specifically for reservoir rock with dense smooth surface (here silica and dolomite).

2 Experimental Procedure

2.1 Materials and Characterization

Anionic alkyl aryl sulfonic acid (AAS), nonionic alcohol ethoxylated (EA, C12-13/7EO) surfactants and Titanium (IV) oxide NPs were used as model formulation (surfactants mixture as chemical agents and NPs as carrier). Five different types of reservoir rock were crushed and sieved. The particle size fraction of 250-425 μm was selected, washed three times with de-ionized water and decanted to remove all dust particles. Then the rock grains were put inside an oven at 80 ºC for 5 days to dry and remove residual humidity to be ready for the BET analysis. A piece of dry rock was polished using different grades of sandpaper (including very-fine sandpaper size) to smooth the rock surface (Fig. 2). The polished and cleaned rocks pieces were then washed with water and dried in an oven. A water droplet (usually 1 to 10 μl) was dispensed on top of rock pieces using a 0.74 mm outer diameter syringe needle and contact angle was calculated using goniometer right after (CAM 2008, KSV instruments Ltd. Finland).

Fig. 2 The polished rock surfaces for contact angle measurement.

The surface chemistry and elemental analysis of rocks were analyzed using a SEM-EDEX analysis. The EDX analysis was performed for specific points or defined area on sample surfaces for elemental analysis. Moreover, the Zeta potential and hydrodynamic size of rock particle as well as TiO_2 NPs were measured in brine by Malvern Zeta-sizer ZS instrument.

2.2 Core-Flooding tests

Fig. 3 shows the schematic of core-flooding set-up. The brine and nanofluid slugs were injected into the core holder using a peristaltic pump and a syringe pump, respectively. The core-holder was filled by 10 g of different rock particles (250-425 micron) and all flooding test were carried out at ambient temperature (22ºC). The permeability value in the range of 90-110 mD was calculated based on Darcy's law using the average pressure gradient at both ends of the packed bed column during brine saturation (Supplementary document). The NP's concentration in the effluent at the outlet of core-holder was measured using UV-spectrophotometer at a wavelength of 450 nm (Shimadzu, UV 1800). Calibration curve of TiO_2 NPs concentration versus UV absorption ratio (at wavelength of 450 nm) was generated with a series of standard samples. The concentration of TiO_2 NPs in effluent solution was estimated using UV intensity by interpolation from calibration curve. On the other hand, the stabilizer's concentration was specified by chemical oxygen demand (COD). Core-flooding experiments for were carried out as follows:

-100 ml brine flooding at a flow rate of 2 ml/min to saturate the rock particles in the core-holder.

-20 ml surfactant slug or nanofluid (functionalized NPs with surfactants) at a flow rate of 0.5 ml/min.

-20 ml brine post flooding at a flow rate of 1 ml/min.

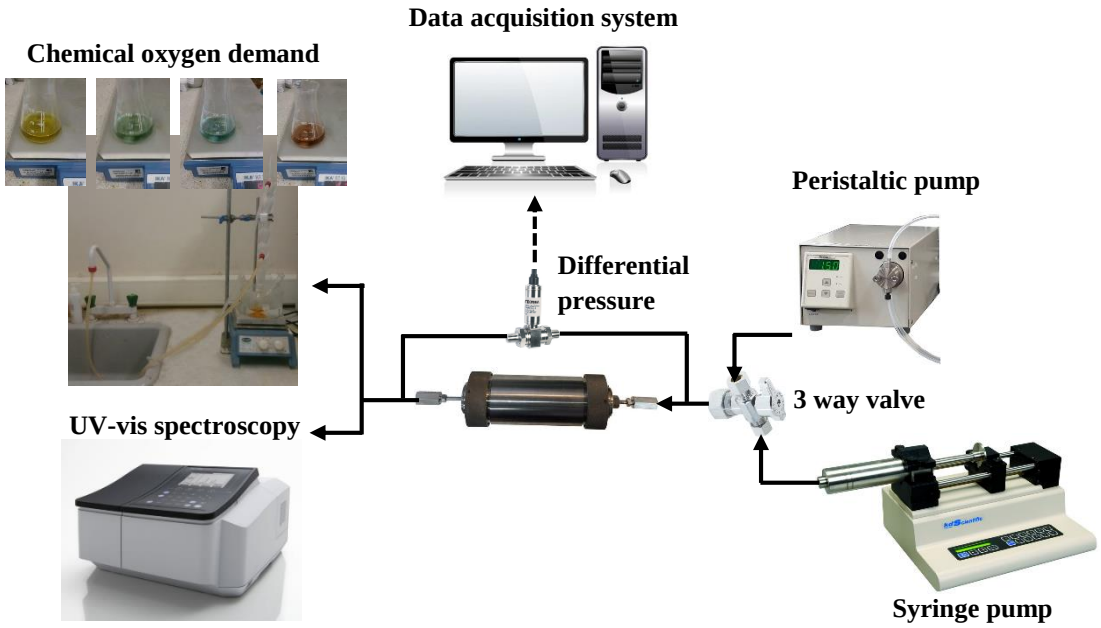


Fig. 3 Schematic of core-flooding set-up.

3 Results and discussion

3.1 Characterization of physical and chemical properties of different rocks

Limestone is a sedimentary rock, which composes large amount of calcium carbonate mineral with some variable amounts of silica. According to SEM photos (Fig. 4) the grains of limestone are irregularly shaped and well-crystallized grains are very rare. Elemental mapping of limestone rocks (Fig. S1) shows the existence of manganese and iron in both limestone. The black limestone contains higher amount of magnesium oxide mineral, which is the main reason of black color. Goethite or hematite are the probable mineralogy of iron in the red limestone as previously investigated by Cai et al. (Cai et al. 2012); however, the existence of hematite is the reason of red color in limestone rock. The elemental mapping also verifies the existence of clay minerals (Alumina and silica composition) in the limestone rocks.

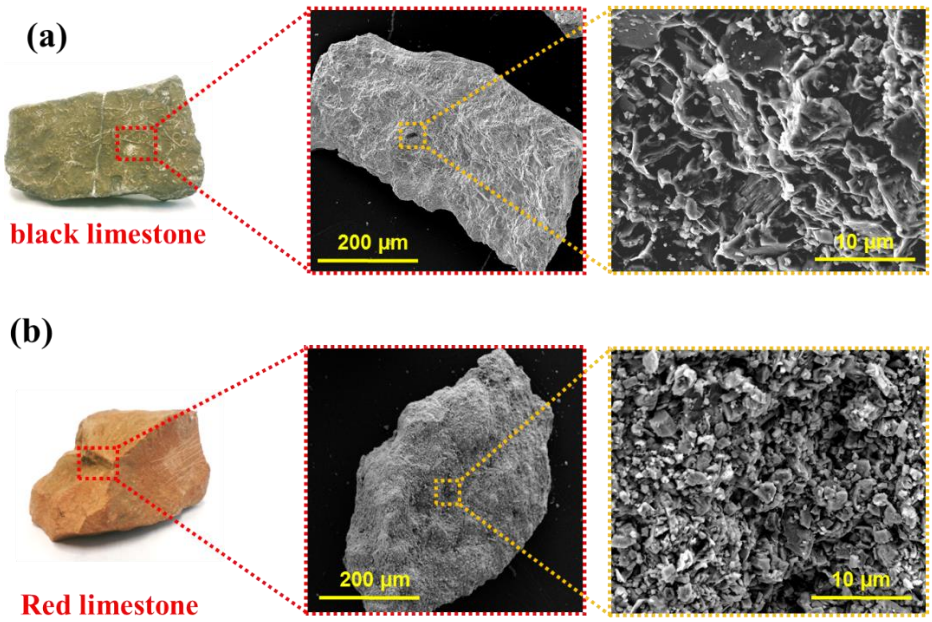


Fig. 4 SEM photos of (a) black limestone and (b) red limestone.

The SEM and EDX images of other types of rocks have been provided in the supplementary document. The SEM photos the calcite rock shows the existence of OOlits structure inside the carbonate rock (Fig. S2). The vein of silica mineral is also detected in calcite rock (Fig. S2) while the composition of dolomite substrate was uniform including magnesium and calcium (Fig. S3). Furthermore, the elemental map of silica rock (Fig. S4) confirms that the silicate crystals is the major fraction of rock structure which combined with a minor fraction of Aluminosilicate mineral. The surface charge of different rocks was obtained using electrophoresis measurements of crushed rock (Schramm, Mannhardt, and Novosad 1991). Rock particles smaller than 45 microns were separated using sieve analysis and suspended in deionized water followed by high-speed centrifuge (5000 RPM for half an hour). The electrophoretic mobility of final suspension then was measured by Malvern zetasizer (Table 1). According to Table 1 all rocks have negative surface charges with the following trend:

Dolomite (least negative) <calcite<black limestone<red limestone < Silica (most negative)

Table 1. The physical and chemical properties of different rocks

Rock type	Silica	Black limestone	Red limestone	Dolomite	Calcite
Specific surface area (m^2/g)	0.877 ± 0.001	1.884± 0.003	3.09 ± 0.004	2.54 ± 0.021	1.46 ± 0.0013

Electrophoretic mobility ($\mu mcmV^{-1}s^{-1}$)	-1.58 ± 0.09	-1.07 ± 0.07	-1.14 ± 0.04	-0.83 ± 0.05	-1.00 ± 0.07
Zeta potential (mV)	-20.6	-14.2	-15.2	-11.1	-12.1
Contact angle	20.09	68.23	37.88	29.83	40.89

Quantitative measurement of CA can determine the wettability of a rock. According to the CA's data (Table 1, Fig. S5) the black limestone and silica have the lowest and highest degree of water wettability between rocks. Surface roughness, fluid composition and rock mineralogy are most important factors which affect the CA of rocks. First time, Wenzel (Wenzel 1936) investigated the effect of roughness on CA and proposed a relationship for the angle observed on both smooth and rough surface. Vijapurapu et al. (Vijapurapu, Rao, and Kun 2002) also studied the impact of mineralogy and surface roughness on wettability of different rocks including quartz, berea sandstone, dolomite and calcite. Both studied reported that the CA values strongly depend on surface chemistry and roughness. However, the Wenzel equation did not match the observation of Vijapurapu.

3.2 Functionalizing of TiO_2 NPs with stabilizers

The AAS surfactant solution samples (15 ml, 0.3 wt%) at different salinities has been shown in Fig. S6. According to Fig. S6 the AAS surfactant made a cloudy solution or even is not soluble at salinity higher than 2 wt%. Clarity and long-term stability are important factors in the design of an injectable surfactant slug. A cloudy and unstable slug indicates an ineffective surfactant solution formulation in the desired salinity range. Thus, it will be necessary to find a suitable composition for formulating single-phase aqueous surfactant solutions at different salinities. Using additive (such as minor fraction of oil phase) or blend of surfactant can produce suitable aqueous solution for injection. In this study, EA surfactant was added to AAS surfactant solution. The ethylene oxide groups in the structure of EA provide tolerance to salinity which produced a clear aqueous solution. In fact, blending of AAS with EA promote the resistance of micelles over high salinity environment and shifts the unsolvable surfactants to become more hydrophilic results in formation of a clear aqueous solution.

Critical micelle concentration (CMC) of AAS was determined by surface tension measurement of surfactant solution with air and conductivity method (Fig. 5). The conductivity of solution was

measured by a Mettler Toledo conductivity Meter (Seven2Go). The conductivity of anionic surfactant solution increased linearly with increasing surfactant concentration until it reached 2.4×10^{-3} g/ml, beyond which the rate of conductivity increasing was slightly reduced. This point on the graph where the slope of conductivity line was changed has been identified as the CMC. Therefore, the selected surfactant concentration for EOR process could be sensible, considering the CMC value.

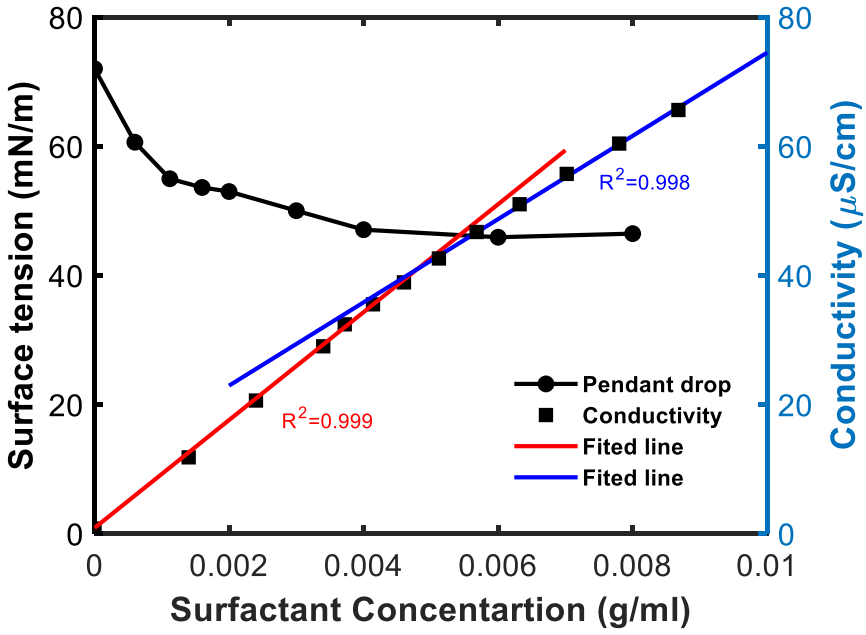
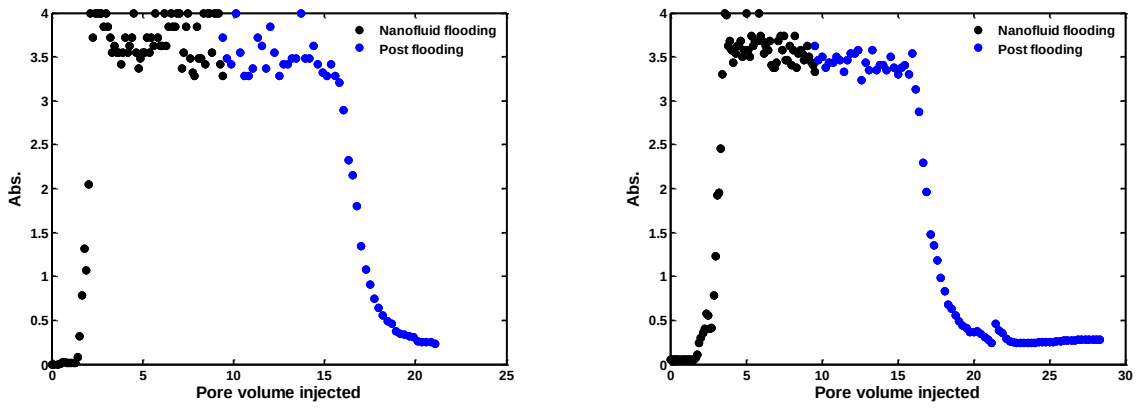


Fig. 5 Critical micelle concentration of AAS surfactant using surface tension measurement of surfactant solution with air and conductivity method

TiO_2 NPs were selected in this study as an example carrier for surfactant molecules in porous media. The optimum condition of functionalizing (concentration of TiO_2 NPs, salinity and optimum surfactants ratio) and formation of non-covalent of grafting surfactants on NPs of solution were evaluated in our previous study (Nourafkan, Hu, and Wen 2018). Briefly, TiO_2 suspensions were prepared by homogenizing 2000 ppm of TiO_2 nanopowders inside the 25% AAS-75% EA surfactants blend solution (4 wt% salinity) by an ultrasound probe running 15 min with amplitude of 25. The reason for choosing 2000 ppm for NPs concentration has been provided in the supplementary document. The stability of nanofluid was checked by UV-visible method and

no change was observed for adsorption peak of nanofluid after 1.5 h immobility. The zeta potential and hydrodynamic size of TiO_2 NPs in brine (4 wt.% salinity, neutral pH) were -10.1 (mV) and 147 nm respectively. The breakthrough curves (BTCs) of NPs were generated using on-line measurement of concentration data using UV-Vis analysis. So, the calculated concentrations in the effluent stream divided by the initial concentration of NPs were drawn versus the injection time expressed in pore volumes (PVs). Finally, the deposition of NPs (mg/g rock and mg/m^2 rock) then calculated by mass balance calculation using BTCs. The breakthrough curves (BTCs) of TiO_2 NP, which shows a relative adsorption, as a function of PV are provided in Fig. 6. The intensity of spectra generally decreases by passing time, which shows that significant amounts of particles were exited from porous media during flooding stage. However, the amount of NPs deposition rate (average intensity of spectral data) are different for different rocks. For example, the average intensity of black limestone and calcite packs is lower compared to silica and dolomite packs which show more retention of NPs in these porous media. The intensity results of post brine flooding (blue points in Fig. 6) show that driving out of NPs is continued following by the brine flooding. However, after totally 20 PV, no more NPs can be cleaned out.



(a) **(b)**

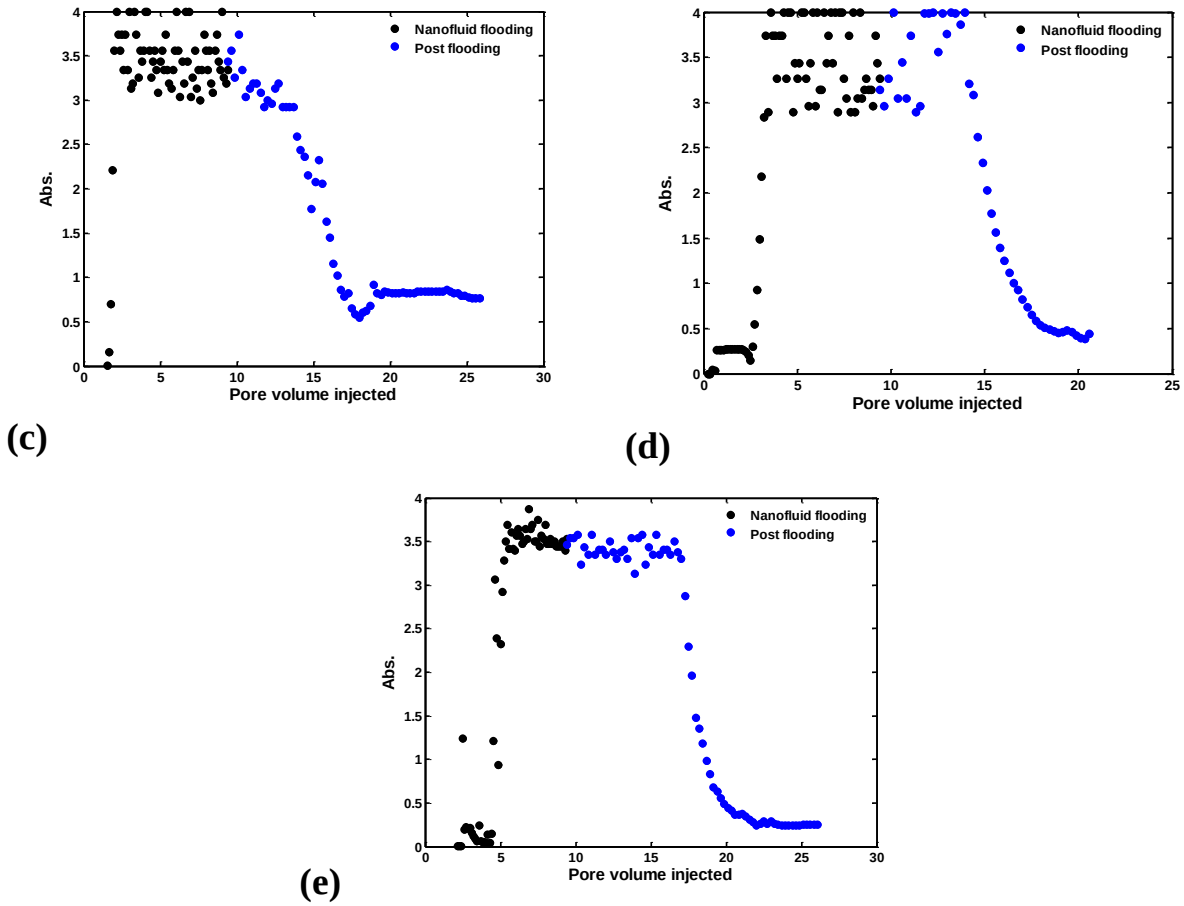
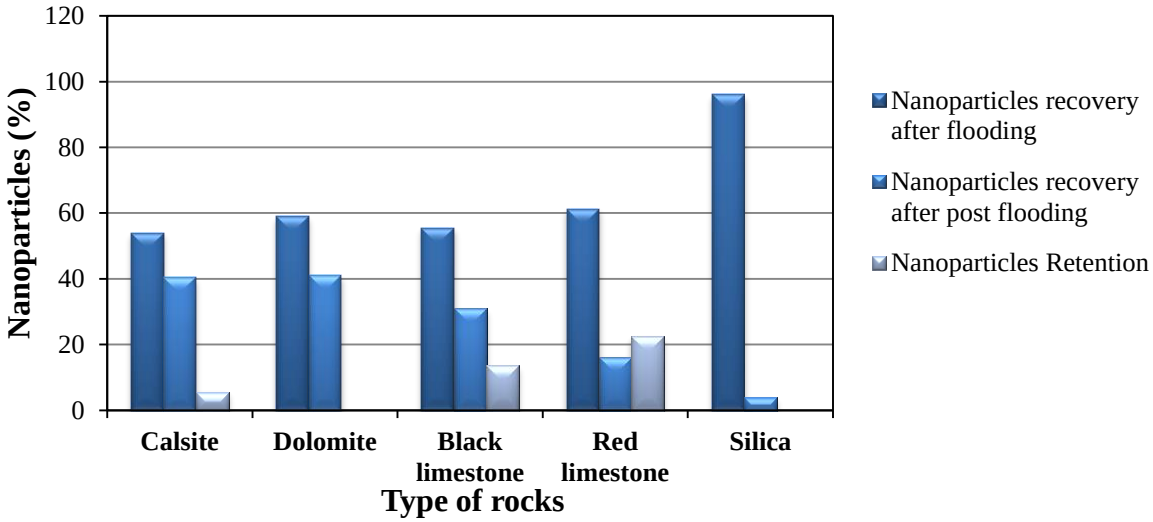


Fig. 6 TiO_2 NPs breakthrough curves transported through different rocks: a) silica, b) black limestone, c) red limestone, d) dolomite, e) Calcite.

Fig. 7-a and Table 2 represented total weigh percent of TiO_2 NPs which trapped in porous media and those discharged during flooding and post flooding which were calculated from BTCs.

(a)



(b)

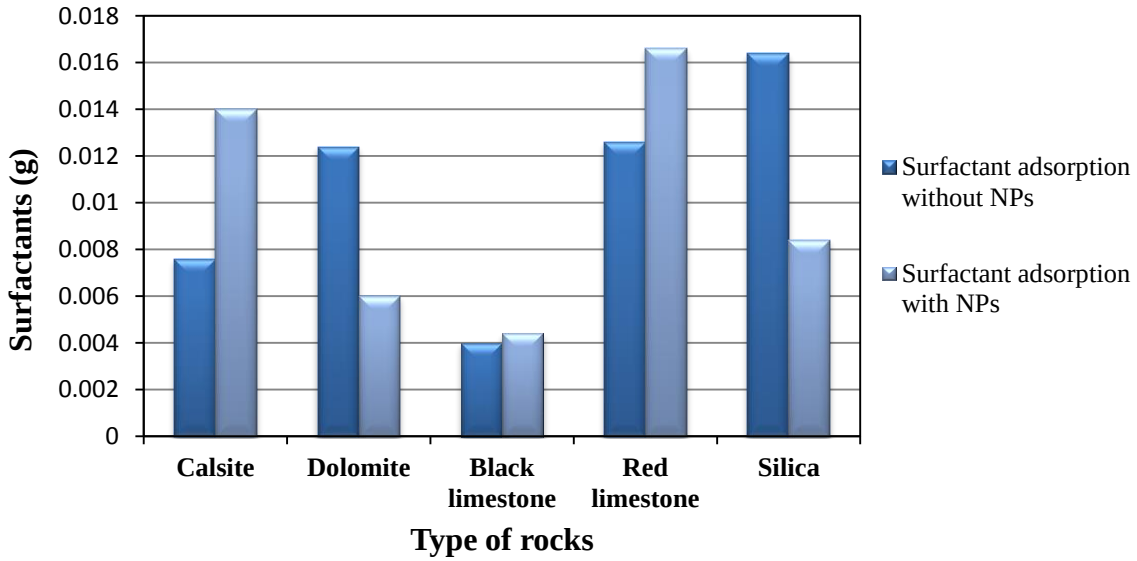


Fig. 7 (a) Weight percent of trapped NPs in porous media, (b) adsorbed surfactants blend (25% AAS-75% EA) on rock surface with and without NPs.

Table 2. TiO_2 NPs retention and surfactants adsorption in different porous medias.

Rock type	Calcite	Dolomite	Black limestone	Red limestone	Silica
Surfactants adsorption without nanoparticles (mg/g rock)	1.16	0.5	1.06	1.98	1.44
Surfactants adsorption with nanoparticles (mg/g rock)	1.5	0.34	1.12	2.38	0.71
Surfactants adsorption without nanoparticles (mg/m^2 rock)	0.529	0.131	0.37	0.427	1.094
Nanoparticles retention (wt%)	5.5	0	13.5	22.4	0
Nanoparticles retention (mg/m^2 rock)	0.075	0	0.186	0.145	0

Fig. 7a and Table 2 indicate that all NPs were discharged from silica and dolomite porous media while other rocks have high degree of NPs retention. Caldelas et al. (Caldelas et al. 2011) stated that specific surface area of rock has a linear effect on particles retention independently of lithology. However, in this study the surface area of dolomite rock is relatively high in compare to other rocks (Table 1) while NPs were completely recovered through porous media of dolomite. Guzman et al. (Dunphy Guzman, Finnegan, and Banfield 2006) also stated that surface charge of rocks is a primary factor in retention of TiO_2 NPs in porous media. Different mechanisms of adsorption, gravitational sedimentation, interception, straining and mechanical trapping have been suggested for the deposition of NPs during transport through porous media, Fig. 8 (Racha Medjda et al. 2020; Agista, Andersen, and Yu 2019).

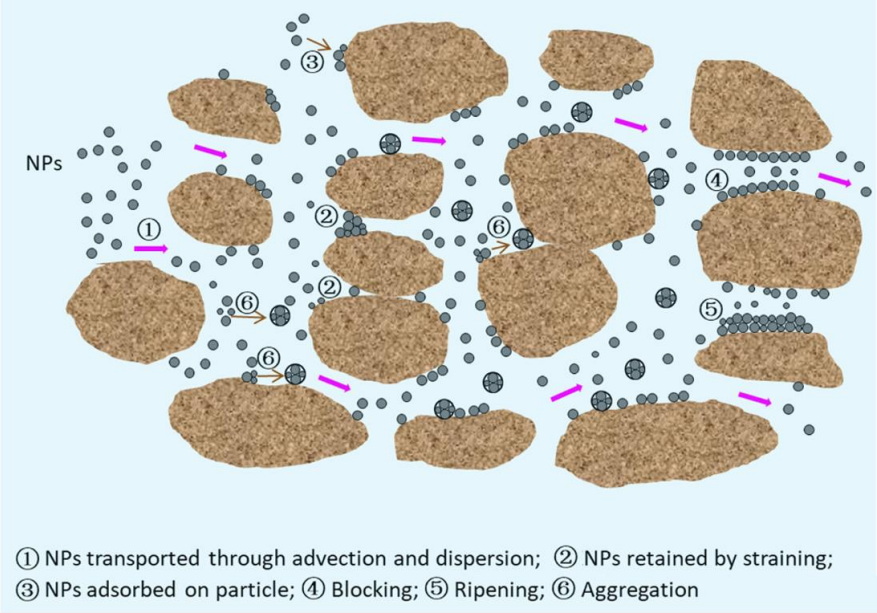


Fig. 8 Schematic diagram of main transport mechanisms of NPs deposition in porous media, reprinted from (Liu et al. 2020).

During this sedimentation process, the particles having greater solid density than water settle on the rock surface. Due to high stability of NPs, sedimentation is unlikely to be the main mechanism for NPs deposition in the current study. Moreover, both Brownian motion and short residence time of NPs could disable gravity sedimentation in the porous media. Independency of NPs deposition amount to surface charge of the rocks could imply that the adsorption doesn't play the main role in trapping the particles. Moreover, the hydrocarbon tail of surfactants do not let the NPs to adsorb on the surface of water wet rocks.

Straining is defined as any physical trapping of agglomerated NPs in pore-throats narrower than the size of larger particles after agglomeration (Babakhani et al. 2017). The process also calls "log-jamming". Here the high stability of TiO_2 NPs confirms the existence of a strong steric repulsion between particles which prevents their agglomeration during transport. According to Table 1 the surface charge of silica has most negativity and dolomite have least negativity while both of them have minimum retention of NPs. With attention to negative zeta potential value of TiO_2 NPs, more retention is expected in dolomite rock compared to other rocks. In fact, it seems that the electrostatic attraction between rock surface and NPs would has a minor effect on particles retention because both silica and dolomite rocks, with opposite surface charge, have the minimum amount of NPs deposition. There is degree of inconsistency between our observation for the effect of surface area and surface charge and other studies which is probably due to two factors: functionalizing of NPs with surfactants blend and surface roughness of rocks. Functionalized surface was covered with a surfactant shell, which reduces the significance of NP's surface charge on NPs retention compared to bare surface.

Moreover, the SEM images and BET analysis together reveal some detail about the surface roughness and topographical of the rocks. The SEM photo illustrated that the silica and dolomite rocks possessed a crystallized particulate morphology. The SEM images of limestone rocks also illustrate the existence of tiny irregular dents and bumps along with submicrometer particles (<1 μm) on surface of rocks which account for the highest measured BET surface area (Fig. 4). The rougher surface of limestone and calcite rocks caused more retention of NPs (Bayat, Junin, Derahman, et al. 2015; Jian et al. 2016). SEM and EDEX analyses also were carried out from the

surface and bulk of different rock's particles to prove the deposition of NPs. The titanium elemental map of bulk grains indicates that lower density of NPs in silica grains in compared to Black limestone and Calcite (Fig. S7). TiO_2 NPs clusters also vividly observed between submicron grains of rock (Fig. S8). Other researchers also stated that the irregular dents and bumps of rock surfaces lead to more NPs to be trapped (Bayat, Junin, Shamshirband, et al. 2015; Bradford and Torkzaban 2008).

In absence of NPs and based on mass of the rock (mg surfactant/g rock), the highest adsorption of surfactants belongs to the red limestone (Table 2); however, based on surface of the rock (mg surfactant/m^2 rock) the silica rock has adsorbed the highest fraction of the surfactants. All evidences confirm that the surfactants intend to adsorb on the rock surface containing Si and Al elements. The Si and Al elements (source of silica and clay mineral) were found in all rocks structure except the dolomite which has the least surfactants adsorption amount. Basically, the surfactant molecules could adsorb by forming electrostatic or hydrogen bonds between hydrophobic tail or hydrophilic head with available surface of porous media (Zhang and Somasundaran 2006). High fraction of EA (75 wt%) and possibility of formation of hydrogen bond between ethylene oxide group the hydroxyl groups at the rock surface is the most probable mechanism for surfactant adoption (Jian et al. 2016). On the other hand, AAS as a ionic surfactant intent to form a electrostatic bond with the opposite charge mineral in the rock structure (Cui et al. 2012; Somasundaran and Krishnakumar 1997). The surface density of hydroxyl groups for different rocks in this study is ordered as dolomite<limestone<Calcite<silica, because of abundance of Si-O-H and Al-O-H groups at rock's surface. The main mechanism of surfactants adsorption at the rock surface schematically illustrates in Fig. 9. Therefore, the amount of surfactants adsorption on dolomite and silica rock's surfaces is expected to be relatively lowest and highest, respectively.

In this research we tried to study the synergistic effect between NPs and surfactant during flooding process through different porous media. The following conclusions can be extracted from this study:

- The rate of surfactants adsorption strongly is a function of surface chare and chemistry of the porous media. A high fraction of surfactants blend (around 36 wt.%) was adsorbed on

silica rock that would drastically reduce the efficiency of practical application of chemical flooding.

- The surfactants adsorption on silica and dolomite rock was reduced to half (around 18 wt.% for silica) after functionalizing the surfactants with TiO_2 NPs. In fact, functionalized NPs have the potential to preserve surfactant molecules from adsorption on the porous walls.
- In spite of usefulness of NPs for reducing adsorption reduction of surfactant in silica and dolomite rocks, the have adverse impact in case of Calcite and limestone rocks. Appling NPs increased the surfactant trapping around 50 and 24 wt.% in Calcite and red limestone porous media.
- We concluded that the synergistic effect between NPs and surfactant has promising result as long as the NPs deposition in porous media be negligible.
- Making a connection between NPs deposition and physicochemical properties of rock's surface (charge, area, roughness and wettability) in this study showed that the surface roughness has the most impact on trapping of NPs. Therefore, the efficiency of functionalized NPs flooding is higher through pore walls with lower micro-roughness.

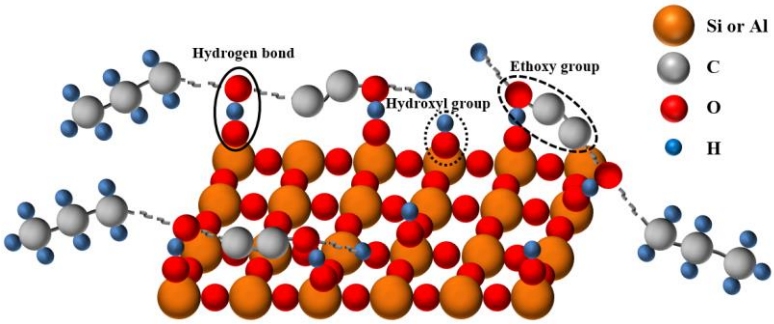


Fig. 9 Proposed mechanism for ethoxylated surfactant adsorption on rock containing silica.

Conclusion

There are several studies dealing with nanoparticles transport through porous media; however, there is still absence of a comprehensive study to evaluate potential of NPs as a chemical agent carrier through different types of porous media. Blend of anionic alkylaryl sulfonates and nonionic alcohol ethoxylated surfactant at optimum composition (25 wt%-75 wt %) and salinity (4 wt%) was used as a stable slug for functionalizing of TiO_2 NPs. The core-flooding experiments has been

performed in five different types of reservoir rocks. According to the results, the surface roughness of rock had most impact on retention of NPs inside the porous media. The SEM photos of limestone grain showed an irregularly surface with rare crystal which caused more retention of NPs inside limestone rocks. The adsorption of alkylaryl sulfonates and alcohol ethoxylated blend greatly depend on mineralogy of rock which was increased at rock surface containing higher amount of silica and alumina. The hydrogen bonding between the oxygen in the ethoxy groups and the hydroxyl groups of silica suggested as likely mechanism which is accrued for adsorption of surfactant. Any specific connection between surfactant attachment with wettability or ability of rock was not disclose in this research. Adsorption of surfactant blend in presence of TiO_2 NPs was proportional with retention of NPs inside column. Therefore, the role of NPs as a carrier for surfactant molecules is outstanding when the transport of NPs through porous media is as much as possible.

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Conflicts of interests The authors declare that they have no conflict of interest.

References

Agista, Madhan Nur, Pål Østebø Andersen, and Zhixin Yu. 2019. 'Modelling nanofluid injection in porous media', *Journal of Petroleum Science and Engineering*, 176: 836-49.

Arsalan, Naveed, Jan J Buiting, and Quoc P Nguyen. 2015. 'Surface energy and wetting behavior of reservoir rocks', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 467: 107-12.

Babakhani, Peyman, Jonathan Bridge, Ruey-an Doong, and Tanapon Phenrat. 2017. 'Continuum-based models and concepts for the transport of nanoparticles in saturated porous media: A state-of-the-science review', *Advances in colloid and interface science*, 246: 75-104.

Bayat, Ali Esfandyari, Radzuan Junin, Mohd Nawi Derahman, and Adlina Abdul Samad. 2015. 'TiO2 nanoparticle transport and retention through saturated limestone porous media under various ionic strength conditions', *Chemosphere*, 134: 7-15.

Bayat, Ali Esfandyari, Radzuan Junin, Farshad Daraei Ghadikolaei, and Ali Piroozian. 2014. 'Transport and aggregation of Al 2 O 3 nanoparticles through saturated limestone under high ionic strength conditions: measurements and mechanisms', *Journal of nanoparticle research*, 16: 1-12.

Bayat, Ali Esfandyari, Radzuan Junin, Rahmat Mohsin, Mehrdad Hokmabadi, and Shahaboddin Shamshirband. 2015. 'Influence of clay particles on Al 2 O 3 and TiO 2 nanoparticles transport and retention through limestone porous media: measurements and mechanisms', *Journal of nanoparticle research*, 17: 1-14.

Bayat, Ali Esfandyari, Radzuan Junin, Shahaboddin Shamshirband, and Wen Tong Chong. 2015. 'Transport and retention of engineered Al 2 O 3, TiO 2, and SiO 2 nanoparticles through various sedimentary rocks', *Scientific reports*, 5: 14264.

Betancur, Stefanía, Francisco Carrasco-Marín, Agustín F Pérez-Cadenas, Camilo A Franco, Jaime Jiménez, Eduardo J Manrique, Henderson Quintero, and Farid B Cortés. 2019. 'Effect of magnetic iron core–carbon shell nanoparticles in chemical enhanced oil recovery for ultralow interfacial tension region', *Energy & Fuels*, 33: 4158-68.

Bradford, Scott A, and Saeed Torkzaban. 2008. 'Colloid transport and retention in unsaturated porous media: A review of interface-, collector-, and pore-scale processes and models', *Vadose Zone Journal*, 7: 667-81.

Cai, Yuanfeng, Xiaoxiao Hu, Xiang Li, and Yuguan Pan. 2012. 'Origin of the red colour in a red limestone from the Vispi Quarry section (central Italy): A high-resolution transmission electron microscopy analysis', *Cretaceous Research*, 38: 97-102.

Caldelas, Federico Manuel, Michael Murphy, Chun Huh, and Steven Lawrence Bryant. 2011. "Factors governing distance of nanoparticle propagation in porous media." In *SPE production and operations symposium*. Society of Petroleum Engineers.

Cui, Z-G, W Li, J-J Qi, and H-J Wang. 2012. 'Individual and mixed adsorption of alkylcarboxylbetaines and fatty amide ethoxylates at Daqing sandstone/water interface', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 414: 180-89.

Dunphy Guzman, Katherine A, Michael P Finnegan, and Jillian F Banfield. 2006. 'Influence of surface potential on aggregation and transport of titania nanoparticles', *Environmental science & technology*, 40: 7688-93.

Foroozesh, Jalal, and Sunil Kumar. 2020. 'Nanoparticles behaviors in porous media: Application to enhanced oil recovery', *Journal of Molecular Liquids*: 113876.

Haruna, Maje Alhaji, Ehsan Nourafkan, Zhongliang Hu, and Dongsheng Wen. 2019. 'Improved polymer flooding in harsh environments by free-radical polymerization and the use of nanomaterials', *Energy & Fuels*, 33: 1637-48.

Hu, Zhongliang, Hui Gao, Srinivasa B Ramisetti, Jin Zhao, Ehsan Nourafkan, Paul WJ Glover, and Dongsheng Wen. 2019. 'Carbon quantum dots with tracer-like breakthrough ability for reservoir characterization', *Science of the Total Environment*, 669: 579-89.

Jian, Guoqing, Maura C Puerto, Anna Wehowsky, Pengfei Dong, Keith P Johnston, George J Hirasaki, and Sibani Lisa Biswal. 2016. 'Static adsorption of an ethoxylated nonionic surfactant on carbonate minerals', *Langmuir*, 32: 10244-52.

Liang, Yan, Jini Zhou, Yawen Dong, Erwin Klumpp, Jiří Šimůnek, and Scott A Bradford. 2020. 'Evidence for the critical role of nanoscale surface roughness on the retention and release of silver nanoparticles in porous media', *Environmental Pollution*, 258: 113803.

Liu, Guansheng, Hua Zhong, Zulfiqar Ahmad, Xin Yang, and Lili Huo. 2020. 'Transport of engineered nanoparticles in porous media and its enhancement for remediation of contaminated groundwater', *Critical Reviews in Environmental Science and Technology*, 50: 2301-78.

Luo, Dan, Feng Wang, Jingyi Zhu, Feng Cao, Yuan Liu, Xiaogang Li, Richard C Willson, Zhaozhong Yang, Ching-Wu Chu, and Zhifeng Ren. 2016. 'Nanofluid of graphene-based amphiphilic Janus nanosheets for tertiary or enhanced oil recovery: High performance at low concentration', *Proceedings of the National Academy of Sciences*, 113: 7711-16.

Neves Libório De Avila, Jocasta, Lorraine Louise Grecco Cavalcanti De Araujo, Santiago Drexler, Jorge de Almeida Rodrigues, and Regina Sandra Veiga Nascimento. 2016. 'Polystyrene nanoparticles as surfactant carriers for enhanced oil recovery', *Journal of Applied Polymer Science*, 133.

Nourafkan, Ehsan, Maryam Asachi, Zhongliang Hu, Hui Gao, and Dongsheng Wen. 2018. 'Synthesis of stable nanoparticles at harsh environment using the synergistic effect of surfactants blend', *Journal of Industrial and Engineering Chemistry*, 64: 390-401.

Nourafkan, Ehsan, Maje Alhaji Haruna, Jabbar Gardy, and Dongsheng Wen. 2019. 'Improved rheological properties and stability of multiwalled carbon nanotubes/polymer in harsh environment', *Journal of Applied Polymer Science*, 136: 47205.

Nourafkan, Ehsan, Zhongliang Hu, and Dongsheng Wen. 2018. 'Nanoparticle-enabled delivery of surfactants in porous media', *Journal of colloid and interface science*, 519: 44-57.

Olayiwola, Saheed Olawale, and Morteza Dejam. 2019. 'A comprehensive review on interaction of nanoparticles with low salinity water and surfactant for enhanced oil recovery in sandstone and carbonate reservoirs', *Fuel*, 241: 1045-57.

Qin, Yunqi, Zong Wen, Wenjing Zhang, Juanfen Chai, Dan Liu, and Shengyu Wu. 2020. 'Different roles of silica nanoparticles played in virus transport in saturated and unsaturated porous media', *Environmental Pollution*, 259: 113861.

Racha Medjda, Bouchenak Khelladi, Chiboub Fellah Abdelghani, Pontié Maxime, and Guellil Fatima Zohra. 2020. 'The trapping of colloid particles in porous media: Mechanisms and applications, review', *Journal of Applied Research in Water and Wastewater*, 7: 180-88.

Schramm, Laurier L, Karin Mannhardt, and Jerry J Novosad. 1991. 'Electrokinetic properties of reservoir rock particles', *Colloids and surfaces*, 55: 309-31.

Somasundaran, P, and S Krishnakumar. 1997. 'Adsorption of surfactants and polymers at the solid-liquid interface', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 123: 491-513.

Venancio, Julio Cesar Carvalho, Regina Sandra Veiga Nascimento, and Aurora Pérez-Gramatges. 2020. 'Colloidal stability and dynamic adsorption behavior of nanofluids containing alkyl-modified silica nanoparticles and anionic surfactant', *Journal of Molecular Liquids*, 308: 113079.

Vijapurapu, Chandra S, Dandina N Rao, and Lian Kun. 2002. "The effect of rock surface characteristics on reservoir wettability." In *SPE/DOE Improved Oil Recovery Symposium*. Society of Petroleum Engineers.

Wenzel, Robert N. 1936. 'Resistance of solid surfaces to wetting by water', *Industrial & Engineering Chemistry*, 28: 988-94.

Wu, Yining, Wenxia Chen, Caili Dai, Yongping Huang, Hao Li, Mingwei Zhao, Long He, and Baolei Jiao. 2017. 'Reducing surfactant adsorption on rock by silica nanoparticles for enhanced oil recovery', *Journal of Petroleum Science and Engineering*, 153: 283-87.

Yekeen, Nurudeen, Muhammad A Manan, Ahmad Kamal Idris, Ali Mohamed Samin, and Abdul Rahim Risal. 2017. 'Experimental investigation of minimization in surfactant adsorption and improvement in surfactant-foam stability in presence of silicon dioxide and aluminum oxide nanoparticles', *Journal of Petroleum Science and Engineering*, 159: 115-34.

Yekeen, Nurudeen, Eswaran Padmanabhan, Ahmad Kamal Idris, and Syed Muhammad Ibad. 2019. 'Surfactant adsorption behaviors onto shale from Malaysian formations: Influence of silicon dioxide nanoparticles, surfactant type, temperature, salinity and shale lithology', *Journal of Petroleum Science and Engineering*, 179: 841-54.

Zhang, Rui, and P Somasundaran. 2006. 'Advances in adsorption of surfactants and their mixtures at solid/solution interfaces', *Advances in colloid and interface science*, 123: 213-29.

Table 1. The physical and chemical properties of different rocks

Rock type	Silica	Black limestone	Red limestone	Dolomite	Calcite
Specific surface area (m^2/g)	0.877 ± 0.001	1.884± 0.003	3.09 ± 0.004	2.54 ± 0.021	1.46 ± 0.0013
Electrophoretic mobility ($\mu m cm V^{-1} s^{-1}$)	-1.58 ± 0.09	-1.07 ± 0.07	-1.14 ± 0.04	-0.83 ± 0.05	-1.00 ± 0.07
Zeta potential (mV)	-20.6	-14.2	-15.2	-11.1	-12.1
Contact angle	20.09	68.23	37.88	29.83	40.89

Table 2. TiO_2 NPs retention and surfactants adsorption in different porous medias.

Rock type	Calcite	Dolomite	Black limestone	Red limestone	Silica
Surfactants adsorption without nanoparticles (mg/g rock)	1.16	0.5	1.06	1.98	1.44
Surfactants adsorption with nanoparticles (mg/g rock)	1.5	0.34	1.12	2.38	0.71
Surfactants adsorption without nanoparticles (mg/m^2 rock)	0.529	0.131	0.37	0.427	1.094
Nanoparticles retention (wt%)	5.5	0	13.5	22.4	0
Nanoparticles retention (mg/m^2 rock)	0.075	0	0.186	0.145	0

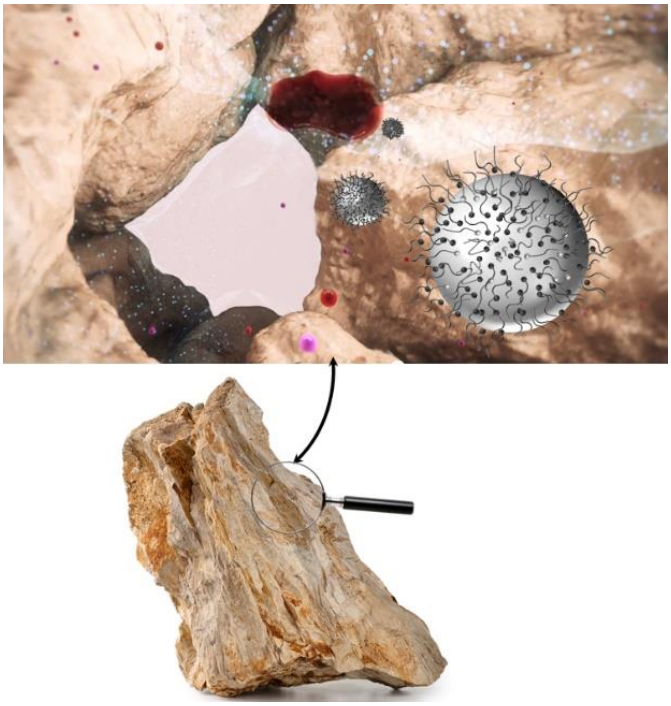


Fig. 1 Employing the synergistic effect between NPs and surfactant for chemical flooding.

Fig. 2 The polished rock surfaces for contact angle measurement.

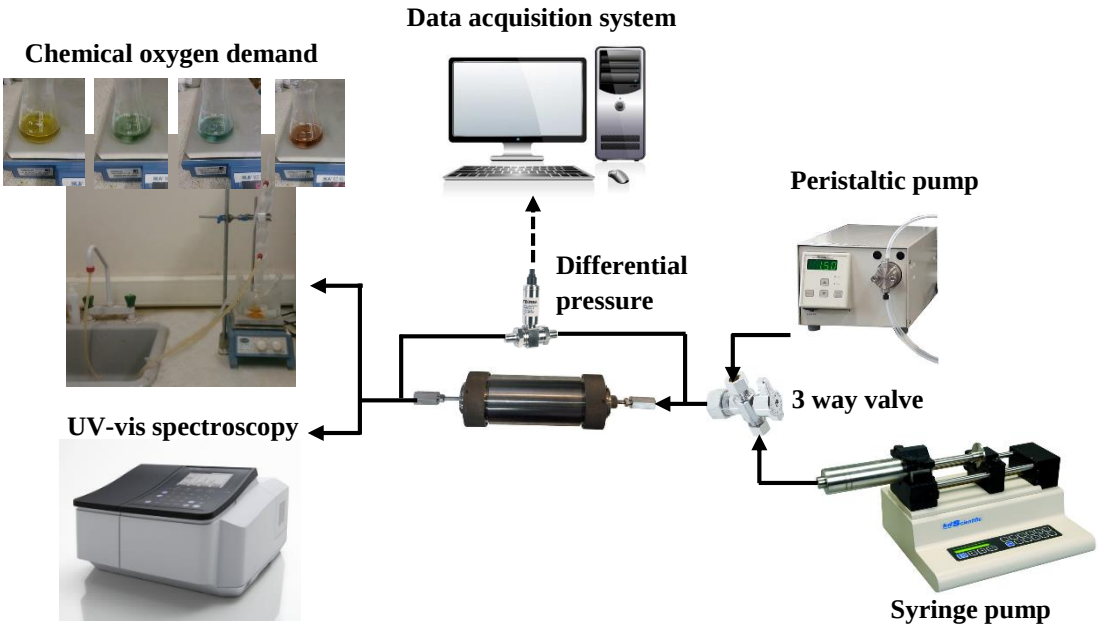


Fig. 3 Schematic of core-flooding set-up.

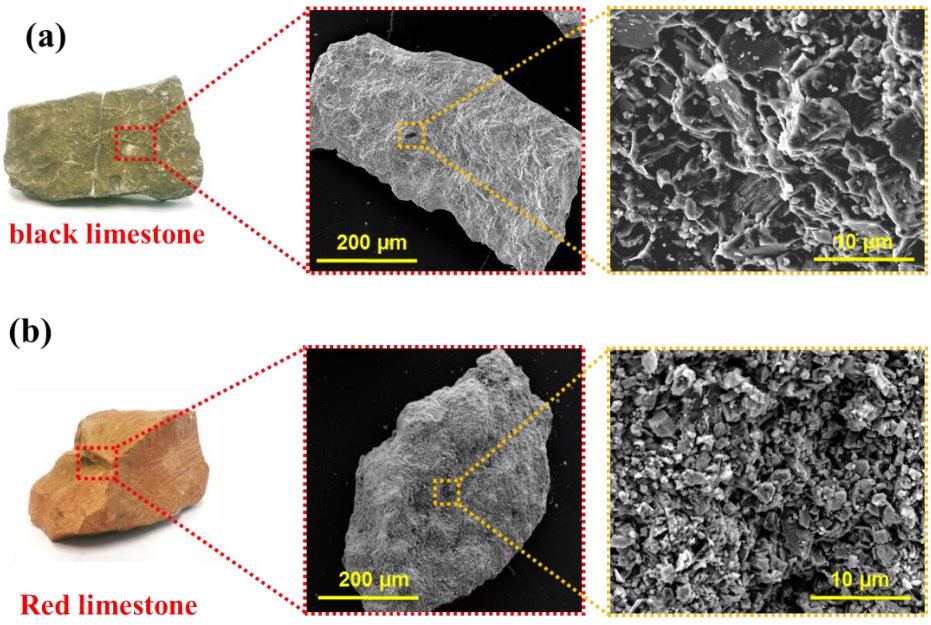


Fig. 4 SEM photos of (a) black limestone and (b) red limestone.

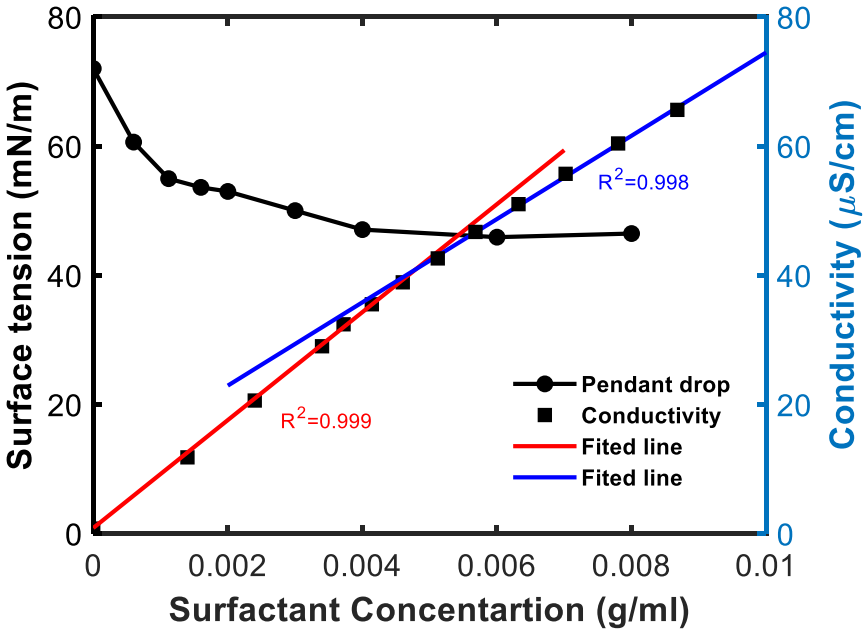


Fig. 5 Critical micelle concentration of AAS surfactant using surface tension measurement of surfactant solution with air and conductivity method

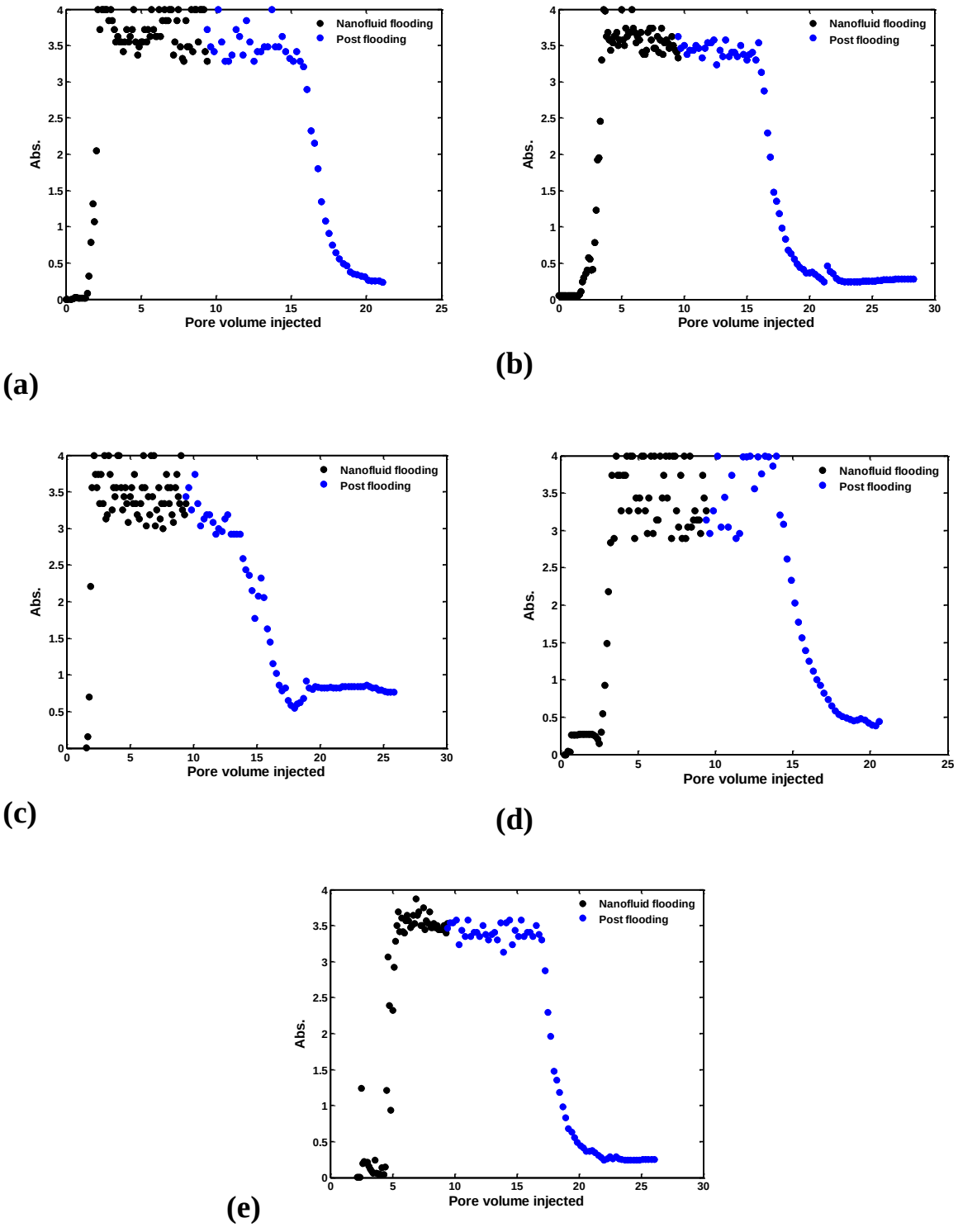
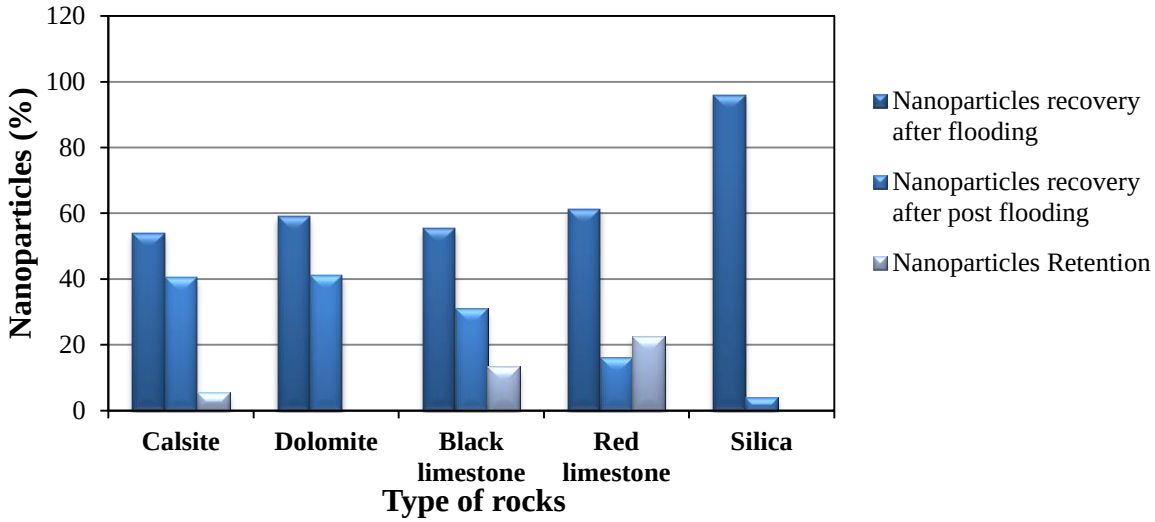


Fig. 6 TiO_2 NPs breakthrough curves transported through different rocks: a) silica, b) black limestone, c) red limestone, d) dolomite, e) Calcite.

(a)



(b)

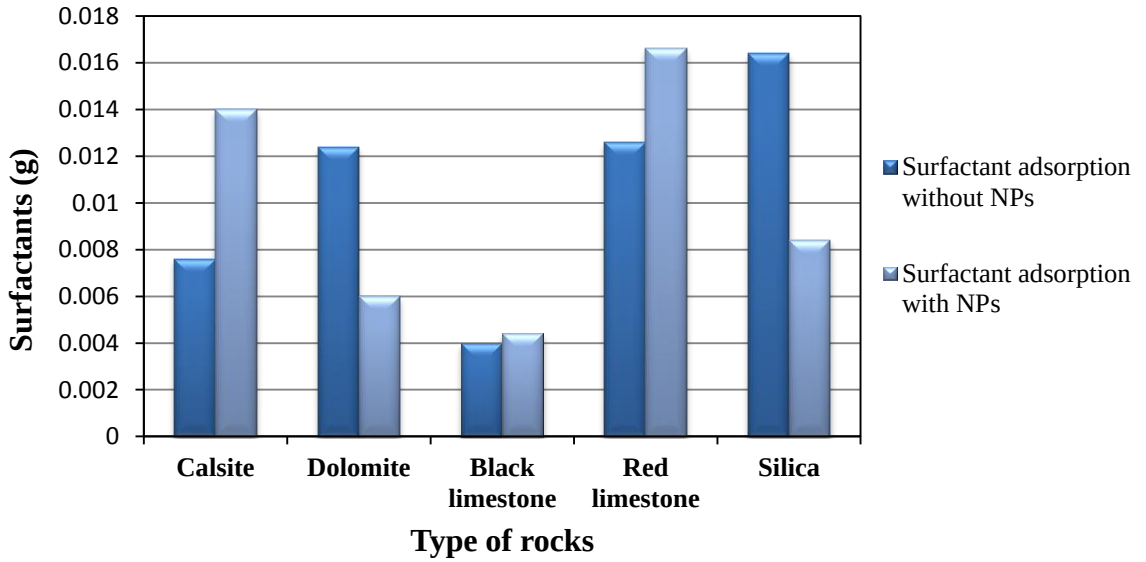


Fig. 7 (a) Weight percent of trapped NPs in porous media, (b) adsorbed surfactants blend on rock surface with and without NPs.

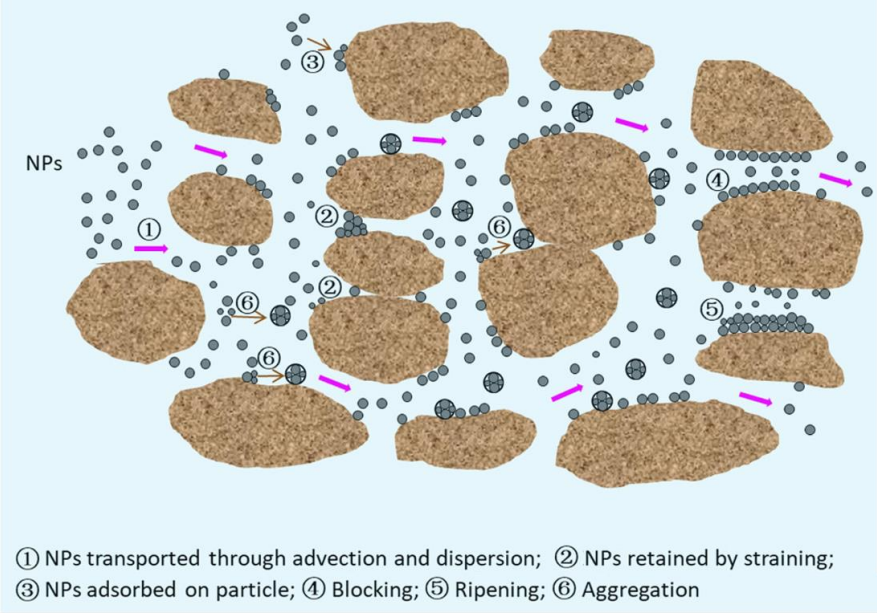


Fig. 8 Schematic diagram of main transport mechanisms of NPs deposition in porous media, reprinted from (Liu et al. 2020).

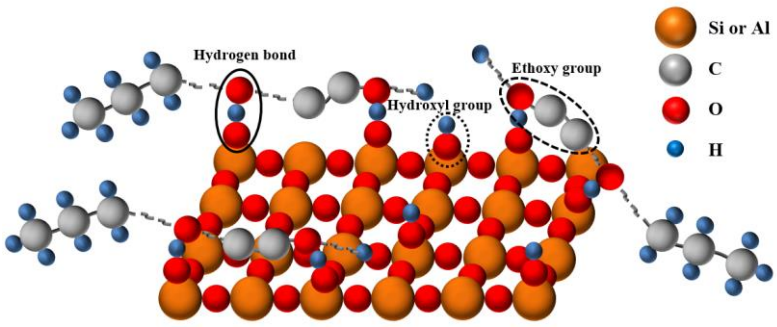


Fig. 9 Proposed mechanism for ethoxylated surfactant adsorption on rock containing silica.

Reply to reviewers:

Nanomaterials for Subsurface Application: Study of Particles Retention in Porous Media

E. Nourafkan[1*], Z. Hu[2], M. Garum[2], H. Esmaeili[3], D. Wen[2,3]

The authors would like to extend their sincere thanks to the reviewers for their valuable and constructive comments. The manuscript has been carefully modified according to the reviewers' suggestions, and the modifications are highlighted in the revised version. A point-by-point reply is appended, where the reviewers' comments are in black color and the replies are in blue. Compared with the previous submission, the major changes are:

- The abstract was rewritten and some important numbers were added to highlight the main achievements of the study.
- More recent research studies have been added to the manuscript to reinforce the literature review of the revised version.
- The CMC measurement and procedure for choosing surfactant/NPs concertations has been discussed in more detail.
- Conducting a thorough proof-reading of the manuscript

A point-by-point reply is appended, where the reviewers' comments are in black colour and the replies are in blue.

Reviewer #2: The manuscript entitled "Nanomaterials for Subsurface Application: Study of Particles Retention in Porous Media" generally is interesting to the audiences of Journal of Applied Nanoscience. However, there are some flaws that need to be corrected before final acceptance. My specific comments are as follows:

1-Abstract should be rewritten. The current form is qualitative and needs to be quantitative.

Response: The author thanks from reviewer for this comment. The abstract was rewritten and quantitative values were added for the surfactant adsorption and nanoparticles retention values.

2- Introduction also needs to be modified and completed by more references such as: *Transport and aggregation of Al2O3 nanoparticles through saturated limestone under high

ionic strength conditions: measurements and mechanisms. Journal of nanoparticle research 16 (12), 1-12.

*Influence of clay particles on Al2O3 and TiO2 nanoparticles transport and retention through limestone porous media: measurements and mechanisms. Journal of Nanoparticle Research 17 (5), 1-14.

*Transport and retention of TiO2 rutile nanoparticles in saturated porous media under lowionic-strength conditions: measurements and mechanisms. Langmuir 27(9):5393-5402.

Response: Thanks for the comment. The recent research relevant to the current study including those are suggested by reviewer were added to the introduction part of the revised version (paragraph 2 page 1-3).

3 -The results revealed in Table 1, in Zeta potential and contact angle sections are questionable. The Zeta potential of limestone and dolomite cannot be negative. The contact angles of limestones and dolomite also show water-wet condition. Please justify how you measure them.

Response: The negative/positive value of Zeta potential of rock particles is significantly a function of pH, salinity and mineralogy of rock. The zeta potential was measurement in the neutral water and zero salinity. There are other studies that reported negative zeta potential values for limestone and dolomite in same condition such as:

https://doi.org/10.2118/175568-MS

https://doi.org/10.1016/0166-6622(91)80102-T

The below image briefly shows the results of zeta potential measurement in this study:

Zetasizer - [ss.dts]

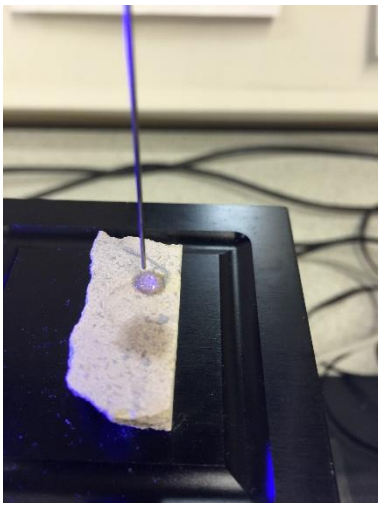
File Edit View Measure Tools Security Window Help

Summary

Records View | Intensity PSD (M) | Zeta Potential (M) | Molecular weight (M) | Autotitration (M) | Aggregation Point (M) | Chromatogram summary (M)

Record	Type	Sample Name	Measurement Date and Time	T	Z-Ave	PdI	Aggregation Index	ZP	Mob	MW	Cond	pH	IEP(s)	IEP Units
				°C	d.nm			mV	µmcm/Vs	kDa	mS/cm			
1	Zeta	red 1	11 August 2016 09:17:13	25.0				-14.1	-1.107		0.366	0.00		
2	Zeta	red 2	11 August 2016 09:19:08	25.0				-15.2	-1.189		0.376	0.00		
3	Zeta	red 3	11 August 2016 09:20:15	25.0				-14.5	-1.140		0.381	0.00		
4	Zeta	calsite 1	11 August 2016 09:22:24	25.0				-13.9	-1.091		0.180	0.00		
5	Zeta	calsite 2	11 August 2016 09:24:22	25.0				-12.5	-0.9786		0.190	0.00		
6	Zeta	calsite 3	11 August 2016 09:25:27	25.0				-12.1	-0.9478		0.196	0.00		
7	Zeta	silica 1	11 August 2016 09:27:22	25.0				-21.3	-1.666		0.159	0.00		
8	Zeta	silica 2	11 August 2016 09:29:17	25.0				-20.6	-1.615		0.169	0.00		
9	Zeta	silica 3	11 August 2016 09:30:22	24.9				-18.9	-1.478		0.174	0.00		
10	Zeta	dolomite 1	11 August 2016 09:35:14	25.0				-10.1	-0.7953		0.909	0.00		
11	Zeta	dolomite 2	11 August 2016 09:37:09	25.1				-11.3	-0.8842		0.967	0.00		
12	Zeta	dolomite 3	11 August 2016 09:38:19	25.0				-14.5	-1.141		0.997	0.00		
31	Zeta	black 1	11 August 2016 10:02:54	24.9				-13.5	-1.062		0.241	0.00		
32	Zeta	black 2	11 August 2016 10:10:35	25.0				-13.1	-1.025		0.282	0.00		
33	Zeta	black 3	11 August 2016 10:12:30	25.0				-14.2	-1.117		0.279	0.00		

For the measurement of contact angle, some pieces of rocks were polished using different grades of sandpaper (including very-fine sandpaper size) to smooth the surface at last (below image):



The polished and cleaned rock pieces were then washed using deionized water and dried in an oven. A water droplet (usually 1 to 10 µl) was dispensed on top of rocks pieces using a 0.74 mm outer diameter syringe needle and contact angle was calculated using goniometer (CAM 2008, KSV instruments Ltd. Finland) right after. The procedure of the contact angle measurement was added into the revised version (page 4, paragraph 2).

Reviewer #3: The authors conducted core-flooding experiments to investigate the transport of functionalized nanoparticles through various porous media including calcite, dolomite, silica, and limestones rocks. The adsorption of surfactants on rock surface and nanoparticles retention in porous media were evaluated by chemical oxygen demand (COD) and UV-Vis spectroscopy.

The work is very interesting. However, there are issues that need to be addressed before the manuscript can be recommended for acceptance.

1-Please improve your abstract. State the significant findings from this study. You can cite values where necessary.

Response: The author thanks from reviewer for this comment. The abstract was rewritten and quantitative values were added for surfactant adsorption and nanoparticles retention values.

2-Change the word "delivering" in line 20 page 2 to a more mature and convenient word. Maybe "propagation"

Response: Done. The "delivering" term was substituted by “transport”.

3-Your manuscript is lacking in recent references, you cited so many old references, there are lot of recent studies in this area. Please consult and cite more recent literature. For instance, in the statement "However, adsorption of surfactant on rock surface reduces the effectiveness of the process and makes it economically unfeasible". In page 2, line 37-39, the most recent reference you cited is in 2011. This is unacceptable in 2021. Please kindly cite recent literature. The following literature that discussed surfactant adsorption in relationship with nanoparticles are suggested for authors. You can cite them if you find them relevant.

i. Journal of Petroleum Science and Engineering Volume 149, 20 January 2017, Pages 612-622

ii. Journal of Petroleum Science and Engineering Volume 179, August 2019, Pages 841-854

iii. Journal of Petroleum Science and Engineering Volume 159, November 2017, Pages 115-134

Response: The comment of reviewer is completely right and authors thank for this comment. The old-fashioned conclusions were substituted with recent studies relevant to the topic of chemical flooding in absence and presence of NPs (including those are suggested by reviewer) (page 2). The authors hope that the revised version now meet the reviewer expectation.

5-The objective of the present study is not very clear. Clearly outline the knowledge gaps that motivate this study with clearer reference to what has been reported so far in previous studies.

Response: The chemicals & NPs flooding inside the porous media is not a novel topic. However, there are lots of unknow facts regarding the synergistic effect between NPs and

chemical for improvement of flooding process by reduction of surfactant adsorption and/or NPs retention inside porous media. Particularly the studies about the effect of physical and chemical properties of pore walls (e.g. wettability, mineralogy, roughness, surface charges, surface area and pores size) on efficiency of functionalized NPs flooding for subsurface applications are very limited and inconclusive. The authors tried to highlight this gap in the last paragraph of the introduction by adding some new sentences.

6-What is the reason for the choice of Titanium (IV) oxide NPs for this study, considering their surface charges and dispersion in aqueous and surfactant solutions? Previous studies showed that silica nanoparticles are better option.

Response: This study has been done as a part of ERC research project entitled NanoEOR (https://cordis.europa.eu/project/id/648375). My colleagues in this project had lots of experience for synthesis, functionalization and characterization of TiO_2 NPs for EOR application. Their result has been published in a several research papers such as:

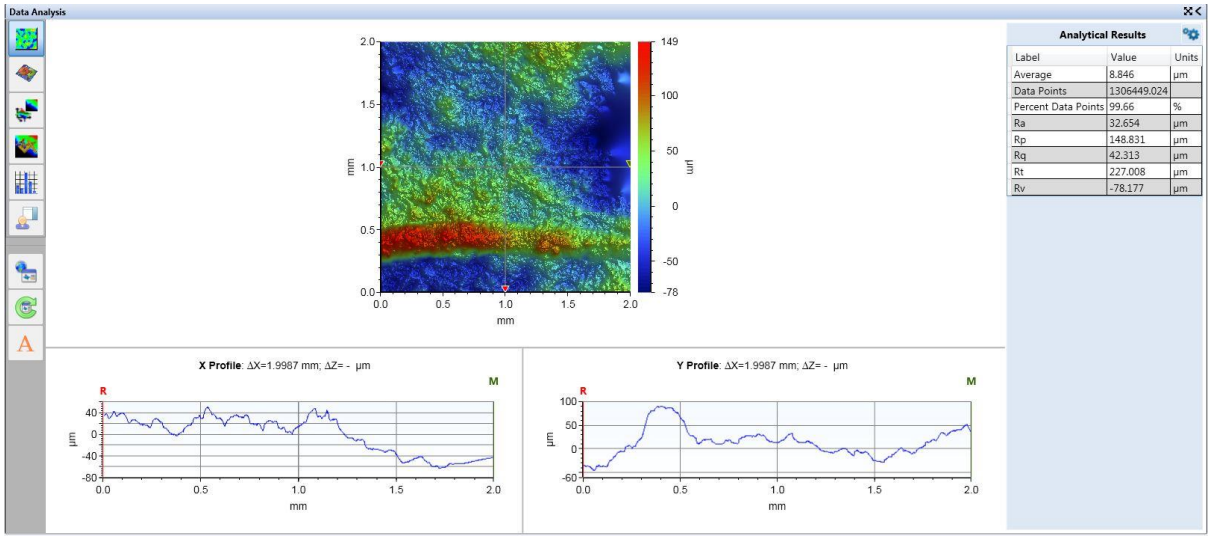
-Ghulam Raza, Muhammad Amjad, Inder Kaur, Dongsheng Wen, Stability and Aggregation Kinetics of Titania Nanomaterials under Environmentally Realistic Conditions, Environ. Sci. Technol. 2016, 50, 16.

Zhongliang Hu, Siddeequah M. Azmi, Ghulam Raza, Paul W. J. Glover, Dongsheng Wen, Nanoparticle-Assisted Water-Flooding in Berea Sandstones, Energy Fuels 2016, 30, 4, 2791–2804.

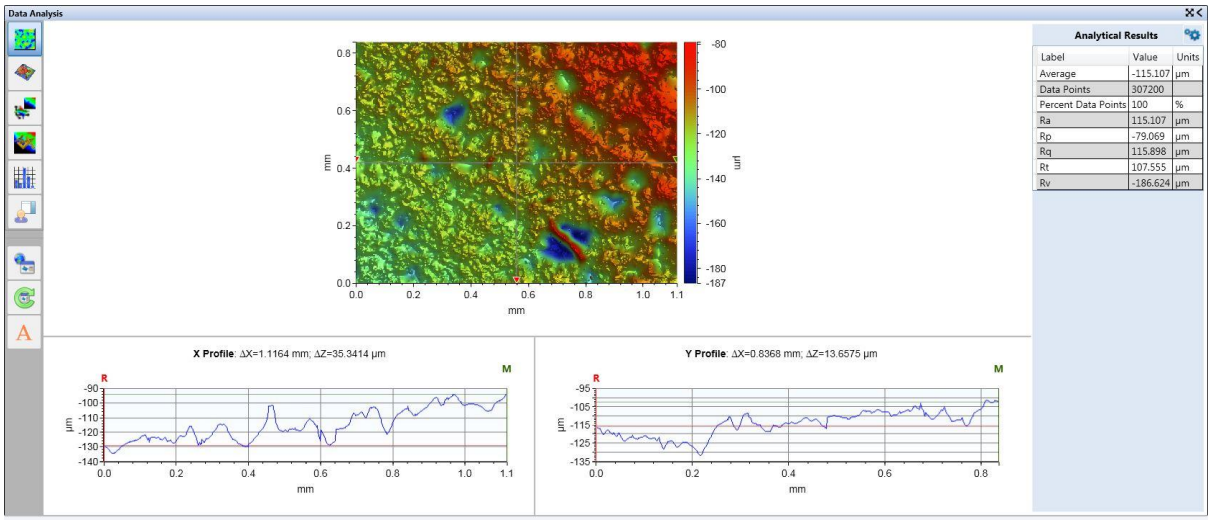
The available experience and promising result of the previous experimental works were the main reasons for selecting the Titanium (IV) oxide NPs.

7-Did the authors measured the rock surface roughness in this study?
In Page 7, line 50-53, the authors stated that "Moreover, it seems other important factor which have effect on retention of NP is surface roughness of rock. The SEM images and BET analysis together reveal some detail about the surface roughness and topographical of different rocks". This is a major issue in this study, firstly, the statement seems like a mere speculation with no mechanistic or experimental evidence to support the statement, Secondly, from the reviewer experience, SEM and BET do not give adequate information regarding surface roughness. Authors are encouraged to use Atomic Force Microscopy to determine the rock surface roughness. This will give more credibility to the results of this study.

Response: The authors agree with the reviewer that the AFM result can drastically improve the quality of manuscript for justifying the NPs retention result. However, we didn't have access to the AFM in our school because it was out of service due to an electronic fault. As an alternative option the authors tried to quantify the surface roughness of the rock using optical profilometer. The below images show the result of profilometer analysis from surface of the rocks. Unfortunately, the resolution of the profilometer was not enough to provide informative information for us to use for justifying the observation.



Optical profilometer image of Silica rock.



Optical profilometer image of dolomite.

The authors believe the combination of SEM and BET results still is valuable to qualitatively justify the NPs deposition in the porous media. The SEM techniques was used for the same purposes in other studies such as:

https://doi.org/10.1038/srep14264

https://doi.org/10.1038/s41598-017-13423-y

8-In Page 8, line 50-55, "The functionalized NPs have the potential to preserve surfactant molecules from adsorption on porous media. However, the actual efficiency is depending upon the retention amount of NPs during flooding process through the porous media". The authors should explain this statement and make it clearer, it is very fundamental to the findings from this study. Did the nanoparticles get adsorbed on the rock surfaces instead of the surfactants? Some explanations are required.

Response: The author thanks from reviewer for this comment. The statement was modified in the revised version. These modifications are incorporated in page 13 and 14 (first paragraph) of the revised version.

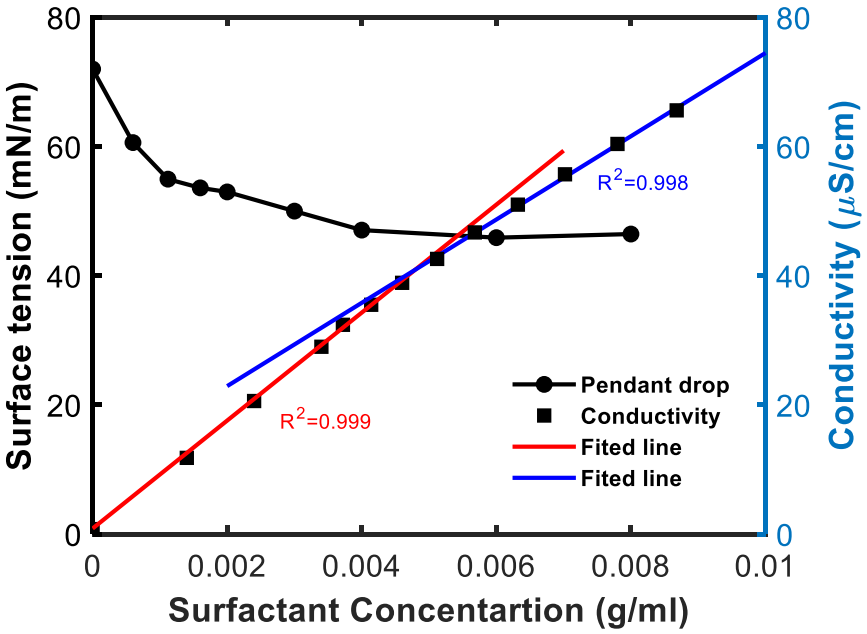
9-In conclusion, the authors mentioned that the optimum surfactant concentration is 25 wt%-75 wt %. It is very uneconomical to use such high concentration of surfactants. Moreover, surfactant optimum performance is at the critical micelle concentration. Was the CMCs of the surfactant determine? The authors should make this clearer please.

Response: Thanks for the comment. Basically, in ASP/SP flooding the surfactant concentration should be in the range of 0.2–1.0 wt% which was stated in several references such as:

-L.L. Schramm, Surfactants: Fundamentals and Applications in the Petroleum Industry, Chapter 6: Surfactant flooding in Enhanced oil recovery, reissue ed., Cambridge University Press, 2006.

-O. Massarweh, A. S. Abushaikha, Review article: The use of surfactants in enhanced oil recovery: A review of recent advances, Energy Reports, Volume 6, November 2020, Pages 3150-3178.

In this study, the total concentration of surfactants blend (AAS-EA) was considered equal to 0.3 wt% (i.e. 0.003 g/ml). Critical micelle concentration (CMC) of AAS was determined by surface tension measurement of surfactant solution with air and conductivity method (below image):



Conductivity measurement of surfactant solution.

The conductivity of anionic surfactant solution increased linearly with increasing surfactant concentration until it reached 2.4×10^{-3} g/ml, beyond which the rate of conductivity increasing was slightly reduced. This point on the graph where the slope of conductivity line was changed has been identified as the CMC. Therefore, the selected surfactant concentration for EOR process could be sensible, considering the CMC value. The CMC measurement of surfactant was added in the revised version (Fig. 5, page 9, first paragraph).

11-Please put your conclusions in bullet points to make it clearer.

Response: Done. The conclusions were put in bullet points as reviewer suggested (page 16).

12-Improve your work with more recent references to show that you are current in this line of research.

Response: Done. The answer was provided in comment number 3.

Reviewer #4: The authors conducted a comparative experiments on loss of surfactant and nanoparticlies in different porous rocks media to justify the potential of functionalized nanoparticles while flowing through porous media. Authors nicely explained the whole study and results are interesting and useful in many applications. The report looks standard and can be considerably suitable for the publication in Applied Nanoscience. However, this study contains very narrow range of study and have some flaws, therefore some considerations should be revised by the authors:

1- Last two lines of the abstract need technical and grammatical revision.

Response: The comment of reviewer is completely right and the authors thank for this comment. The abstract was rewritten and quantitative values were added for surfactant adsorption and nanoparticles retention.

2-Nanotechnology has been widely utilized for drug delivery in nanomedcine field….this statement has been mentioned without having any correlations with the rest of the statements in the introduction.

Response: Done. The text has been modified in the revised version.

3-Introduction is not in line with the research theme in context of the used surfactant and nanoparticles. It would be better to add one more paragraph to compare the novelty of work with recent published works or previous research in presence of similar surfactants and nanoparticles or functionalized nanoparticles.

Response: Done. The recent studies relevant to the current study including those are suggested by reviewer were added to the introduction part of the revised version (page 3). The authors tried to highlight the novelty of the work in the last paragraph of the introduction and to identify which gaps have been addressed in this study.

4-It would be better to discuss the science behind the particles retention in terms of particles-rock interactions, physical and chemical heterogeneity (already mentioned but not clear even no references have been referred), rock types (surface charges, pore size, fluid-rock interaction, mineralogy etc.) instead of just mentioning the different rock properties (in the second last line of the introduction).

Response: Done. The format of discussion in the revised version was completely modified which was supported with recent references. At first discussion about the retention of bare NPs in pore walls and science behind that has been provided. Then advantage of chemical flooding following by the available opportunity of chemical flooding using NPs has been explained. Finally, the gap in the literature and objective of the current study were highlighted.

5-Overall, the introduction need revision and need suitable discussion in line with the current research theme. It would be better if authors talk about the results and limitation reported so far relevant to the current studies and why this studies is now required at current situation.

Response: Thanks for the comment. The authors modified the introduction part to highlight the importance of synergistic effect between NPs and surfactant for improvement of chemical flooding process. Several recent studied were added to elucidate the state of art of this topic. A new paragraph also was added to explain the gap in the literature for the effect of rock properties on efficiency of the functionalized NPs flooding. The authors hope introduction now meets the expectation of reviewer.

Experimental Procedure:

6-At what pH the Zeta potential and hydrodynamic size of rock particle were measured? Is it same to the pH of injecting fluid(s)? Same about the salinity (it is 4% for the sample fluid). Justify the case for the nanoparticle and rock's particles.

Response: The zeta potential and hydrodynamic size of TiO_2 NPs was measured in the brine (4 wt.% salinity, neutral pH) and Zeta potential of the rock's particles was measured in the deionized water (neutral pH). The condition of measurement was added into the revised version.

7-What was the condition of rock while measuring contact angle, whether dry and polished or saturated (with oil or water) and polished?

Response: For measurement of contact angle, some pieces of dry rocks surfaces were polished using different grades of sandpaper (including very-fine sandpaper size) to smooth the surface at last (Fig. 2 in revised version). The polished and cleaned rocks pieces were then washed with water and dried in an oven. A water droplet (usually 1 to 10 µl) was dispensed on top of rocks pieces using a 0.74 mm outer diameter syringe needle and contact angle was calculated using goniometer (CAM 2008, KSV instruments Ltd. Finland) very quick and in a couple of seconds after that. The procedure of contact angle measurement was added into the revised version (page 4, paragraph 2).

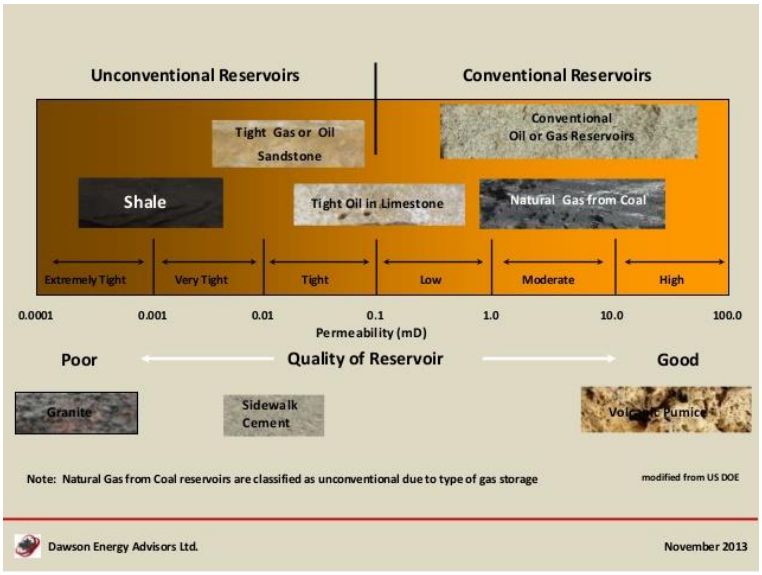
8-Why the flow rate in each three injection period is not same? Is there any effect of flow rate on particle retention; such as at high flow rate, fraction of retained nanoparticle can flow out to the porous media or less retention at higher interstitial velocity?

Response: Thanks for the comment. Basically, the core flooding tests are time consuming and due to high number of tests, we considered the rate of brine flooding (initial stage) equal to 2 ml/min. This stage is just for saturation of core sample and don't have any adverse impact on the final results. The rate of injection for chemical fluid was 0.5 ml/min (0.1 cm/min for core holder with 2.44 cm internal diameter) which is close to the field application numbers (1-1.5 m/day). The flooding rate could influence the NP's deposition rate; but study of such a parameter was beyond the scope of this study. The authors just applied the injection rate in domain of practical field applications.

9-The rock particles size range is 250-425 micron; it would be better if the particle size distribution will be added as a supplementary data. Also on the basis of rock's particle size, average pore-size should be mentioned (or a range of pore size variation, for example 25-70 micron) to justify that whether the few retention were due to the mechanical trapping or not.

Response: As the authors mentioned in the manuscript, five different types of reservoir rock were crushed, sieved using Test Sieves (Retsch) and collected in different vessels (e.g. below image).

The standard sieves size of 45, 53, 106, 150, 180, 250, 425 and 500 microns were used for particles screening. The rock particles of 250-425 μm size fraction then was selected because this fraction produced a desirable permeability value. Unfortunately, more detail for size distribution of the selected fraction size (between 250-425 μm) is not available to put in the supplementary document. The permeability was calculated based on Darcy's law by using the average pressure gradient at the both end of packed bed column during brine saturation. The authors provided the data for pressure drop and permeability calculation in the supplementary document of revised version. The calculated permeability values were in the range of 90-125 mD and so the packed porous media is well representative of conventional oil reservoir rocks.



Results and discussion:

10-Please justify the huge variation in the contact angle (29-68 degree) of different rock samples (except silica). If all the rock samples were cut and polished identically, how the surface roughness differ largely. If the rock were dry, whether the average pore size were

similar so that the water droplet spreading was influenced due to different entry capillary pressure in different rock samples?

Response: Thanks for the comment. However, the authors didn't fully realize that the reviewer's comment is for the possibility of contact angle variation or the reasons behind this variation. So, we tried to address both of them. As authors provided some references in the manuscript, both surface chemistry and roughness could change the wettability of rock surface. The research studies for the effect of surface mineralogy on wettability are limited, but several studies showed that the surface rock minerals can drastically change the wettability of rocks:

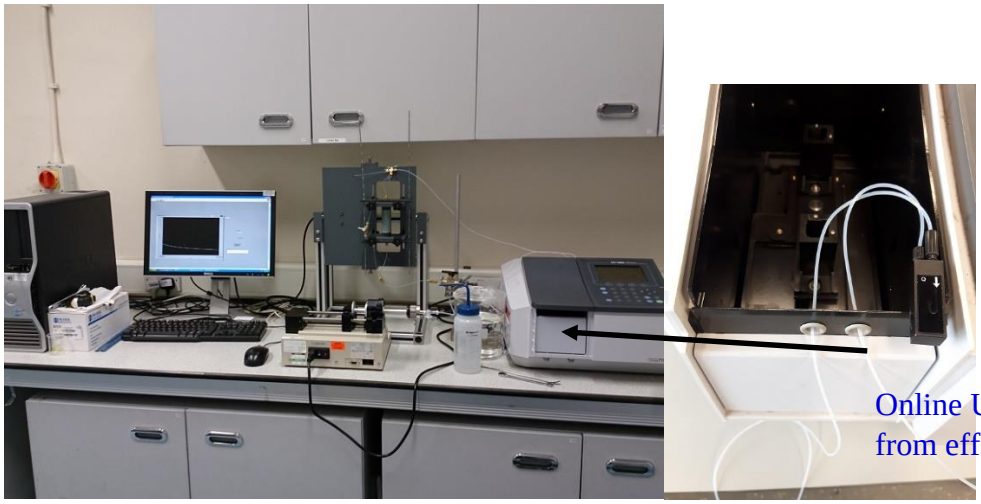
M.H. Alqam, S.A. Abu-Khamsin, A.S. Sultan, T.M. Okasha, H.O. Yildiz, Effect of Rock Mineralogy and Oil Composition on Wettability Alteration and Interfacial Tension by Brine and Carbonated Water, Energy Fuels 33 (2019) 1983-1989.

-I. Mohammed, D. Al Shehri, M. Mahmoud, M. S. Kamal, O. S. Alade, Impact of Iron Minerals in Promoting Wettability Alterations in Reservoir Formations, ACS Omega (2021) 4022-4033.

Alqam et al. showed that the contact angle for the crude oil changed from 127.9°on dolomite to 88.5°on calcite. Mohammed et al., also showed how just iron mineral influenced the wettability of rock surface. In addition to effect of minerals, the surface roughness of rock surface is different is nanoscale which may change the wettability. The objective of this research from wettability measurement is to investigate any connection between NPs deposition and rock properties such as wettability. We cannot for sure propose a mechanism or reason for the contact angle variation because it needs further investigation in a separate research.

11-The mass balance was done for calculating the deposition of NPs. Please mention whether the effluent sample was first dried and then measured the concentration or it was done without drying.

Response: The concentration of TiO_2 NPs was at the outlet stream was species using UV-Vis spectroscopy (below image):



Online UV spectral collection from effluent solution

For this purpose, a series of standard TiO_2 sample solution (with known concentration) was prepared and a calibration curves of TiO_2 NPs concentration versus UV absorption ratio (at wavelength of 450 nm) was generated. The concentration of the TiO_2 NPs in the outlet stream was specified by interpolation from calibration curve each 30 second. A sentence was added to the revised version to clarify the procedure.

12-Double check the statement in line 38-42 at page 6 about intensity and mineralogy. Do the authors have compositional analysis of minerals present in the different rocks?

Response: Thanks for the comment. The text was modified to be clear for the readers.

13-Please update the caption of Fig. 4 with the surfactant name.

Response: Done. The caption of Fig. 4 was modified as reviewer suggested.

14-Why the tracer test were not carried out before conducting the nano-fluid injection? It would be better if a brief discussion will be added about tracer test results in case of used rocks based on the previously reported research.

Response: This study has been done as a part of ERC research project entitled NanoEOR (https://cordis.europa.eu/project/id/648375). Our team had several sub-groups which worked on different projects including: NPs application for 1-EOR, 2- for reservoir characterization and 3-for drilling applications. Characterization of reservoir rocks using tracer tests (QD particles) was the research topic of another team; however, I had a minor contribution for that work. Due to the conflict of interest, it was rarely possible to do the test in this study. Many thanks for your understanding.

15-Based on the data provided in table 2 and figure 5; the surfactant are attached or grafted to the nanoparticles surface (probably electrostatically); please mention whether all the surfactant molecules were enough to cover the nanoparticle's surface or less or more? For example, if the total amount of surfactant was just equal to the required concentration to cover the complete surface of each nanoparticles, if the nanoparticle retention was zero (seems to ideal) or almost zero, why the adsorption of surfactant onto the rock's surface were not zero. Please discuss this in the context of surfactant-particle interaction and surfactant-rock interaction and which one was dominating. Also incorporate the properties of functionalized nanoparticles before the injection and after or in the effluent sample, whether are they identical?

Response: The conductivity measurement was also used to specify the amount of NPs which is required for attachment of all surfactants molecules on NPs surface. For this purpose, the conductivity of surfactant solution (0.3 wt%), deionized water and TiO2 nanofluid (500, 1000, 1500, 2000 ppm of TiO2 NPs) were measured (supplementary document). The nanofluids have been kept in a dark place immobile for 20 days for sedimentation of NPs. According to Fig. S10, the supernatants conductivity of 2000 ppm TiO2 nanofluid is close to pure TiO2 nanofluid (without surfactant) which confirms a small fraction of surfactant molecules are free inside nanofluids. Therefore 2000 ppm concentration was selected for coreflooding experiment since the higher concentration is not more efficient for surfactant delivery. The conductivity of supernatants solution shows in Fig. S10. According to the figure, the supernatants conductivity of 2000 ppm TiO_2 nanofluid is close to pure TiO_2 nanofluid (without surfactant) which confirms a small fraction of surfactant molecules are free inside nanofluids.

The method of grafting surfactants to NPs can be classified as covalent assembly and non-covalent adsorption. There are several types of linkage groups such as thiol, ether, phosphonate, carboxylate, sulphate, alkene and amines, which can be introduced onto oxide and graft to NPs with terminal OH groups. As we showed in our previous research, the AAS molecule makes hydrogen bonds to the oxide surface of TiO_2 NPs via condensation that occurs between the Sulphate-OH groups to form S-O-Ti bond. A similar procedure is proposed for grafting EA molecules to surface of NPs via oxygen atom in ethoxylated group. Such a hydrogen bonds could be break during the core flooding which leads to adsorption on the surfactant on pore walls. Therefore, a degree of surfactants adsorption is observed even in the presence of NPs. However, the efficiency of chemical flooding process could increase by drastically reducing the surfactant amount (around 50%) which is interesting for EOR or soil remediation

applications. Moreover, according to authors estimation (based on conductivity measurement), 5.17 wt% of surfactant molecules are free in TiO_2 nanofluid before coreflooding. Therefore, the small fraction of free surfactants molecules was not removed before core flooding experiments. In fact, the total efficiency of application of NPs for surfactant delivery was calculated after injecting of TiO_2 nanofluid containing a fraction of free surfactant molecules.

Supplementary data:

16-Please cross check the Figs. S5 (d) and (e); they seem identical. Also mention the condition of the rock samples (dry or saturated) in the caption.

Response: Thanks for the comment. The comment of reviewer is completely right and the authors apologise for the mistake. The authors reviewed the data again and modification was done in the revised version.

17-It would be better, if data that represents contact angle in presence of surfactant and nanoparticles system are added.

Response: Thanks for the comment. Unfortunately, because of addressing high number of comments within one month and prioritizing the experimental tests, the authors did not find any time to measure the contact angle in presence of surfactant and NPs. The authors accept that are interesting for the readers; however, they do not have any effect on main messages of the manuscript. The authors are more than happy to provide these data in next run of comments, if the reviewer still think it is urgent to provide the data before publication.

18-Additional references are required to support some of the research statements that are just reported in the current format.

https://doi.org/10.1016/j.phpro.2011.11.009
https://doi.org/10.1016/j.molliq.2020.113079
https://doi.org/10.1016/j.molliq.2020.113876
https://doi.org/10.1021/acs.energyfuels.6b00152
https://doi.org/10.1016/j.apsusc.2013.07.029
https://doi.org/10.2118/124418-MS
https://doi.org/10.3390/nano8070547

https://doi.org/10.1016/j.petrol.2018.11.002
https://doi.org/10.1016/j.fuel.2018.12.122

Response: The recent studies relevant to the current study including those are suggested by reviewer were added to the introduction part of revised version (paragraph 3).