Evaluation of nanoparticle-based fluids with regard to the enhanced oil recovery (EOR) efficiency and energy cost of their synthesis

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Introduction

Globally the overall oil recovery efficiency for primary and secondary recovery range from 35% to 45% and a tertiary recovery method that can increase the enhanced oil recovery (EOR) efficiency by 10-30% could contribute to energy supply. The tertiary (EOR) methods are commonly based on the injection of materials to displace the trapped oil. During EOR processes, the physicochemical properties of the rock alter to favor the mobilization of trapped oil ganglia. This might occur with: (i) the reduction of the interfacial tension thus decreasing the capillary forces; (ii) the increase of the viscosity of water, thus increasing the mobility ratio between water and oil; (iii) the alteration of the wettability, thus facilitating the detachment of oil from the rock surfaces.

Conventional EOR methods include chemical flooding (CEOR), gas injection, thermal recovery, microbial enhanced oil recovery (MEOR), low-salinity waterflooding, and foam-EOR. Chemical EOR (CEOR) includes different methods of injecting polymers, surfactants, salts and alkalis into the reservoirs. Studies have shown that the polymer flooding might increase oil recovery by 5-30% of original oil in place (OOIP). The use of polymers in enhanced oil recovery (EOR) processes comprise an emerging and well-promising approach. While surfactants injection into geological sites has been a commonly practiced EOR method, the chemical flooding by the injection of polymer solutions or polymer-coated nanoparticle suspensions is still at its early stages.

Objectives

- Development of "smart fluids" by grafting adequately synthesized polymers to the surface of nanoparticles, and use them as agents for the synthesis of Pickering emulsions.
- Correlation of the stability / longevity of nano-colloids, and rheological behavior of Pickering emulsions with their composition (salinity, ionic strength, divalent ion concentration, oil to water volume ratio,).
- Correlation of the interfacial and rheological properties of "smart fluids" with their capacity to mobilize oil ganglia from glass-etched pore network.
- Cost benefit analysis and selection of the most efficient "smart fluids" for EOR processes.

Methodology

- **Synthesis** of two different types **of nano-colloids** in brine (aqueous solutions of NaCl, $CaCl_2$) and their use to prepare Pickering oil-in-water emulsions.
  1. **Polymer-coated nanoparticles (PNPs) of silica** synthesized by free radical polymerization of the monomers 2-acrylamido-2methyl-1-propanesulfonic acid (AMPSA) and dodecyl methacrylate (DMA) on the surface of acrylic-modified spherical silica nanoparticles [1].
  2. **Iron oxide nanoparticles (IONPs)** synthesized and stabilized by biosynthetic routes using the polyphenols extracted from plant leaves (parsley) [2].
- Measuring the **properties of PNPs and IONPs.**
  1. **Nano-colloid suspensions.** The **nanoparticle size distribution** was determined with **dynamic light scattering** (DLS); the **stability of nano-colloids** was confirmed by measuring the **ζ-potential** as a function of the **ionic strength**; the **surface / interfacial tension** was measured by **static method** (duNuoy Ring); the **wettability** was quantified by measuring the **oil/water contact angle** on glass surface.
  2. **Pickering emulsions**. Oil-in-water emulsions were generated by mixing the **PNPs and IONPs with n-C_{10}** at volume ratio 2:1 with the aid of a **high energy ultrasound probe**. The **shear viscosity** of emulsions was recorded **as a function of time** on a stress rheometer. The **stability** of emulsions was inspected by observing the **phase separation** (macro-scale) and measuring the **drop size distribution** (micro-scale).
- Assessing the **Enhanced Oil Recovery efficiency** of "smart fluids".
  Flow-controlled immiscible displacement visualization tests were conducted on a **glass-etched pore network** [3] in the following order:
  (i) *Drainage step.* The fully saturated by brine (salt solution) porous medium was displaced by paraffin oil.
  (ii) *Primary imbibition step*. The residual oil of the previous step was displaced by brine.
  (iii) *Secondary imbibition step.* The residual oil of the previous step was displaced by PNP- or IONP-based fluid.
  The oil saturation was measured as a function of time with image analysis of successive snap-shots captured by a CCD camera [3], and the transient response of the pressure drop across the porous medium was recorded with the aid of two pressure transmitters and a data acquisition card.

Conclusions

✓ Polymer-coated nanoparticles (PNPs) and Polyphenol-coated iron oxide nanoparticles (IONPs) were synthesized and the nano-colloid suspensions were stabilized successfully.
✓ The decrease on the interfacial tension and contact angle facilitates the emulsification and detachment of oil ganglia from the solid surface by the nano-colloid suspensions
✓ The EOR efficiency is maximized when using Pickering emulsions, due to the high viscosity ratio, and the creation of stable displacement front
✓ The selection of the most suitable emulsion should be based on a balance between the EOR efficiency and energy cost (which increases remarkably with the viscosity of injected emulsion increasing)

References

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Acknowledgements

H.F.R.I. Hellenic Foundation for Research & Innovation

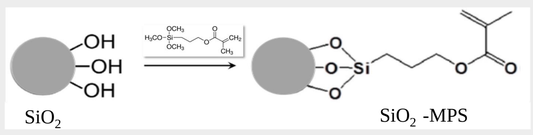
EORPNP

The research project is supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "1st Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment" (Project Number: HFRI-FM17-361, Title: Enhanced oil recovery by polymer-coated nanoparticles, Acronym: EOR-PNP).

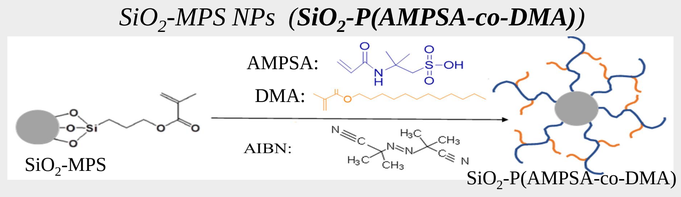
Synthesis and stabilization of nano-colloids

Polymer-coated nanoparticles (PNPs)

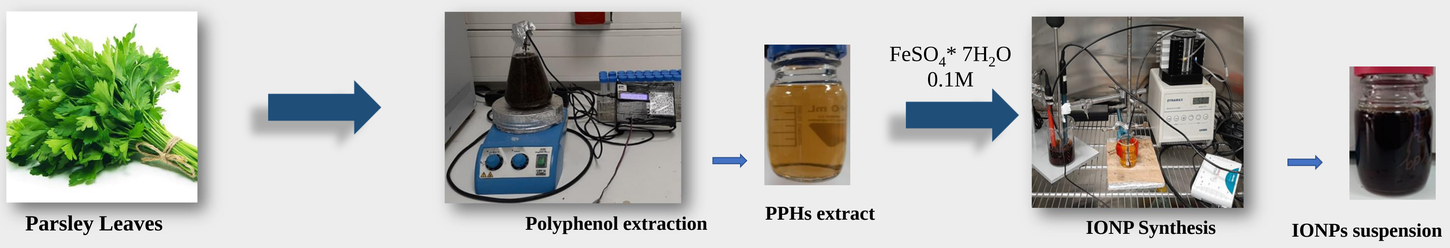
a. *Functionalization of SiO_2 NPs with 3-(trimethoxysilyl)-propyl methacrylate (**SiO_2-MPS**)*



b.*Polymerization of AMPSA and DMA monomers onto the functionalized SiO_2-MPS NPs (**SiO_2-P(AMPSA-co-DMA)**)*



Polyphenol-coated iron oxide nanoparticles (IONPs)

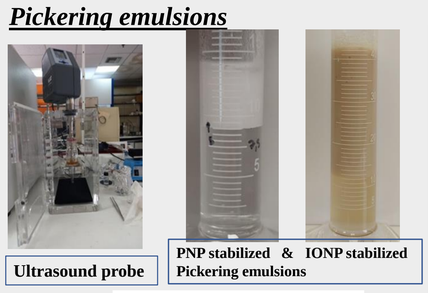


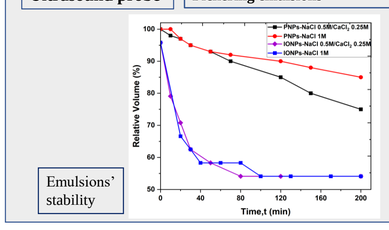
Properties of PNPs and IONPs

Nanoparticle suspension	Surface tension (mN/m)	Interfacial tension (mN/m)	Contact angle air / suspension θ(°)	Contact angle paraffin oil / suspension θ(°)	Average diameter of nanoparticles (nm)
SiO2-P(AMPSA-co DMA)0.25% w/v – NaCl 0.5M-$CaCl_2$ 0.25M	55.40±0.21	28.04 (56.0)	59.10 ± 0.99	79.00 ± 1.56 (86.1)	190.4±4.0
SiO2-P(AMPSA-co-DMA)0.25% w/v –NaCl 1.0M	53.07±0.46	30.28 (60.6)	63.80 ± 0.28	62.75 ± 0.05 (85.5)	255.0±2.1
IONPs 0.25g/L – NaCl 0.5M-$CaCl_2$ 0.25M	50.69±0.09	20.80 (56.0)	73.85±0.60	67.78±3.92 (85.5)	295.3±9.4
IONPs 0.25g/L- NaCl 1.0M	48.55±0.45	21.90 (60.6)	74.06±1.74	69.95±0.46 (86.1)	295.3±10.2

***ζ-potential of suspensions*:**
- PPHs -20.4mV
- IONPs -19.7mV
- PNPs -38.8mV

Pickering emulsions





The rheology of Pickering emulsions follows the power law model: $\mu = \mu_{inf} + (\mu_1 - \mu_{inf})\dot{\gamma}^{n-1}$

Emulsion	μ_1 (Pa s)	μ_{inf}(Pa s)	*n*
PNPs–NaCl 0.5M-$CaCl_2$ 0.25M	0.279	0.001	0.425
PNPs–NaCl 1M	0.397	0.001	0.128
IONPs–NaCl 0.5M-$CaCl_2$ 0.25M	0.559	0.015	0.162
IONPs–NaCl 1M	0.456	0.012	0.165

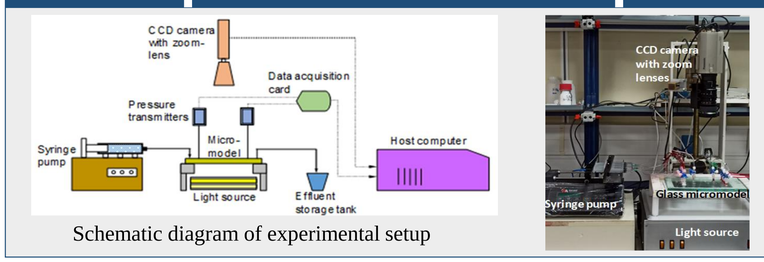
Values of μ_{inf} , μ_1 , n were calculated by *ATHENA Visual studio* and the $<\mu>$ by:

$$\langle\mu\rangle = \mu_{inf} + \left(\frac{\mu_1 - \mu_{inf}}{n}\right)\gamma_w^{n-1}$$

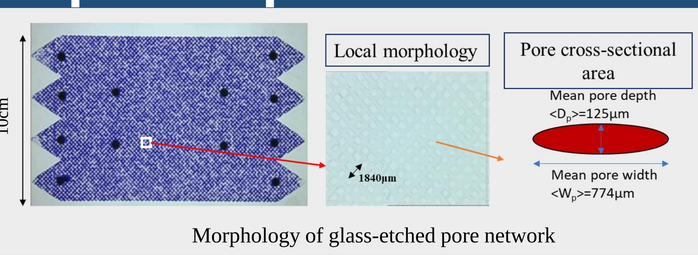
$\gamma_w = \left(\frac{8u_p}{4r_H}\right)\left(\frac{3n+1}{4n}\right) \rightarrow u_p = \frac{u_0}{\varphi_V} \rightarrow \varphi_V = \frac{\pi\langle W_p\rangle\langle D_p\rangle}{4L_p^2}$

γ_w is the shear rate at pore-wall, φ_V is the porosity of the planar porous medium at the vertical direction, r_H is the equivalent hydraulic pore radius (r_H=45 μm) [4]

Experimental setup - transparent pore network



Schematic diagram of experimental setup

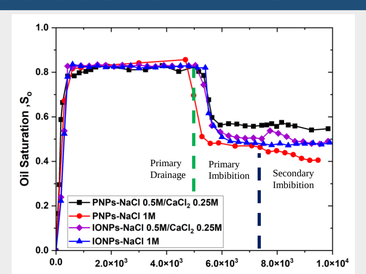


Morphology of glass-etched pore network

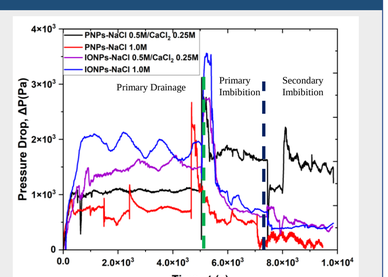
Visualization tests of EOR

Results- Nanoparticles Suspensions

Displacing **suspension** in Secondary Imbibition	Primary Drainage $^*S_o$	Primary Imbibition S_o	Secondary Imbibition S_o	Oil recovery efficiency (%)
PNPs –NaCl 0.5M/$CaCl_2$ 0.25M	0.82	0.56	0.54	34.1
PNPs–NaCl 1.0M	0.85	0.47	0.40	52.9
IONPs–NaCl 0.5M/$CaCl_2$ 0.25M	0.83	0.50	0.49	40.9
IONPs–NaCl 1.0M	0.82	0.47	0.48	41.4



Oil saturation

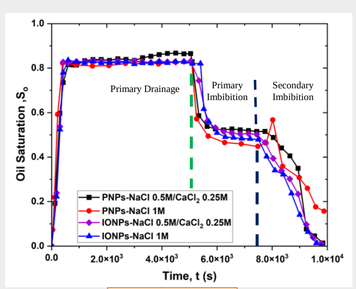


Pressure drop

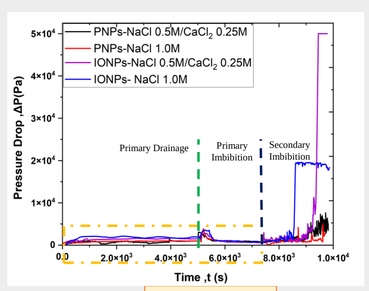
Results- Pickering emulsions

Displacing **emulsion** in Secondary Imbibition	Primary Drainage $^*S_o$	Primary Imbibition S_o	Secondary Imbibition S_o	<μ> (mPa s)	κ	Cax10^{-5}	Oil recovery efficiency (%)
PNPs –NaCl 0.5M/$CaCl_2$ 0.25M	0.86	0.52	0.014	74	3.71	4.50	98.4
PNPs–NaCl 1.0M	0.83	0.45	0.16	61	3.08	3.45	80.7
IONPs–NaCl 0.5M/$CaCl_2$ 0.25M	0.83	0.50	0.011	103	3.96	8.41	98.7
IONPs–NaCl 1.0M	0.82	0.47	0.0	84	3.23	6.52	100

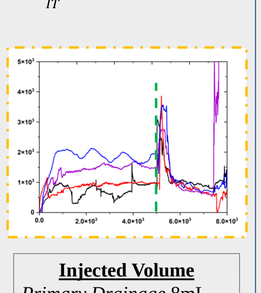
S_o Residual oil saturation; <μ> Viscosity of emulsion averaged over a single pore; Viscosity ratio: $\kappa = \frac{\langle\mu\rangle}{\mu_o}$ where μ_o = 0.026 Pa s for IONPs experiments and 0.02 Pa s for PNPs; Capillary number: $Ca = \frac{u_0\langle\mu\rangle}{IT}$



Oil saturation



Pressure drop



Flow rate at: *Primary Drainage* 0.08ml/min & *Primary/Secondary Imbibition* 0.2ml/min

Injected Volume
Primary Drainage 8mL
Primary Imbibition 8mL
Secondary Imbibition 8mL

Displacements of Secondary Imbibition step