Pickering emulsions synthesized from iron oxide nano-colloids and used as agents for the residual oil displacement in porous media

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Introduction

The removal of residual oil that has been trapped in the pore space of underground geological settings is of critical importance for environmental processes such as the remediation of vadoze / saturated zones of the subsurface, and energy production like the enhanced oil recovery from oil-bearing reservoir rocks. The remediation of soils polluted by non-aqueous phase liquids (NAPLs) resulting from leaking storage tanks, spills and improper waste disposal is considered as one of the most significant challenges. NAPLs have caused widespread subsurface contamination, while they tend to sink in groundwater systems, resulting in complex dispersal and plume patterns, which are extensive long-term sources of subsurface pollution, and difficult to clean-up. Moreover, the continuous dissolution of NAPLs may lead to the extensive contamination of groundwater.

Concerning energy production, due to population and economic growth, the global energy consumption is estimated to increase by almost 50% in the next thirty years. The overall oil recovery efficiency for primary and secondary recovery range from 35% to 45% and tertiary recovery methods that can increase the enhanced oil recovery (EOR) efficiency by 10-30% could contribute to energy supply. Conventional methods include chemical flooding, 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, alkaline, emulsions, and foams.

The use of nanoparticles and Pickering emulsions in EOR processes comprise emerging and well-promising approaches. The green synthesis and stabilization of aqueous suspensions of iron oxide nanoparticles from plant extracts is an environmental-friendly approach utilizing the extracted polyphenols as reductants and polymeric coatings.

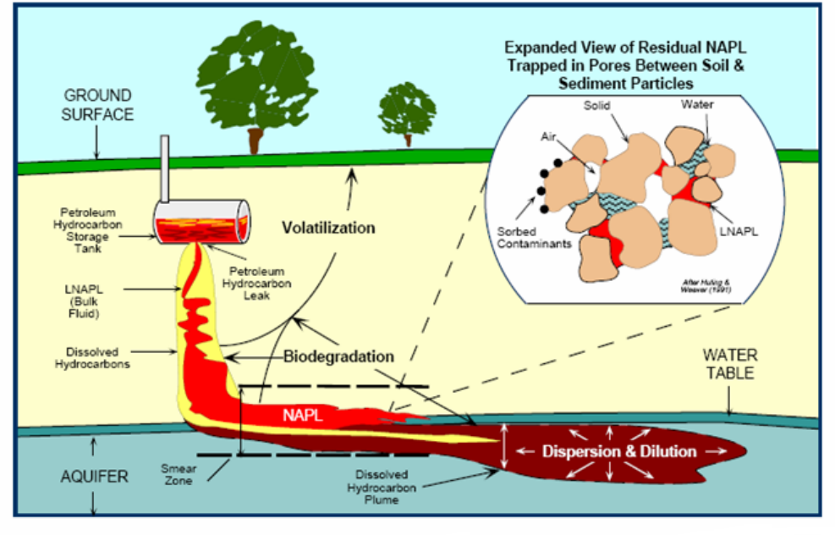
Objectives

- 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, oil to water volume ratio).
- Correlation of the interfacial and rheological properties of "smart fluids" with their capacity to mobilize oil ganglia from porous media (micromodels, sandpacks).
- Cost benefit analysis and selection of the most efficient "smart fluids" for EOR or remediation of oil-polluted soils.

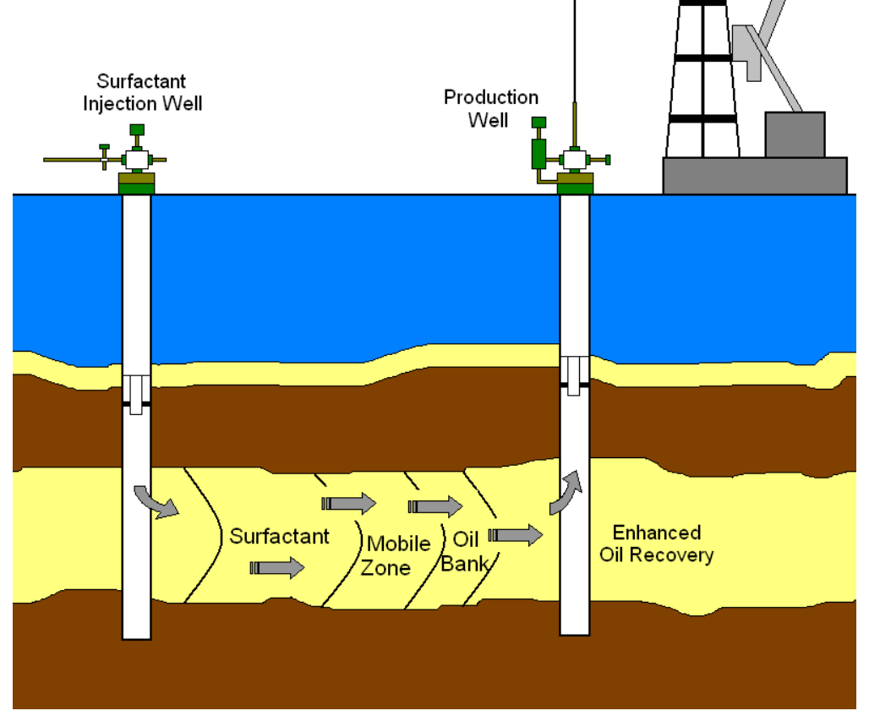
Methodology

Oil recovery from subsurface and reservoir rocks

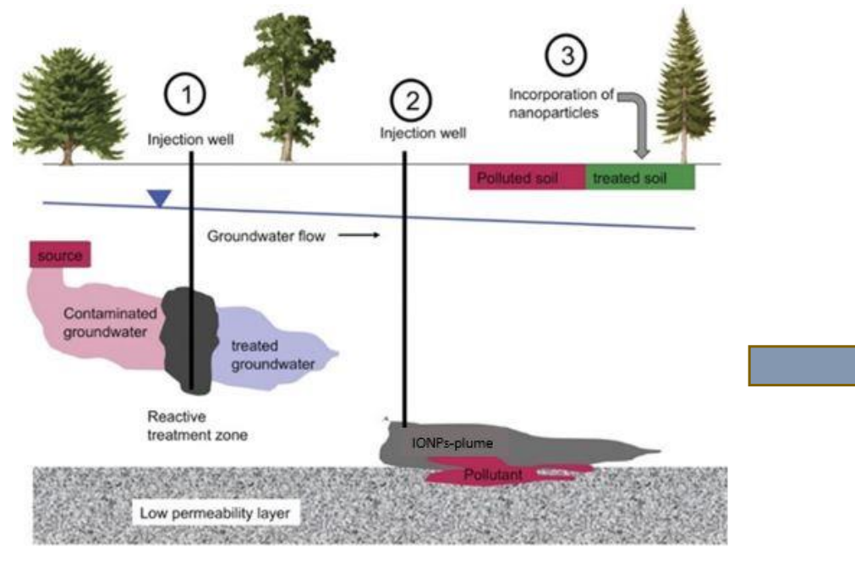
Source zone pollution



Enhanced Oil Recovery

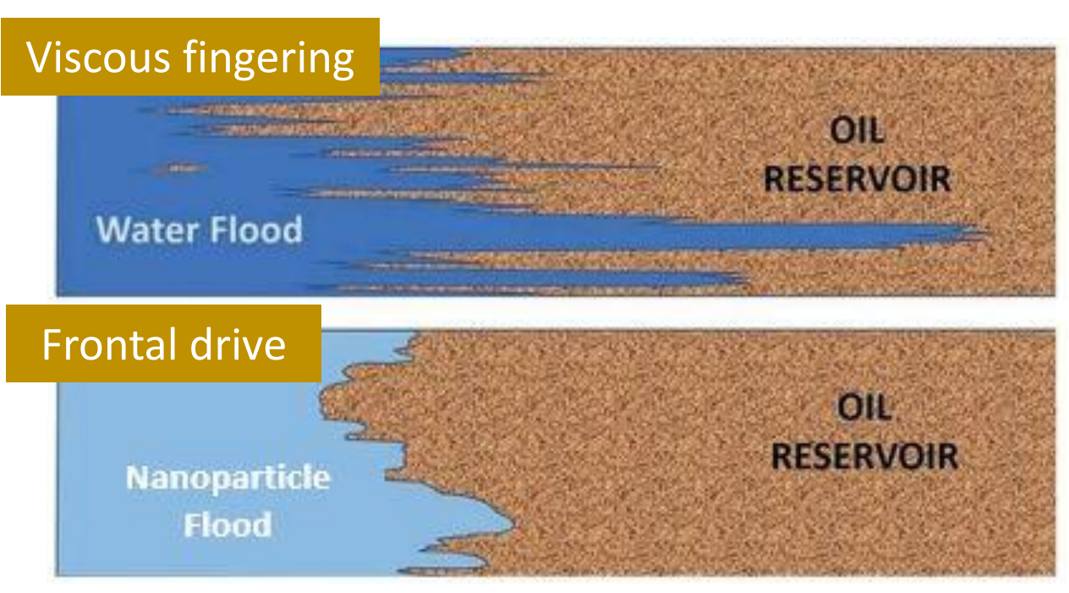


nZVI injection



Viscous fingering

Frontal drive



Synthesis and stabilization of nano-colloids

Polyphenol-coated iron oxide nanoparticles (IONPs)

Parsley Leaves

Polyphenol (PPH) extraction

PPH extract

IONP Synthesis

$FeCl_3$ 0.1M

IONP suspension

Properties of Iron Oxide Nanoparticles (IONPs)

	PPHs : pH = 6.36 , ζ-potential = -37.7mV IONPs : pH = 6.05 , ζ-potential = -22.9mV				
Nanoparticle suspension	Surface tension (mN/m)	Interfacial tension (mN/m)	Contact angle air / suspension θ(°)	Contact angle synthetic oil / suspension θ(°)	Average diameter of nanoparticles (nm)
IONPs 1.0g/L	52.89±0.29	53.54	21.7 ± 0.02	9.6± 8.7	141.8±5.8
IONPs 0.75g/L	54.47±0.41	55.31	25.7 ± 0.20	20.7 ± 5.1	164.2±2.2
IONPs 0.5g/L	56.48±0.27	58.12	33.4±2.4	24.9±3.1	105.7±8.2
IONPs 0.25g/L	59.78±0.17	58.35	25.4±1.20	19.1±0.6	105.7±16.2
PPHs 3.0g/L	45.29 ±0.13	49.05	-	-	68.06±8.3

During 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 increasing the capillary number; (ii) the increase of water viscosity, thus increasing the mobility ratio; (iii) the alteration of the wettability, thus facilitating the detachment of oil from the rock surfaces.

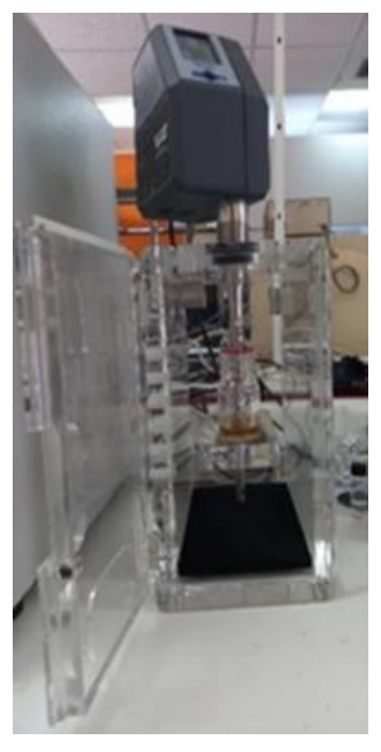
Suspension of iron-oxide nanoparticles (IONPs) as injection fluid in Secondary Imbibition

Nanoparticle suspension	Primary Drainage S_o	Primary Imbibition S_o	Secondary Imbibition S_o	Total Oil recovery efficiency (%)
IONPs 1.0g/L	0.85	0.52	0.50	41.2
IONPs 0.75g/L	0.84	0.511	0.518	38.3
IONPs 0.5g/L	0.81	0.45	0.45	44.4
IONPs 0.25g/L	0.81	0.53	0.52	35.8
PPHs 3.0g/L	0.82	0.542	0.541	34.0

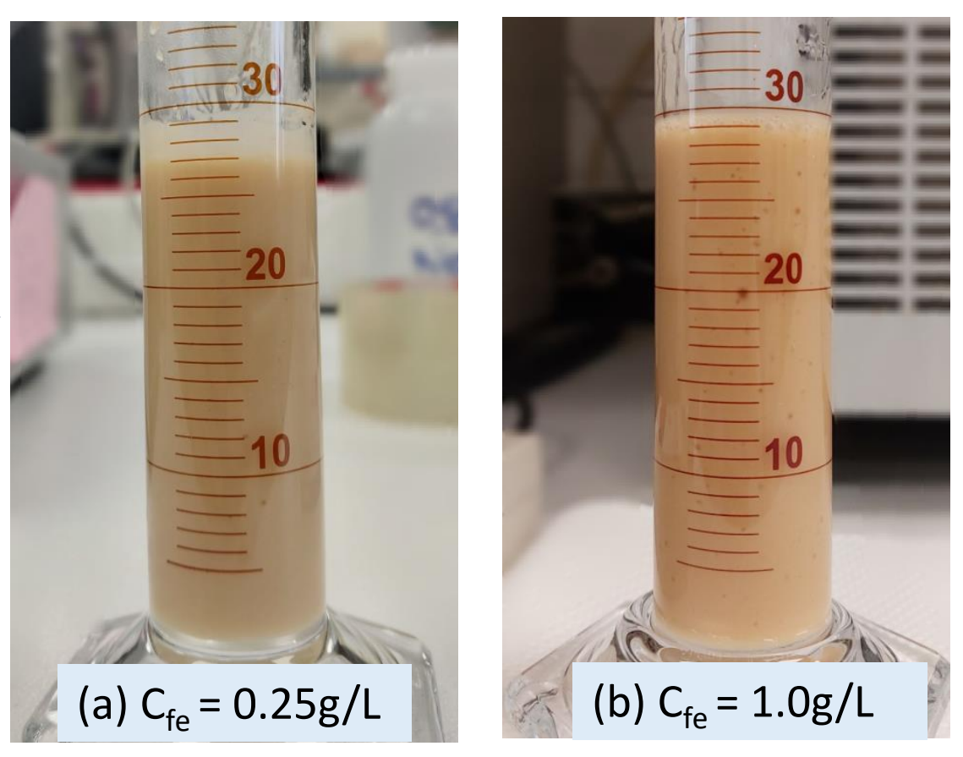
Experimental tests in glass etched pore network with nanoparticle suspensions at various concentrations gave the aforementioned residual oil saturation values per each cycle, namely **Primary Drainage** (oil displaces water), **Primary Imbibition** (water displaces oil) and **Secondary Imbibition** (nanoparticle suspension displaces oil). The changes of oil saturation between primary and secondary imbibition tests are quite small, thus the potential to stabilize Pickering emulsions and use them as injection fluids in Secondary Imbibition was investigated.

For assessing emulsions: (1) their stability is quantified by the macroscopic- phase separation and microscopic oil-drop size distribution; (2) the shear viscosity is measured as function of time with steady-state tests, and the loss and storage moduli are measured with dynamic frequency sweep tests on a stress rheometer .

Synthesis and Properties of Pickering Emulsions



Ultrasound probe



(a) C_{fe} = 0.25g/L (b) C_{fe} = 1.0g/L

IONP stabilized Pickering emulsions

Volume ratio: IONPs suspension – nC_{10} [2:1]

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

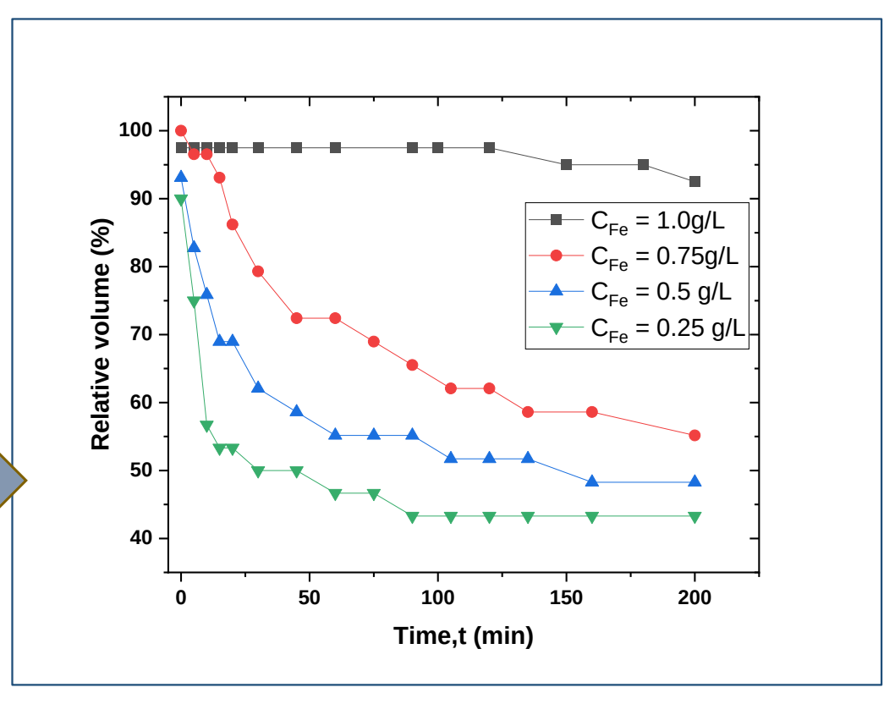
$$\langle\mu\rangle = \mu_{inf} + \left(\frac{\mu_1 - \mu_{inf}}{n}\right)\gamma_w{}^{n-1} \qquad Ca = \frac{u_0 < \mu >}{\gamma_{ow}} \qquad \kappa = \frac{<\mu>}{\mu_{oil}}$$

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

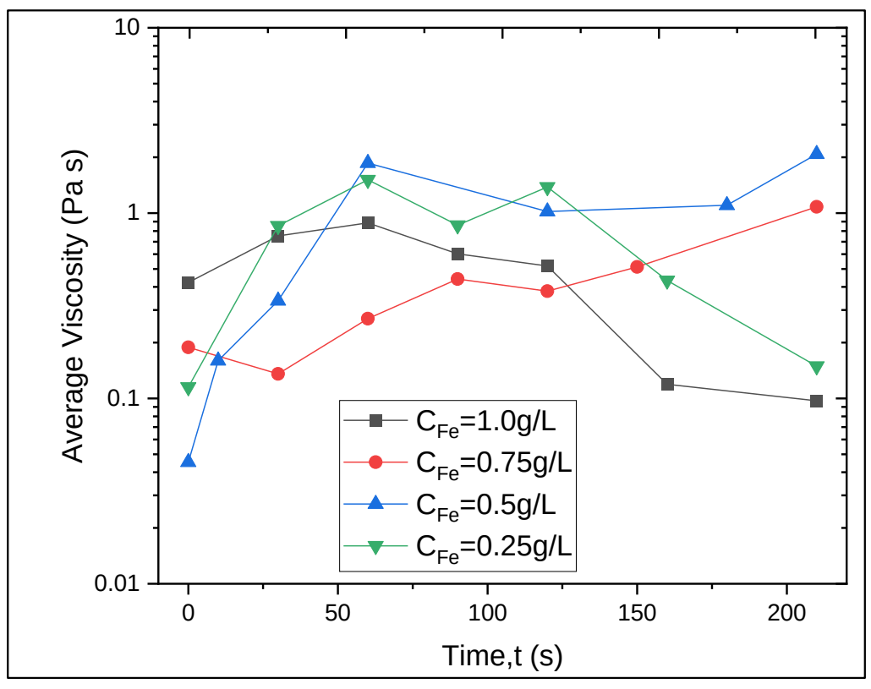
γ_w is the shear rate at pore-wall, φ_V is the porosity of the planar porous medium at the vertical direction, r_H is the equivalent hydraulic pore radius (r_H=45 μm) [3] , Ca is the capillary number, κ is the viscosity ratio , μ_{oil} = 0.026 Pa s

Emulsion	μ_1 (Pa s)	μ_{inf} (Pa s)	*n*	<μ> (Pa s)	*Ca* (10^{-5})	*κ*
C_{Fe} =1.0 g/L	2.468	0.001	0.196	0.423	11.9	1.63
C_{Fe} =0.75 g/L	1.053	0.003	0.217	0.189	5.98	0.72
C_{Fe} =0.50 g/L	0.213	0.006	0.252	0.045	1.37	0.17
C_{Fe}=0.25 g/L	0.564	0.002	0.287	0.115	3.45	0.44

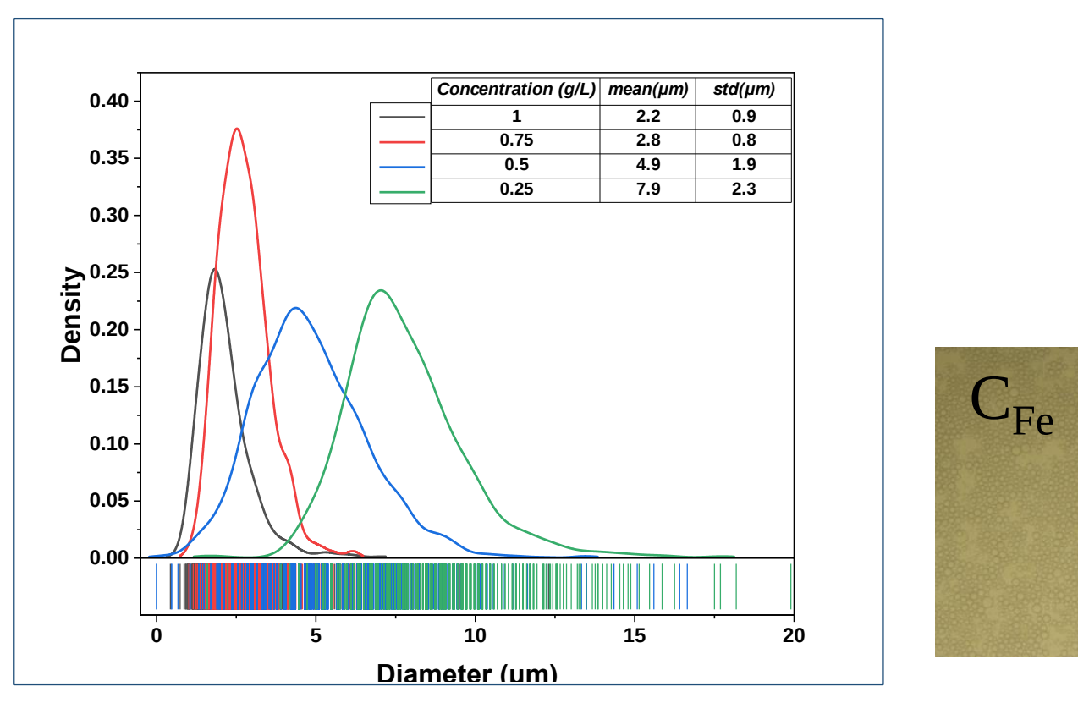
Emulsion stability vs time



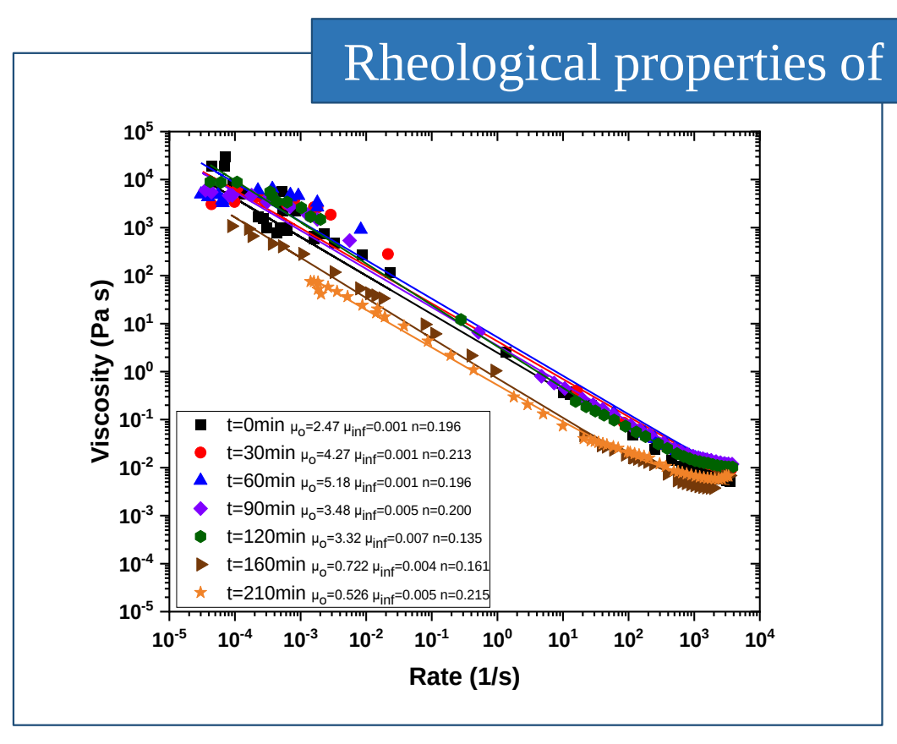
Average viscosity vs time

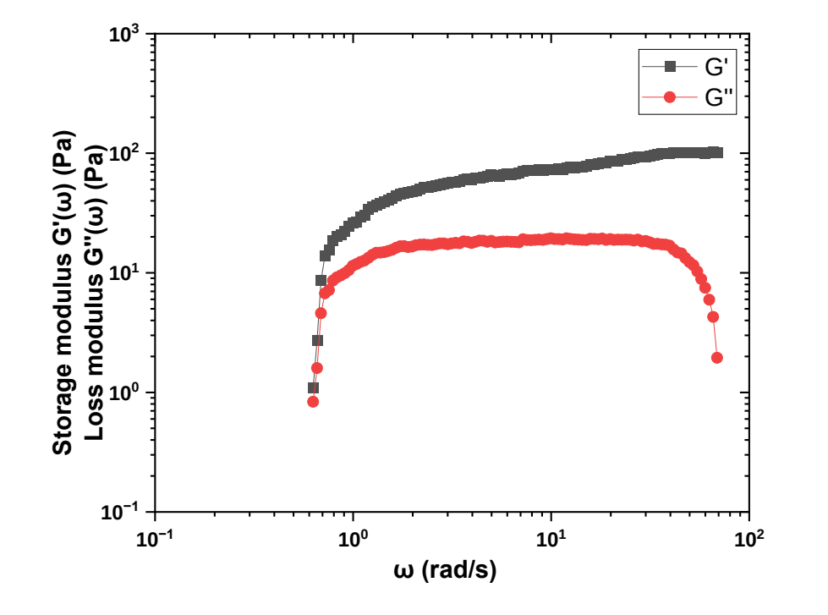


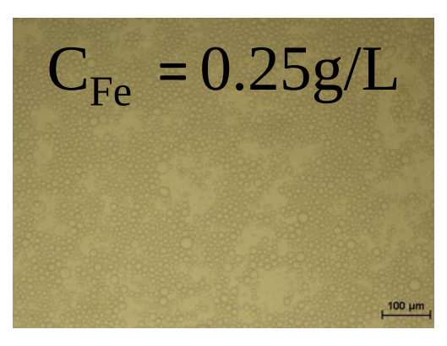
Oil-drop size distributions in emulsions

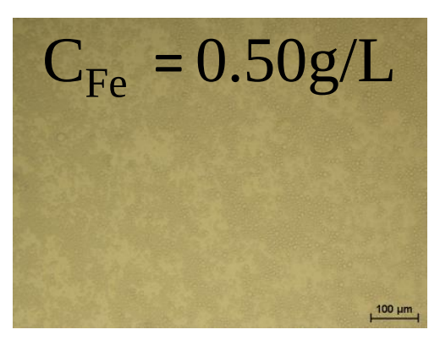


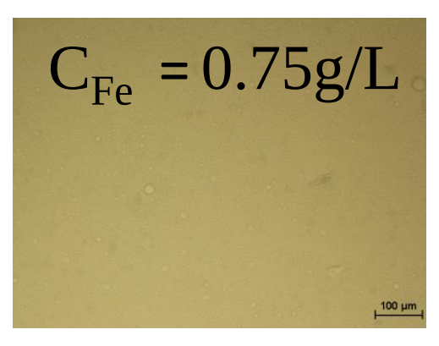
Rheological properties of emulsion C_{Fe} =1.0g/L

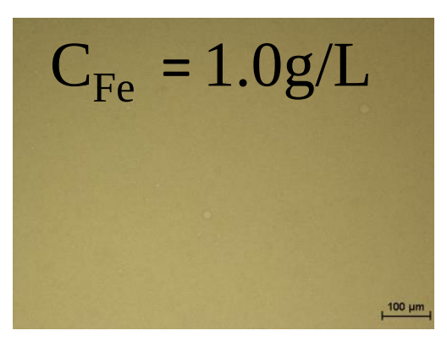






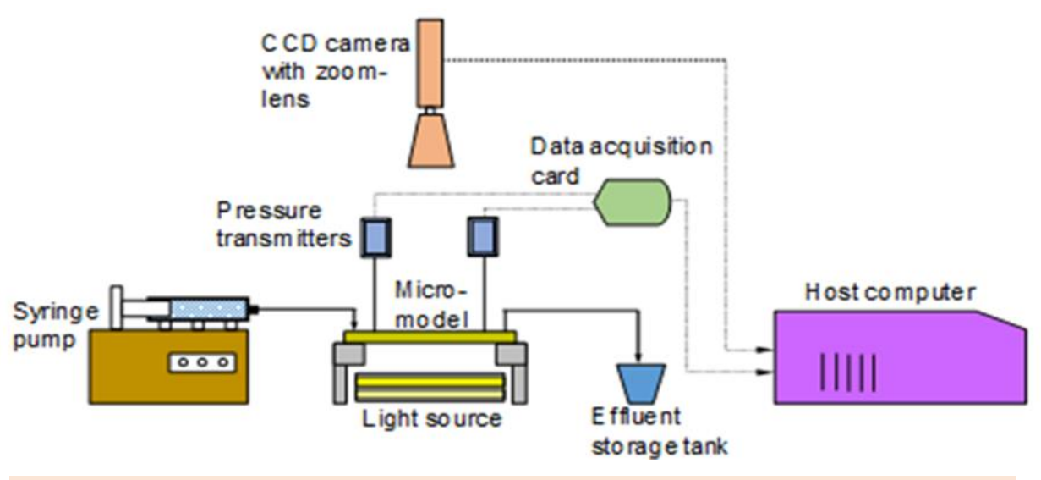




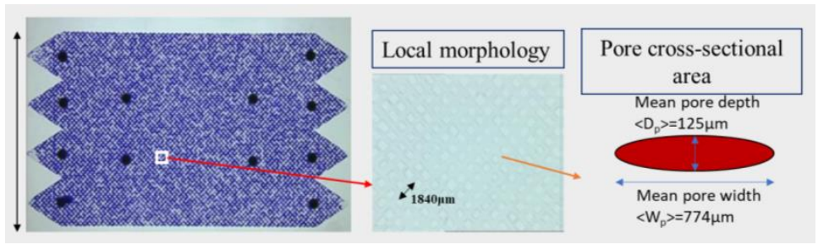


Assessing the displacement efficiency of Pickering emulsions

Visualization tests on a transparent pore network



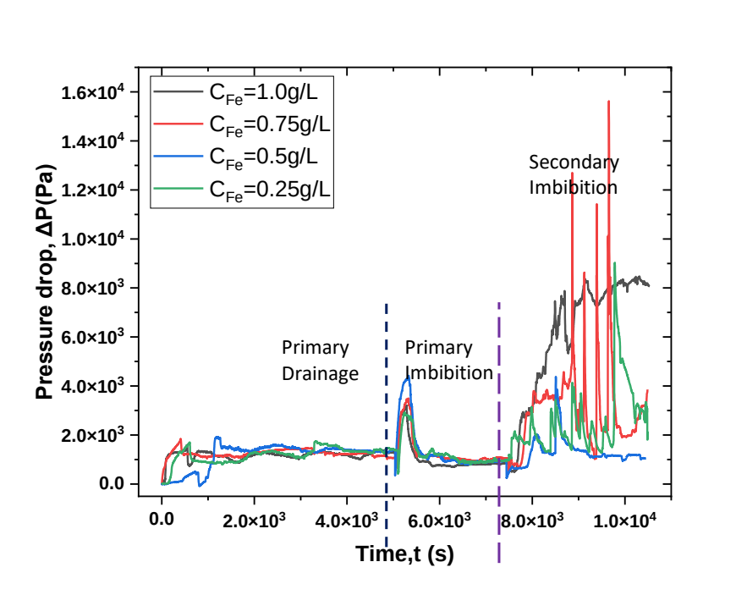
Schematic diagram of experimental setup

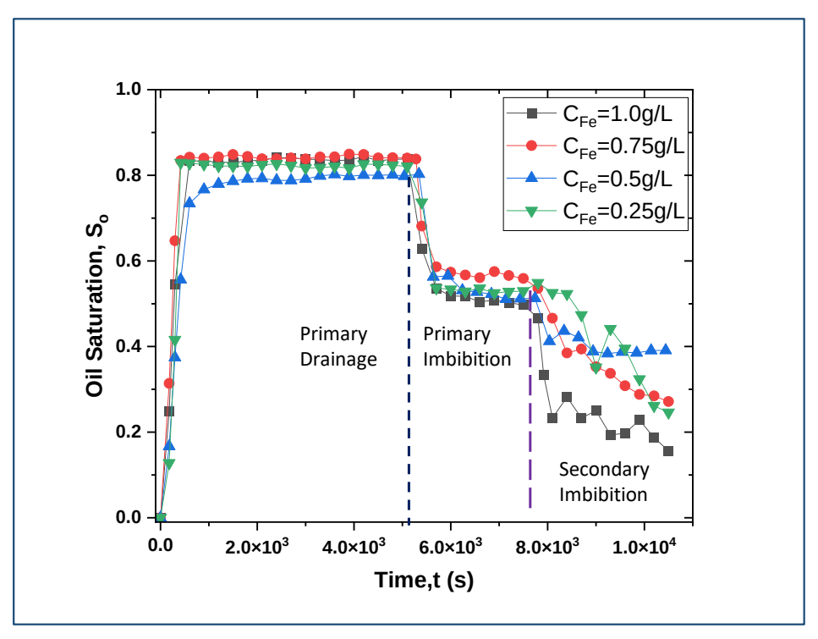


Morphology of glass-etched pore network

Permeability k=20.5 Da
Porosity φ=0.65
Pore volume 2mL

IONP concentration in Pickering emulsion	Primary Drainage $^*S_o$	Primary Imbibition S_o	Secondary Imbibition S_o	Sec. Imbib. oil recovery efficiency (%)
1.0 g/L	0.83	0.49	0.15	69.4
0.75g/L	0.84	0.55	0.27	50.9
0.50g/L	0.80	0.51	0.39	23.5
0.25g/L	0.82	0.52	0.24	53.8



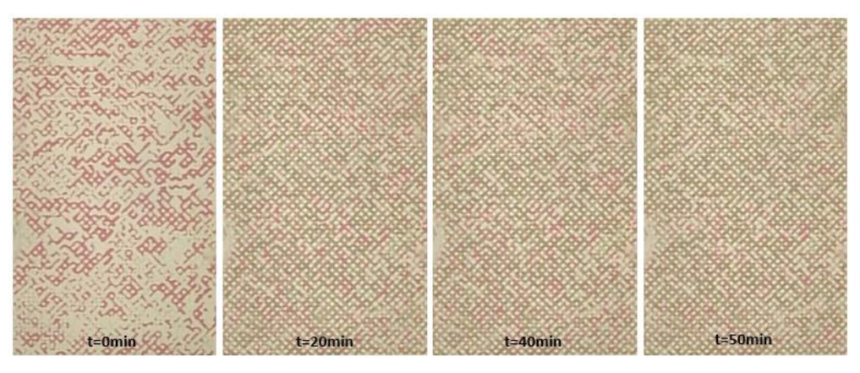


Flow rate at *Primary Drainage:* 0.08mL/min
& *Primary/Secondary Imbibition:* 0.2mL/min

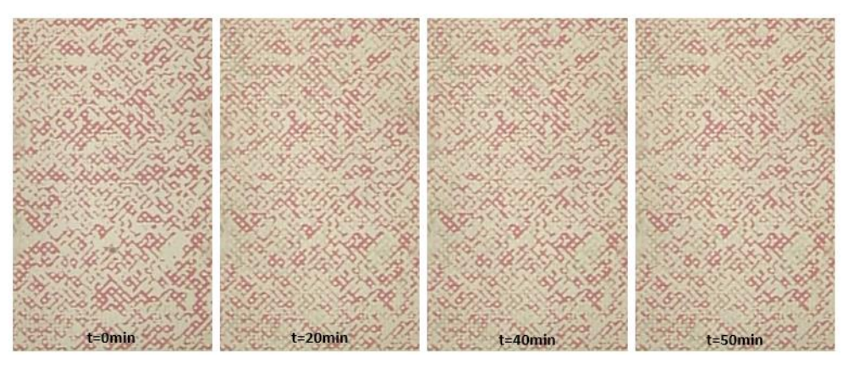
Injected Volume
Primary Drainage: 8mL
Primary Imbibition: 8mL
Secondary Imbibition: 10mL

Secondary Imbibition by Pickering Emulsions

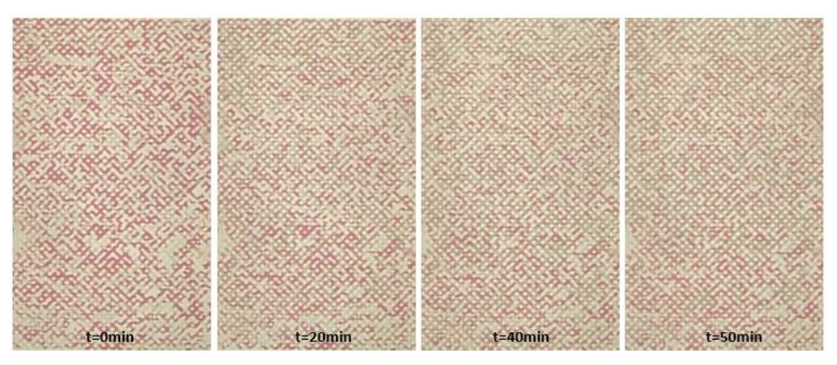
C_{fe} =1.0g/L



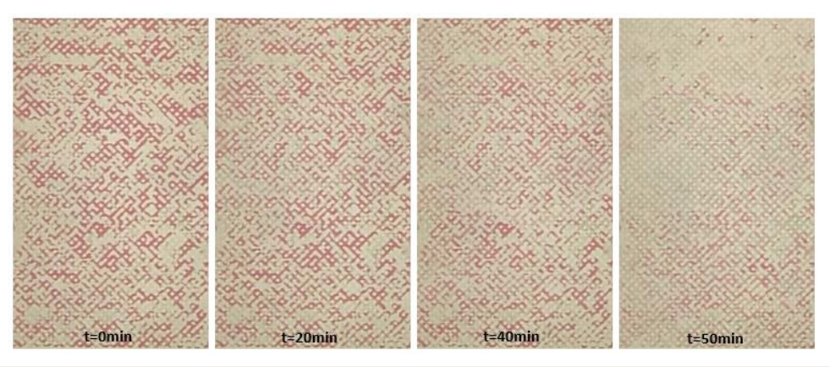
C_{fe} =0.5g/L



C_{fe} =0.75g/L



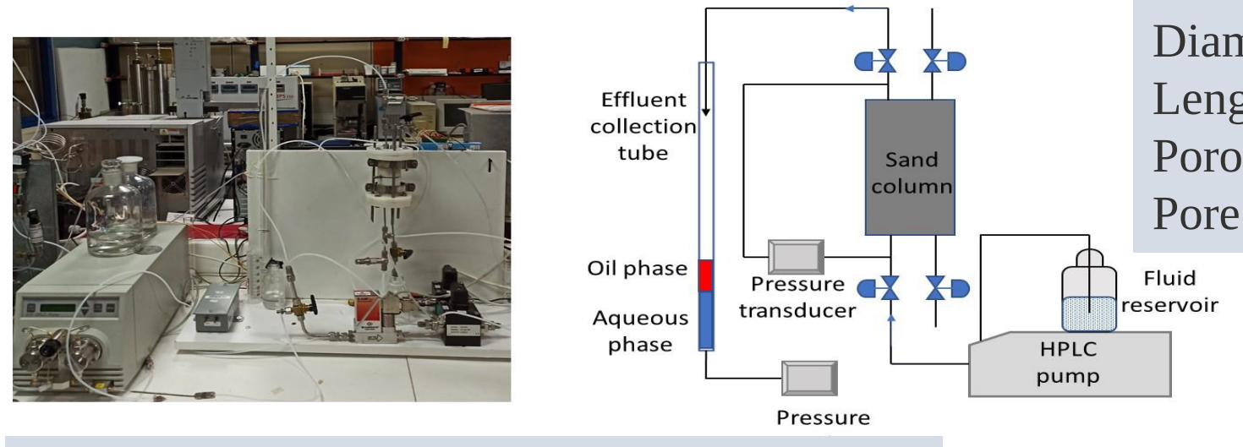
C_{fe} =0.25g/L



Displacement tests on a sandpack

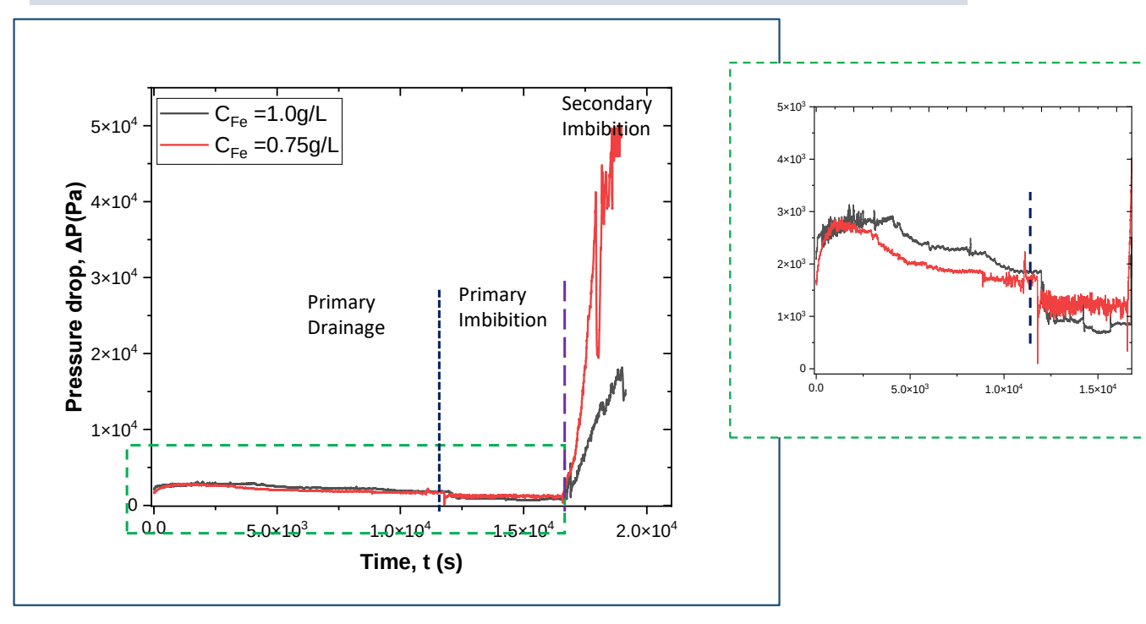
Permeability k=11.9 Da
Diameter=3.0 cm
Length=6.6 cm
Porosity φ=0.49
Pore volume 19.7 mL

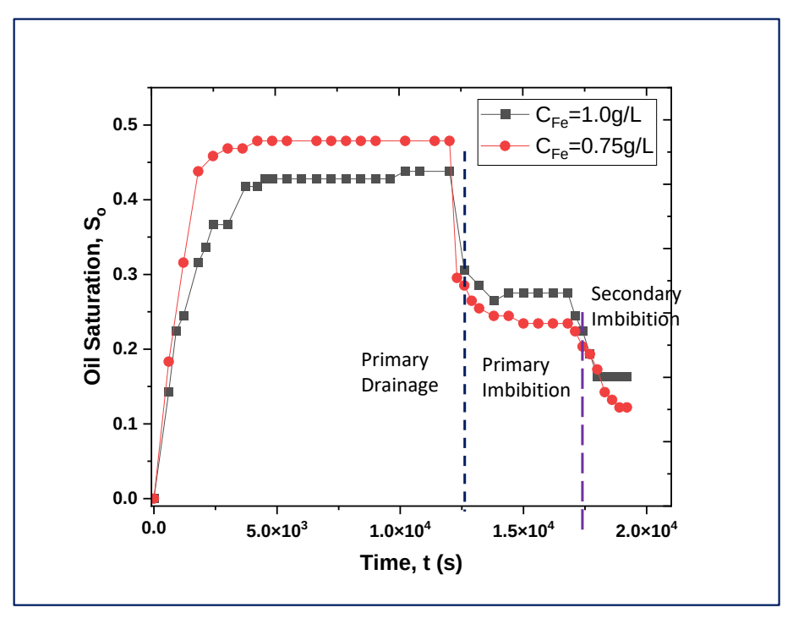
Flow rate at: *Primary Drainage:* 0.4ml/min
& *Primary/Secondary Imbibition:* 1.0ml/min



Schematic diagram of experimental setup

Injected Volume
Primary Drainage: 80mL ,
Primary Imbibition: 80mL,
Secondary Imbibition: 40mL





Displacing **emulsion** in Secondary Imbibition	Primary Drainage $^*S_o$	Primary Imbibition S_o	Secondary Imbibition S_o	Oil recovery efficiency (%)
1.0 g/L	0.44	0.28	0.16	42.8
0.75g/L	0.48	0.23	0.12	47.8

$^*S_o$ →Oil saturation

References

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Conclusions

- ✓ 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 oil recovery efficiency is maximized when using Pickering emulsions, due to the high viscosity ratio, and the creation of stable displacement front.
- ✓ The maximum oil efficiency is attained by the emulsion prepared at the highest IONP concentration (1.0 g/L), composed of small oil drops of narrow size distribution, and characterized by the lowest viscosity at late times (maximum stability).

Acknowledgments

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