10th International Conference on Environmental Management, Engineering, Planning and Economics & SECOTOX Conference

Synthesis of smart fluids for the efficient removal of residual oil from subsurface

Ch. Ntente[1,2], A. Strekla[1,3], M. Theodoropoulou[1], C.D. Tsakiroglou[1]

[1] Foundation for Research and Technology Hellas - Institute of Chemical Engineering Sciences (FORTH/ICE-HT), 26504 Patras, Greece
[2] University of Patras, Department of Chemistry, 26504 Patras, Greece
[3] University of Patras, Department of Physics, 26504 Patras, Greece

Problem

- **Remediation of oil spills** is a global challenge due to their devastating impact on the *environment and human health*
- Synthesis of **smart fluids** with iron oxide nanoparticles (IONPs) via green synthesis is an *innovative and eco-friendly approach*

Characteristics of IONPs

- Unique *magnetic properties*
- High *surface area*
- *Stability*
- Ability to *decrease Interfacial Tension (IT)* of oil and water

Stable Pickering emulsions

Objectives

- Synthesis of ***stable aqueous suspensions of iron oxide nanoparticles*** *(IONPs)*
- Measurement of the ***interfacial and wetting properties*** of IONPs suspensions
- Preparation of the ***IONPs – stabilized Pickering emulsions***
- Assessment the ***oil removal efficiency of Pickering emulsions***

Preparation of polyphenol extract

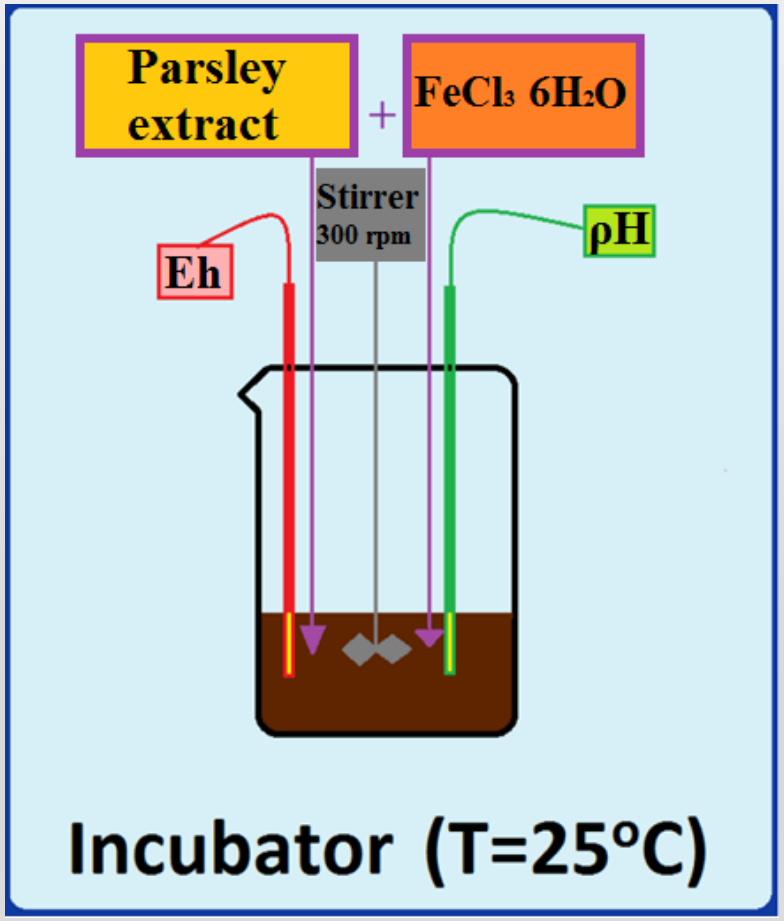
Polyphenol extract preparation

Parsley extract

Gallic acid samples after Folin – Ciocalteau reagent

- ✓ Fresh parsley leaves **washed several times with 3D–water** and **dried at 50 ^{o}C** in oven **for 24 h**
- ✓ Heat **3D - water until 80 ^{o}C**
- ✓ Add **dried parsley leaves in water** under vigorous stirring
- ✓ **Stirring and heating** at stable temperature for 1h
- ✓ **Filtrated** under vacuum and **centrifuged** at 10000 rpm for 10 min
- ✓ Estimating the **total polyphenol concentration (TPC = 3 g/L)** using the **Folin – Ciocalteau method**

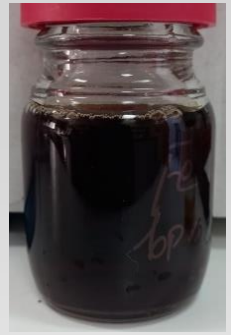
Synthesis of iron oxide nanoparticles (IONPs) suspensions



Schematic diagram of IONPs synthesis

Experimental setup for IONPs synthesis

- ✓ Add dropwise the **$FeCl_3$ * $6H_2O$ solution** (c = 0.1M) **in parsley extract (2:1)** under vigorous stirring at **25°C**
- ✓ Identification of IONPs suspension by **colour change to dark brown**
- ✓ **pH adjustment to 6.0** with NaOH solution
- ✓ Place suspension in refrigerator



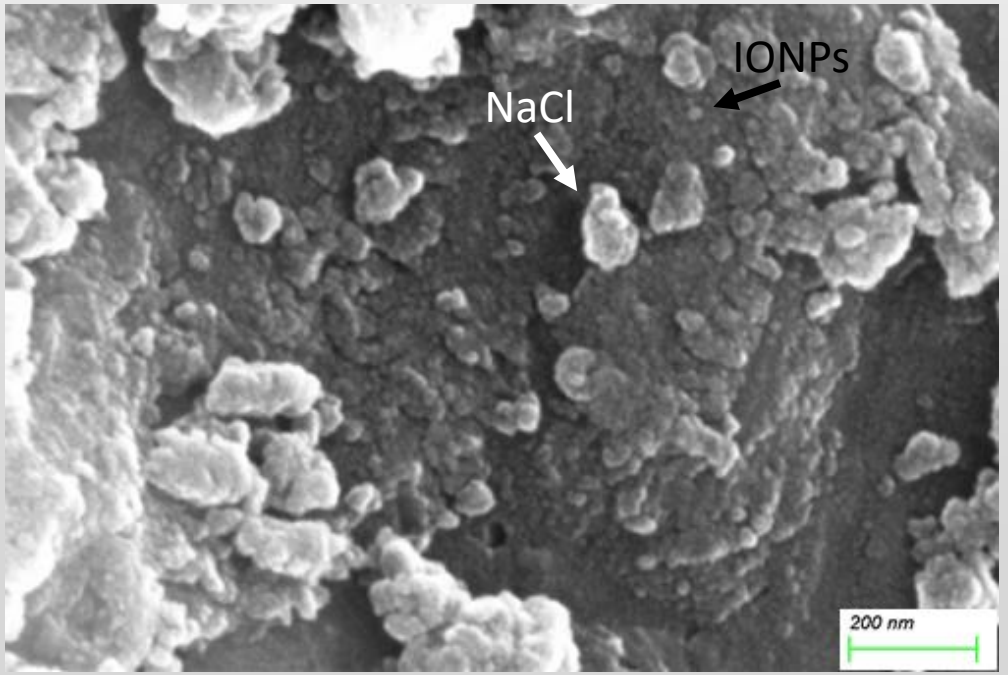
IONPs suspension

Characterization of iron oxide nanoparticles (IONPs)

DLS measurements for different suspensions

Aqueous suspension	Particle size distribution $\langle D_p \rangle \pm \sigma_p$ (nm)	ζ-potential (mV)
Parsley extract	58.77 ± 3.4	-11.3
IONPs, C_{Fe}=0.25g/L	18.17 ± 17.9	-28.5
IONPs, C_{Fe}=0.5 g/L	32.67 ± 15.4	-29.2
IONPs, C_{Fe}=0.75 g/L	24.36 ± 11.5	-20.3
IONPs, C_{Fe}=1.0 g/L	15.69 ± 5.5	-25.1

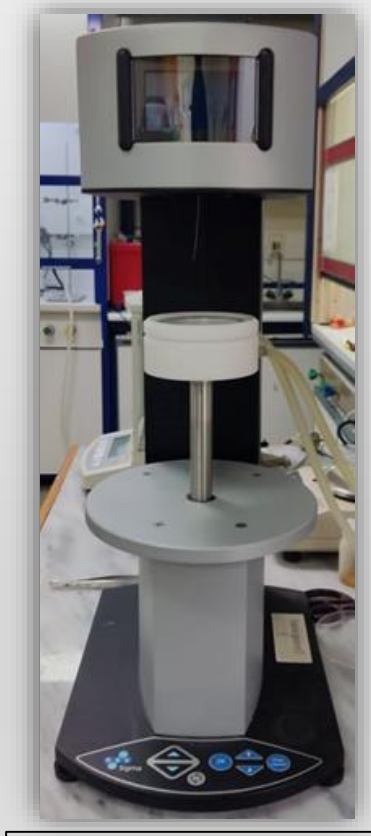
SEM image



Evaluation of Interfacial and Wetting properties

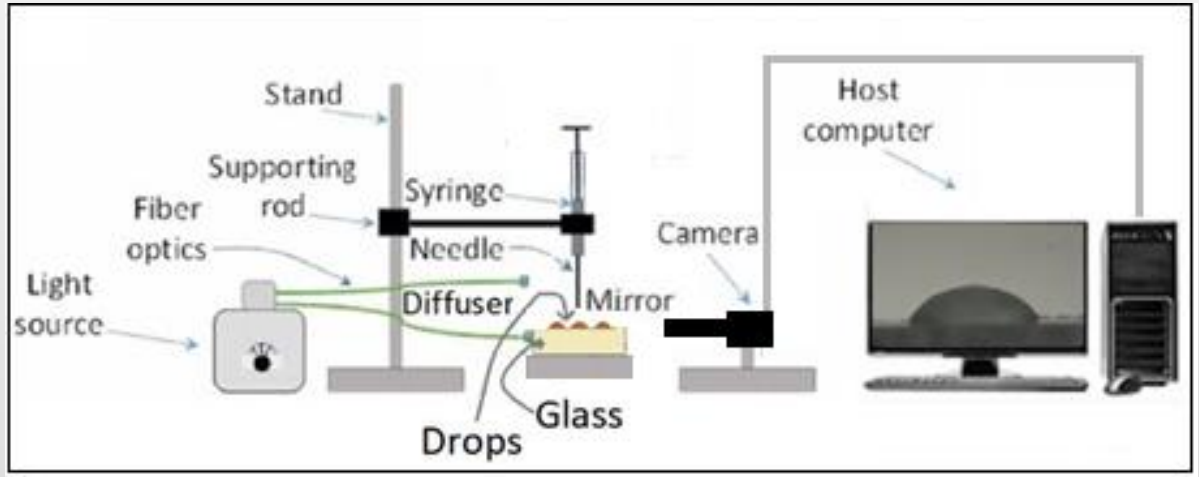
Static Surface and Interfacial Tension measurements

*with **Du Nouy ring method***



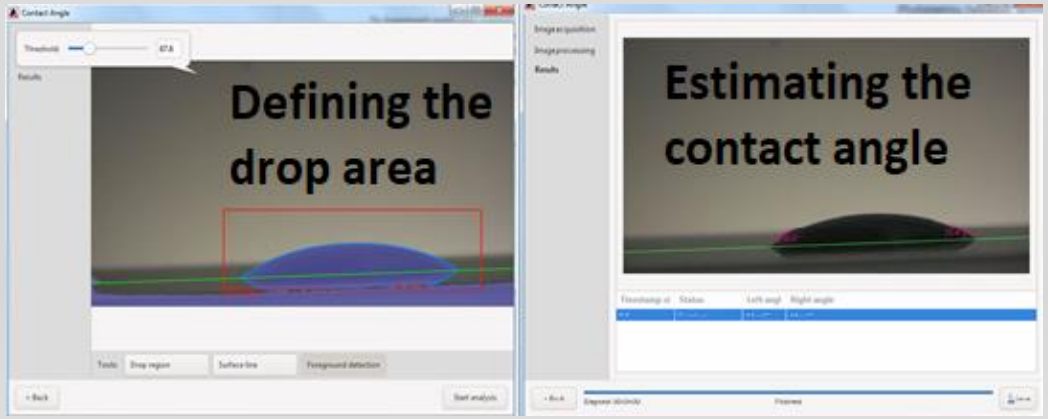
Tensiometer Sigma -702

Contact angles measurements



*Schematic diagram of **contact angles measurements***

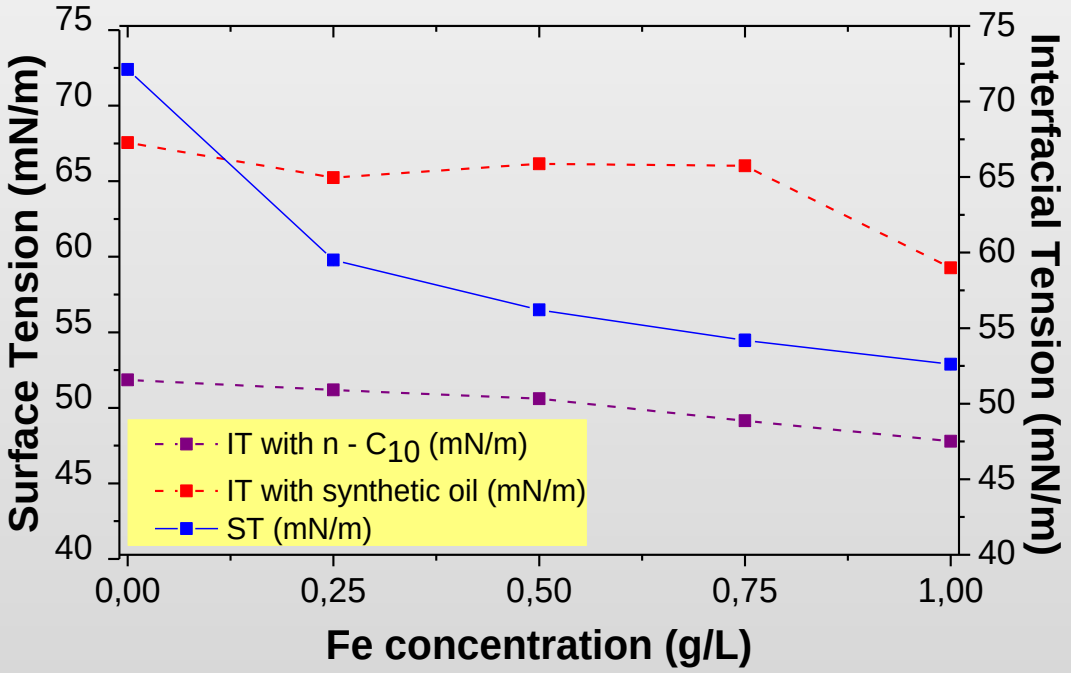
*"Analyzing the recorded contact angles configurations with the open **access OpenDrop software**"*



*Estimation of contact angle by **OpenDrop software***

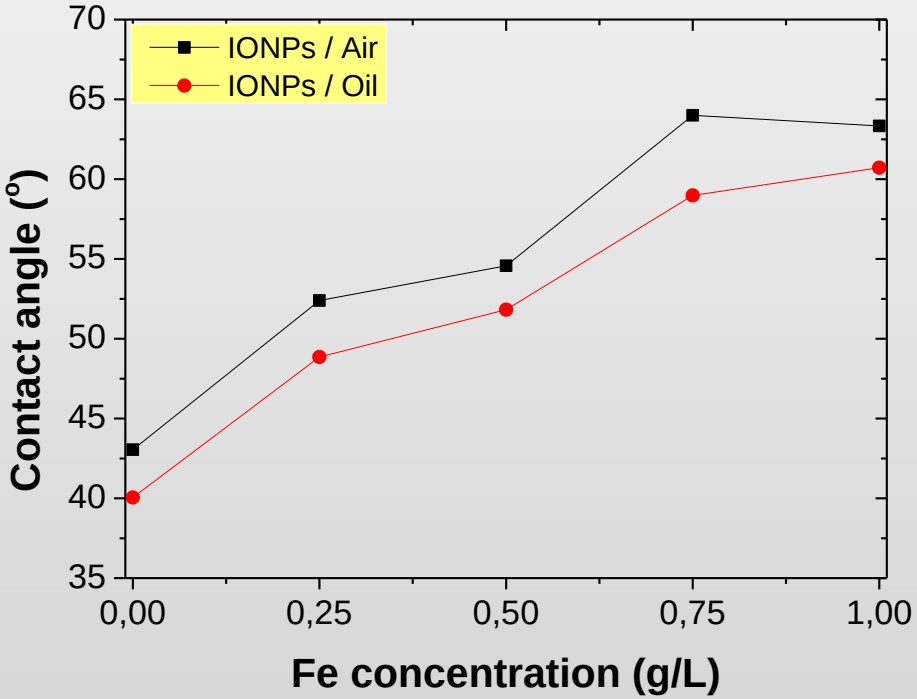
Evaluation of Interfacial and Wetting properties

Surface and Interfacial Tension measurements



Lower **ST, IT** values were indicated at increased **Fe concentrations**

Contact angles measurements



IONPs suspensions indicate **intermediate wetting** on **glass** surface

Pickering emulsions

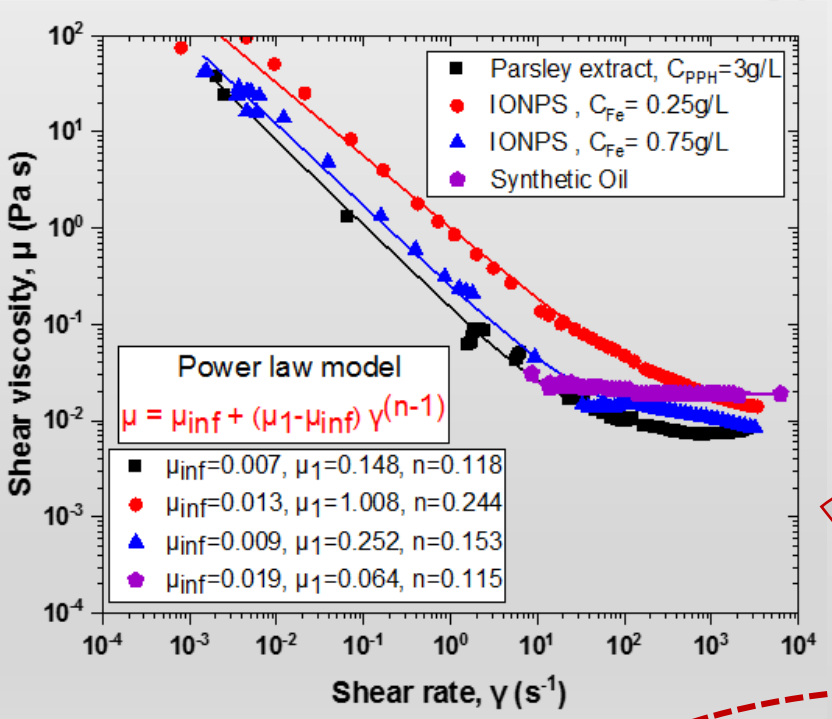
Preparation Process

Homogenizing ***aqueous phase*** (parsley extract or IONPs suspension) ***with n-C10 (2:1)*** in an ultrasound probe ***for 10min***

Immiscible phases

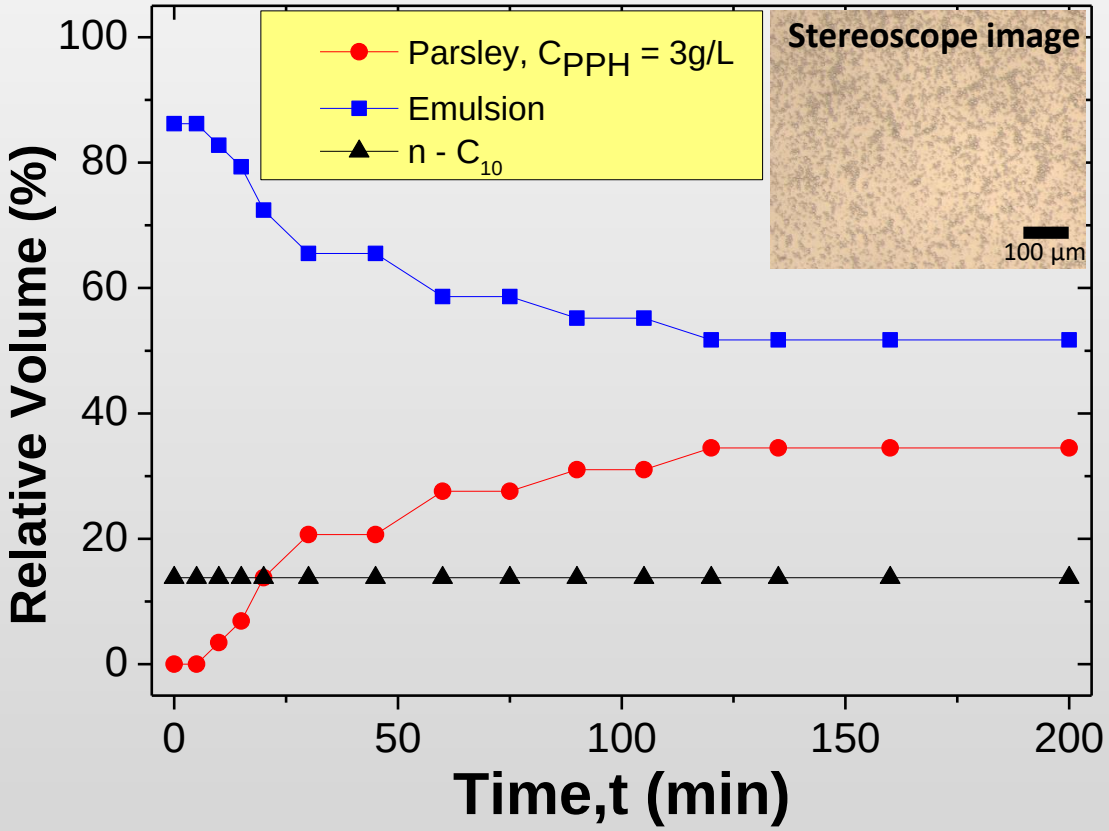
Pickering emulsions

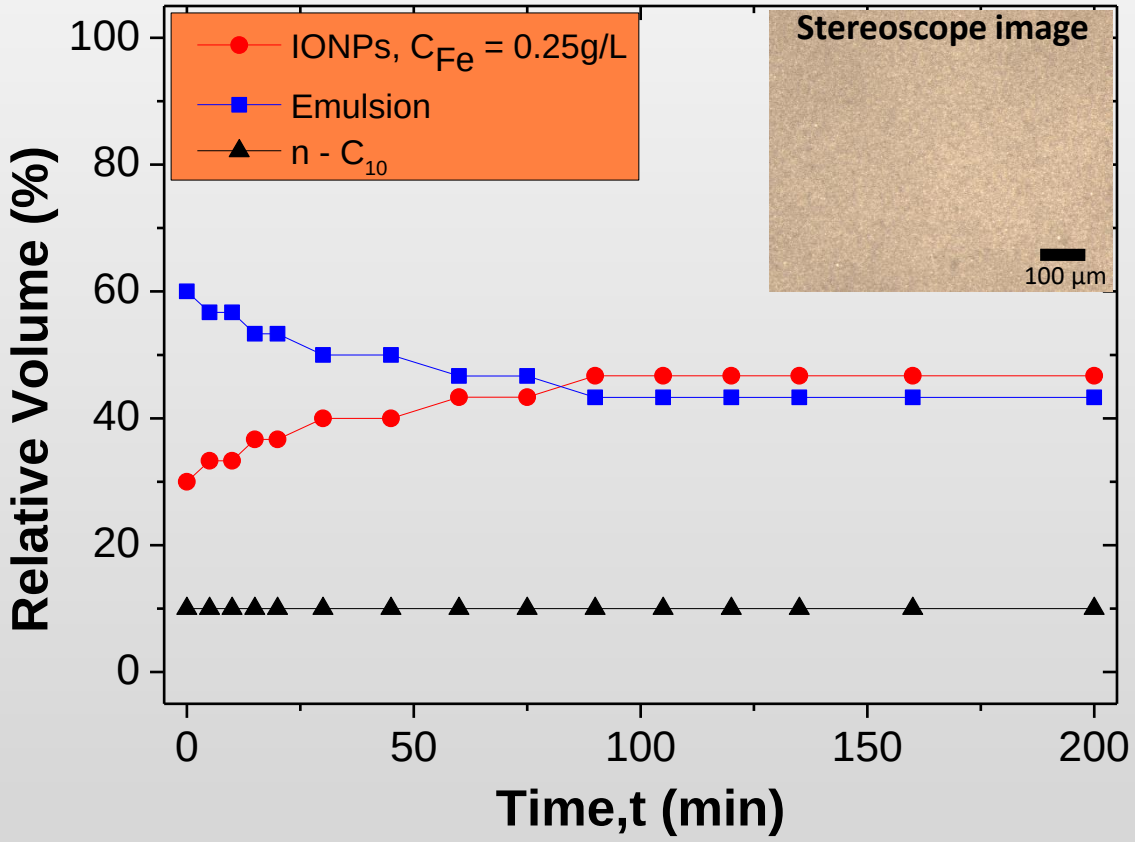
Rheology



The ***shear thinning rheology*** of the Pickering emulsions were fitted satisfactorily with the ***Power law model***

Stability of the Pickering emulsions

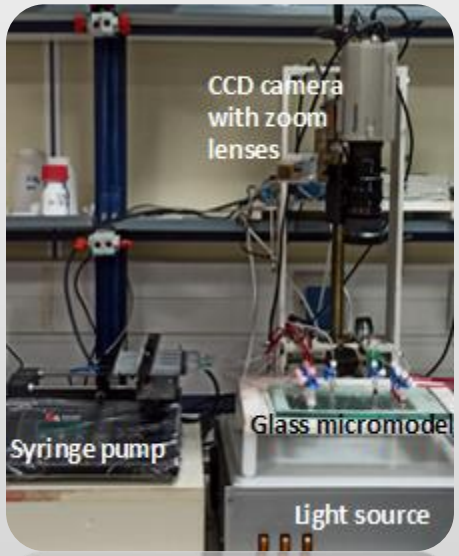


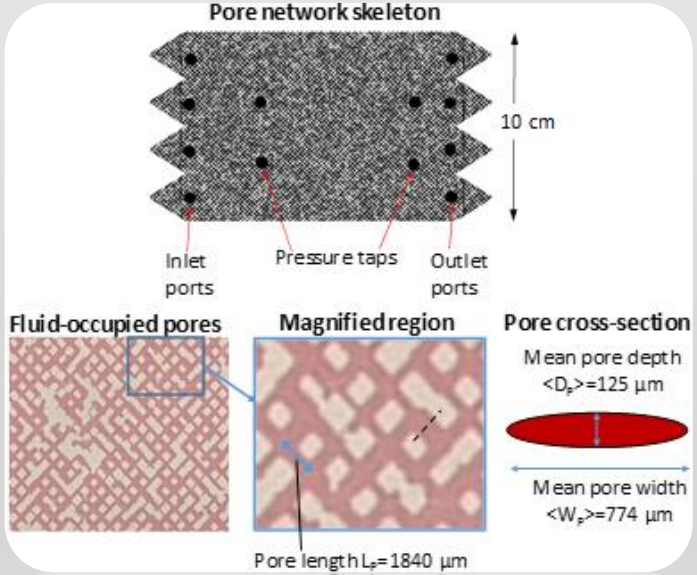


Stable Pickering emulsions *over time*

Displacement Test on a glass – etched pore network model

Experimental setup





Morphology of glass-etched pore network model

Steps for the evaluation of IONPs – fluids to the in situ removal of residual oil from subsurface

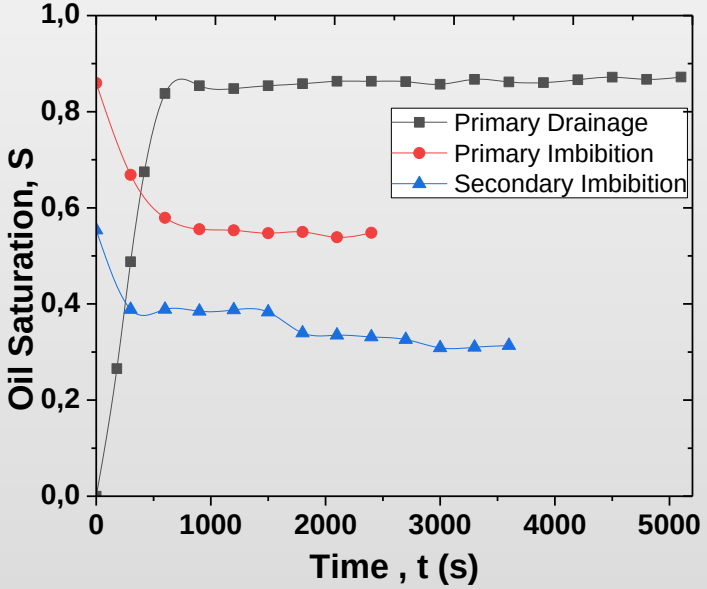
Transient responses of **synthetic oil saturation** for displacement tests,

- **3D – water in primary imbibition**
- **displacing fluid in secondary imbibition:**
  - **Pickering emulsion** stabilized by parsley extract:

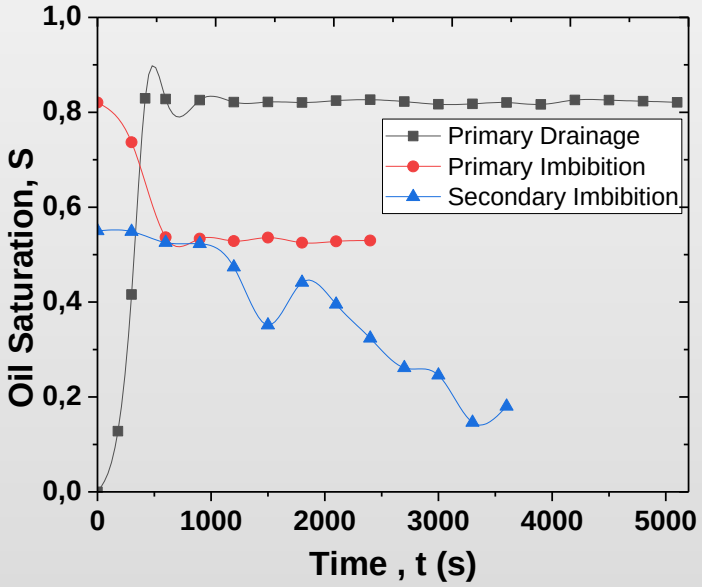
  or
  - **Pickering emulsion** stabilized by IONPs suspension

Synthetic oil: Mixture of paraffin oil with n – C_{10} (4:1)

(a) Pickering emulsion stabilized by parsley extract

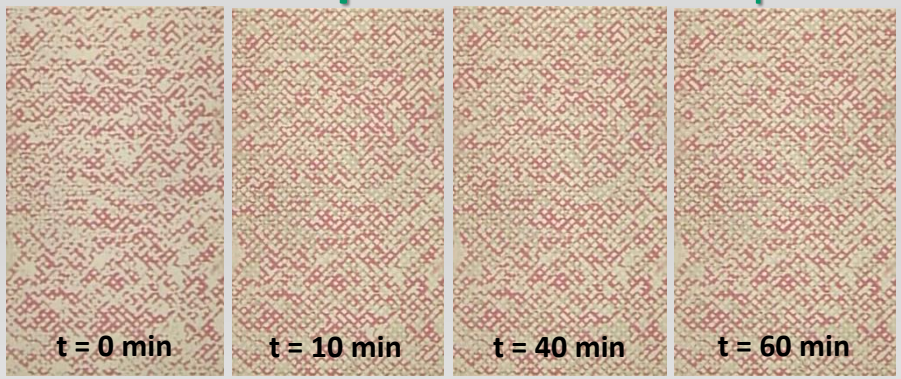


(b) Pickering emulsion stabilized by IONPs suspension

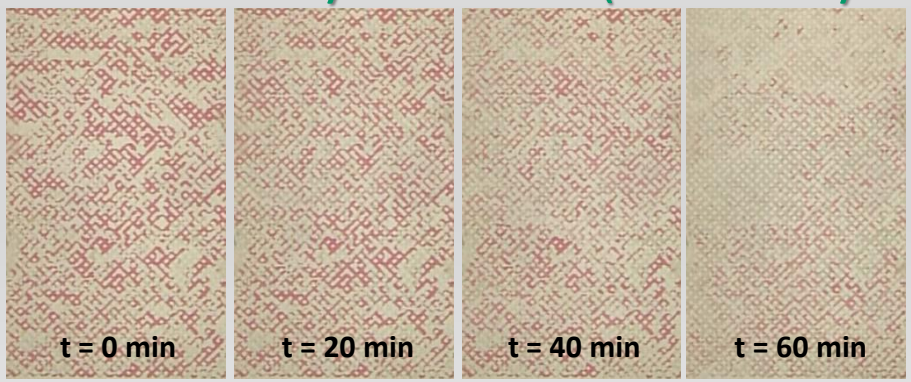


Significant oil removal efficiency** achieved by **Pickering emulsions

Successive snap-shots of the displacement of residual synthetic oil (secondary imbibition) by:



(a)



(b)

Displacement tests conducted in a glass – etched pore network

Type of displacement	Displaced fluid	Displacing fluid	Flow rate (mL/min)	Injected volume (mL)	Oil saturation	Oil removal efficiency (%)
Drainage	3D - water	Synthetic oil	0.08	8.0	0.87	-
Prim. Imbib.	Resid. synthetic oil	3D - water	0.20	8.0	0.55	-
Sec. Imbib.	Resid. synthetic oil	Emulsion*	0.20	11.2	0.31	64.4
Drainage	3D - water	Synthetic oil	0.08	8.0	0.82	-
Prim. Imbib.	Resid. synthetic oil	3D - water	0.20	8.0	0.53	-
Sec. Imbib.	Resid. synthetic oil	Emulsion**	0.20	11.2	0.18	78.0

*Parsley extract / n-C_{10}, ** IONPs suspension (C_{Fe} = 0.25 g/L) / n-C_{10}

Conclusions

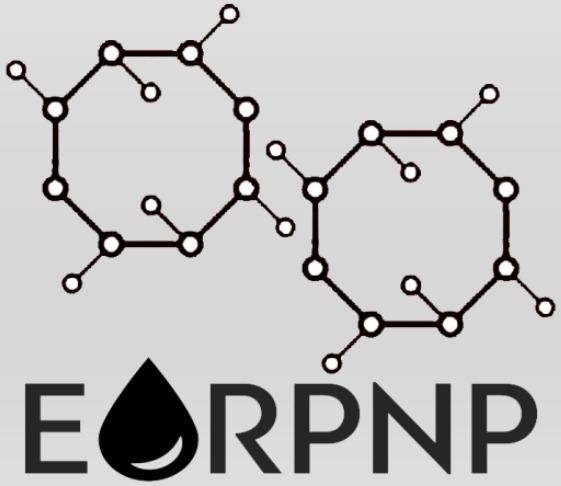
- ✓ Successful synthesis of ***stable IONPs suspensions*** via *green synthesis*
- ✓ ***Surface and Interfacial tension*** depends on the *concentration of Fe*
- ✓ IONPs suspensions appear ***intermediate wettability*** on *glass surface*
- ✓ Formation of ***stable Pickering emulsions*** was fitted reliably with the *Power law model*
- ✓ ***Significant oil removal efficiency*** was achieved by injecting *Pickering emulsions*

Future research

- Synthesis of ***IONPs*** *suspensions* by ***different plants extracts***
- Study of the ***kinetics of the reaction***
- Measurement of ***size distribution, zeta – potential*** and other physicochemical properties ***over time***
- Estimation of ***drops distribution and rheology measurement*** of the *Pickering emulsions* ***over time***

Acknowledgments

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)



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


Best Regards!
Thank you!