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

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Abstract

Aqueous solutions of polyphenols extracted from the leaves of plants are used to synthesize and stabilize aqueous suspensions of iron oxide nanoparticles by green chemistry routes. The interfacial properties and wetting properties of nano-colloids are measured to assess their capacity to generate stable Pickering emulsions. The rheological properties of emulsions are measured, and their stability is inspected by observing the phase separation (macro-scale) and measuring the drop size distribution (micro-scale). The capacity of emulsions to remove residual oil from soils is evaluated with visualization tests of drainage / primary imbibition / secondary imbibition performed on a glass-etched pore network for an oil / aqueous solution system. In each test, the transient changes of the fluid saturation along with the pressure drop across the porous medium are measured and correlated with dimensionless parameters, such as the capillary number and viscosity ratio.

Keywords: *iron oxide nanoparticles (IONPs), interfacial tension, wettability, oil displacement, soil remediation*

1. INTRODUCTION

The remediation of oil spills is an urgent global challenge due to their devastating impacts on the environment and human health [1].Conventional methods for oil spill remediation, such as mechanical recovery and chemical dispersants, have drawbacks and limitations, including potential harm to marine life and ecosystems. Therefore, alternative and environmentally-friendly approaches are needed for efficient oil spill remediation [2].

One promising approach is the use of smart fluids synthesized via green synthesis with iron oxide nanoparticles. Iron oxide nanoparticles (IONPs) are attractive materials for environmental remediation due to their unique magnetic properties, high surface area, and stability [3,4]. Green synthesis with plant extracts is a sustainable and eco-friendly method for producing iron oxide nanoparticles [5]. IONPs can decrease the interfacial tension of oil and water, which can lead to more stable Pickering emulsions [6-8].

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Several studies have demonstrated the potential of smart fluids synthesized via green synthesis with iron oxide nanoparticles for the efficient removal of residual oil from subsurface environments. In these 'greener' processes, plant extracts were used for the synthesis of nanoparticles through biosynthetic routes which involve primarily the extraction of polyphenols, which are natural polymers acting as reducing agents and stabilizers [9-11].In summary, the synthesis of smart fluids via green synthesis with iron oxide nanoparticles is a promising approach for the efficient removal of residual oil from subsurface environment.

In this work, aqueous solutions of polyphenols are extracted from parsley leaves and mixed with a ferric chloride hexahydratesolution to produce IONPs suspensions. An ultrasound probe is used for the production of stable oil-in-water emulsions by mixing the suspensions with n-decane. The performance of the emulsions as agents for the efficient removal of residual oil from subsurface, is assessed with secondary imbibition tests, performed on a transparent glass-etched pore network,after having completed a drainage / imbibition cycle,by usingas oil phase a synthetic one of controlled viscosity which was prepared by mixing paraffin oilwith n-decane.A comparative analysis of the displacement efficiency of Pickering emulsionsenabled us to classify them, in terms of their rheological properties.

2. MATERIALS AND METHODS

2.1 Synthesis of iron oxide nanoparticles (IONPs) suspensions and emulsion preparation

For the preparation of parsley extract, 1000 mL of triple distilled water (3D - water) was heated on a hot plate, andwhen the temperature reached at 80 °C, 50 g of parsley leaves was added in water, and left for60 min, under stirring. Then, the mixture waswithdrawn from the hot plate,left to equilibrate to ambient conditions, filtrated under vacuum on 4 μm and 2.5 μm pore size filters (Whatman) and centrifuged at 10000 rpm for 10 min (Heraeus Megafuge-16) toseparate the liquid extract from the solid residue. The total polyphenol concentration (TPC) of the extract was measured in terms of gallic acid equivalent (g/L GAE), using the Folin-Ciocalteu method [12] andUV-Vis spectroscopy (Shimadzu UV-1900).

The synthesis of iron oxide nanoparticles (IONPs) was achieved by adding 0.1 M $FeCl_3$ solution inthe polyphenol extract (PPH), at a volume ratio of 2:1 [13]. The colour change of the solution to dark brown certified the end of the reaction. The pH was measured with a pH-meter (CONSORTC830), adjusted to 6.0, and the suspension was placed in a refrigerator for further use.

The preparation of emulsions was done by mixing 20 mL of IONPs suspension with 10 mL of oil (n-decane) at a volume ratio 2:1 for 10 min by using an ultrasound probe (Hielscher, UP400St).The synthetic oil was prepared by mixingparaffin oil (Labkem, Spain) with n-decane (Sigma – Aldrich) at volume ratio 4:1 [14].

2.2 Characterization of IONPs suspensions and emulsions

Suspensions of IONPs were prepared at four iron concentrations 0.25, 0.5, 0.75 and 1.0 g/L. The particle size distribution, and ζ-potential of IONPs suspensions were measured with Dynamic Light Scattering -DLS (Zetasizer Nano System, Malvern) after having diluted each suspension at volume ratio 1:50 with 3DW.

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The static surface tension of the suspensions, as well their interfacial tension with n-decane and synthetic oil were measured at 25°C on a Sigma 702 (KSV Instruments) tensiometer by using the DuNouy Ring method.

The static contact angles were measured by placingdrops of aqueous phase,surrounded by air or oil, on a glass surface under a stereoscope (Nikon)and capturing the images with an HY-2307 CMOS camera (Hayear) connected via USB with PC and equipped with image capturing software.

The stability of Pickering emulsions was inspectedmacroscopically, by observing the phase separation as a function of time, and microscopically, by a CCD video camera (Micropublisher 6, Photometrics-Teledyne).

2.3. Visualization tests

Immiscible displacement tests were performed on a glass pore network model (Figure 1), to assess the capacity of IONP-stabilized emulsions to enhance the recovery of residual oil entrapped in the pore network after a primary drainage (displacement of 3-distilled water (3DW) by synthetic oil at rate q=0.08 mL/min),and primary imbibition (displacement of oil by 3DW at rate, q=0.2 mL/min). During this secondary imbibition stepthe emulsion displaces the residual oil at flow rate q=0.2 mL/min. Each displacement step started at the point that the previous step was completed, so that theoil saturation varied continuously with time. At each series of displacement tests, images were captured every 20 s by a CCD video camera (Panasonic AW-E300E). The absolute pressure was measured with two pressure transmitters (SGM, Electrosystems)(Figure 1)properly connected with a data acquisition system (ADAMS-4561 & ADAMS-4117, Advantech). Recorded snap-shots of the flow pattern were processed with image analysis software (ImageJ) to determine the gradual variation of residual oil saturation.

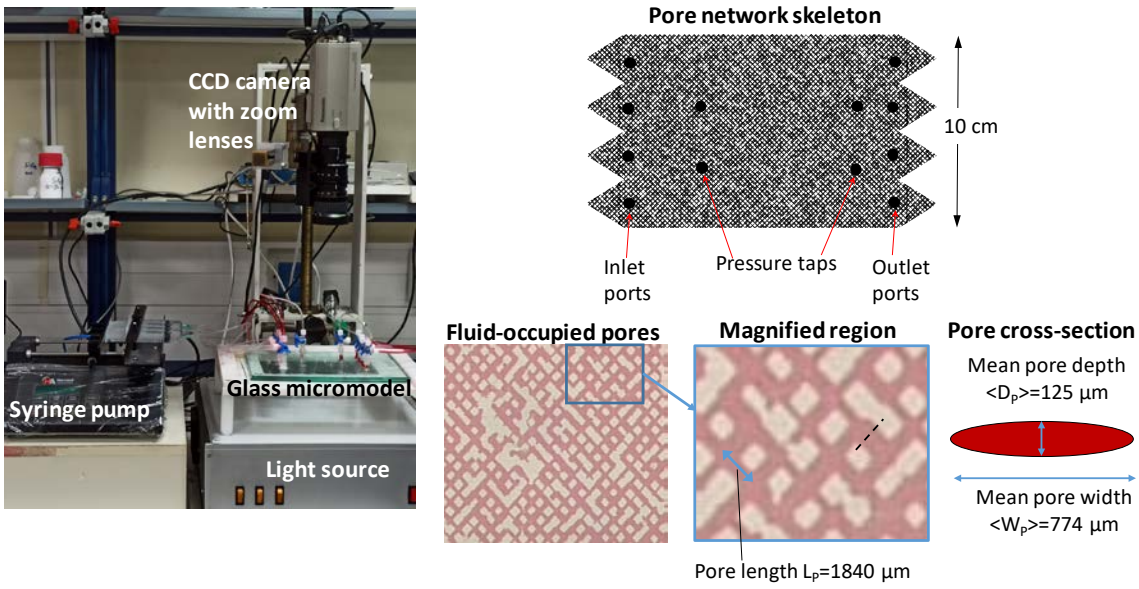

Figure 1. *Experimental setup and micromodel morphology.*

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3. RESULTS AND DISCUSSION

3.1 Physicochemical and interfacial properties of aqueous suspensions

The polyphenol concentration in PPH extract was measured by Folin-Ciocalteu method and estimated ~2.0 – 3.0 g/L GAE, while its pH was found 6.5.Moreover, the surface tension of PPH extract was found equal to45.3 ± 0.13mN/m, whereas the PPH extract / n-decane,and PPH extract / synthetic oil interfacial tensions, all measured at 25^{o}C,were found equal to 36.8 and 48.2 mN/m, respectively.The physicochemical, wetting, and interfacial properties of nanoparticle suspensions as functions of IONP concentrationare shown in Table 1, Table 2, and Figure 2, respectively.

The IONP suspensions are stable, and the nanoparticle sizes exhibit a narrow size distribution (Table 1). The air/IONP suspension and oil/IONP suspension contact angle vary (50^{o} – 75^{o})over the intermediate wetting range (Table 2). The surface tension of suspensions is a clearly decreasing function of IONP concentration (Figure 2) while the interfacial tensionof aqueous IONPssuspensionswith oils is a weakly decreasing function of IONP concentration (Figure 2).

Table 1. Physicochemical properties of aqueous suspensions.

Aqueous suspension	Particle size distribution		ζ-potential(mV)
	$\langle D_p \rangle$ (nm)	σ_p (nm)	
Parsley extract, C_{PPH}=3.0 g/L	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	-10.3
IONPs, C_{Fe}=1.0 g/L	15.69	5.5	-25.1

Table 2. Wetting properties of aqueous suspensions.

Aqueous suspension	Air/water contact angle		Oil/water contact angle	
	$\langle \theta_{aw} \rangle$(^{o})	$\sigma_{\theta aw}$ (^{o})	$\langle \theta_{ow} \rangle$(^{o})	$\sigma_{\theta ow}$ (^{o})
Parsley extract, C_{PPH}=3.0 g/L	73.95	2.86	69.59	1.61
IONPs, C_{Fe}=0.25g/L	52.39	7.95	48.85	7.49
IONPs, C_{Fe}=0.5 g/L	54.57	2.95	51.82	2.58
IONPs, C_{Fe}=0.75 g/L	64.00	3.18	58.98	3.61
IONPs, C_{Fe}=1.0 g/L	63.33	4.63	60.72	3.17

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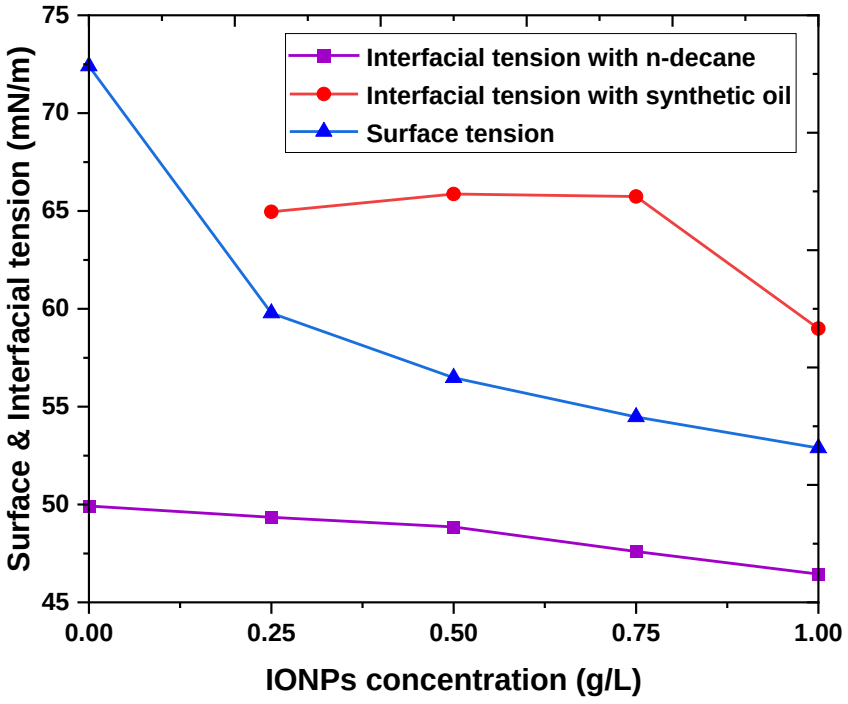

Figure 2. *Interfacial properties of aqueous IONPssuspensions*

3.2 Emulsion characterization

Macroscopically, examiningthe relative volume of each phase as function of time, all emulsions appear comparable stability, with the emulsified phase occupying 50-60% of the total volume 3hrs after their preparation (Figure 3). Rheological measurements (Figure 4) show all Pickering emulsions are shear-thinning fluidswhich are fitted satisfactorily with theextended power law model:

$$\mu = \mu_{inf} + (\mu_1 - \mu_{inf})\dot{\gamma}^{n-1} \quad (1)$$

where $\dot{\gamma}$is the shear rate, μ_{inf} is the asymptoticvalue of viscosity as the shear rate tends to infinity, μ_1 is the viscosity at $\dot{\gamma} = 1\ s^{-1}$, and *n*is a power law exponent. The higher the values of μ_1 , μ_{inf} ,the more viscousthe emulsion. The lower the exponent *n*, the sharper the reductionof viscosity at increasing shear rates (Figure 4).

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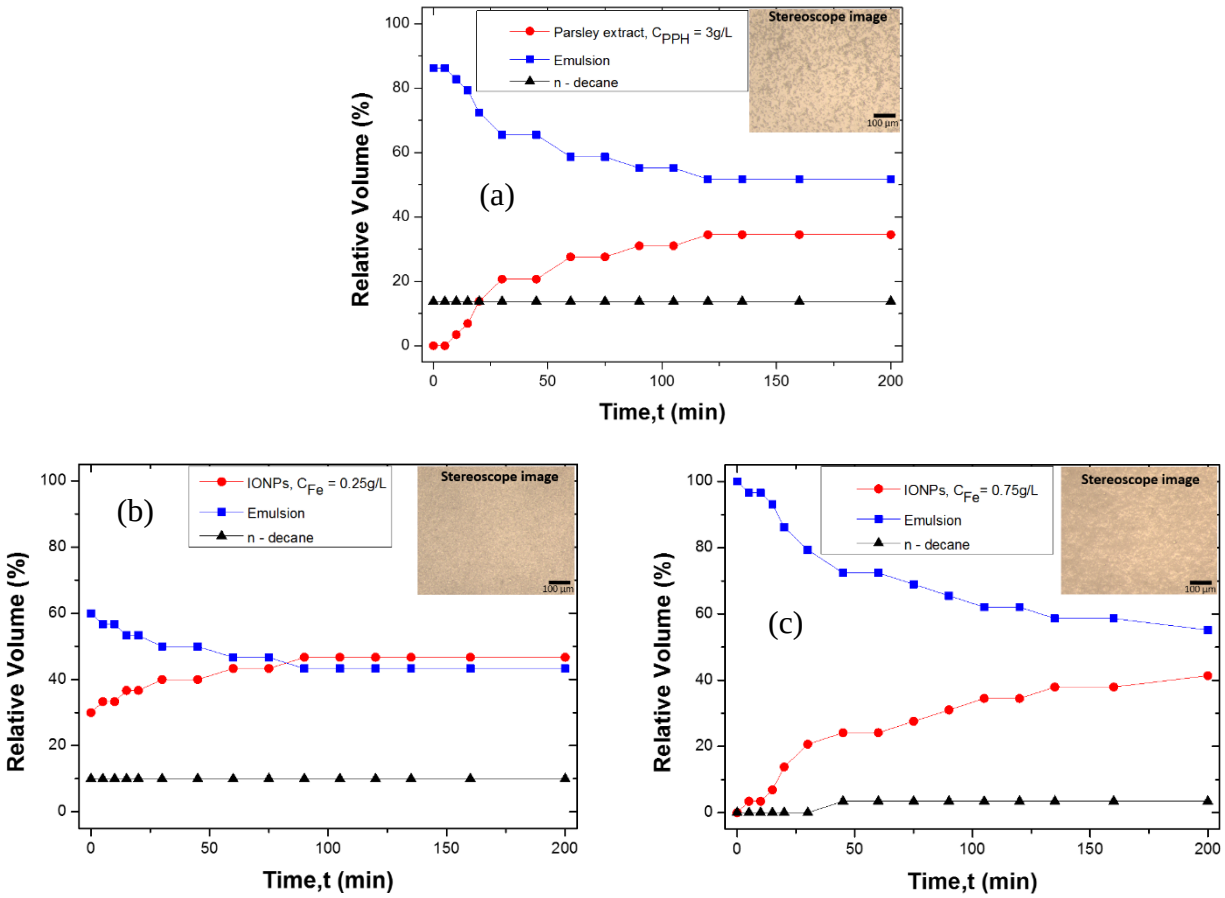

Figure 3. *Transient response of the relative volume of the various phases of emulsions. (a) Aqueous phase: parsley extract, C_{PPH}=3.0g/L. (b)Aqueous phase: IONPs, C_{Fe}=0.25g/L.(c) Aqueous phase: IONPs, C_{Fe}=0.75g/L.*

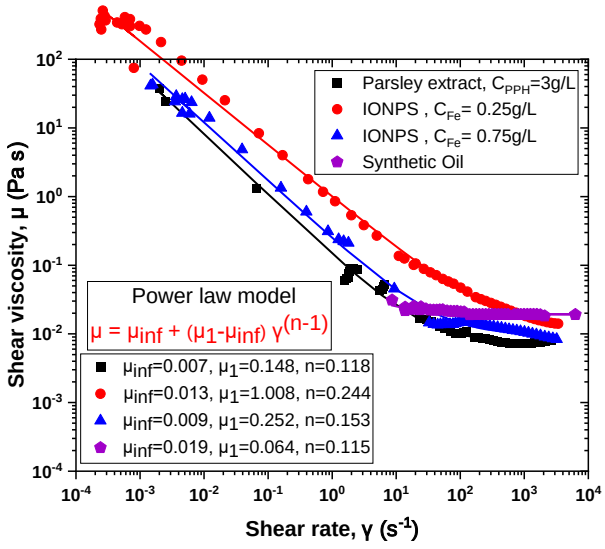

Figure 4. *Shear viscosity of Pickeringemulsions and synthetic oil, fitted with the extended power law model.*

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3.3 Visualization tests

Successive images of the primary drainage/primary imbibition /secondary imbibition cyclesfor the most effective Pickering emulsion (IONP with C_{Fe}=0.25 g/L) are shown in Figure 5. In addition, the corresponding transient response of the oil saturation and pressure drop across a central region of the porous medium are shown in Figures 6, 7 and 8 for the three emulsions tested.The highest oil recovery efficiency of secondary imbibition was achieved with the highest values of viscosity ratio and capillary number, favouring the frontal drive flow pattern (Figure 5c). The strong shear thinning viscosity of displacing fluid during the secondary imbibition is reflected in the high amplitude of the pressure drop fluctuations (Figure 7a, 8a).

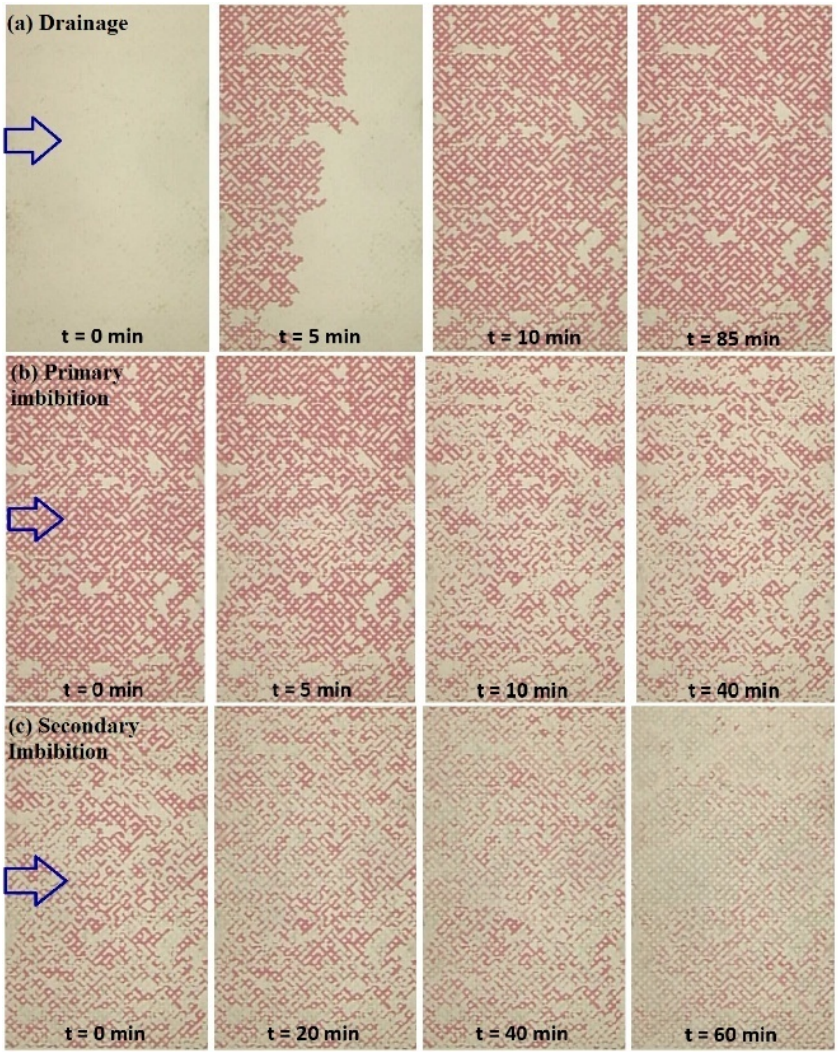

Figure 5. *(a) Displacement of 3D-water by synthetic oil (μ=0.026 Pa s). (b) Displacement of synthetic oil by 3D-water. (c) Displacement of residual synthetic oil by Pickering emulsion (aqueous suspension=IONPs withC_{Fe}=0.25g/L; oil phase: n-decane; volume rate 2:1).*

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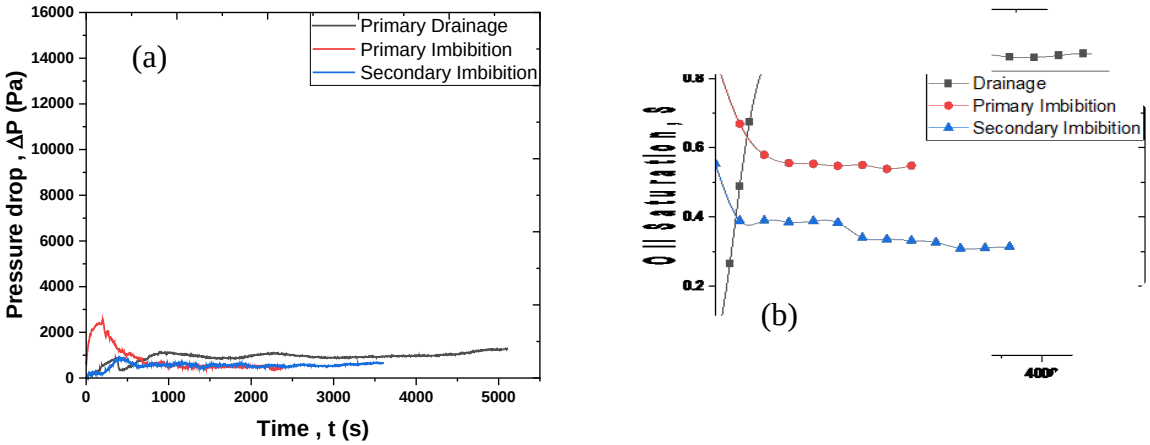

Figure 6.*Transient response of (a) pressure drop, and (b) oil saturation, as a function of time. Pickering emulsion of parsley extract, C_{PPH}=3g/L, was injected at the secondary imbibition step.*

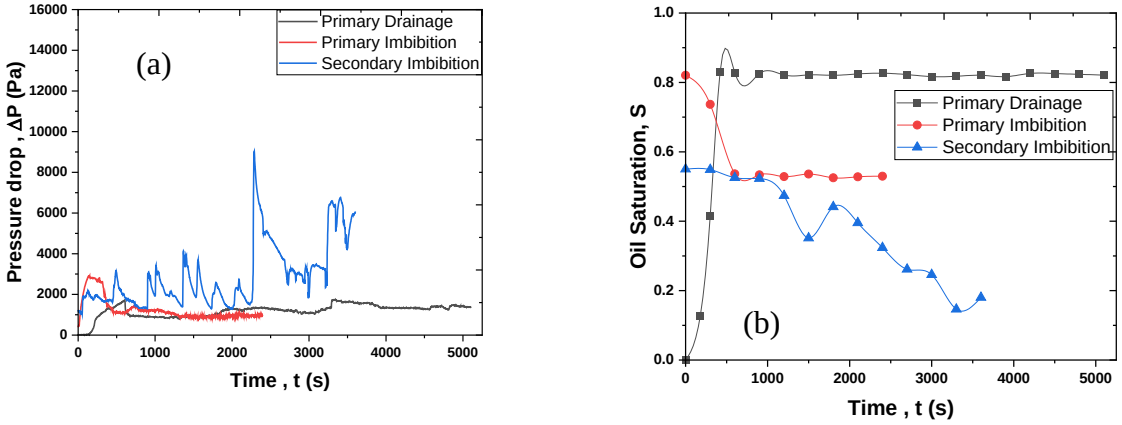

Figure 7. *Transient response of (a) pressure drop, and (b) oil saturation, as a function of time. Pickering emulsion of IONPs suspension, C_{Fe}=0.25g/L, was injected at the secondary imbibition step.*

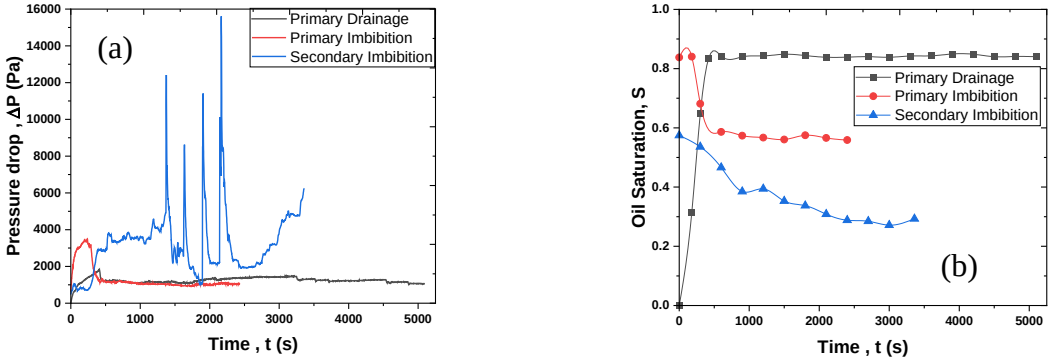

Figure 8. *Transient response of (a) pressure drop, and (b) oil saturation, as a function of time. Pickering emulsion of IONPs suspension, C_{Fe}=0.75g/L, was injected at the secondary imbibition step.*

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Table 3. Summary of results from visualization tests

Displacing fluid in Secondary Imbibition	Primary Drainage* S_o	Primary Imbibition S_o	Secondary Imbibition S_o	+μ_{av} (mPa s)	&κ	$Cax10^{-5}$	Oil recovery efficiency (%)
Pickering emulsion C_{PPH}=3.0g/L	0.87	0.55	0.31	28	1.08	0.98	64.4
Pickering emulsion C_{Fe}=0.25g/L	0.82	0.53	0.18	197	7.58	5.2	78.0
Pickering emulsion C_{Fe}=0.75g/L	0.84	0.56	0.29	47	1.81	1.2	65.5

*Residual oil saturation; +Viscosity of emulsion averaged over a single pore; &Viscosity ratio:$\kappa = \frac{\mu_{av}}{\mu_o}$ where μ_o = 0.026 Pa s;$ Capillary number: $Ca = \frac{u_0 \mu_{av}}{\sigma_{ow}}$, σ_{ow} is the aqueous suspension / synthetic oil interfacial tension

4. CONCLUSIONS

IONP suspensions are synthesized and stabilized by mixing ferrous (FeIII) chloride solution with the polyphenol extract of parsley. Visualization tests are performed on a glass-etched pore network to examine the potential of emulsions to enhance the residual oil recovery after a primary drainage / imbibition cycle.It seems that the oil displacement efficiency is maximized when injecting the emulsion ensuring the highest values of viscosity ratio, and capillary number which favour a frontal two-phase flow pattern (Table 3).

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