



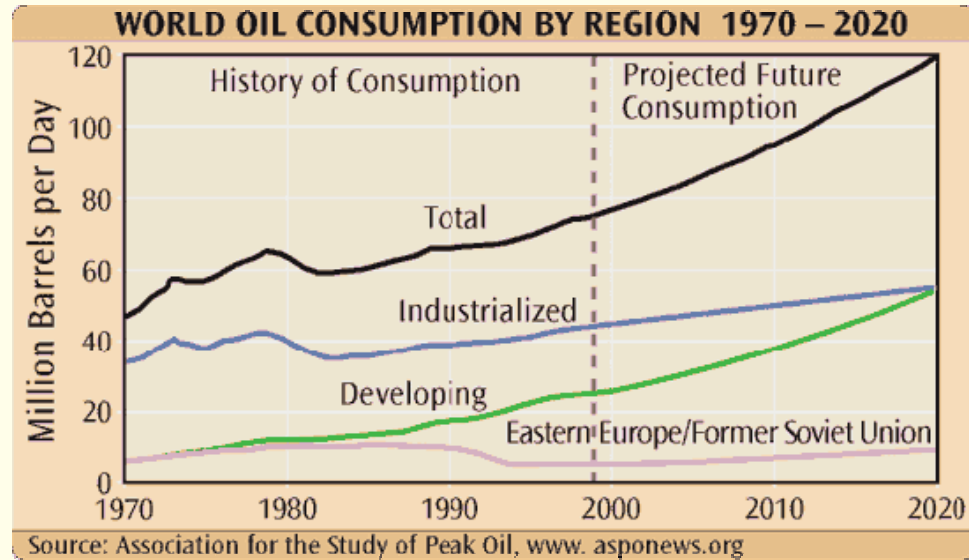
Magnetite nanoparticles and ferromagnetic bionanocomposites for crude oil removal from water

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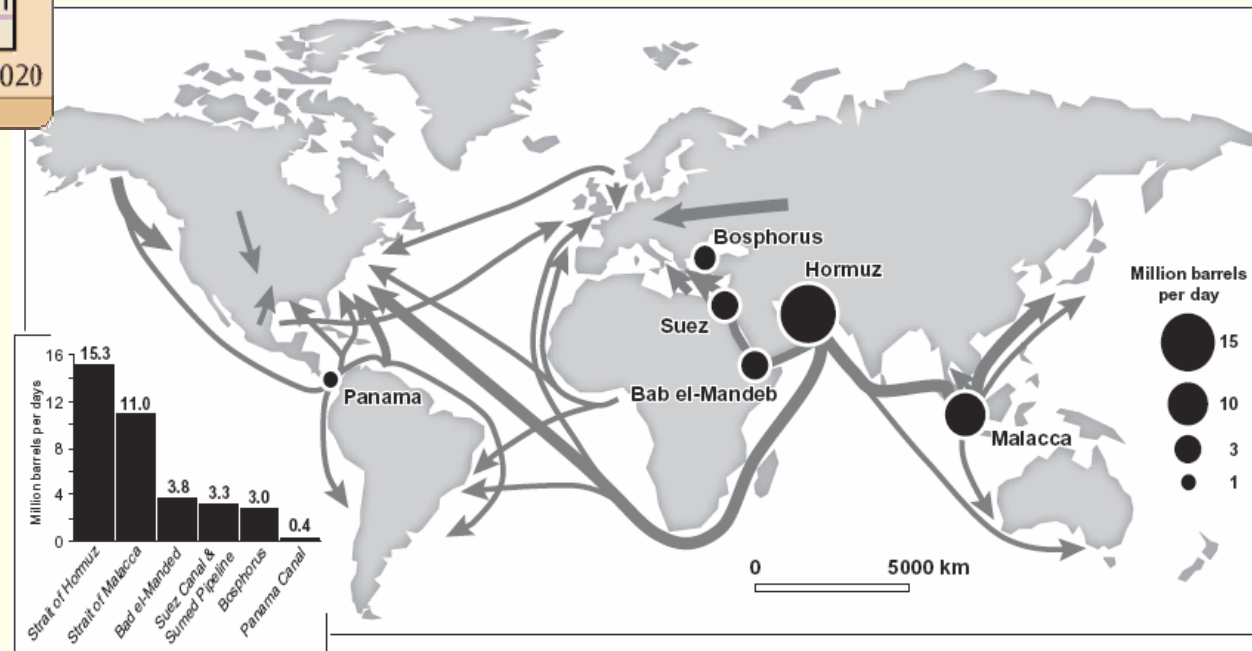
¹Department of Chemistry
Federal University of São Paulo



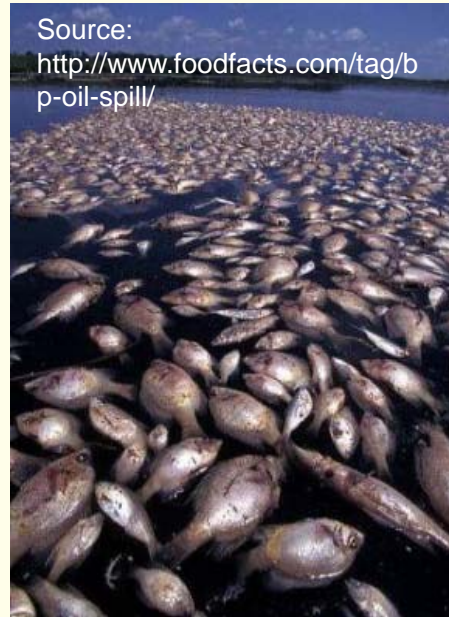
Basis of our motivation



Main oil routes in the world



Source: <https://www.erudit.org>





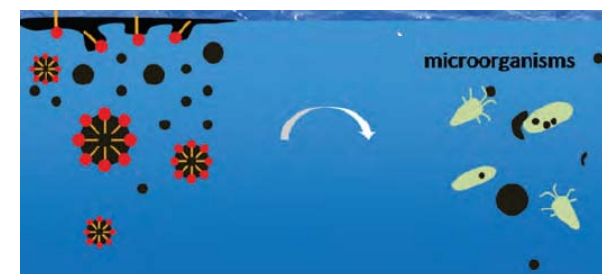
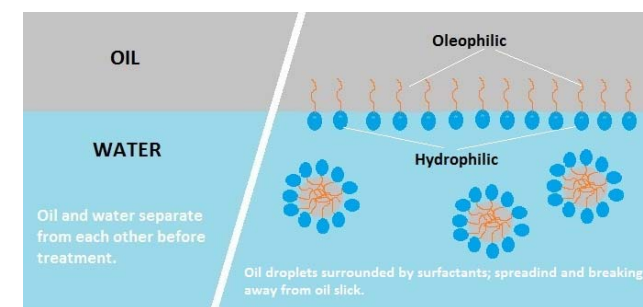
Source: <http://response.restoration.noaa.gov>

Gulf of Mexico oil spill in 2010 -- the worst
environmental disaster in U.S. history -- to cost
it \$ 40 billion.



Recovery of Spilled Oils Today

Methods	Exemples	Limitations
Mechanicals	<i>booms, skimmers</i>	<ul style="list-style-type: none">Do not remove all oil
Chemicals	dispersants, surfactants and solidifiers	<ul style="list-style-type: none">Introduction of new substances in environmentDoes not necessarily allow the oil to be removed
Biologicals	biodegradation	<ul style="list-style-type: none">Introduction of microorganisms and dispersantsIt is necessary the prospection and the control of ideal conditions for each microorganismsDo not permit the oil recovery



NEWS ALERT

French President Emmanuel Macron's party projected to win overwhelming majority in parliamentary election



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Cleaning up oil spills with magnets and nanotechnology

By Tom Levitt, for CNN

Updated 1404 GMT (2204 HKT) September 21, 2012



Researchers hope the use of magnets will allow them to recover more oil and lead to an easier clean up operation.

Story highlights

Oil companies could soon be using an innovative new technique involving nanotechnology and magnets to help clean up offshore oil spills.



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How to clean up oil spills

MIT researchers devise a surprisingly simple but effective method for magnetically separating oil and water.

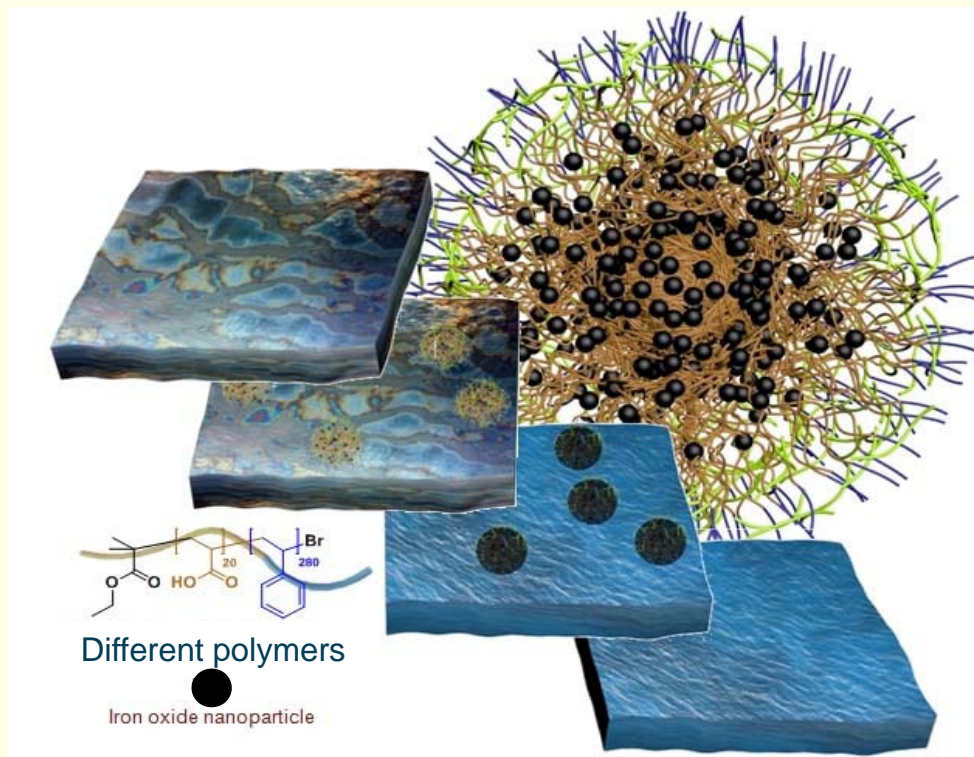
Larry Hardesty, MIT News Office
September 12, 2012

Press Inquiries

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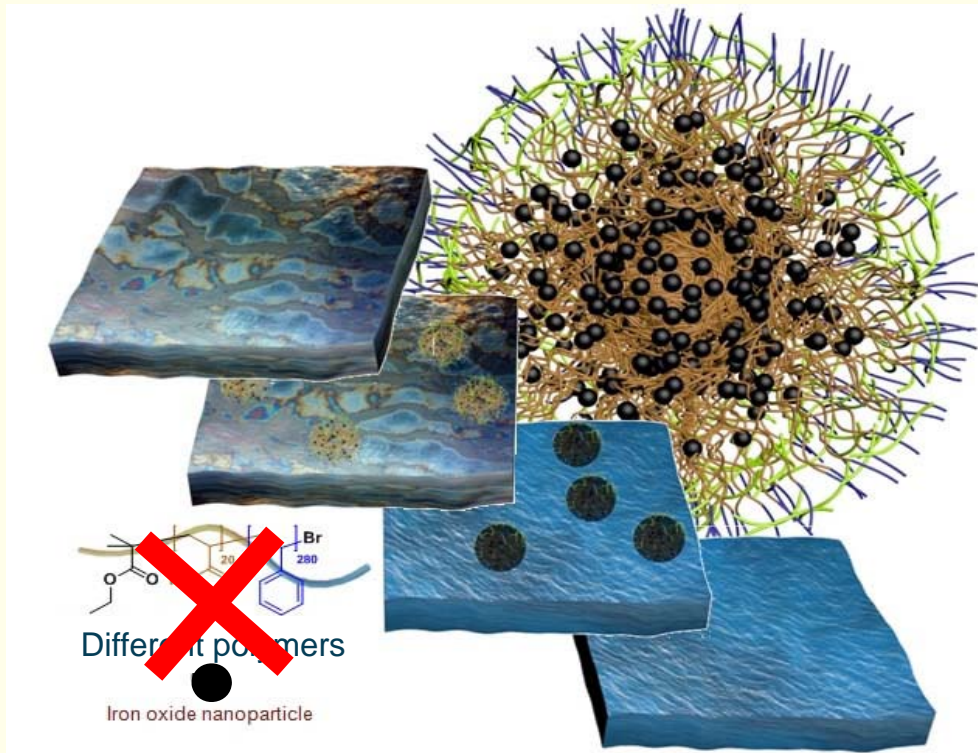
ATHENS2017

Magnetic nanoparticles and composites: *Biosorption*



Source: <http://www.science.tamu.edu>

Magnetic nanoparticles and composites: **Biosorption**



Source: <http://www.science.tamu.edu>

Biomasses:

Low cost

Inactive biological materials

Renewable sources

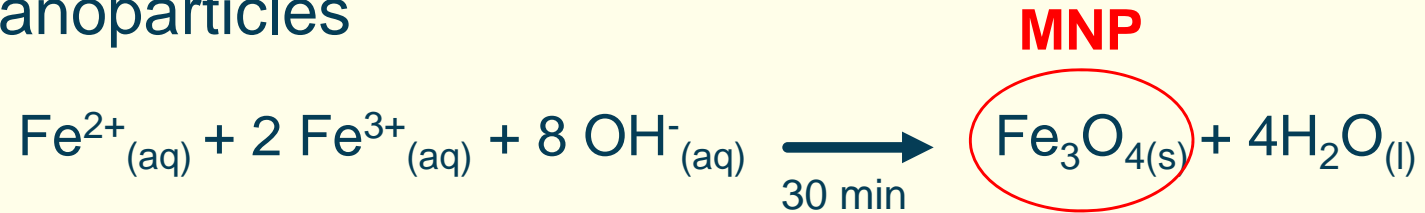
Residues

Hydrophobic surfaces

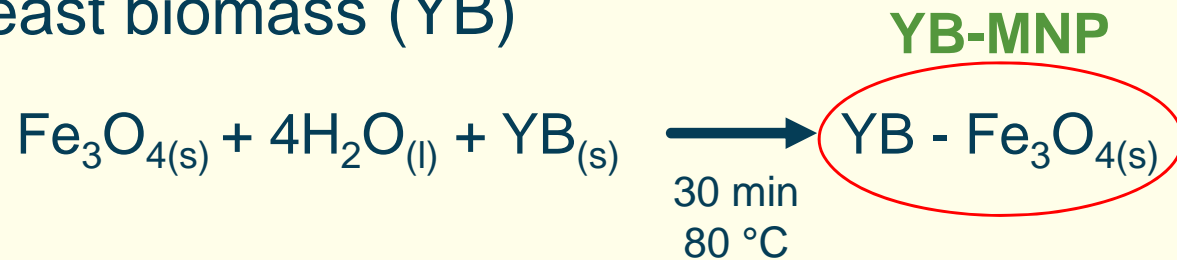
Development of new materials
(such as composites)

Synthesis

Magnetite nanoparticles



Addition of yeast biomass (YB)



Yeast biomass
(YB)



Magnetic nanoparticles
(MNP)

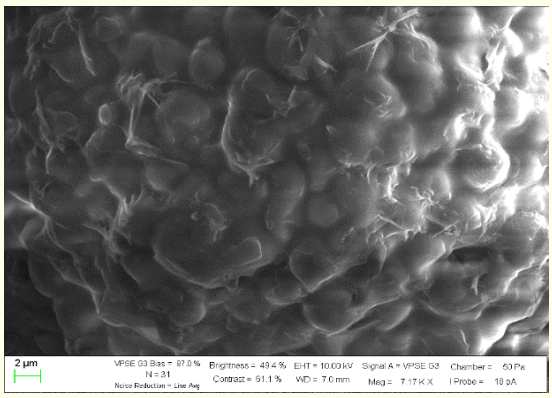
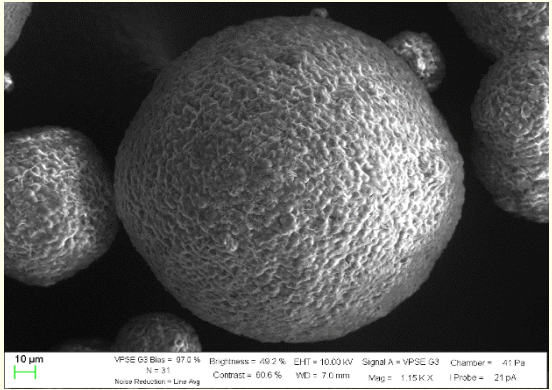


Yeast Magnetic
bionanocomposite
(YB-MNP)

Characterization

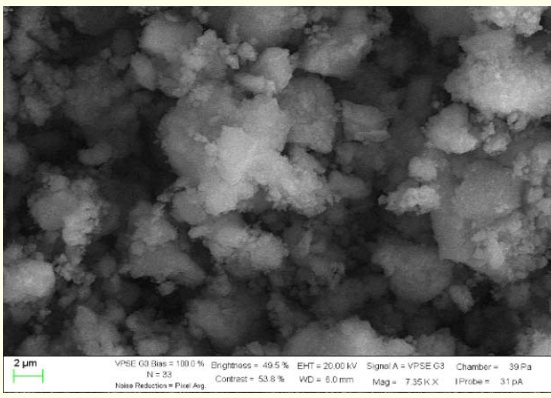
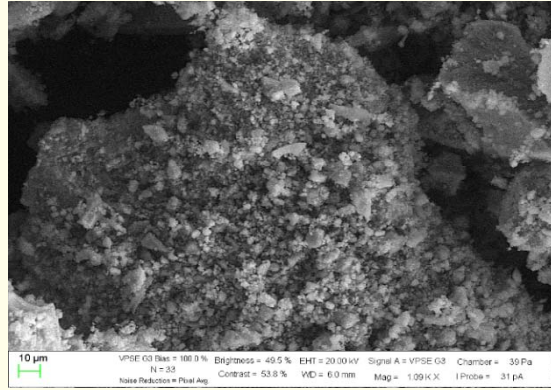
scanning electron microscope (SEM)

YB



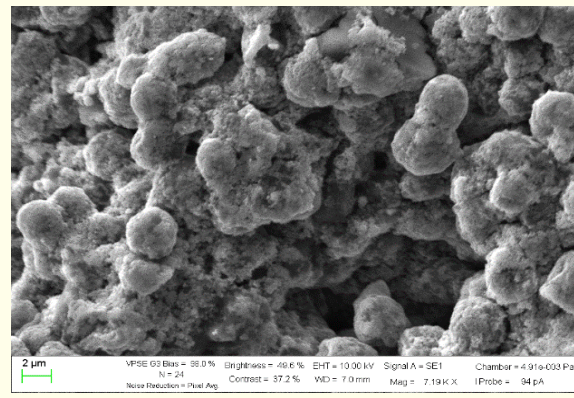
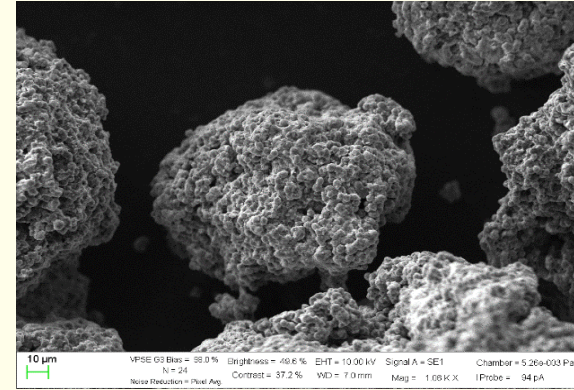
N = 6.14%
C = 41.0%
H = 6.21%

MNP



N = 0.40%
C = 3.5%
H = 1.0%

YB-MNP



N = 3.8%
C = 29.7%
H = 4.3%

magnified 1000X

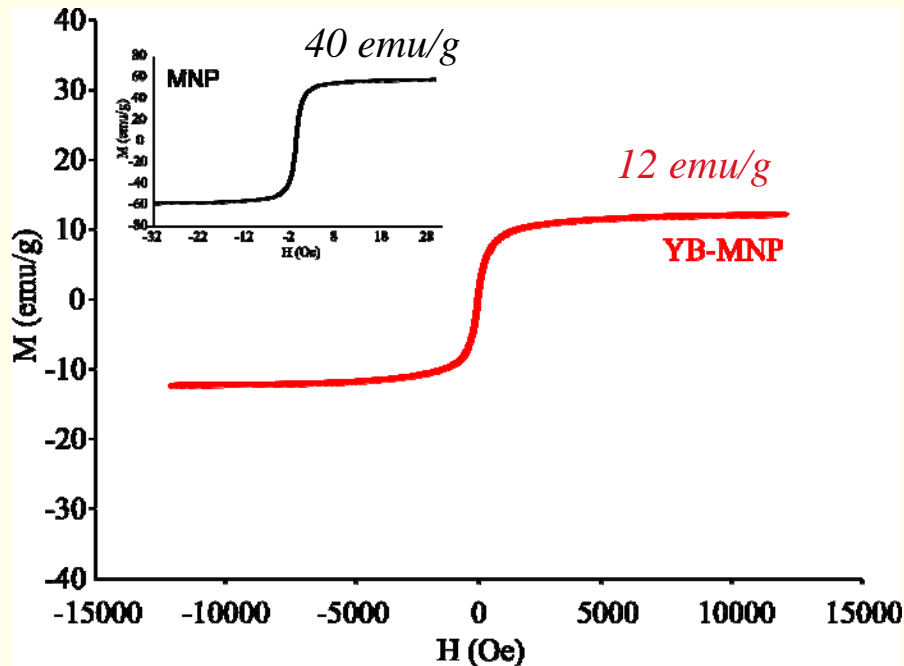
magnified 7000X

Elemental Analyses



Characterization

Magnetization



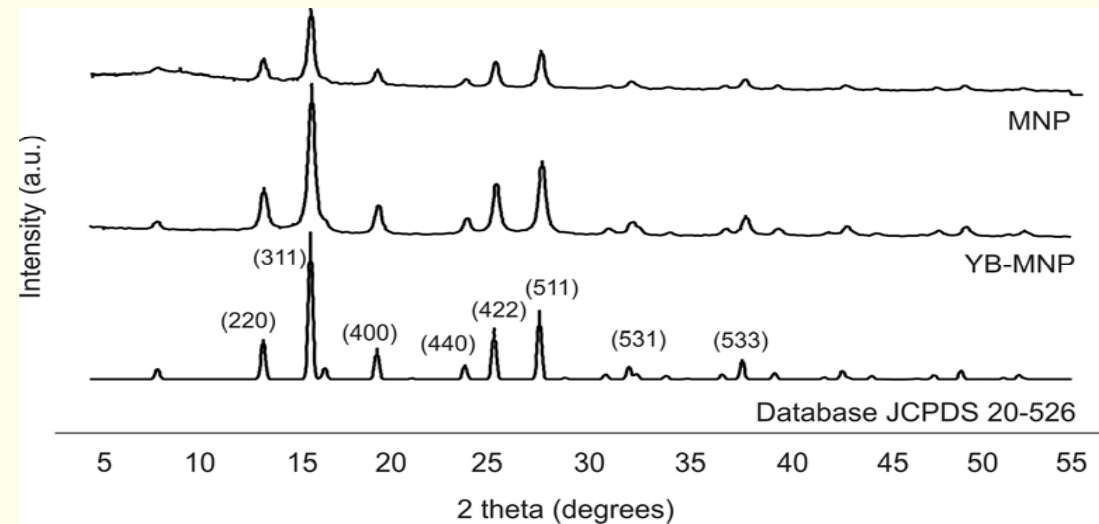
zeta potential

YB = -9.39 ± 0.86 mV (negatively charged)

YB-MNP = -13.9 ± 0.5 mV (negatively charged)

MNP = $+20.3 \pm 0.4$ mV (positively charged)

- Superparamagnetism: Strong magnetic response with low magnetic fields
- Easy removing by a magnetic field
- Fe_3O_4 nanoparticles are environmental friendly, naturally present



X-ray powder diffractograms from representative MNP; YB-MNP and MNP from Database JCPDS 20-526 nanoparticles displaying the Bragg peak reflections of magnetite.

Oils removing

Fractional Factorial Design (two-layers procedure)

Experimental design varying four parameters: material, contact time, temperature and mass.

Condition	Material	Contact time	Temperature	Mass
C1	-1	-1	-1	-1
C2	+1	-1	-1	+1
C3	-1	+1	-1	+1
C4	+1	+1	-1	-1
C5	-1	-1	+1	+1
C6	+1	-1	+1	-1
C7	-1	+1	+1	-1
C8	+1	+1	+1	+1

New Motor Oil (NMO) $d = 0.8983 \text{ kg/m}^3$

Mixed Used Motor Oil (MUMO) $d = 0.9046 \text{ kg/m}^3$

Petroleum 28 °API (P28API) $d = 1.0366 \text{ kg/m}^3$

Material -1 = YB-MNP

Material +1 = MNP

Mass -1 = 50 mg

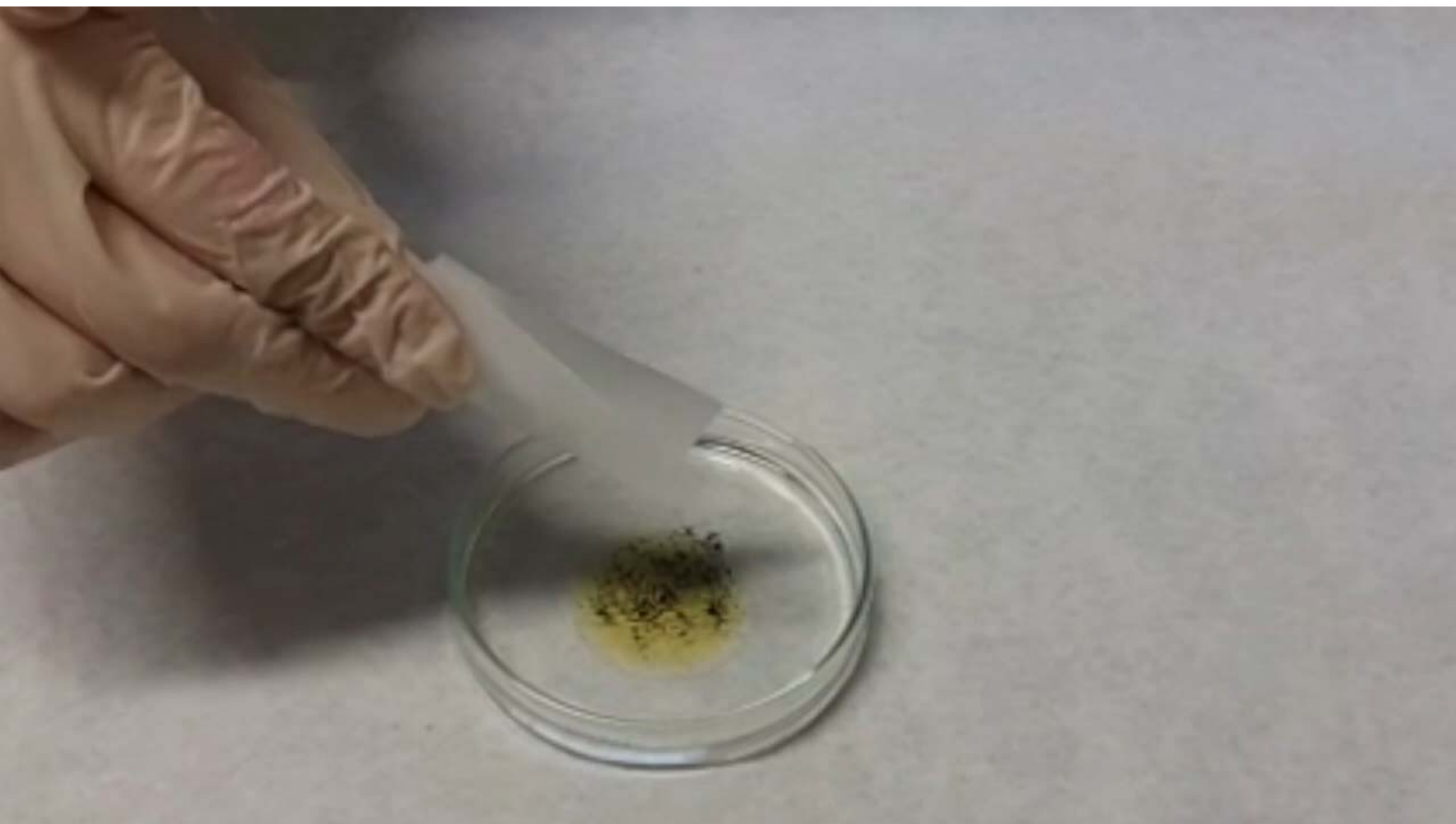
Mass +1 = 70 mg

Contact time -1 = 2 min

Contact time +1 = 30 min

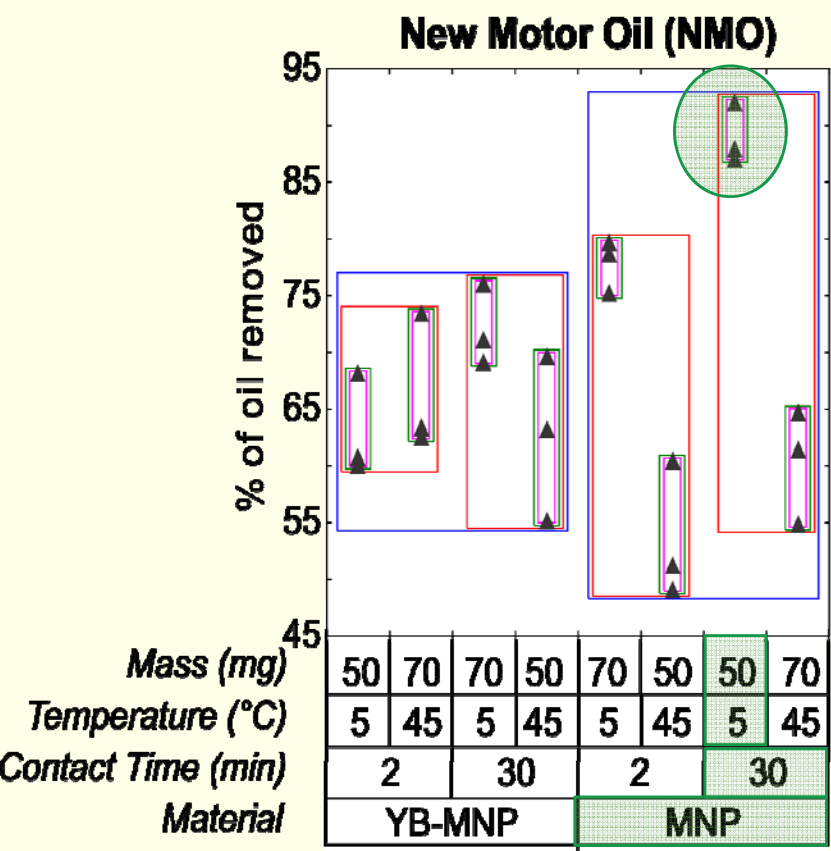
Temperature -1 = 5 °C

Temperature +1 = 45 °C

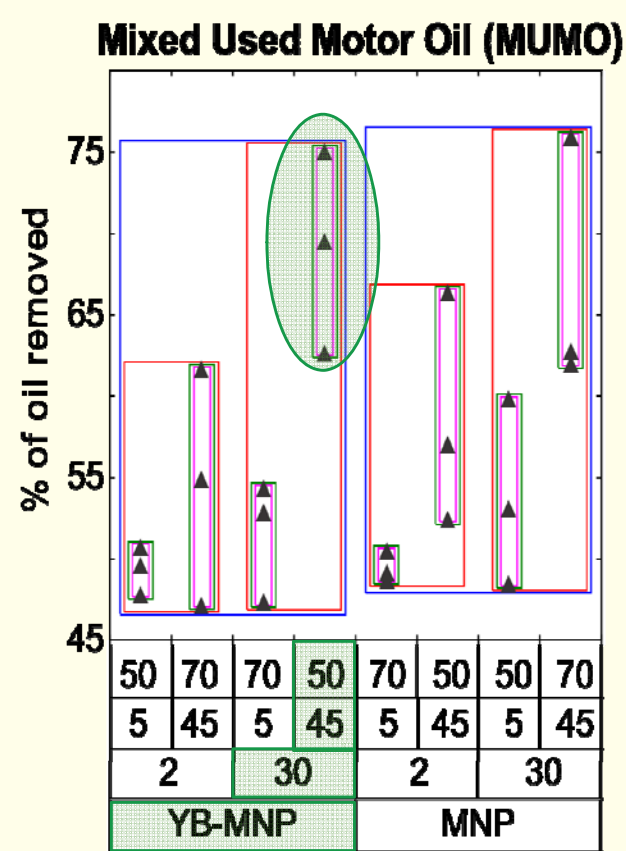


Results

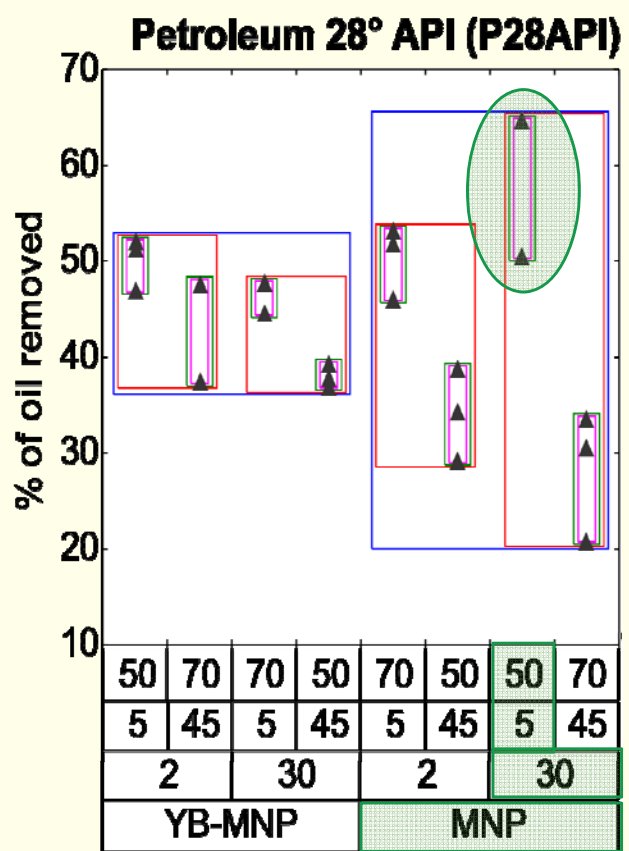
D-Optimals



3.5 ± 0.1 kg oil/kg MNP



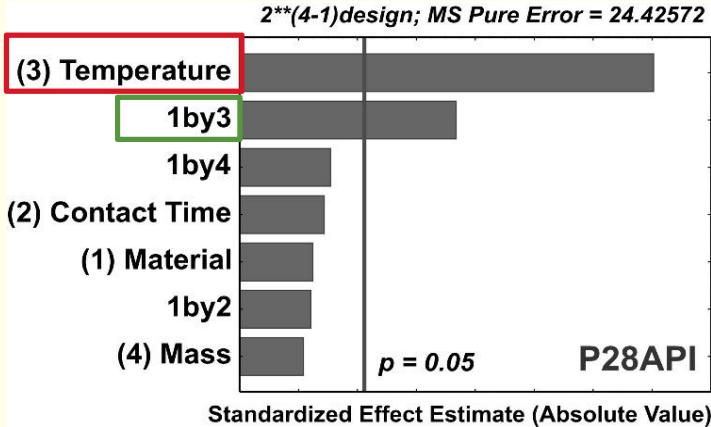
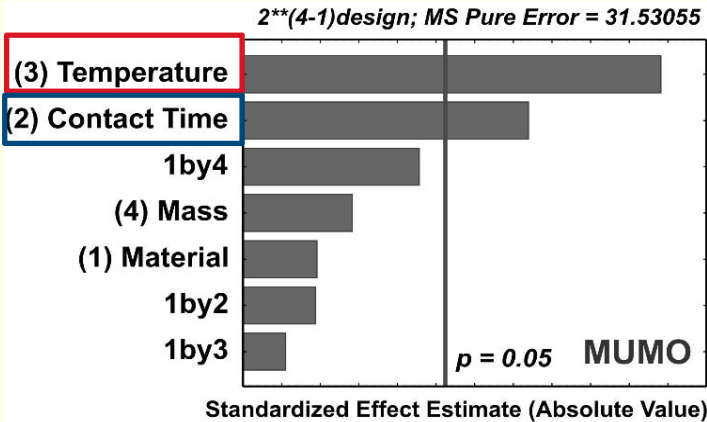
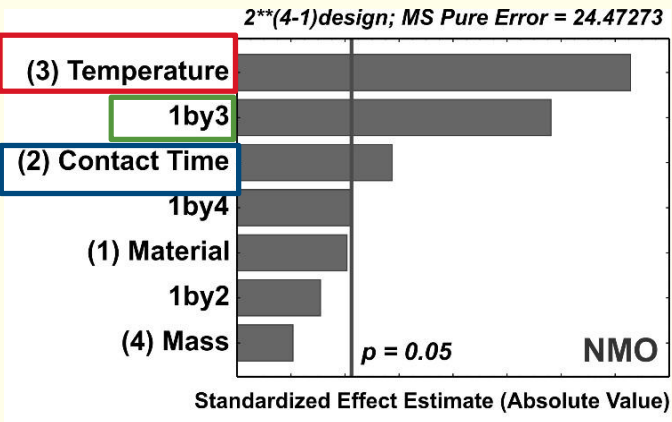
2.8 ± 0.3 kg oil/kg YB-MNP



2.2 ± 0.3 kg oil/kg MNP



Results

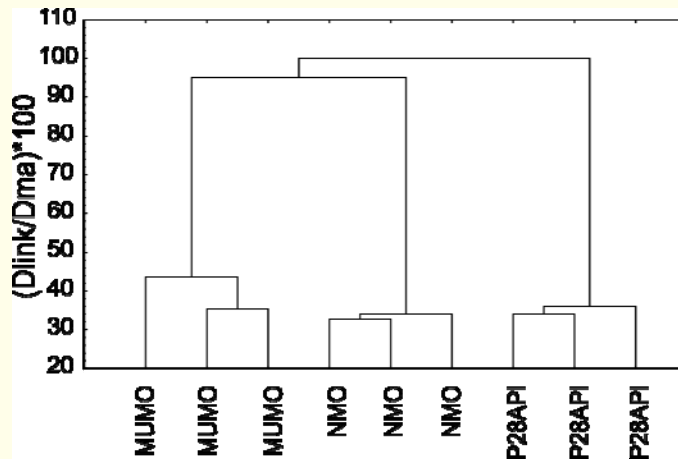
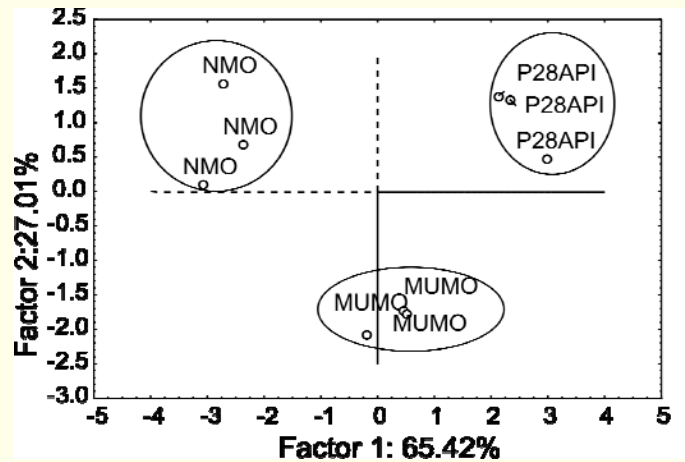


Pareto's graphics for removing of different oils by magnetic materials YB-MNP (yeast magnetic bionanocomposite) and MNP (magnetite nanoparticles).

New Motor Oil (NMO)
Mixed Used Motor Oil (MUMO)
Petroleum 28 °API (P28API)



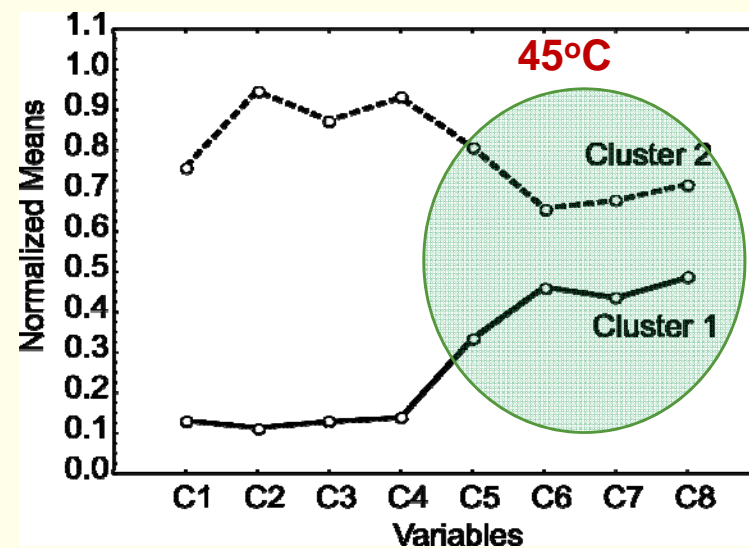
Principal Components Analyses Hierarchical Components Analyses



Graphics for de complete data set of oils removal from water by the different evaluated magnetic materials.

New Motor Oil (NMO)
Mixed Used Motor Oil (MUMO)
Petroleum 28 °API (P28API)

Graph of cluster (K-Means) for the different conditions of fractional factorial design employed for oils removal.



Results

Table 1. Regression analyses for oils uptakes by magnetic materials YB-MNP (bionanocomposite of yeast biomass) and MNP (magnetite nanoparticles). Material: -1 (YB-MNP) and +1 (MNP); Contact Time: -1 (2 min) and +1 (30 min); Temperature: -1 (5 °C) and +1 (45 °C); Mass: -1 (0.05 g) and +1 (0.07 g).

Oil	Parameter				Experimental	Applied Regression Model				
	Material	Mass (mg)	Temperature (°C)	Contact time (min)	Maximum Experimental Mean (%) (just like D-Optimal)	D-Optimals	Multiple regression	MARS (Multivariate Adaptive Regression Splines)	Neural Networks	Models Mean
NMO	+1	-1	-1	+1	89.0 ± 2.6	89.0 (0.0) $r^2 = 0.87$	79.5 (10.7) $r^2 = 0.54$	62.8 (29.4) $r^2 = 0.87$	89.7 (0.8) $r^2 = 0.94$	80.3 ± 31.3**
MUMO	-1	-1	+1	+1	69.1 ± 6.2	69.1 (0.0) $r^2 = 0.70$	66.5 (3.8) $r^2 = 0.65$	69.1 (0.0) $r^2 = 0.71$	68.8 (0.4) $r^2 = 0.86$	68.4 ± 3.8**
P28API	+1	-1	-1	+1	55.3 ± 8.2	55.7 (0.7) $r^2 = 0.82$	48.8 (11.8) $r^2 = 0.62$	38.1 (31.1) $r^2 = 0.82$	57.5 (4.0) $r^2 = 0.90$	50.0 ± 33.5**
Mean NMO + MUMO + P28API					71.1 ± 9.8*	71.3 ± 0.7**	64.9 ± 16.4**	56.7 ± 42.8**	72.0 ± 4.1**	

*Standard Error, **Propagated Error

New Motor Oil (NMO), Mixed Used Motor Oil (MUMO), Petroleum 28 °API (P28API)

Our conclusions

- Temperature was the most significant parameter for improve oils removal capacities. However, contact time and magnetic material are also important.
- Greater contact time and smaller masses of magnetic materials improve oil removing.
- The oil characteristics affect its removal from water by this proposed method.
- The cluster analysis showed that the temperature increasing turns the behavior of the other oils similar to MUMO (from C5, temperature = 45°C).
- The theoretical models satisfactorily fitted experimental data, denoting the capacity of explanation of the observed phenomena.
- Bionanocomposite reduces de cost with reagents to produce magnetite nanoparticles maintaining the desired magnetic characteristic.

We are grateful to



UNESPetro



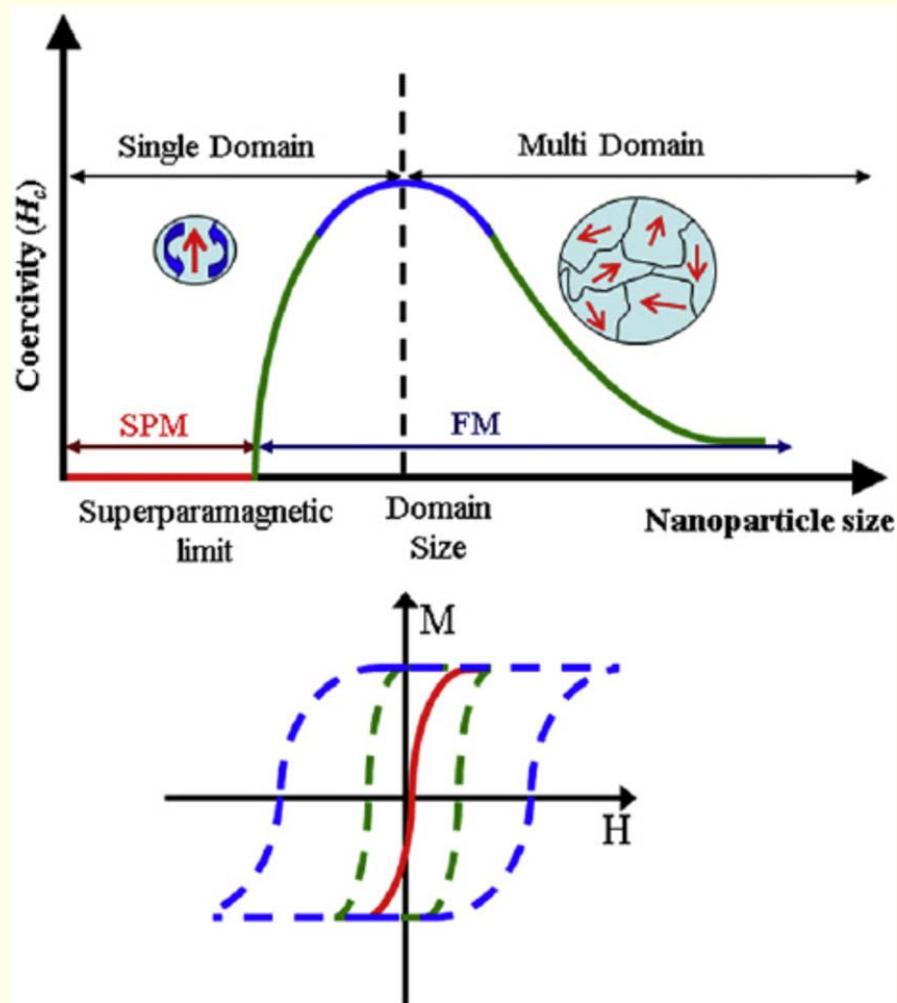


Group of Applied Chemical Analyses

Geórgia Labuto

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The qualitative behavior of the size-dependent coercivity of magnetic particles. The magnetic behavior of superparamagnetic (SPM) nanoparticles is demonstrated by the solid line, while ferromagnetic (FM) particles are presented by dashed lines. Here H denotes the applied magnetic field strength and M is the measured magnetization. Superparamagnetism occurs in particles with sizes smaller than the superparamagnetic limit.

ÓLEOS				
Tipo de Óleo	SAE 90	25W-60	SAE 50	20W-50
	Óleo Original	LUBRAX	LUBRAX	LUBRAX
Marca		Petrobras	Petrobras	Petrobras
GRAU SAE	90	25W-60	SAE 50	20W-50
GL		-	-	-
Densidade a 20/40°C		0,8983	0,8997	0,8846
Ponto de Fulgor (VA) (°C)		240	272	240
Ponto de Fluidez (°C)		-21	-6	-24
Viscosidade a 40°C (cSt)	180	267,7	226,2	183,7
Viscosidade a 100°C (cSt)	13,5 - 24,0	25,18	19,4	20,8
Índice de Viscosidade		121	97	134