Magnetite nanoparticles and ferromagnetic bionanocomposites for crude oil removal from water


1Department of Chemistry
Federal University of São Paulo
Basis of our motivation

![Graph showing world oil consumption by region from 1970 to 2020, with projections.](https://www.erudit.org)

Main oil routes in the world

![Map illustrating main oil routes around the world.](https://www.erudit.org)
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

<table>
<thead>
<tr>
<th>Methods</th>
<th>Examples</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanicals</strong></td>
<td><em>booms, skimmers</em></td>
<td>• Do not remove all oil</td>
</tr>
</tbody>
</table>
| **Chemicals**  | dispersants, surfactants and solidifiers | • Introduction of new substances in environment  
                          • Does not necessarily allow the oil to be removed |
| **Biologicals** | biodegradation            | • Introduction of microorganisms and dispersants  
                          • It is necessary the prospection and the control of ideal conditions for each microorganisms  
                          • Do not permit the oil recovery |
Cleaning up oil spills with magnets and nanotechnology

By Tom Levitt, for CNN

Updated 14:04 GMT (22:04 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 contain oil spills.

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
Magnetic nanoparticles and composites: Biosorption

Source: http://www.science.tamu.edu
Magnetic nanoparticles and composites: **Biosorption**

- Biomasses:
  - Low cost
  - Inactive biological materials
  - Renewable sources
  - Residues
  - Hydrophobic surfaces
  - Development of new materials (such as composites)

Source: [http://www.science.tamu.edu](http://www.science.tamu.edu)
**Synthesis**

**Magnetite nanoparticles**

\[ \text{Fe}^{2+}_{(aq)} + 2 \text{Fe}^{3+}_{(aq)} + 8 \text{OH}^-_{(aq)} \rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O}(l) \]

Addition of yeast biomass (YB)

\[ \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O}(l) + \text{YB}(s) \rightarrow \text{YB} - \text{Fe}_3\text{O}_4(s) \]

30 min

80 °C

**MNP**

**YB-MNP**

Yeast biomass (YB) + Magnetic nanoparticles (MNP) = Yeast Magnetic bionanocomposite (YB-MNP)
Characterization

YB

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

MNP

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

YB-MNP

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

Elemental Analyses

scanning electron microscope (SEM)

Magnified 1000X

Magnified 7000X
**Characterization**

**Magnetization**

- **Superparamagnetism**: Strong magnetic response with low magnetic fields
- **Easy removing by a magnetic field**
- **Fe$_3$O$_4$ nanoparticles** are environmentally friendly, naturally present

![Magnetization graph](image)

- **YB** = $-9.39 \pm 0.86$ mV (negatively charged)
- **YB-MNP** = $-13.9 \pm 0.5$ mV (negatively charged)
- **MNP** = $+20.3 \pm 0.4$ mV (positively charged)

![X-ray powder diffractograms](image)

X-ray powder diffractograms from representative MNP; YB-MNP and MNP from Database JCPDS 20-526 nanoparticles displaying the Bragg peak reflections of magnetite.
Experimental design varying four parameters: material, contact time, temperature and mass.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Material</th>
<th>Contact time</th>
<th>Temperature</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>C2</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>C3</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>C4</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>C5</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>C6</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>C7</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>C8</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
</tbody>
</table>

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

**New Motor Oil (NMO)**

- Mass (mg): 50, 70, 70, 50, 70, 50, 70
- Temperature (°C): 5, 45, 5, 45, 5, 45, 5
- Contact Time (min): 2, 30, 2, 30
- Material: YB-MNP, MNP
- % of oil removed: 95, 85, 75, 65, 55, 45, 35, 25

3.5 ± 0.1 kg oil/kg MNP

**Mixed Used Motor Oil (MUMO)**

- Mass (mg): 50, 70, 70, 50, 70, 50, 70
- Temperature (°C): 5, 45, 5, 45, 5, 45, 5
- Contact Time (min): 2, 30, 2, 30
- Material: YB-MNP, MNP
- % of oil removed: 95, 85, 75, 65, 55, 45, 35, 25

2.8 ± 0.3 kg oil/kg YB-MNP

**Petroleum 28° API (P28API)**

- Mass (mg): 50, 70, 70, 50, 70, 50, 70
- Temperature (°C): 5, 45, 5, 45, 5, 45, 5
- Contact Time (min): 2, 30, 2, 30
- Material: YB-MNP, MNP
- % of oil removed: 95, 85, 75, 65, 55, 45, 35, 25

2.2 ± 0.3 kg oil/kg MNP
Pareto’s graphics for removing of different oils by magnetic materials YB-MNP (yeast magnetic bionanocomposite) and MNP (magnetite nanoparticles).
Graph of cluster (K-Means) for the different conditions of fractional factorial design employed for oils removal.

Principal Components Analyses

Hierarchical Components Analyses

Graphics for the 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)

45°C
## 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).

<table>
<thead>
<tr>
<th>Oil</th>
<th>Material</th>
<th>Mass (mg)</th>
<th>Temperature (°C)</th>
<th>Contact time (min)</th>
<th>Maximum Experimental Mean (%) (just like D-Optimal)</th>
<th>D-Optimals</th>
<th>Multiple regression</th>
<th>MARS (Multivariate Adaptive Regression Splines)</th>
<th>Neural Networks</th>
<th>Models Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Motor Oil (NMO)</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>89.0 ± 2.6</td>
<td>89.0 (0.0)</td>
<td>79.5 (10.7)</td>
<td>62.8 (29.4)</td>
<td>89.7 (0.8)</td>
<td>80.3 ± 31.3**</td>
</tr>
<tr>
<td>Mixed Used Motor Oil (MUMO)</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>69.1 ± 6.2</td>
<td>69.1 (0.0)</td>
<td>66.5 (3.8)</td>
<td>69.1 (0.0)</td>
<td>68.8 (0.4)</td>
<td>68.4 ± 3.8**</td>
</tr>
<tr>
<td>Petroleum 28 °API (P28API)</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>55.3 ± 8.2</td>
<td>55.7 (0.7)</td>
<td>48.8 (11.8)</td>
<td>38.1 (31.1)</td>
<td>57.5 (4.0)</td>
<td>50.0 ± 33.5**</td>
</tr>
<tr>
<td>Mean NMO + MUMO + P28API</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>71.1 ± 9.8*</td>
<td>71.3 ±0.7**</td>
<td>64.9 ± 16.4**</td>
<td>56.7 ± 42.8**</td>
<td>72.0 ± 4.1**</td>
<td></td>
</tr>
</tbody>
</table>

*Standard Error, **Propagated Error
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

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SÃO PAULO RESEARCH FOUNDATION

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

CAPES

UNESPetro

UFSCar

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