The Use of Magnetic Nanocomposites

For Treating Bilge Water

By

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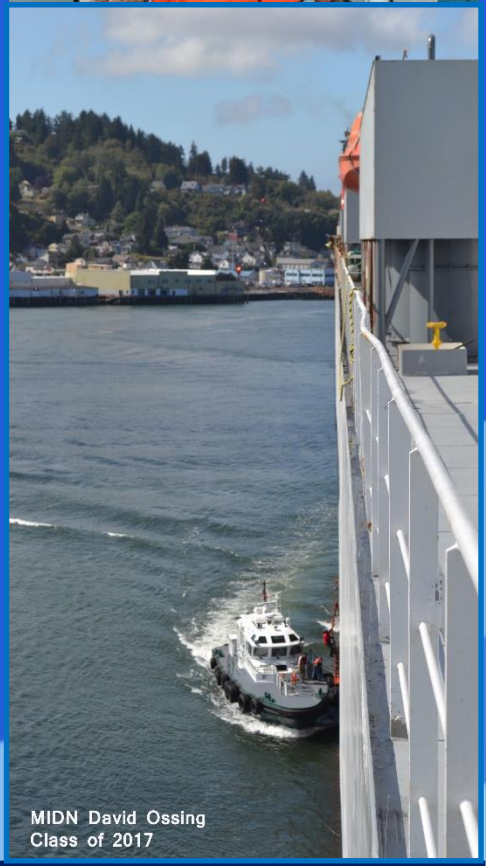
United States Merchant Marine Academy
Maritime Administration of the United States of America
Department of Transportation

Outline

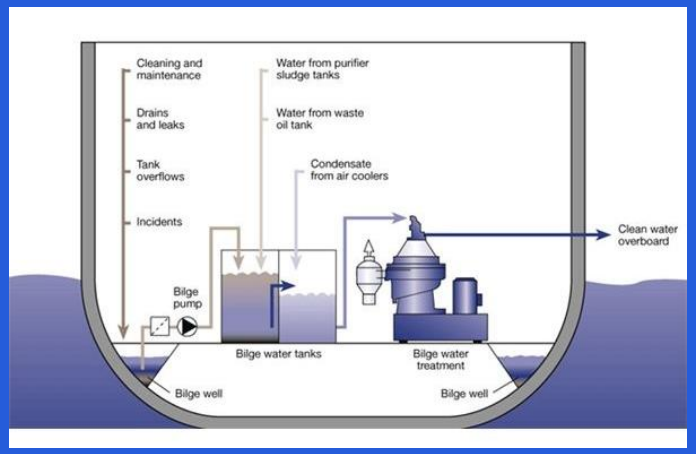
- Shipping & Economy
- Bilge Water & MARPOL Regulation
- Challenges
- Magnetic Separation Based on Nanocomposites – A Promising Technology
  - Magnetic Polydimethyl Siloxane (PDMS) Sponges
  - Properties: Magnetic Properties, Contact Angle, Chemical Resistivity, & Reusability
  - Factors Affecting Sorption Ability:
    - Preparation Conditions: Templates, Amounts of Solvent Used & Composition
    - Sorption Media: Oil Types, Detergent, Emulsion.
    - Temperature
  - Meeting MARPOL Standards: <15 ppm Oil Content!
- Summary

Shipping & Economy

- Water covers 71% Earth's Surface
- Shipping transports 90% of world's food, products, and energy
- Shipping is safer, greener & more efficient
- U.S. waterway uses per year:
  - 70, 000 port calls for commercial vessels
  - 110,000 fishing vessels
  - 20 million recreational vessels
- Shipping contributes > $649 billion to U.S. GDP
- Increased demand for expanding water transportation



Bilge Water & MARPOL Regulation



Bilge Water:

- Water in the lowest space
- Leaks/spills, cleaning, drains
- Water, lubricating oils, grease, detergent, emulsified fuels and other contaminants
- 1000-5000 gals daily that require periodical discharges

- Shipping/bilge put 137 million gals of oil in the oceans per year, 4 times > big oil spills (source: NASA-Ocean Planet, 1995)
- International Maritime Organization (MARPOL) imposes <15 ppm of oil contain when bilge water is discharged

Challenges

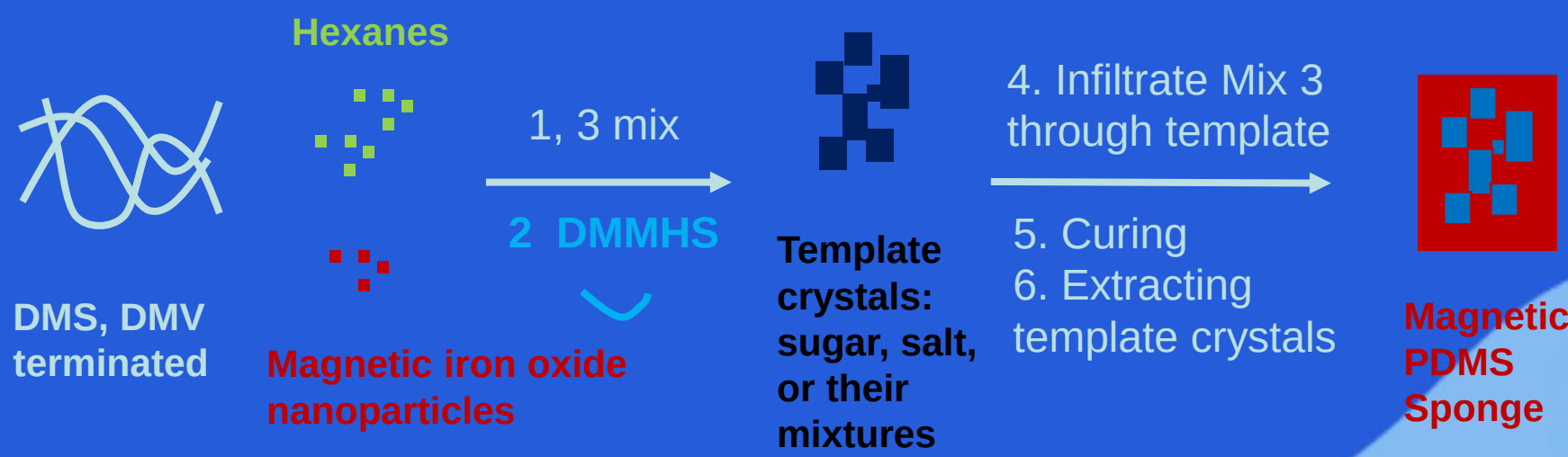
- Oily Water Separator (OWS) is used to treat bilge water
- Based on gravity separation
- Requires several technologies
- Expensive, may require heating and can be troublesome to operate
- Designed to work under ideal conditions (e.g. Laminar flow, no detergents)
- May not meet the 15 ppm set oil content limit

Magnetic Separation Based on Nanocomposites–A Promising Technology

- Nanocomposite: synergistic and/or hybrid properties
- Polydimethyl siloxane (PDMS) sponge embedded with magnetic iron oxide nanoparticles offers crucial properties:
  - Instant and magnetically controllable actions by the well integrated and dispersed iron oxide nanoparticles for easy separation
  - Reusability and oleophilic properties of the PDMS sponge for effective sorption of oils, detergents, suspended or dissolved hard-to-separate emulsified oil droplets and contaminants
  - Chemical resistivity and low-cost

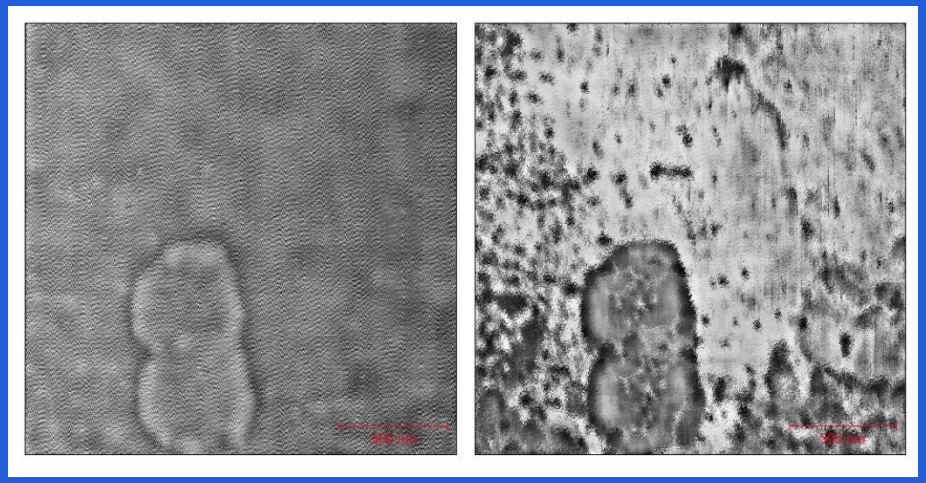
Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic Polydimethyl Siloxane (PDMS) Sponges**



Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges - Properties**



AFM images of 20-50 nm iron oxide particles

%wt. Iron Oxide	g Magnetic Force per g Sponge*
4	5
8	12

* Magnetic field by 5 Earth Magnets, 3/4” x 1/8”

Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges - Properties**

Highly Hydrophobic
& Oleophilic

Magnetic Separation Based on Nanocomposites–A Promising Technology

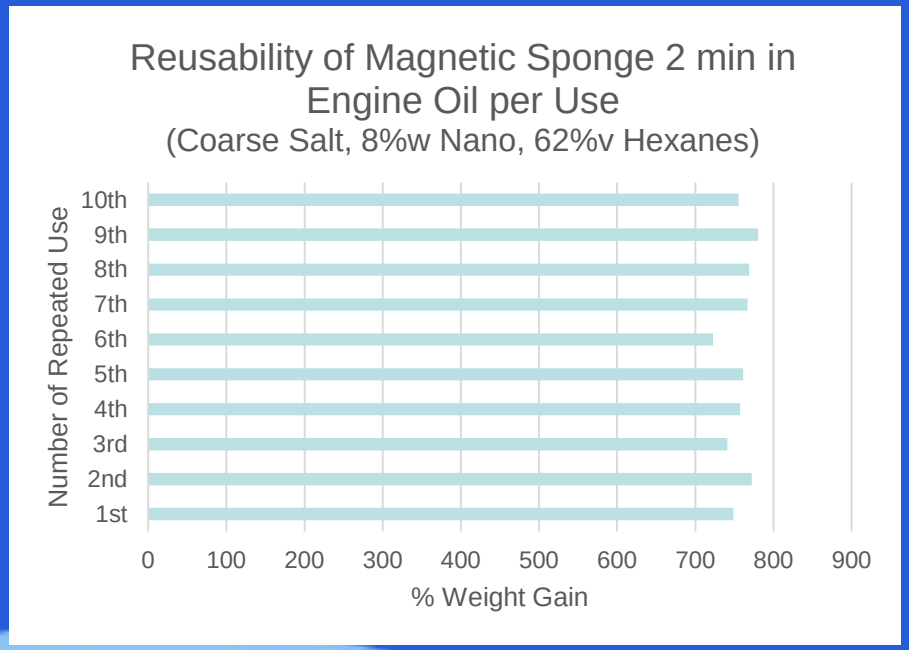
- **Magnetic PDMS Sponges - Properties**

	M_o, g	Treatments	M_f, g	Notes
1	0.099	• 18 days in pH=5 solution • 24 hours in pH=1 solution • Washed, dried	0.099	No change in appearance
2	0.096	• 18 days in pH=8 solution • 24 hours in pH=13 solution • Washed, dried	0.096	No change in appearance

Highly Chemical Resistant

Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges - Properties**



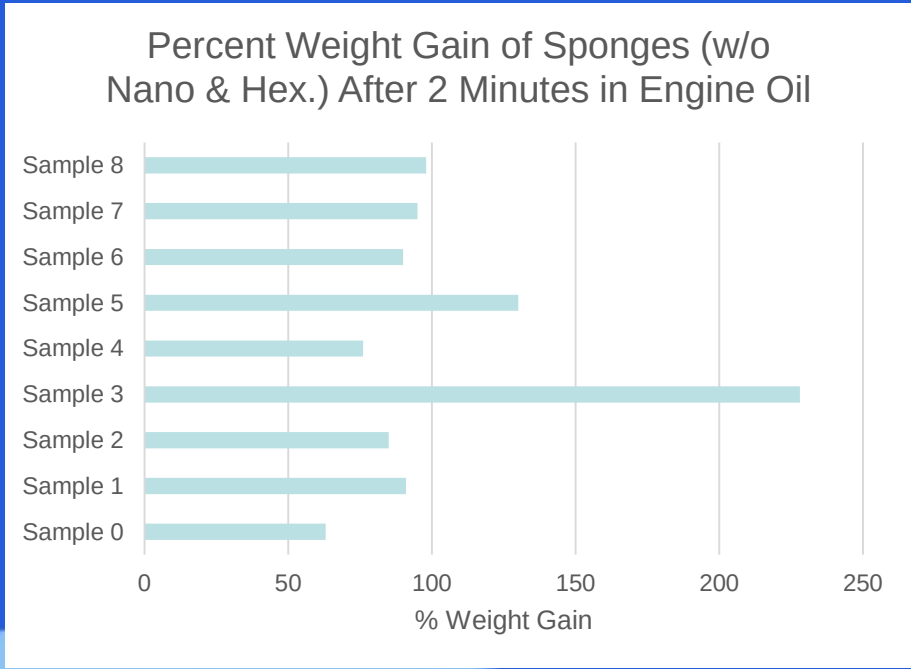
Reusable and Highly Robust

% Wt. Gain= $\frac{M_f - M_o}{M_o}$ **x100%**

M_o = initial weight of sponge
M_f = final weigh of sponge

Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges – Factors Affecting Sorption Ability**



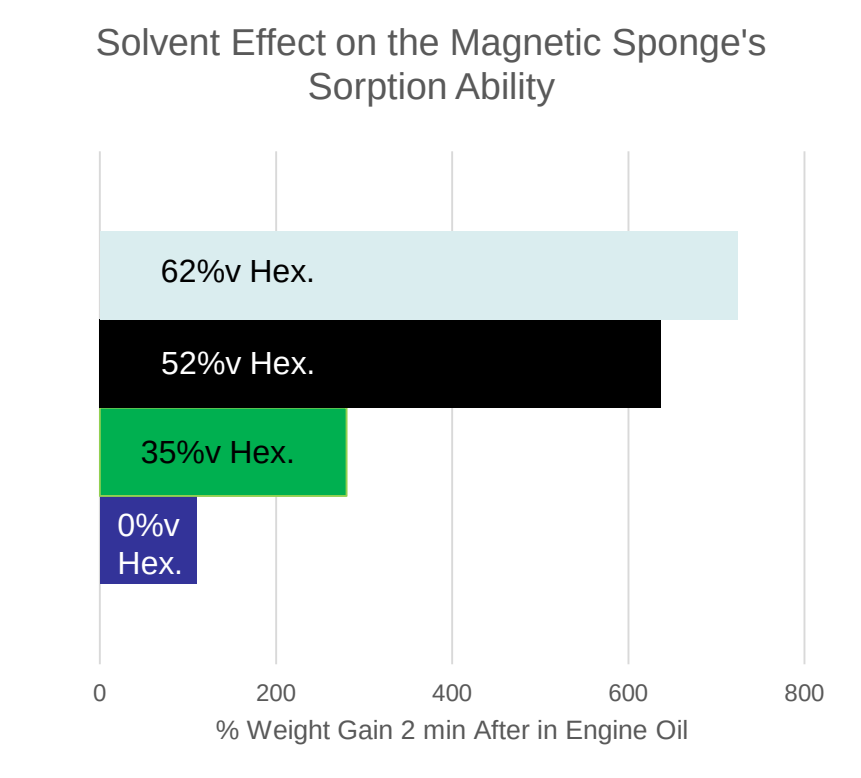
Preparation Conditions:
Template Types and Sizes

Sugar crystals:
500 μm, 500-1000 μm
Salt Crystals:
500 μm, 1000-2500 μm (coarse)

Least Sorption:
S0: Sugar, 500 μm
Most Sorption:
S3: Coarse Salt

Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges – Factors Affecting Sorption Ability**

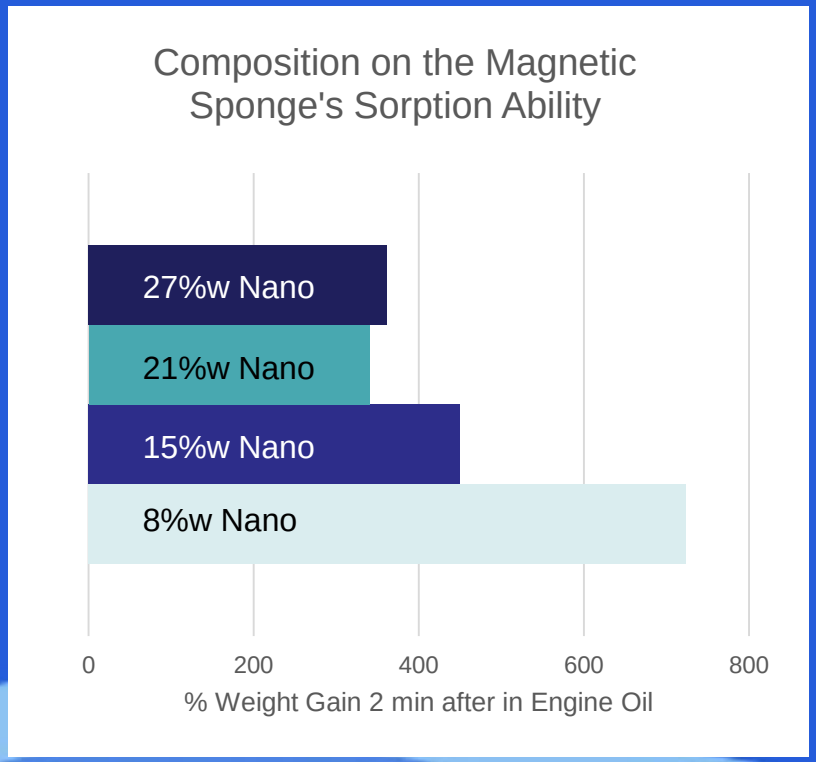


Preparation Conditions:
Amount of Hexanes (Hex.)
- Hex. as infiltrate thinner

0-62%v Hexanes Range:
More solvent, higher sorption-
100% - 700% Wt. Gain Range
(8%w Nano Sponges, Coarse Salt Templated)

Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges – Factors Affecting Sorption Ability**



Preparation Conditions:
Amount of Iron(III) Oxide (Nano)

8-27%w Nano Range:
More Nano, lower sorption-
700% - 300% Wt. Gain Range
(Nano Sponges, Coarse
Salt Templated w/ 62%v Hex.)

Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges – Factors Affecting Sorption Ability**

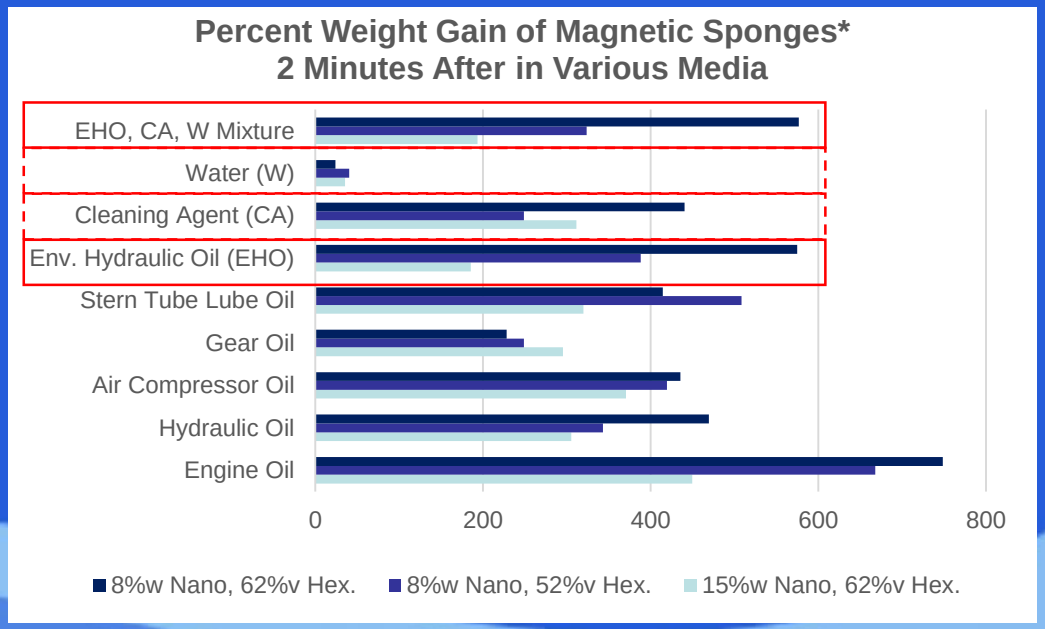
Sorption Media Effect: Higher Viscosity, Lower Density → Higher Sorption
* 8%w Nano sponge templated with 500 μm sugar crystals w/o hexanes

Oil Use	Oil Type	Viscosity (*cSt, 40°C*)	Density (*kg/m³, 16°C*)	Magnetic Sponge* %Wt. Gain (2 min)
Engine Oil	Mineral Oil	158	900.0	180
Gear Oil	Mineral Oil	150	897.0	154
Stern Tube Lube Oil	Mineral Oil	100	881.0	-
Env. Hydraulic Oil (EHO)	**Sat. Syn. Ester Based**	**70.6**	**918.0**	**126**
Hydraulic Oil	Mineral Oil	32	875.0	114
Air Compressor Oil	Synthetic Oil	39.3	982.6	93
Cleaning Agent (CA)	Cleaner-Degreaser	"Like Water"	1010.0-10300	61
Water (W)	-	1	1000.0	53
EHO, CA, W Mixture	**-**	**-**	**-**	**131**

Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges – Factors Affecting Sorption Ability**

Sorption Media Effect: Higher Viscosity, Lower Density → Higher Sorption
*Nano sponge templated with coarse salt crystals and hexanes (w/ exception)



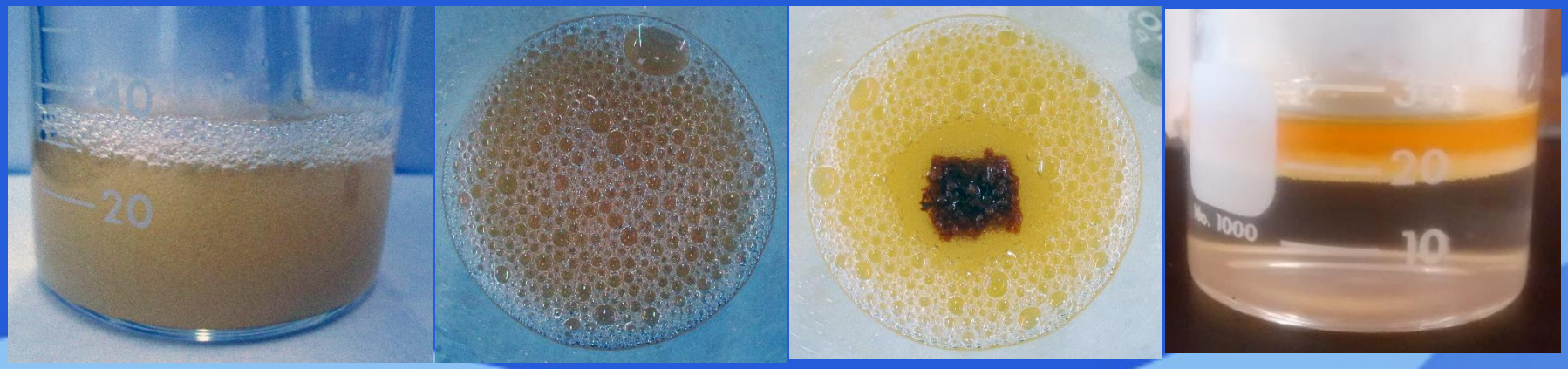
Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges – Factors Affecting Sorption Ability**

Sorption Media Effect**:** **Emulsion Sorption Mirrors Oil Sorption**

Magnetic PDMS Sponge = An Oil Coalescer !!!

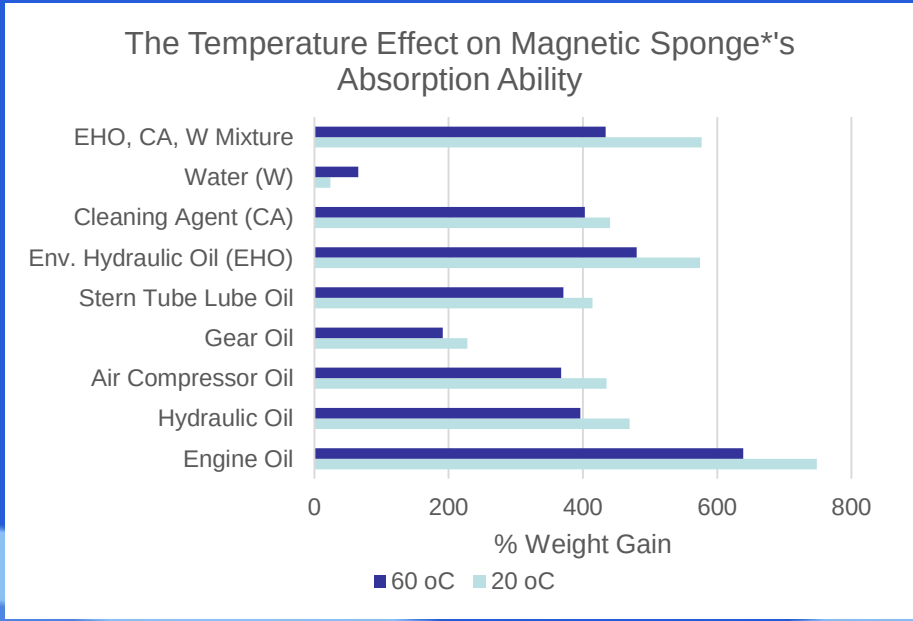
Equal parts of oil, detergent, & water | Immediate Effect | Two weeks later



Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Magnetic PDMS Sponges – Factors Affecting Sorption Ability**

Temperature Effect: Higher Temperature, Lower Sorption for ALL but Water
*8%wt Nano sponge templated with coarse salt crystals and 62%v hexanes



Magnetic Separation Based on Nanocomposites–A Promising Technology

- **Meeting MARPOL Standards – Below 15 ppm Oil Content!**

Oil & Water Mixture

Summary

- Magnetic PDMS Nanocomposite Sponges
  - Simple & low-cost to prepare
  - Very magnetic for easy control & fast separation
  - Highly hydrophobic and oleophilic
  - Highly chemical resistant
  - Reusable and highly robust
  - Effective absorbers with fast sorption for detergents, emulsified oil droplets, and oils of varied viscosities & densities
  - Oil coalescers that break oil emulsion
  - No requirement for heating & for laminar flow
  - May remove oil from water to well below 15 ppm
- Offer a Promising New Technology for Treating Bilge Water!

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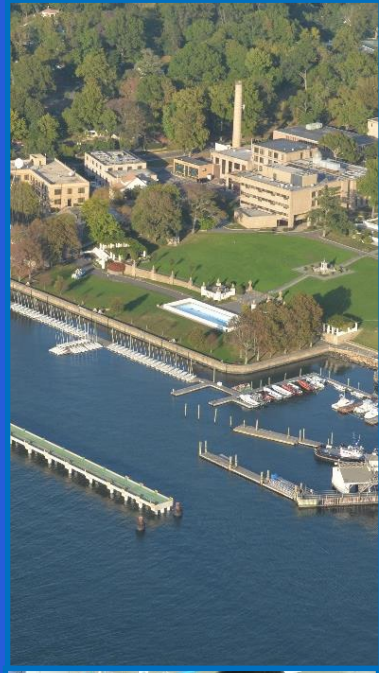

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