



OIL SPILL SCIENCE

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In the immediate aftermath of the Deepwater Horizon spill, BP committed \$500 million over a 10-year period to create the Gulf of Mexico Research Initiative, or GoMRI. It is an independent research program that studies the effect of hydrocarbon releases on the environment and public health, as well as develops improved spill mitigation, oil detection, characterization, and remediation technologies. GoMRI is led by an independent and academic 20-member research board.

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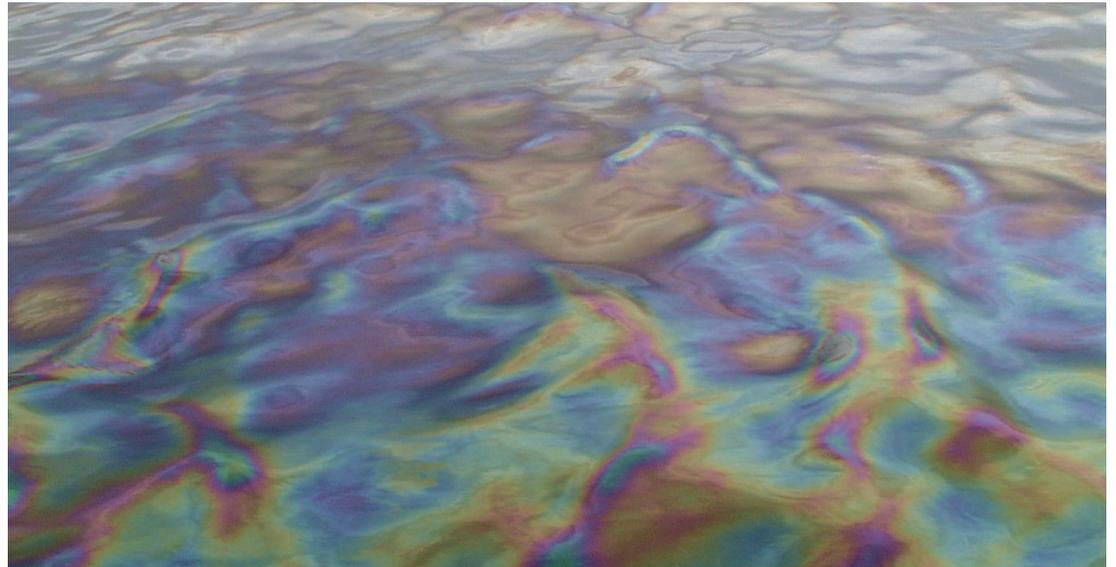


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EMERGING SURFACTANTS, SORBENTS, AND ADDITIVES FOR USE IN OIL SPILL CLEAN-UP

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Responders used the oil dispersants Corexit 9527A and 9500A to combat the 2010 Deepwater Horizon oil spill. What other products are currently available or in development to remove oil from water in future spills?



Scientists are continually developing new technologies for use in cleaning up oil spills in coastal and marine environments. Pictured above is an oil sheen from a spill in New Bedford, Massachusetts. (Massachusetts Department of Environmental Protection)

CURRENT APPROACHES

Deepwater Horizon (DWH) oil spill responders used **sorbents** and chemical **dispersants** to lessen the 172 million gallon spill's impact on ecologically sensitive and valuable marine habitats in the Gulf of Mexico.

Because oil and water do not mix, oil slicks occur on the water's surface. Booms, which often include sorbent materials to absorb oil, help keep slicks from spreading. Man-made materials like plastic, and natural materials like peat moss, straw, clay, and

felted wool all work as sorbents.^{1,2} When responders retrieve sorbent booms, they also remove any absorbed oil.³

Dispersants do not remove oil from the water. Instead, **surfactants** in dispersants like **Corexit 9527A and 9500A** help break the oil into small droplets. Microscopic sea life called microbes live throughout the marine environment. Some types of microbes ingest the easy-to-break-down portions of oil as part of their natural diet. Certain types of oil and small oil droplets are more readily consumed by microbes

and can be more completely broken down than other types of oil.

DWH oil spill responders applied 1.84 million gallons of dispersants at the wellhead and on the slick to reduce aquatic life and shoreline oiling and to enhance the natural breakdown of oil by microbes. Tests conducted by the U.S. Environmental Protection Agency (U.S. EPA) show that Corexit 9500A has toxicity levels similar to other commercially available chemical dispersants.⁶ Despite these findings, lingering concerns over human and aquatic health has led community members to ask what other approaches might be available for oil spill response.⁷ More rigorous studies documenting human health risks are ahead in the future. These studies will better inform impacted communities.

EMERGING SOLUTIONS

Surfactants inspired by microbes

The abundance of oil-consuming microbes increases where an oil spill occurs.^{4,5} Laboratory tests show that some types of microbes can degrade as much as 65 percent of oil in the water in a little more than one week, depending on the type of oil.⁸

Multiple species of microbes produce their own surfactants to help them digest oil.⁹⁻¹⁰ These natural surfactants show promise for use in oil spill response because they are effective, disintegrate easily in the environment, and tend to have low toxicity. The surfactants produced by microbes consist of compounds including sugars, **amino acids**, and **lipids**.¹⁰⁻¹² Because of the great need for such surfactants, scientists in the laboratory are creating surfactants

modeled after microbial-based ones and searching for the genes that produce these surfactants.^{12,13} Surfactin is an example of a compound naturally produced by microbes that is effective at breaking up oil slicks. However, it does not mix well with water. Scientists are modifying microbes to produce a form of surfactin that effectively breaks down oil and mixes with water.¹¹

Everyday materials – Finding treasure in unexpected places

Everyday items can be useful during oil spill response, too. Soy lecithin, a soybean by-product, is a natural surfactant commonly used to create smooth, creamy textures in processed foods. Because it attracts both water and oily, fatty substances, scientists think it might work well as a surfactant in oil spill response. Soy lecithin's safety for human consumption makes it an attractive alternative to current chemical dispersants. But applying soy lecithin alone to an oil slick does not get lasting results — the droplets eventually reform slicks. Scientists are mixing soy lecithin with other food-grade surfactants or altering soy lecithin in the lab to keep oil slicks from reforming (Figure 1).¹⁴⁻¹⁶ Soy lecithin-surfactant mixtures produce smaller and more stable oil droplets than Corexit 9500A to provide microbes with a steady meal of oil.¹⁴

Sorbents also can be crafted from everyday materials. Using plastic for oil spill clean-up combines old and new technologies and offsets oil and plastic pollution. Scientists have discovered they can create a thin, oil-absorbing film by melting and mixing together different types of plastics.¹⁷ The combination creates a gooeey, gel-like material that later is chemically treated and stretched out to dry. The

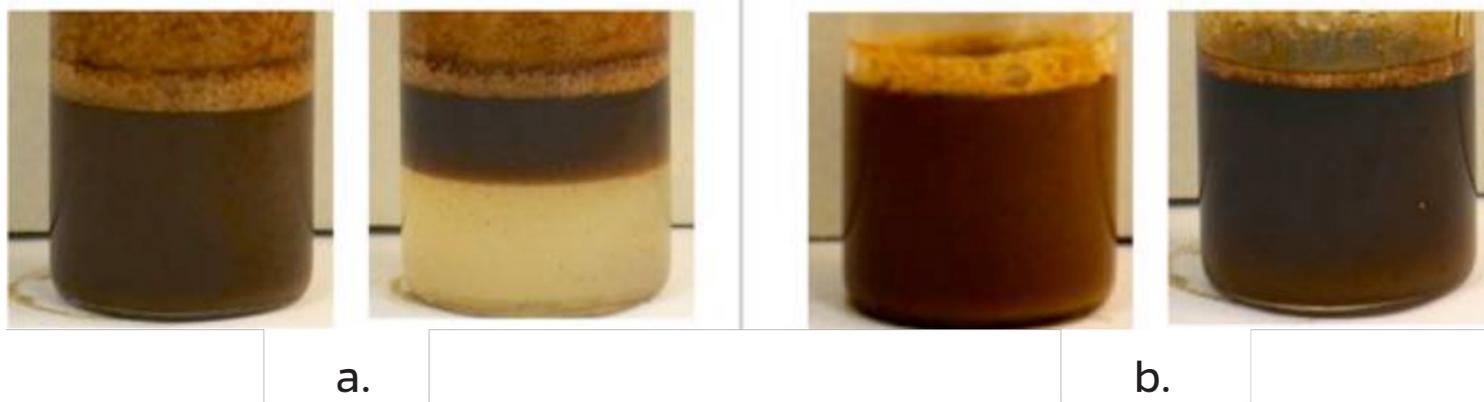


FIGURE 1. While soy lecithin disperses oil (left image on panel a), it forms large oil droplets which re-form oil slicks over time (right image on panel a). A 60 percent-40 percent mixture of soy lecithin with another food-grade surfactant creates tiny oil droplets (left image on panel b) that stay evenly distributed in water over time (right image on panel b). (Adapted with permission from Athas, J. C., Jun, K., McCafferty, C., Owoseni, O., John, V. T., & Raghavan, S. R. (2014). An effective dispersant for oil spills based on food-grade amphiphiles. *Langmuir*, 30(31), 9285-9294. Copyright (2016) American Chemical Society.)



FIGURE 2. A worker, left panel, extracts jute fiber from the stem of jute plants. (Susantab) The resulting jute fiber fabric, right panel, is commonly used in rugs and sacks, but increasingly also used as a sorbent to soak up oil after a spill. (Luigi Chiesa)

finished product is a thin film with many microscopic holes that trap oil.

Natural materials like jute and bagasse make great sorbents after some laboratory modifications. Jute is a natural plant fiber commonly used to create burlap sacks and rug backings (Figure 2). The remains of sugarcane stalks after processing are tough and full of fibers called bagasse (Figure 3). Both of these biodegradable fibers can serve as sorbents. However, it is not as simple as placing these fibers directly on an oil slick. Both materials absorb water, reducing their ability to take in oil. Scientists can modify the fibers to repel water and absorb more oil,

making them more effective than sorbents made of plastic fibers.^{3,18} Bagasse modified in this way can absorb almost twice as much oil as traditional plastic-based sorbents.¹⁸

Some sorbents and newly-developed **dispersant additives**, including carbon black (CB) and chitosan, work differently. CB can be produced in a number of ways, including charring natural materials like wood, tar, and bone. It not only helps microbes break down oil, it attracts and bonds with potentially toxic oil-based compounds.¹⁹ When these potentially toxic oil-based compounds adhere to the CB, they are less likely to impact aquatic animals. When chitosan is added to Corexit, it reduces the amount

FIGURE 3. Sugarcane, top and bottom left images, can be used as more than a natural food sweetener. (top panel, LSU AgCenter; bottom left panel, Rufino Uribe) After the sugar is processed, the remaining stalks contain bagasse, bottom right panel, a product used to create sorbents to soak up oil. (Anna Frodesiak)



of Corexit needed.²⁰ Made by chemically modifying crustacean shells in the lab, chitosan works by preventing oil droplets from gathering together to re-form slicks.²¹ It also helps create a gel-like substance that stops oil droplets from moving, making oil physically easier to remove from water.

WHEN WILL THESE EMERGING PRODUCTS BE USED?

The new products mentioned in this bulletin are fascinating and many answer the increasing need for low-cost response tools that will not only breakdown oil, but also breakdown in the environment afterward. However, much testing, both in the lab and the field, and regulatory steps lay ahead before these products may be utilized during an oil spill.

To learn about the legal framework, including some of the testing requirements, governing the use of dispersants, visit the Mississippi-Alabama Sea Grant Law Center site and click on the keyword 'oil spills'.

<http://masglp.olemiss.edu/publications/index.html>

Nanotechnology – Tiny materials with big impact

Engineered **nanomaterials** are made up of pieces only nanometers in size. For reference, a nanometer is equivalent to 0.00000025 inches. That is 100,000 times smaller than the diameter of a human hair.²² Industry uses these tiny materials in everything from computers and cellular phones to workout clothing. Their next application could be oil spill clean-up.

Some nanomaterials show great promise as sorbents because of their ability to absorb oil and repel water.

Carbon nanotube (CNT) sponges are one example. CNT sponges look like their name suggests, resembling large household sponges up to 10 inches in length (Figure 4). However, the sponges' fibers are actually tiny tubes made of carbon. CNT sponges repel water, and some can absorb up to 23 times their weight in oil in only 15 minutes. Traditional sorbent materials like plastic fibers and felted wool can only take in eight to nine times their weight (Figure 5).²

How do responders remove these innovative nanomaterials from the water after they have soaked up unwanted oil? Magnets may be the answer. Highly-engineered, magnetic CNTs effectively isolate and remove oil-based compounds from water, but CNTs can be expensive.²³ Scientists have created relatively inexpensive, magnetic, iron-based nanoparticles in the laboratory. They

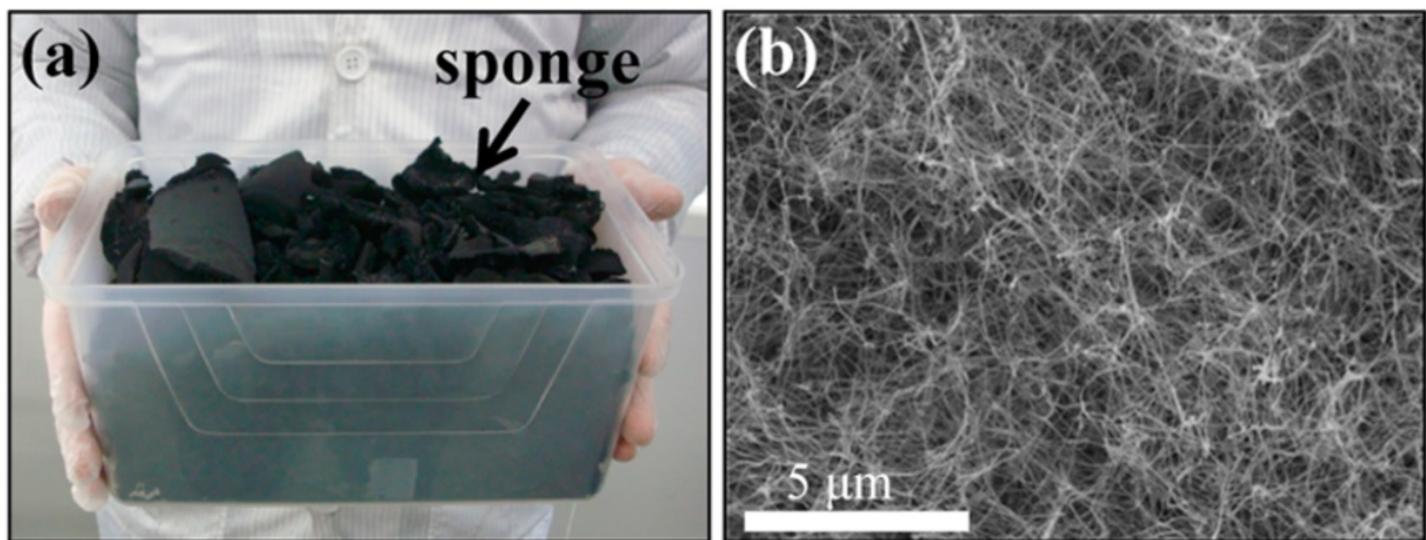


FIGURE 4. Carbon nanotube (CNT) sponges (panel a) resemble ordinary, household sponges. The nano-sized tubes of carbon making up the sponge are evident through a high-powered microscope (panel b). (Reprinted with permission from Gui, X., Zeng, Z., Lin, Z., Gan, Q., Xiang, R., Zhu, Y., ... & Tang, Z. (2013). Magnetic and highly recyclable macroporous carbon nanotubes for spilled oil sorption and separation. *ACS applied materials & interfaces*, 5(12), 5845-5850. Copyright (2016) American Chemical Society.)

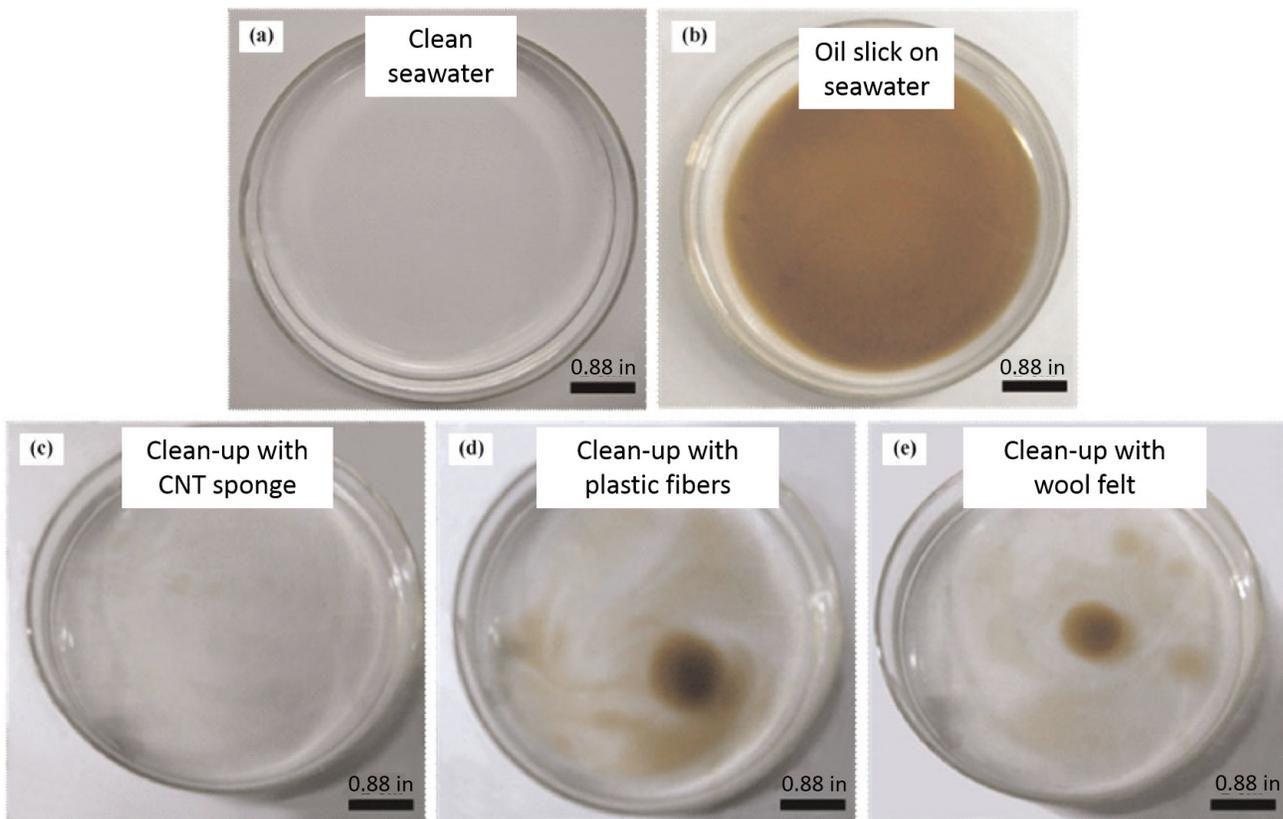


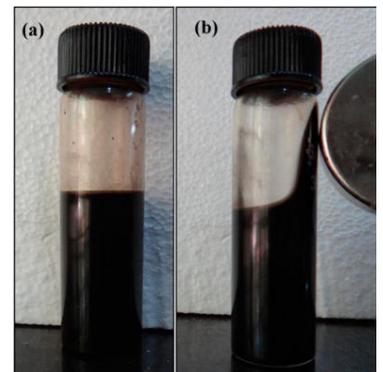
FIGURE 5. Laboratory testing shows that the effectiveness of sorbents varies by material. The top panels show clean seawater (panel a) and seawater with an oil slick (panel b). The bottom panels (c-e) show the effectiveness of three sorbents at soaking up an oil slick (each the one shown in panel b) after 15 minutes. (Reprinted with permission of Springer. Zhu, K., Shang, Y. Y., Sun, P. Z., Li, Z., Li, X. M., Wei, J. Q., ... & Zhu, H. W. (2013). Oil spill cleanup from sea water by carbon nanotube sponges. *Frontiers of Materials Science*, 7(2), 170-176. Copyright (2017) Springer.)

add tiny, magnetized particles to coconut oil to create a **suspension** called a nanofluid. Magnetic coconut oil nanofluids are 91 percent effective at removing motor oil from water in lab tests.²⁴ The coconut oil attracts and attaches to oil, allowing magnets to remove the mixture of magnetic particles, oil, and coconut oil from the water (Figure 6).

Nanotechnology can be used to do more than absorb oil. It efficiently carries and applies dispersant directly to individual oil droplets too.

Scientists are investigating how additives made from nanomaterials might combine with existing surfactants to improve oil spill clean-up. Nano-sized particles of **silica** create stable oil-water mixtures in the lab when paired with certain surfactants.²⁵ Oil droplets in these mixtures are well-distributed, creating excellent conditions for natural breakdown by microbes. **Halloysite nanotubes (HNTs)** are another nanomaterial scientists combine with surfactants

FIGURE 6. A mixture of magnetic particles and coconut oil can be added to remove crude oil from seawater (panel a). The coconut oil in the mixture attracts crude oil. When a magnet is applied (panel b), the magnetic particles are pulled by the magnet, carrying the coconut oil and crude along with it and out of the seawater. (Reprinted with permission from Nabeel Rashin, M., Kutty, R. G., & Hemalatha, J. (2014). Novel coconut oil based magnetite nanofluid as an ecofriendly oil spill remover. *Industrial & Engineering Chemistry Research*, 53(40), 15725-15730. Copyright (2016) American Chemical Society.)



to improve oil spill clean-up.²⁶ Scientists form them by rolling microscopic sheets of a naturally occurring clay called halloysite into nanometer-sized tubes. They fill these HNTs with the surfactant used in the dispersants Corexit

9500A and 9527A. The HNTs stabilize oil-water mixtures and act as a delivery system for the surfactant (Figure 7). The mixtures' stability improves as more HNTs are added, meaning the oil droplets are less likely to recombine into a slick. The number of small oil droplets increases with the amount of surfactant loaded on the nanotubes. This system makes the dispersant more efficient and increases microbes' ability to consume the oil.

The Gulf of Mexico Research Initiative (GoMRI) and

others continue to explore new possibilities in the realm of oil spill clean-up. To learn more about this and the research being conducted on the Deepwater Horizon spill, visit the Gulf of Mexico Research Initiative website at www.gulfresearchinitiative.org. Visit the Gulf Sea Grant program website at <http://gulfseagrant.org/oilspilloutreach> to view other publications that provide additional information on the dispersants and the impact of oil and dispersant mixtures on aquatic animals.

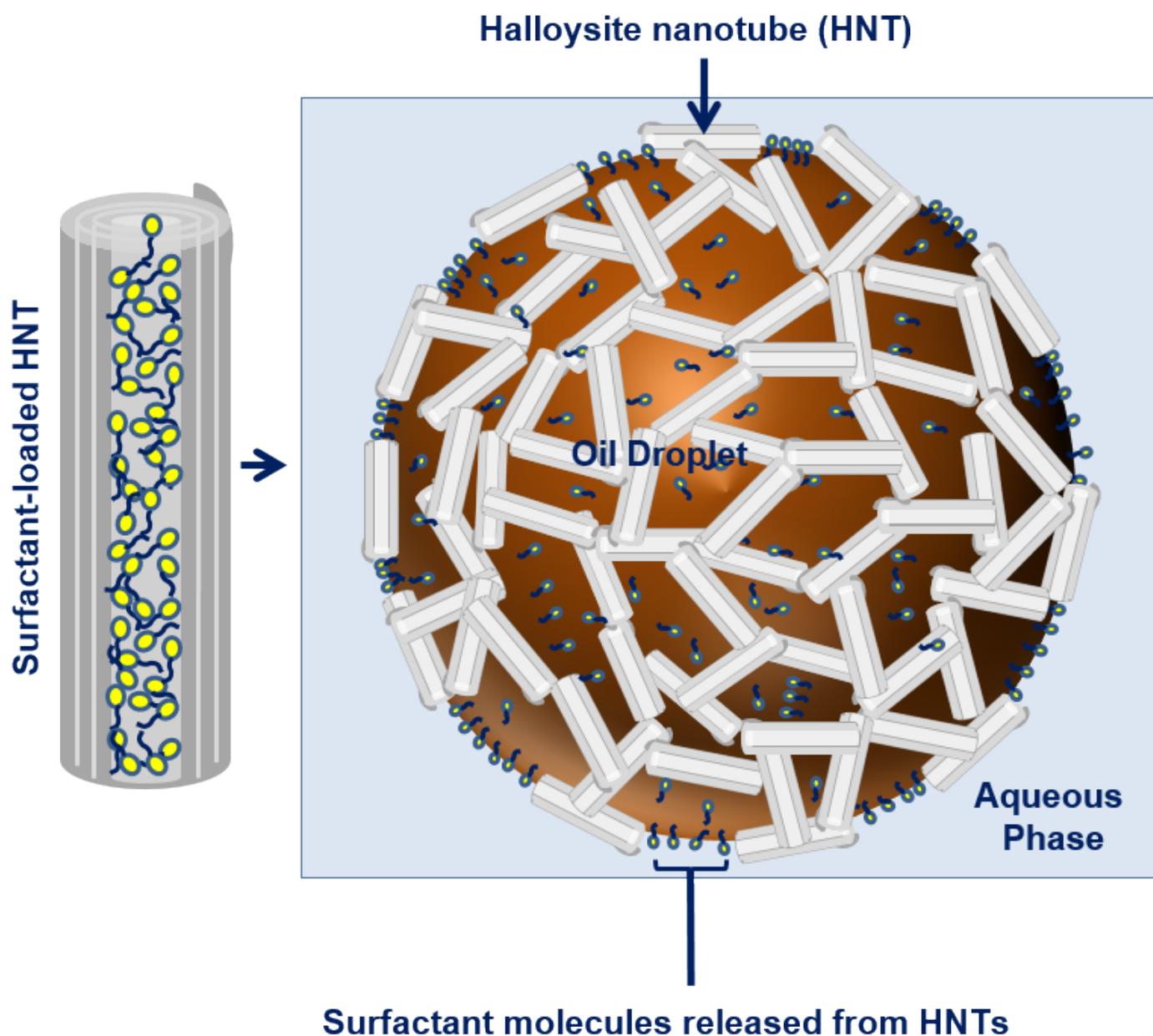


FIGURE 7. Nanotechnology has many applications, including in oil spill response. Pictured are halloysite nanotubes (HNTs) filled with surfactant. They coat oil droplets and release surfactant on the droplet's surface. (Reprinted with permission from Owoseni, O., Nyankson, E., Zhang, Y., Adams, S. J., He, J., McPherson, G. L., ... & John, V. T. (2014). Release of surfactant cargo from interfacially-active halloysite clay nanotubes for oil spill remediation. *Langmuir*, 30(45), 13533-13541. Copyright (2016) American Chemical Society.)

GLOSSARY

Amino acids — A collection of 22 compounds, all containing a minimum of nitrogen, oxygen, carbon, and hydrogen. Chains of amino acids make up protein. For this reason, they are sometimes referred to as the chemical building blocks of protein.

Carbon nanotube (CNT) — A nano-scale (1-100 nanometer, which equals 1-100 billionth of a meter) cylinder of carbon molecules. CNTs have novel properties that make them potentially useful in a wide variety of applications in electronics, optics, and other fields of materials science, as well as oil spill response.

Corexit 9527A and 9500A — Dispersants approved for use in U.S. waters and those that were used to minimize the presence of surface oil slicks during the Deepwater Horizon oil spill.

Dispersants — Chemicals that are used during oil spill response efforts to break up oil slicks. Their use can limit floating oil from impacting sensitive ecosystems such as coastal habitats.

Dispersant additives — Compounds added to enhance the abilities of dispersants.

Halloysite nanotubes (HNTs) — A nano-scale (1-100 nm) cylinder constructed from a naturally occurring

aluminosilicate (halloysite). They have properties that make them potentially useful in a wide variety of applications including drug delivery, technology, and oil spill response.

Lipids — A group of compounds, including natural plant and animal oils, waxes, and fats, that do not dissolve easily in water.

Nanomaterials — Engineered materials of which a single unit is sized between 1 and 1000 nanometers (nm), but is usually 1–100 nm.

Silica — A mineral composed of silicon and oxygen. In nature, this mineral is a component of quartz and a major component of some sands. It is used by humans in some toothpastes, electronics, and pharmaceuticals.

Sorbents — Materials used to absorb oil during oil spill clean-up operations.

Surfactants — Compounds that work to break up oil. Dispersants contain surfactants that break the oil slick into smaller droplets that can more easily mix into the water column.

Suspension — A mixture of particles that are dispersed throughout a bulk of fluid.

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Workers clean up oil that made its way to Port Fourchon, Louisiana's shore during the Deepwater Horizon oil spill. The development of emerging surfactants, sorbents, and additives, like those described in this bulletin, have the potential to reduce the amount of on-shore oiling that occurs in future spills. (PO3 Patrick Kelley)

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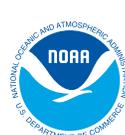
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