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TECHNICAL RESEARCH NOTE

CytoSol – Cleaning Oiled Shorelines with a Vegetable Oil Biosolvent

RANDALL VON WEDEL *,[1]
CytoCulture International, Inc., 249 Tewksbury Avenue, Point Richmond, California 94801, USA

A cleanup process has been developed to aid in the removal of crude or fuel oil from shorelines using CytoSol "biosolvent" formulation based on vegetable oil methyl esters in combination with bioremediation enhancers. The CytoSol biosolvent dissolves and floats the oil, the oil/biosolvent mixture is rinsed off with ambient temperature water for collection as a consolidated layer with skimmers. The collected oil mixture can be recycled as a burner fuel. Nutrient enhancers in the formulation then stimulate the natural biodegradation of the remaining residual hydrocarbons. This new approach minimizes physical and chemical impacts to marine organisms, cleans oiled surfaces effectively, and allows the oiled ecosystem to recover with less mortality than conventional methods involving hot water, detergents or other chemical cleaners. CytoSol is ideally suited for port facilities and waterfronts dealing with occasional small oil spills and has undergone extensive laboratory testing for the US EPA. In 1997, the CytoSol biosolvent was licensed in the state of California as a shoreline cleaner and set up for commercial distribution.
CytoSol biosolvent can extract heavy petroleum (crude, fuel oils) off shoreline habitats, mussel-encrusted breakwaters or pilings, and estuary vegetation. The viscosity of the product tends to limit the penetration of the CytoSol/oil mixture into sand and gravel beaches, allowing more of the dissolved oil to be removed from the shoreline by washing. The product has a low specific gravity (0.87), tends to consolidate oil, and is practically immiscible with water, so it facilitates the recovery of spilled oil with conventional skimming and absorbent boom technologies. Since it is non-volatile and non-flammable, there is little danger of explosion or fire when spraying it inside confined spaces.

Application

The CytoSol process is a two step cleanup technology for removing spilled oil accumulated on shorelines, breakwaters, piers, river banks and other waterway structures. CytoSol can be applied with a variety of spraying or washing equipment depending on the scale and type of surface to be cleaned. The product is shipped to the site in bulk containers or 55-gal drums for direct application to the oil. In small-scale applications, the biosolvent may be applied with hand sprayers, or with portable pumps, hoses and nozzles to spray the product directly onto oiled surfaces and shorelines.

The dissolved oil is floated off the shoreline or washed off vegetation and shellfish-encrusted structures using ambient temperature, low pressure water spray to minimize damage to the affected ecosystems. In laboratory efficacy tests and pilot field trials, CytoSol bioreleased 50–98% of the original oil adhering to or trapped in various shoreline sediments ranging from oiled coral beach sand collected at the San Juan, Puerto Rico spill (1994) to coarse California beach sand and intertidal gravel from Prince Williams Sound.

Bioremediation

The remaining CytoSol and residual petroleum hydrocarbons are biodegraded through a proactive bioremediation program focused on the nutrient enhancement of indigenous, hydrocarbon-degrading bacteria already present at the site. This second step generally takes six weeks (at warmer temperatures,

*Tel.: +1-510-233-0102; fax: +1-510-233-3777.
E-mail address: rvw@cytoculture.com (R. von Wedel).
[1] Web site: www.cytoculture.com

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PAGES 1-3 DISPATCH 18 April 2000
SSTB 257 A
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e.g., Puerto Rico spill) to several months in cooler weather for the residual petroleum to break down to levels acceptable for site closure. Biodegradation rates can be substantially improved in stockpiled oiled gravel or sand by tilling to improve mixing and oxygen transfer, and by periodic irrigation to maintain adequate moisture levels.

The biodegradation of residual hydrocarbons in shoreline and estuarine environments can be accelerated through controlled nutrient addition, particularly through the use of oleophilic nitrogen and phosphorous fertilizers that support acclimated hydrocarbon-degrading bacteria living at the oil–water interface. The vegetable oil methyl esters of CytoSol have been shown in laboratory studies and field trials to further boost the populations of bacteria that break down petroleum. In bioremediation studies of oiled sand and slurries of oiled sediments, the bacteria that acclimated to the biosolvent as a sole food source were at least as active at degrading crude oil as bacteria grown up on the crude oil alone.

Dose rates for application of CytoSol will vary with the type and amount of petroleum spilled, the extent of weathering, and other site-specific conditions. In general, the ratio of applied CytoSol to crude oil is between 0.5:1 and 1:1 parts of CytoSol to immobilized oil, although it could be used at higher dose rates for direct application to release inaccessible, trapped or weathered oil.

Recovery of Oil/Biosolvent Mixture

Shoreline washing with ambient temperature seawater (e.g., header flooding systems or moderate pressure hoses) is essential for releasing the extracted oil/biosolvent mixture. CytoSol facilitates the collection of adherent oil by reducing the oil's adhesion to surfaces and consolidating the floating mixture into discrete patches. As a result, weir (or disc) skimmers and vacuum recovery systems work more effectively in collecting the consolidated oil. The oil/biosolvent mixture's lower viscosity and greater cohesion dramatically increases the extracted oil penetration into absorbent pads and booms compared to results obtained with dispersed oil and sheen.

Marine Toxicity and Biodegradation Studies

In laboratory simulations conducted at CytoCulture using California Department of Fish and Wildlife protocols, the dissolved phase CytoSol esters (saturation = 14 ppm at 17°C) biodegraded with naturally-occurring bacteria in San Francisco Bay water with a half life of approximately 4 days. Bacterial populations cultured on CytoSol as their only Carbon/energy source were then shown to be at least as active in breaking down crude oil fractions as bacteria cultures raised on the crude oil alone.

Acute toxicity bioassay studies were conducted on two marine larval species as required by US EPA protocols for testing shoreline washing agents to be listed in the NCP schedule of products used at oil spills. *Mysidopsis bahia* shrimp larvae and *Menidia beryllina* fish larvae were exposed to increasing concentrations of the CytoSol added as an emulsion to agitated sea water during a 48-h survival test. A third test species, abalone larvae (*Haliotis rufescens*), was used to evaluate the CytoSol in a leachate bioassay test required for licensing in the State of California by the Department of Fish and Game. Marine toxicity levels for emulsified CytoSol were found to be 15–20 times lower than for reference fuel oil.

Pilot Demonstrations of the CytoSol Process

CytoCulture has performed a series of pilot demonstrations with CytoSol since the first demonstration at the *Berman* barge fuel oil spill in San Juan, Puerto Rico in January 1994. These demonstrations have been conducted for the US Coast Guard, NOAA, the US Environmental Protection Agency, and the US Department of Agriculture, as well as for local regulatory agencies in California, Washington and Alaska. A similar, larger pilot demonstration was performed for Japanese authorities on the west coast of Japan (Kaga) in April 1997 as they cleaned heavy oil from a major tanker spill.

In the demonstrations, heavily oiled (saturated) sand is treated in confined pools with the CytoSol and then rinsed with cold water to float off the consolidated petroleum. The floating oil/biosolvent mixture is collected by a weir skimmer and recycled as burner fuel. Over 80% of the fuel oil can be recovered from the sand by a single CytoSol application and water rinse in the first step of the process.

For step two, the treated sand is fertilized with time release and dissolved nutrients, and then inoculated with cultures of hydrocarbon-degrading bacteria grown up on site in seawater. The sand is tilled and irrigated on a weekly basis to promote the biodegradation of remaining hydrocarbons. In the Puerto Rico demonstration, the total hydrocarbon concentrations had dropped by over 90% to less than 200 ppm after six weeks of tilling. In oiled sediments obtained from a crude oil production field in Mexico, the population of hydrocarbon-degrading bacteria in CytoSol treated samples increased 2–3 logs to over 10^7 colony forming

units per gram. Similar results were obtained after CytoSol was used to treat an oiled creek bed in Santa Barbara, CA.

Cytosol Field Tests

In a 1995 San Francisco Bay field test, a single application followed by a passive water wash released over 60% of the trapped oil near the high tide zone as measured by samples collected and analyzed by the California Department of Fish and Game, Office of Oil Spill Prevention and Response. Subsequent field tests of oiled creek beds (Santa Barbara), oiled mussel beds and pilings (Long Beach Harbor) have confirmed removal of oil from shoreline communities without major disruption to these sensitive ecosystems.

CytoSol research briefly summarized in the above were supported by the United Soybean Board and the US Department of Agriculture from 1994–1997.

In June of 1997, CytoSol was licensed by the California Department of Fish and Game as a shoreline cleaning agent available for potential use by Regional Response Teams at oil spills in marine and aquatic habitats.

In May of 1999, CytoSol was used as a "degreaser" for cleaning the inside of the engine room in the stranded stern section of the beached *New Carissa* in Coos Bay, Oregon. Under US Coast Guard supervision, the CytoSol was sprayed inside the ship to release trapped oil and tars for recovery by skimmers and absorbents.