Advances in Biological Cleaning

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Biological cleaning integrates two proven technologies: emulsion cleaning and the microbial biodigestion of the removed oils and greases. The cleaner is continuosly rejuvenated avoinding the necessity of waste treating spent solutions. While the process has been validated in a large number of industries, the present applications have been limmited to the soak cleaning of oils and greases. To extend the range of the technology, new procucts were formulated, that combined biological cleaning related pocesses, such as phosphating and electrocleaning. The combined processes have the extended life found in biological cleaning, eliminating the necessity of waste treatment of spent solutions. A limitation to the use of biological cleaners has been the necessity to observe operational constraints (such as temperature, concentration and pH) to maintain the microbial activity during the process. The development of microbes that have better environmental tolerance may further improve the uses and productivity of biological cleaning.

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Introduction

Biological cleaning is a novel technology based on the simultaneous use of two processes: surface cleaning and bioremediation. The cleaning process actually takes place in two separate operations. When parts come in contact with the solution, the oil and impurities are emulsified into micro-particulates. The particulates are then consumed by microorganisms, which are present in the bath or spray. The microbe consumption of the oil present in the bath, as its food source. The microbes are naturally present in industrial oils and greases, and the main species responsible for biodegradation has been identified as *pseudomonas stutzeri*, a microorganism found in the environment

While microorganisms have been used for many years to digest oil from wastes and spills, the integration of biodegradation with aqueous cleaning for industrial cleaning applications is a relatively recent process. Most of the conventional cleaners will not allow the survival of oil consuming microbes due to high operating pH and temperatures. By formulating a mild alkaline emulsifying cleaner that operates at relatively low temperatures it is possible to integrate the removal of oil and particulates with the biological digestion of the residues. The system is essentially self-regulating, since the microbial activity will adjust itself to the amount of oil present in the system.

The basic biological cleaning system was evaluated by the Concurrent Technologies Corporation under a Cooperative Agreement with the U.S. Environmental Protection Agency was presented under the title "Evaluation of BioClean USA, LLC Biological Degreasing System for the Recycling of Alkaline Cleaners" during the 22nd Annual AESF/EPA Conference on Pollution Prevention and Control for the Surface Finishing Industry, January 29-31, 2001, in Orlando, FL. A number of case histories using the same were presented in a paper delivered at the same Conference under the title "Field Experience with an Integrated Biological Degreasing System". The biological cleaning process is working in a large variety of industries such as general metalworking, electroplating, anodizing, painting and powder coating. Still, the present system has limitations and process improvements are necessary to further expand the uses of biological cleaning.

Principles of Biological Cleaning

To understand the implications of the new technical advances, it is necessary to review the principles of bioremediation. The consumption of emulsified oils and greases in the cleaning process by microorganisms is essentially bioremediation. In the simplest terms, bioremediation is the use of microorganisms (fungi or bacteria) to decompose pollutants into less harmful compounds. Bioremediation is the technological application of biodegradation. Biodegradation is a natural process by which microbes alter and break down petroleum hydrocarbons, natural oils and fats into other substances. The resulting products can be carbon dioxide, water, and partially oxidized biologically inert by-products.

Bioremediation is the optimization of biodegradation by fertilizing (adding nutrients) and/or seeding (adding microbes). These additions are necessary to overcome certain environmental factors that may limit or prevent biodegradation. Certain enzymes produced by microbe's attack hydrocarbon molecules, such as oil, causing degradation. The degradation of oil relies on having sufficient microbes to degrade the oil through the microbes' metabolic pathways (series of steps by which degradation occurs). However, even when these microbes are present, degradation of hydrocarbons can take place only if all other basic requirements of the microbes are met.

Bacteria differ dramatically with respect to the conditions that allow their optimal growth. In terms of nutritional needs, all cells require carbon, nitrogen, phosphorus, sulfur, numerous inorganic salts (potassium, magnesium, sodium, calcium, and iron), and a large number of other elements called micronutrients. The survival of a microorganism depends on whether or not it can meet its nutritional needs. Carbon is the most basic structural element of all living forms and is needed in greater quantities than other elements. The nutritional requirement ratio of carbon to nitrogen is 10:1, and carbon to phosphorus is 30:1. Organic carbon is a source of energy for microbes because it has high energy yielding bonds in many compounds. In the decomposition of oil, there is plenty of carbon for the microorganism due to the structure of the oil molecule.

Nitrogen is found in the proteins, enzymes, cell wall components, and nucleic acids of microorganisms and is essential for microbial metabolism. Because only a few microorganisms can use molecular nitrogen, most microorganisms require fixed forms of nitrogen, such as organic amino nitrogen, ammonium ions, or nitrate ions. These other forms of nitrogen can be scarce in certain environments, causing nitrogen to become a limiting factor in the growth of microbial populations. Phosphorous is needed in the membranes (composed of phospholipids), ATP (energy source of cell) and to link together nucleic acids.

Along with nutrients, microbes need certain conditions to live. Microbial growth and enzymatic activity are affected by stress ultimately impacting the rate of biodegradation. As the stress increases (less favorable conditions occur) the microbes have a harder time living in their environment. Just as humans need certain conditions to live (like oxygen) so do microbes. There is a certain range of conditions in which microbes can live. As conditions reach the extremes microbial growth slows down, but when conditions are perfect the microbial community can thrive.

Oxygen is needed, since biodegradation is predominantly an oxidation process known as heterotrophic metabolism. Bacteria enzymes will catalyze the insertion of oxygen into the hydrocarbon so that the molecule can subsequently be consumed by cellular metabolism. Because of this, oxygen is one of the most important requirements for the biodegradation of oil. The primary source of oxygen for biodegradation is atmospheric oxygen. Aeration is required to allow biodegradation to take place. Oxygen is important in hydrocarbon degradation because the major pathways for both saturated and aromatic hydrocarbons involve molecular oxygen or oxygenases. Theoretical calculations show that 3.5 g of oil can be oxidized for every gram of oxygen present.

Biodegradation can also occur under anaerobic conditions by processes called anaerobic respiration, in which the final electron acceptor is some other inorganic compound, such as nitrates, nitrites, sulfates, or carbon dioxide. The energy yields available to the cell using these acceptors are lower than in respiration with oxygen - much lower in the case of sulfate and carbon dioxide - but they are still substantially higher than from fermentation.

Water is needed by microorganisms since it makes up a large proportion of the cell's cytoplasm. Water is also important because most enzymatic reactions take place in solution. Water is also needed for transport of most materials into and out of the cell. Several variables, including pressure, concentration, temperature and pH, may also have important effects on biodegradation rates. Bacteria have adapted to a wide range of temperatures. Although hydrocarbon degradation has been found to occur at a wide range of temperatures (as low as below 0°C to as high as 70°C) it is an important factor on the rate of biodegradation. Raising the temperature will increase the possibility of reactions taking place and increase the rate of diffusion. Without reactions and diffusion life cannot exist. In general the rate of enzymatic reactions can be doubled for every 10°C rise in temperature as long as the enzymes are not denatured. The higher the rate of the enzymatic reactions the faster the biodegradation will occur. However, there is a maximum temperature at which these microorganisms successfully survive. While higher temperatures are conducive to cleaning, temperatures in excess of 60ºC will kill the bacteria. For this reason the temperatures for Biological Cleaning are maintained between 40º and 57ºC (104-131ºF).

In the Biological Cleaning process the pH of the cleaner is also an important variable and it is maintained in a relatively narrow range of 8.8 to 9.2. At pH values above this limit the microbial activity decreases, while at lower pH values the microbe population will grow too fast and will consume not only the oils present but also the biodegradable surfactant needed for cleaning.

The concentration of pollutants is an important factor. If the concentration of petroleum hydrocarbons is too high then it will reduce the amount of oxygen, water and nutrients that are available to the microbes. This will create an environment where the microbes are stressed thereby reducing their ability to break down the oil.

Biodegradable Materials

Once the necessary requirements are present either naturally or by addition, the oil and other organic materials can begin to be broken down by the microbes. Favorable conditions for the microbes will help optimize the degradation of the oil.. Petroleum is the main source of industrial oils and greases. Petroleum is a complex mixture of hydrocarbons, but it can be fractionated into aromatics, aliphatics, asphaltics and a small portion of non-hydrocarbon compounds. The general outline bioremediation pathways for aliphatic and aromatic hydrocarbons have been formulated and continue to be developed in greater detail with time. All of these pathways will result in the oxidation of at least part of the original hydrocarbon molecules. The content of a particular petroleum mixture will also influence how each hydrocarbon will degrade and the type and size of each hydrocarbon molecule will determine the susceptibility to biodegradation.

The type and size of the hydrocarbon molecule will affect its ability to be metabolized by microorganism. The straight-chain alkane (n-paraffin) compounds with 10 to 24 carbon atoms are degraded the fastest because they are easiest to metabolize. As the length of a chain increases, it becomes resistant to biodegradation, and those compounds with molecular weights of 500 to 600 are no longer able to serve as a carbon source. Branching of alkanes will reduce the biodegradability. Aromatic hydrocarbons are made up of at least one benzene ring or substituted benzene ring. These compounds can be degradable when they are simple and have a low molecular weight. However, as they increase in complexity and molecular weight they are not as easily degraded. Aromatics with five or more rings are not easily attacked and may persist in the environment for long periods of time. Asphaltic petroleum components do not or are slow to biodegrade. No uniform degradative pathway, comparable to the pathways established for aliphatic and aromatic hydrocarbons, has yet emerged for the asphaltenes.

Metal working lubricants are the most common sources of the contaminants in the industrial cleaning of metals. These materials are based mainly on petroleum hydrocarbons, but contain a variety of additives, such as natural and sulfurized oils and greases, synthetic polymers, chlorinated parafins, etc. that exhibit different degrees of biodegradability. In most cases manufacturing uses a variety of metal working fluids that will be removed and mixed in the emulsion cleaner, requiring a biodigestive process that is at the same time robust and flexible.

Process Improvements

The present biological cleaning process employs an alkaline cleaning solution that operates at relatively low temperatures (104ºF - 131ºF) (40ºC - 55ºC) and a pH range of 8.8 - 9.2, which is a viable habitat for these microorganisms.. The cleaning solutions from the cleaning baths are pumped continuously into a separator module that feeds the system. After treatment the cleaning solution is returned into the holding tank and then pumped back into the cleaner tanks. This operation is run in a continuous mode without interruptions for solution dumping and new solution make-up. As a result of the dynamics of the process and the re-circulation of the bath solution, the consumption of oil by the microbes occurs throughout biological degreasing system. For an efficient operation the oil must be emulsified and oil must be present at all time to keep an active population of microorganisms. In the case of a longer interruption that may be conducive to the total depletion of the oil present in the system, to keep the microbes alive it is necessary to render them dormant by increasing the pH to 10.5 or alternatively, to feed them with small amounts of oil during the down time.

This basic biological cleaning process is undergoing major developments to improve the productivity and to overcome some of the present limitations. Some of the improvements can be found in the following areas:

Microbial Enhancement

This project is being carried out in a partnership with a the chemical engineering department of a major university. This work focuses on identifying bacteria which can enhance the existing technology and which can expand the process for use at different temperatures. Studies are conducted to investigate the rates of degradation as well as improve the process. In addition, bacterias are identified which synthesize their own surfactants to enhance the emulsification of the grease (and thereby improve degradation rates), and bacterias are evolved specifically for the degreasing operations. The specific objectives are:

- Determine the rates of degradation of the common metal working lubricants, optimizing these degradation reactions by adding additional limiting nutrients.
- Identify the active bacteria in the process so that the process may be made more reliable, pairing up bacteria with difficult metal working lubricants..
- Develop a high-temperature process.
- Develop a low-temperature biological cleaning process to create new markets
- Evolve bacteria for degrading contaminants which are currently difficult to degrade.
- Utilize bacteria capable of producing their own surfactants.

Another new activity is focused on the initial acclimation phase during which the biodigestion process is not evident. An explanation of the acclimation process is based on the proliferation of small populations. The process uses a community of microbes. A small number of microbes of this community are more capable to digest the specific oils and greases present in an emulsion cleaner than the rest of the population and therefore their number will grow exponentially after a relatively slow start. At the present we are examining several approaches to accelerate the acclimation period.

Equipment Development

As mentioned before, the system employs an alkaline cleaning solution and control system that utilizes microbes in the solution to consume the oil/grease that is removed from parts. The system is managed by a separator control module (Fig. 1), consisting of a process tank, inclined plate clarifier, aerator, heaters and heat control, pH meter, transfer pump, chemical metering pumps. The module is essentially a Biostat that maintains the chemical and biological equilibrium of the system by adjusting the temperature and the pH, and the replenishment of surfactants and nutrients. It is possible to operate the system without downtime for extended periods (up to many years), eliminating the need of dumping spent cleaning solutions. The enhanced productivity and the reduced use of chemicals and water have made the system well suited to fulfill the present needs of the industry.

At the present about one hundred control modules have been installed in a variety of industries. Many operations have been in service continuously for extended periods (up to six years) representing the long term experience and proving the efficiency of the design and the dependability of the components of the system. The present work on a amore advanced design has as an objective to introduce on line control and recording capabilities and to expand the analytical equipment of the unit to measure additional variables. The new unit is microprocessor controlled and is capable of remote adjustments.

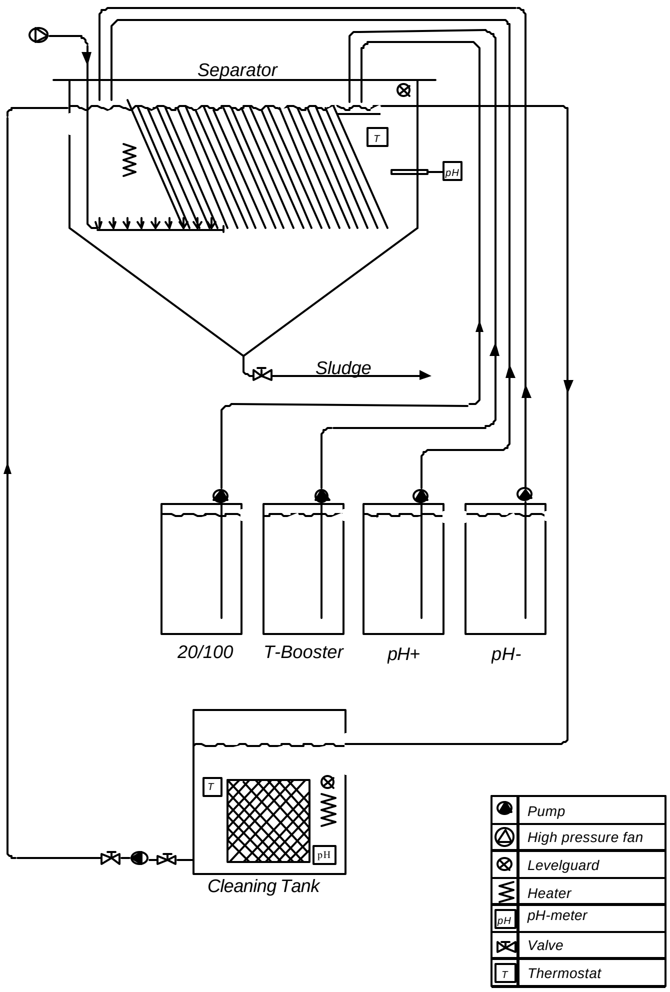

Figure 1: Biological Cleaning Control Module

Pre-cleaning and Post- cleaning

While the biological approach to cleaning has proven its effectiveness in a large number of installations, under certain conditions the original contaminants are not totally removed from the surface. In these cases the biological cleaning is further improved either by treating the parts with a precleaning solution that assists in removing the oils and greases, or by treating with post cleaning solutions, that remove the residual films after the biological cleaning. A combination of pre and post operations can also be used to remove difficult contaminants.

While these additional procedures may improve the effectiveness of the cleaning, they share a common inconvenient, namely that they become contaminated by the oils and greases and age quickly, requiring frequent dumping and waste disposal. To overcome this limitation, a novel approach has been invented. The pre and/or post treatment solutions are selected and formulated with materials that are compatible with the biological cleaner, avoiding the use of materials that can damage the microbial action. Portions of the pre and/or post treatment materials are introduced periodically or continuously into the biological cleaning system where they take part in the biodegradation process. The process is maintained by replenishing only the pre or post cleaning tanks, without the necessity of adding fresh materials to the main soak cleaner.

By adapting this approach, it will be possible to operate the integrated cleaning system (including pre and/or post treatments) in a steady state mode and the solutions will have the extended life and steady composition of the present biological cleaning process. Initial testing of the advanced biological cleaning systems have confirmed that they can handle the most difficult cleaning demands in an effective way, expanding the potential of this novel technology.

New Applications

A large number of industries are potential targets for biological cleaning. To expand the uses of this technology and to develop new markets, new products are formulated and new techniques are being introduced on an ongoing basis. We will mention here three new applications: that are being field tested presently.

Electrocleaning

In many cases electrocleaning is required after soak cleaning to prepare the surfaces for electroplating or electropainting. Unfortunately the electrocleaners also become contaminated and require dumping and waste disposal. The contaminants can not be biodigested, since the electrolytic process will kill the bacteria. One way to obviate this problem is to add portions of the electrocleaner transferred into the biological soak cleaner where it will take part in the biodegradation process. The electrocleaner is replenished by adding portions of fresh material, consequently rejuvenating these solutions and the system is working in a zero discharge, closed loop mode. It is possible to return the drag out to the soak cleaner tank to further reduce the consumption of replenisher.

Phosphating

Many of the iron phosphating products (used in painting and powder coating) contain surfactants to clean and conversion coat simultaneously. The oils and greases that are removed in the cleaning phosphates will contaminate the bath. By formulating a cleaner phosphate that contains no biocides and controlling the pH between 5.0 and 5.5 it was possible combine phosphating with biological cleaning. The product is working well in a beta site with improved results of both cleaning and phosphating. Additional work has been carried out to extend the cleaning phosphate to treat steel, aluminum and galvanized surfaces.

Wire Drawing

One of the most difficult cleaning operations has been the removal of lubricating compounds from wire that has been submitted to the heat and pressure during the drawing process. The lubricating compounds are generally sodium and calcium soaps and the wire rods are treated with borax and lime after pickling to remove the scale. Emulsion cleaners have proven to be effective in removing these materials, but insoluble materials, such as calcium compounds will be building up in the cleaner. These insoluble contaminants can be removed by filtration and the clarified bath will support microbes that will degrade the soluble soaps. Experience in a large production line has proven the practicality of this novel approach to wire cleaning.

Hot Dip Galvanizing

At the present the hot dip galvanizing lines are using conventional alkaline cleaners to degrease before removing scales and oxides in the acid pickling step. It is necessary to rinse thoroughly the parts between degreasing and pickling to avoid carrying alkaline materials into the pickling acid. Using a specially formulated biological cleaner, the rinsing step can be avoided, with the added benefit that the carried over cleaner activates the removal of oxides, inhibiting at the same time the attack of the clean deoxidized surfaces. With this process it is possible to use pickling solutions with reduced free acidity and to increase the capacity of the pickle to tolerate higher iron contents.

GENERAL REFERENCES

Atlas, Ronald M. and Bartha, R. ***Microbial Ecology,*** Benjamin/Cummings Science Publishing, Menlo Park, CA.1998

Alexander, M. ***Biodegradation and Bioremediation,*** Academic Press, London, UK 1999

Byers, J. P. ***Metalworking Fluids,*** Marcel Dekker, New York, NY 1994.