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Come Together

Polymeric surfactant technology bridges the gap between oil water separator capability and the parameters that must be met for regulatory compliance and industrial closed-loop processing

By Hal Alper

Water conservation and prevention of water pollution have become global issues affecting the life and health of people and the ecosystems they inhabit. The ability of ecosystems to recover has been stretched to the limit by overpopulation. As population reduction is unlikely and in fact, the obverse is anticipated, minimization of environmental impact is critical for the survival of the human species.

Organic and oily compounds[1] are a major component of water pollution. The need to reduce discharges of oily and organic pollutants from industrial process streams, marine bilge water and discharges to publicly owned treatment works (POTW) has overwhelmed the capabilities of current technologies. This article addresses organic cleanliness requirements for wastewater discharge and industrial closed-loop processing as compared to the capability of existing organic pollution control devices. Physical, chemical and performance requirements are discussed for a technology capable of bridging the gap between current capability and desired performance. A novel technology based on polymeric surfactant (PS) chemistry[2] is one way to bridge the gap.

Overview

Removal of oils and organic compounds from water is required before discharge to comply with regulations (i.e., Clean Water Act, International Maritime Organization (IMO) and local regulations) or to allow or enhance further treatment in order to facilitate closed-loop industrial processing.

There are a variety of local, national and international laws governing discharge of oils into freshwater and into the oceans. It is not the purpose of this article to address all the various regulations. A review of the current laws and international regulations indicates that maximum allowable oily discharge will be 15 parts per million (ppm) and in many areas, zero discharge will be required. Interestingly, a recent study conducted by the Center for Strategic and International Studies (CSIS) indicated that many of the major wars to come in the next fifty years would be over water rights.

Examples of Polymeric Surfactant Technologies

As population increases, clean water and healthy ecosystems become crucial to economic viability and mandate as close to zero discharge as possible.

Types of Organic Pollutants

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On December 10, 2000, 122 countries agreed to ban, restrict and clean up 12 highly toxic organic compounds known as persistent organic pollutants (POPs) tagged "The Dirty Dozen," (Aldrin, Chlordane, Dioxin, Dieldrin, Endrin, Furan, Heptachlor, Hexachlorobenzene, Mirex, Polychlorinated Biphenyls (PCBs) and Toxaphene). These compounds are especially pernicious because they do not readily biodegrade, are mutugenic and worse in very low concentrations, are slightly soluble or emulsifiable in water and are extremely fat-soluble. This combination of properties produces bioaccumulation of the POPs ascending up the food chain resulting in a variety of deleterious outcomes (i.e., increased cancer rate).

Although it is facile to group pollutants based on toxicity, we find it more useful for purposes of technology characterization and evaluation to group pollutants based on physical and chemical properties as follows.

Non-aquesous Phase Compounds

These compounds tend not to emulsify or dissolve in water without help of detergents and will sink or float. Long chain parafinnic oils are an example. These materials are amenable to gravity separation techniques but tend to clog filtration processes (i.e., membrane filtration, clay filters, etc.).

Slightly Soluble (SS) Organic Compounds

Before today's very sensitive analytical capabilities, many of these compounds were considered insoluble. For our purposes, these compounds have solubilities ranging from one ppb to 100 parts per million (ppm). One example would be benzene, toluene, ethylbenzene, and xylene (BTEX). BTEX are aromatic hydrocarbons. As a class, aromatic hydrocarbons are the most water-soluble constituents of crude oil. Polyaromatic hydrocarbons (PAHs) are not as water-soluble but are generally better bioaccumulators. Many of the POPs are PAHs.

Emulsions

Ordinarily insoluble or SS organic compounds can be made to form sufficiently small droplets so as to have close to neutral buoyancy and therefore remain suspended in water for an indefinite time. Emulsification occurs as a result of mechanical agitation and/or chemical emulsification. Solvents, detergents and surfactants are some common emulsifying agents. We will not address the mechanisms of emulsification or the characteristics of emulsions in any detail in this article except as relates to treatment technology. An excellent reference book for more details is *Surfactants and Interfacial Phenomena* (Wiley John & Sons Inc., 1994) by Milton Rosen.

Only totally soluble organic compounds (i.e. low molecular weight (mw) alcohols) are more difficult to treat using physical or chemical methods than emulsions are. Stable and pseudostable emulsions resist gravity separation due to having neutral or nearly neutral buoyancy. Adsorption using conventional oleophilic filter substrates is not very effective because the droplet/water interface is relatively hydrophilic rendering oleophilic filters less effective. High pressure buildup across the filter after capturing higher molecular weight organic compounds is also an occasional problematic contingency.

Water Soluble Organic Compounds

These compounds are generally polar, therefore hydrophilic, and tend to have lower molecular weights. Ethanol and ethylene glycol, two water-soluble organic alcohols are an example. Membrane filtration and biodigestion are two possible ways to effectively treat this group, provided high mw organics and oils are removed upstream to prevent fouling.

Current State of the Art

Bulk Removal, OWS. Most oils and organic compounds tend to have a lower specific gravity than water, and therefore tend to float. This fact provides the basis for gravity-driven oil/water separator devices (OWS). There are various OWS configurations (e.g., parallel plate, centrifugal, underflow wear), but they are all driven by gravity acting on the density difference between immiscible components. More advanced OWS devices strive to enhance the rate and extent of separation by magnifying density differences through increased g-force (a unit measuring the inertial stress of a body during acceleration in multiples of the acceleration of gravity) and/or by maximizing iterations of the coalescing step. Gravity-driven OWS technology is well established and the equipment is capable of achieving high purity in simple waste streams with strictly non-aqueous phase constituents. Until recently, gravity OWS devices were the primary and sole treatment for oily waste in most cases. Current discharge and processing requirements, however, exceed performance capability, especially if emulsified droplets are present. Emulsified droplets having zero or close to zero buoyancy provide only a tiny density difference available for exploitation by gravity.

We have found that in the case of complex organic waste streams, where some emulsification and dissolution have occurred, typical effluent concentrations range from 30 to 200 ppm for lightly emulsified systems and up to 2,000 ppm for solutions heavily loaded with solvents and surfactants. Discharge requirements for naval bilgewaters where OWS are extensively used is 15 ppm. Recycled industrial process water needs to be in the low ppm to ppb range in order for membrane filtration and other downstream fine polishing devices to be effective. Discharge standards for many solvents (i.e., benzene) are in the low ppb range. It is obvious that gravity oil water separation alone is insufficient to meet these requirements, however, gravity oil water separation is the proven best and most robust first cut.

Polishing. As elucidated above, gravity OWS alone is insufficient and therefore a variety of post OWS polishing technologies have been evaluated. Some of the polishing methods which have been explored include sorbents, membrane technology, flocculation, dissolved air flotation, bioreactors/bio-remediation and air stripping. Two of the more ubiquitous and successful means are as follows.

Sorbents. Sorbents such as modified clays and/or granulated activated carbon (GAC) have been tested as post-OWS polishers. For the most part, effluent sufficiently emulsified or dissolved to get through the OWS also tend to readily desorb from the sorbent when influent concentrations decrease or when less hydrophilic organic compounds are present that then displace the emulsified or soluble compounds. This phenomenon makes it necessary to use massive amounts of sorbent to remove relatively small amounts of pollutant. Sometimes even massive amounts of sorbent will not remove highly emulsified or water soluble materials. Conversely, sorbent materials readily clog and foul if exposed to slugs of higher molecular weight oils as happens regularly due to entrainment in the OWS. The result is breakthrough or downtime for maintenance.

Crossflow Membrane Technology. Membrane polishing technologies are covered in detail in a previous article (See "Protection from Organic Fouling," June 2001, under Archives at www.eponline.com). For our purposes, it is sufficient to note that membrane technologies excel at removing low concentrations of low molecular weight organics and inorganics. They are limited in their ability to remove higher molecular weight organic compounds due to fouling and high-pressure build up across membranes. Membrane technologies are well suited to producing very pure water if they are presented with fairly pure water to polish.

Bridging the Gap

The following properties are required of any technology that can bridge the gap between bulk organic removal and fine polishing of organic and inorganic compounds in order to achieve pure water and/or zero discharge:

Permanent Affinity -- Part of the problem with sorbents is that they tend to desorb. This results in use of large quantities of sorbent and therefore large equipment footprint. Permanent affixing of pollutant is required to eliminate this problem.

Low Pressure Drop --Conversely, sorbents and membranes tend to build up high pressures with higher molecular weight compounds which do permanently affix to them. Any equipment able to bridge the gap must be able to capture high molecular weight organic compounds without significant pressure build-up.

High Flow Rate -- Process must be robust enough to accommodate the range of flow rates, which exist in industry. Again, the low-pressure drop quality is crucial for achieving high flow rate.

Small Footprint -- Sorbents and membranes are dependent on contact area or contact time. In other words, in order to increase the flow rate, the contact area or contact time must also be increased, leading to a larger equipment footprint. Adsorption should be independent of contact time in order to achieve equipment, which can accommodate a variety of flow rates with the same small footprint.

Energy Efficient -- Large amounts of the energy used in filtration devices results from the requirement of pumping to overcome the pressure differential across the filter. Filter technology with very low-pressure differential will also use less energy.

One technology which attempts to address the above requirements consists of utilizing curable visco-elastic oleophilic PS[3]. PS infused filters have the ability to remove slightly soluble organics, emulsified organics and non-aqueous phase compounds from water and to permanently affix these materials into the PS infused filter matrix. This property results in the filters demonstrating extremely high first-pass efficiencies without desorption.

Attempts have been made in the past to enhance the oleophilic attraction of filters by treating them with oleophilic polymers. These attempts have all been unsuccessful due to the simple fact that oleophilic polymers swell when they come in contact with organic compounds. This quickly produces extremely high and unmanageable pressure differentials across the filter media. PS chemistry has the property of being visco-elastic. Visco-elastic materials essentially contract when they are sheered. When visco-elastic oleophilic materials are infused in filter media, organic compounds are able to be captured with less than one pound per square inch (psi) pressure differential cost to filter. This is because water passing through the filter essentially acts as a sheering agent upon the PS/organic coagulate thereby causing contraction.

Another salient property of PS technology that allows it to fulfill the requirements listed above is extremely high first-pass efficiency independent of contact time. Conventional filtration equipment is dependent upon contact time or contact area. This means that a piece of equipment required to handle 10 times the flow rate has to be approximately 10 times bigger. The time invariance of the PS affinity reaction allows equipment size to remain constant over a broad range of flow rates. This is especially useful where space is at a premium and small-equipment footprint is required, as is the case with most ship board applications.

References

[1] For purposes of this article "oily compounds" will represent oils and other oily and organic pollutants (i.e., benzene and toluene, ethyl benzene (BTEX), polychlorinated biphenyls (PCBs), pesticides, etc.)

[2] For purposes of this article, MYCLEX® Technology will be represented as polymeric surfactant (SF) chemistry.

[3] For purposes of this paper, PS will represent MYCELX® curable polymeric surfactant infused filtration technology.

Examples of Polymeric Surfactant Technologies

Case Study: Oily Bilge Water

Ship bilge water is typically a cocktail of oils, greases, solvents, detergents and water. Generally the level of emulsification is high. Until recently, OWS were used exclusively to treat this waste stream and were able to achieve effluent concentrations of anywhere from 30 ppm to 2,000 ppm depending on the degree of emulsification. Since the promulgation of the uniform national discharge standard (UNDS), maximum allowable bilge effluent concentration has been set at 15 ppm. PS infused filters have been deployed successfully post OWS and have produced effluents of no greater than one ppm practically independent of degree of emulsification.

Case Study: Membrane Technology Prefiltration

Approximately half the cost of operating membrane systems to achieve industrial closed-loop water processing is directly or indirectly a result of organic fouling. Conventional prefiltration methods have had limited success in this application due to filter clogging and fouling caused by high molecular weight organic compounds. PS filters deployed premembrane filtration in various field applications has extended membrane life 10 to 20 fold while reducing downtime to operating time ratio from four to one to one to four. PS infused prefilters render membrane systems much more robust and economically viable.

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