

INDUSTRIAL TREATMENT

By George R. Alther

Oil and Grease (O&G) are a common occurrence in wastewater. An EPA commissioned study recently concluded that O&G is an indicator of the presence of numerous other organics in a wastewater, the types that partition into oil. The most famous one is PCB, which partitions into transformer oil.

The EPA is debating new rules that would set specific limits for O&G content in wastewater, thereby encompassing an entire range of organics that partition into oil. Such organics also would include solvents such as benzene and phenols.

Removing oil and grease from wastewater is relatively simple and cheap. Process industries should take the lead in addressing these questions, so that they are ready when the law takes effect. Furthermore, if they design their system such that the wastewater can be recycled, they actually can use this new law to save costs and lessen public concern about discharge of contaminated wastewater.

Effective removal of O&G requires an understanding of emulsions, mechanical versus chemical. Furthermore, the operator must know how to break emulsions and how to test effective treatment methods in the

How to Remove Emulsified Oil from Wastewater with Organoclays

laboratory. He then must know how to remove the now mechanically emulsified oil most economically (i.e., how to coalesce the oil droplets effectively and how to reduce the O&G content to non-detect) so that recycling of the wastewater is feasible. This means being familiar with post-polishing techniques, particularly the use of organically modified clays (organoclays). Organoclays remove oil and grease from water at seven times the rate of activated carbon.

Oil

Oil appears in wastewater in a number of different forms including free oil and

grease (FOG), mechanically emulsified oil, oil wet solids, chemically emulsified oil and dissolved oil.

Free Oil and Grease

Free oil rises rapidly to the surface of the water tank under calm conditions. The droplet size is ≥ 150 microns. This oil can be removed by an overflow weir in the tank and a skimmer. The traces can be removed by passing the wastewater through an adsorber tank (such as a carbon tank) filled with organoclay.

Mechanically Emulsified Oil

These oil droplets range in size from 20–150 microns. Mechanically emulsified oil is stabilized by electrical charges and other forces that result in the coating of suspended solids. Such oils mix with water due to shear that can result from the wastewater traveling through a pump, wastewater splashing into a tank and anything that will break up and disperse larger oil droplets.

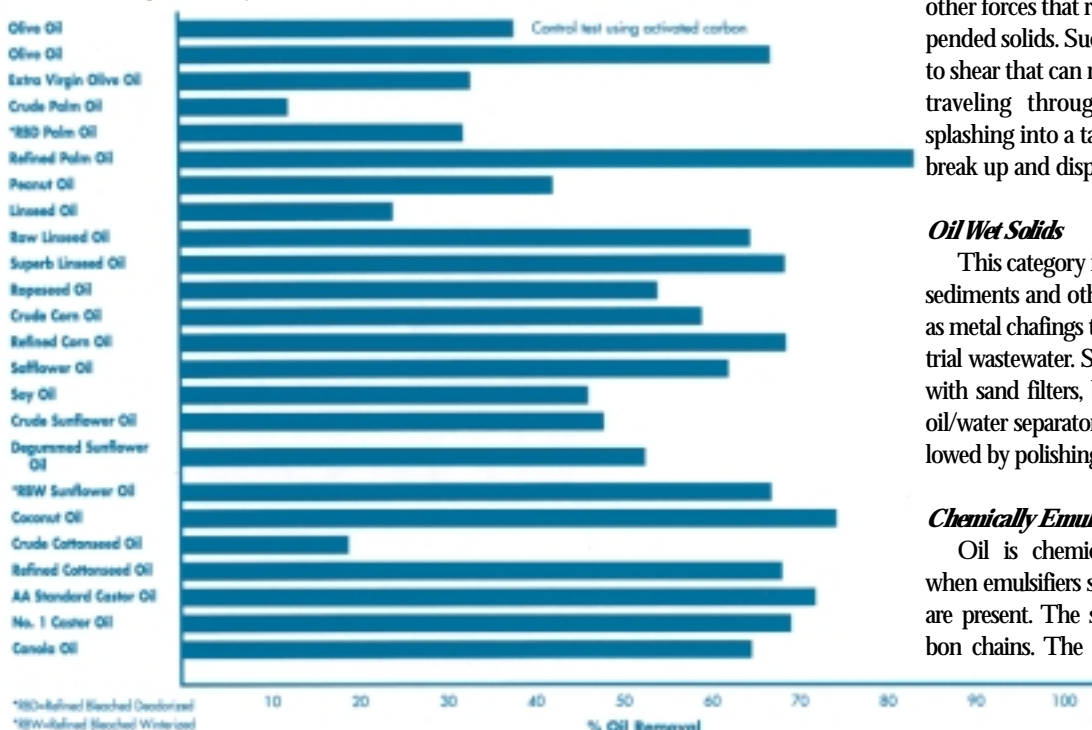
Oil Wet Solids

This category includes oil that adheres to sediments and other particulate matter such as metal chafings that are common in industrial wastewater. Such oil solids are removed with sand filters, bag filters, flocculants and oil/water separators. These processes are followed by polishing with organoclay.

Chemically Emulsified Oil

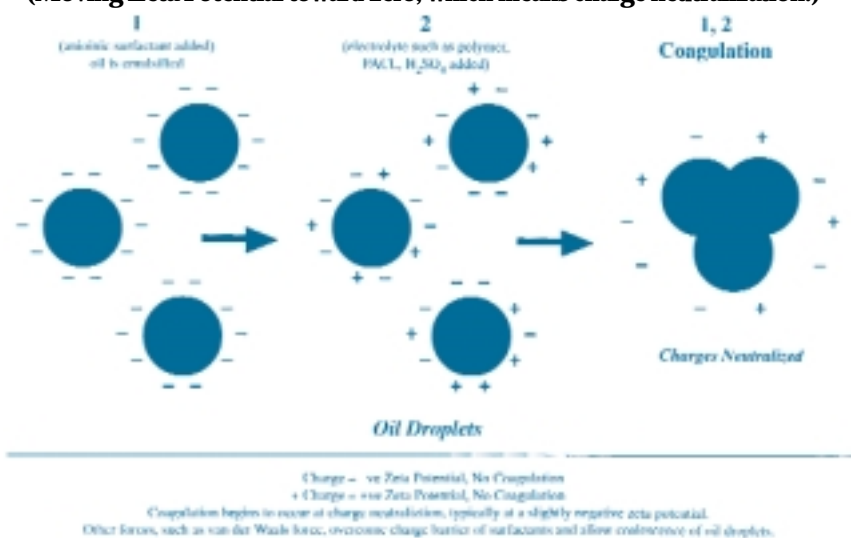
Oil is chemically emulsified in water when emulsifiers such as surfactants or soaps are present. The surfactants have hydrocarbon chains. The simplest ones are sodium

Figure 1: Percent of Plant Oil Removed by Non-Ionic Organoclay Powder from Water (500 ppm) Jar Tests



*RBD=Refined Bleached Deodorized
*RBD=Refined Bleached Winterized

Figure 2: Coagulation of Oil Droplets or Destabilization of Emulsion (Moving Zeta Potential toward zero, which means charge neutralization.)



laurel sulfate or stearic acid, which have a hydrophilic (water loving) and a lipophilic (oil loving) end. The lipophilic end enters the oil droplet, while the hydrophilic end remains in the water. Since this creates a charge on the otherwise neutral oil droplet, the droplets will repel each other and disperse. This is called a chemically stabilized emulsion. The droplets are less than 20 microns, while the color of the water is white. The white color is an indicator that the emulsion must be split to allow removal of the oil. The source of such oils is metal working fluids, coolants, lubricants, motor oil, hydraulic fluids, etc.

Dissolved Oil

These are oils from the light end of the oil spectrum such as benzene, toluene and xylene. The molecules are less than five microns in size. They are removed very effectively by activated carbon.

Emulsion Description

If oil is not emulsified, it floats on top of the water as a sheen. Oil can be either mechanically or chemically emulsified. This means that the oil is broken up into droplets that disperse in the water. The smaller the droplets, the more stable the emulsion. When the drops contact each other they tend to coalesce and rise to the surface.

In chemical emulsions, an emulsifier (usually a surfactant, detergent or soap) is present. Surfactants consist of a hydrophilic/oleophobic end and a hydrophobic/oleophilic/lyophobic end.

They act as a coupling agent between the oil/water phase. Because the emulsifier is polar on one end (i.e., it has a charge) and is non-polar at the other end, it prevents the oil from approaching and coalescing.

Thus, an emulsion is a heterogeneous system that consists of at least one immiscible liquid intimately dispersed in another liquid in the form of droplets, whose diameter generally exceeds 0.1 micron. Surfactants and finely divided solids increase the stability of the emulsion.

What are Organoclays?

Organoclays are manufactured by modifying bentonite with quaternary amines, a type of surfactant that contains a nitrogen ion. The nitrogen end of the quaternary amine (the hydrophilic end) is positively charged and ion exchanges onto the clay platelet for sodium or calcium. Bentonite is chemically altered volcanic ash that consists primarily of the clay mineral montmorillonite. The bentonite has a charge of 70–90 meq/gram. After it is treated with the quaternary amine, some 30–40 meq/gram remain, resulting in the organoclay also removing small amounts of the common heavy metals such as lead, copper, cadmium and nickel.

As the organoclay is introduced into water, the quaternary amine is activated and extends perpendicularly off the clay platelets into the water. A chlorine or bromine ion is loosely attached to the carbon chain. Since the sodium ions that were replaced by the nitrogen are positively

charged, they will bond with the chlorine ion, resulting in sodium salt that is washed away. The end result is a neutral surfactant with a solid base that is the organoclay.

The hydrophilic end of the amine dissolves into the oil droplet, because “like dissolves like,” thus removing that droplet from water. Because the partition reaction takes place outside of the clay particle, in contrast to adsorption of oil by carbon that takes place inside its pores, the organoclay does not get fouled quickly. The granular organoclay is blended with anthracite, which also has oil removal capability and has about the same bulk density (56 lb/ft³) as the organoclay, to prevent the interstitial pores from immediately being filled with oil.

Organoclays also remove chlorinated phenols and other hydrophobic, chlorinated sparingly soluble compounds effectively such as PNAHs, PCBs and others. In combination with activated carbon, BTEXs are removed much more economically, because the organoclay removes the compounds with lower solubility such as xylene and toluene, while the carbon concentrates on removing benzene.

The organoclay is used as a granular material in carbon vessels, or as a powder in batch treatment systems. Some industrial applications for this material include air compressors, boiler steam condensate, cooling water, stormwater, refinery wastewater, amine gas sweetening, steel mill wastewater and motor vehicle wash water.

Recent laboratory work has revealed that the same type of organoclay can be used to remove some synthetic and semi-synthetic coolants from water as well as surfactants. Surfactants tend to compete with organoclay for the oil, which is why the water must first be deemulsified. The organoclay prefers the oil to any other chemical, which is the reason why the surfactant often passes through the organoclay bed, requiring an activated carbon as a polisher. At a pH of 5, glycol can be removed from water. On the other hand, if the flow is fast enough, oil can be removed from antifreeze without the removal of ethylene glycol. Figure 1 shows laboratory data that indicates the capacity of organoclay to remove plant oil from water.

Techniques for Splitting Oily Emulsion

The design of oil/water separators is based on Stoke’s Law. The lighter oil

droplets impact on the slant ribs of the media, coagulate and rise to the surface. The principle of air flotation is that oil droplets will adhere to air and gas bubbles and rise to the surface of the tank. Chemically emulsified oil can be removed by heating the water from 150 to 220° F. However, this can become expensive.

Evaporators remove the water and leave the oil. This process also is expensive and results in difficult clean ups of the elements of the evaporator. The addition of salts, polymers, bentonite powders and pH adjustment are the most difficult but most successful methods of breaking emulsions and removing the oil.

When chemical treatment is applied, prior bench testing is required. The first step is the addition of an inorganic salt such as magnesium or aluminum sulfate. This may be sufficient to break emulsions, or deemulsify the oil, if sodium soaps are the emulsifier. If this process is not successful, a cationic coagulant may be added. The purpose is to neutralize the charges on the oil droplet caused by the emulsifier (i.e., drive the zeta potential towards zero). If this does not work, the pH may have to be adjusted downward to 3.5 with sulfuric acid to break up the surfactant. Coagulants and flocculants then may be added to remove the oil. This step is followed by passing the water through a bed of organoclay to remove the last traces of oil (polymers are not economical below 330 ppm), adjustment of the pH to 5 or higher and a pass through an activated carbon bed. The water now can be reused.

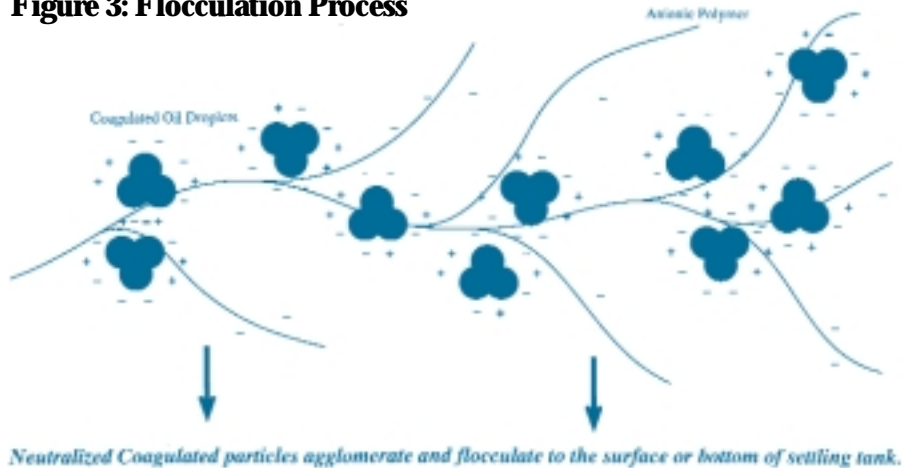
Emulsion Breaking

Both sulfuric and hydrochloric (HCl) acids are used to break emulsions, however, hydrochloric acid often seems to be superior. A step-by-step guide to both acid breaking and coagulant breaking is presented below.

Acid Breaking Process

After the pH is measured, add acid until the pH reaches a level of 4 or 5. Observe the turbidity. If the oil does not already rise to the surface, lower the pH to 3. Filter the water to remove the oil sheen. Measure the oil content. If the oil content still is relatively high, you may add 10–50 ppm of a non-ionic coagulant to help coalesce the remaining oil droplets. Remeasure the oil content.

Figure 3: Flocculation Process



There are two post-polishing methods with organoclay for the removal of traces of oil. In one method, organoclay powder is added (2 gram per 100 ml) and mixed for ten minutes, then flocculated out with an anionic polymer. One also can pass the filtered water through a column of granular organoclay and remeasure the oil in the effluent. These methods allow for recycling of the water with oil at non-detectable levels.

After the water has been polished with granular organoclay, raise the pH back to 7 with sodium hydroxide. Next, pass the water through an activated carbon column to remove the surfactants. If removal of the surfactants (soaps) is not required, carbon polishing may not be necessary.

Coagulant Breaking

Method 1: For emulsions that break at a pH of 7 or 6, add polyaluminum chloride (PAC), aluminum sulfate or ferric chloride at 50–200 ppm or more as needed. Make sure you are aware of aluminum discharge limits in your locality.

Method 2: Add cationic (or nonionic) polymer. Start at 50 ppm (mg/l) to 1000 ppm or more, if needed, and observe the reaction. You may want to use inorganic and organic coagulants in combination. Inorganics generate a gel-like sludge, but are much cheaper than organic coagulants. Sometime better results are achieved by combining the inorganic and organic coagulants. The principle of coagulation is shown in Figure 2. In order to cause the flocs that the coagulants generate to settle to the bottom of the tank, an anionic flocculant may have to be added. The princi-

ple of their operation is shown in Figure 3. After the floc has formed, filter the wastewater, measure the remaining oil content and conduct a column test using organoclay media as the post-polisher.

Jar Test Method

In order to establish the best emulsion breaking method for the application, a jar test can be set up.

Requirements: A 1,000 ml jar and a paddle mixer. Ideally, a five-jar, five-mixer multi-station paddle mixing kit is used.

Establish the pH, turbidity, and the emulsion method (mechanical or chemical). Perform the acid breaking test and the coagulant breaking test in separate jars, and determine the best demulsification method for the application. The turbidity meter can generate a relative number to determine the presence of oil.

Mixing technique: Mix it fast for three minutes, slowly for another seven minutes, and allow it to rest for 10 minutes. Once a floc has formed, filter the water and test for the presence of oil.

Now use the chemical that gave the best results and do a dosage curve (i.e., determine the minimum dosage required for maximum results).

Finally, perform a column test using granular organoclay to polish the filtrate, and establish the amount of organoclay required to polish the water.

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