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Organically modified clays have long been used by industry to remove oil from water. A study was undertaken to verify results from real-world applications and develop a better understanding of the chemical conditions under which organoclays are most effective. Systematic testing was conducted on some 50 oils, including mineral oils, vegetable oils, animal fats, fish oils, and synthetic oils. In addition, the adsorption capacity of activated carbon was tested in order to compare the effectiveness of the two media. Tests also investigated the removal capacity of organoclays for various surfactants as well as the influence such surfactants exert on the removal efficiency of the organoclays. Results showed organoclays are more effective than activated carbon in removing oil from water and cationic organoclays are superior to nonionic organoclays for some removal applications.

# Removing oils FROM WATER with organoclays

**G**ranular organoclays have been used for a number of years as a prepolisher to activated carbon and for removal of small amounts of oil from industrial processing water and groundwater. However, neither industry nor academia has conducted studies to determine whether organoclays work with all oils, including mineral oils, plant oils, animal oils, crude oils, and refined oils. In addition, data are sparse as to which chemical conditions are most conducive to organoclay efficiency or whether one particular type of organoclay fits all circumstances. This article provides the results of a systematic laboratory study conducted to investigate various organoclay applications.

## ALL ABOUT OIL

An understanding of the removal mechanism of organoclays requires familiarity with oil and its classifications. The sidebar on page 116 details the various kinds of oils, including crude oil, mineral oil, petroleum, animal oils, vegetable oils, and essential oils. Table 1 lists oils by type and function.

**Oil contaminants in water.** Oil and grease are commonly found in many process waters and groundwater. Oil found in contaminated water can be classified into five areas:

# Types of Oils

Crude oil (also called mineral oil) is composed of liquid hydrocarbons, which have a lower specific gravity than water. Crude oil is found in porous rock formations underground and is pumped out of the ground and refined, at which point it becomes petroleum. Before it is shipped to a refinery, crude oil is heated and treated with chemicals to remove gases, solids, and water.

**Mineral oil** is a bituminous hydrocarbon. It is a viscous liquid that is insoluble in water but soluble in alcohol or ether. Mineral oil is flammable.

**Petroleum** is made up of gaseous, liquid, and solid components and is used for such purposes as motion power, lubrication, fuel, dyes, drugs, and cooling. Petroleum's consistency (i.e., viscosity) varies from very thin and light to so heavy that it can barely be poured. Petroleum is subdivided into three generic classes:

- Paraffins (which contain waxes) have twice as many hydrogen atoms as carbon plus two.
- Naphthenes (which contain few or no waxes) have twice as many hydrogen atoms as carbon.
- Mixtures of naphthenes and paraffins are categorized based on their viscosity into five base stocks, which serve as the basic components of all lubricants.

Petroleum is a highly complex mixture of paraffinic, cycloparaffinic (naphthenic), and aromatic hydrocarbons, containing low percentages of sulfur and trace amounts of nitrogen and oxygen compounds. It consists of aliphatic and aromatic organic compounds.

The aliphatic group of organic compounds is characterized by straight or branched-chain arrangements of the constituent carbon atoms. Aliphatic hydrocarbons comprise three subgroups. (1) Paraffins (alkanes) are saturated (i.e., all carbon electrons satisfied with hydrogen or other ions) and

comparatively unreactive. The branched chains of paraffins are suitable for gasoline. (2) Olefins (alkenes or alkyl-dienes) are unsaturated and therefore quite reactive. (3) Acetylenes (alkynes) contain a triple bond and are very reactive. In complex structures, the chains may be branched or cross-linked.

The aromatic (arene) organic compounds are a major group of unsaturated cyclic hydrocarbons containing one or more rings. This category, which includes naphthenes, is typified by benzene, which has a six-carbon ring containing three double bonds. The term "aromatic" derives from the somewhat pleasant odor of these compounds.

**Animal oils** are carbon-hydrogen-oxygen compounds, called fatty oils or fixed oils. Animal oils differ from fats only in that they are liquid and fats are solids. Animal oils include such oils as tallow oil derived from beef, lard oil from hogs, whale oil, and cod liver oil. They are extracted by boiling the tissue of these animals in hot water, which results in the fat floating to the surface of the boiling liquid. Animal oils can be further classified as drying and nondrying oils.

**Vegetable oils** are derived from the kernels or leaves of soybeans, cottonseed, olives, palms, jojoba, aloe vera, and other plants. Tall oil is derived from pine trees. Vegetable oils can be further classified as drying (linseed, tung, oiticica), semidrying (soybean, cottonseed), and nondrying (castor, coconut). Vegetable oils are used primarily for cooking purposes; however, the category does include volatile and essential oils, which are derived from specific plants (e.g., palm, coconut) and used for fragrances and cosmetics.

**Essential oils** are complex, volatile liquids derived from flowers, stems, leaves, and often the entire plant. They contain terpenes (e.g., pinene, dipentene) and are usually admixed with resinous products. Turpentine is a highly residuous essential oil.

- Free oil is oil that rises rapidly to the surface under calm conditions.
- Mechanically emulsified oil consists of fine droplets ranging in size from microns to a few millimetres. These droplets are electrostatically stabilized without influence of surfactants.
- Chemically stabilized emulsions have surface active agents that provide enhanced stability because of interaction at the oil-water interface.
- Chemically emulsified or dissolved oil includes finely divided oil droplets (0.5- $\mu$  diameter), benzene, and phenols.

- Oil-wet solids are oils that adhere to sediments, metal shavings, or other particulate matter in wastewater (Braden, 1991).

Types of oil found in wastewater can include fats, lubricants, cutting fluids, and heavy hydrocarbons such as tar, grease, crude oil, and diesel oil. Other oils are classified as light hydrocarbons (e.g., kerosene, jet fuel, and gasoline) and can also be found in wastewater.

The major components of oils found in contaminated groundwater are benzene, toluene, xylene, naphthalene, benzo(a)anthracene, benzo(a)pyrene, polychlorinated