Innovative Uses of Organophilic Clays for Remediation of Soils, Sediments and Groundwater - 9507

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ABSTRACT

PCBs and similar low-solubility organic compounds continue to offer significant challenges in terrestrial and sediment remediation applications. While selective media such as granular activated carbon (GAC) have proven to be successful at absorbing soluble organics, these media may have reduced performance due to blinding in the presence of high molecular weight organic matter.

An alternative technology addresses this problem with a clay-based adsorption media, which effectively and efficiently stabilizes low-solubility organic matter. Organoclay™ reactive media utilizes granular sodium bentonite, which has been chemically modified to attract organic matter without absorbing water. The unique platelet structure of bentonite clays provides tremendous surface area and the capacity of the media to absorb over 60 percent of its own weight in organic matter. Because of these properties, organoclays allow for several cost-effective in-situ remediation techniques, such as:

- **Flow-through filtration for removal of organic matter from aqueous solutions**
  Organoclay can be utilized as a fixed-bed media in a column operation. This specialty media offers a high efficient alternative to Granular Activated Carbon (GAC) when applied as a flow through media to remove oil, PCB and other low soluble organic contaminates from water.
- **Placement in a Reactive Core Mat™**
  Organoclay may be encapsulated into carrier textiles which are adhered together to create a thin reactive layer with high strength and even distribution of the reactive media. This type of delivery mechanism can be successfully applied in a sub aqueous or terrestrial environment for sediment capping applications
- **Permeable reactive barriers**
  Organoclay can deliver high sorption capacity, high efficiency, and excellent hydraulic conductivity as a passive reactive media in these applications.

INTRODUCTION

Bentonite is an ore composed mostly of montmorillonite formed millions of years ago from the deposition of volcanic ash. Bentonite can be found all over the world and has hundreds of commercial uses. Typically, bentonite is categorized as either swelling or non swelling to determine its use and functionality. The dominant exchangeable cation will determine the swelling properties of the clay. While the predominant ion will usually be sodium or calcium, magnesium and potassium may also be present.

Na Bentonite Clay Typical Properties	
Aspect Ratio:	**100nm – 1000 nm**
Surface Area:	**560 – 800 m^2/g**
CEC:	**80 – 125 milliequivalent/100g**
Specific Gravity:	**2.6 g/cm^3**

In its natural state, sodium bentonite is very hydrophilic and expands or swells many times (by volume) as it absorbs water. Bentonite is comprised of individual platelets, which are typically less than 1nm in thickness but as much as 1000 nm in length. The result is a structure with significant surface area and exposed reactive sites which are occupied by the clay's exchangeable ion complex. Sodium bentonite also has important electrochemical properties. The platelets have an overall

negative charge and carry a relatively high charge density. It is this high charge density and capacity for cation exchange (CEC) that makes sodium bentonite clay desirable for chemical modification.
Sodium bentonite clay has been used for many years to treat and clarify water. Its natural occurring anionic charge makes this mineral a very effective coagulant aid for the removal of multivalent cations. As early as the 1930s and 1940s it was discovered that sodium bentonite clay could be surface modified to allow the sorption of organic molecules into the clay matrix (1). Researchers found that these modified clays were capable of irreversibly adsorbing high amounts of organic matter. Further research has shown that organic loading by as

much as 65% (by weight) can be achieved by taking advantage of the high amount of surface area unique to these specialty minerals. These modified clays were initially introduced as a flow through filtration media to treat process water generated in oilfield drilling operations. More recently these products have been effectively applied for environmental remediation applications involving treating contaminated groundwater and industrial process streams. Organoclays have also proven effective in stabilizing organic constituents migrating in contaminated soils, sludge and sediments. They are now being applied in both sub aqueous and terrestrial conditions in a variety of innovative ways.

CREATING ORGANOPHILIC CLAY

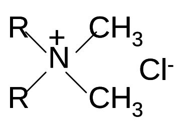
The high CEC of sodium bentonite makes this mineral an ideal platform for surface modification. During this process the naturally occurring Na^+ ion is substituted with an organic cation, which can be typically introduced during various processes. The resulting product is a hydrophobic media that will not swell in water but has a high affinity for low soluble organic matter. The Organoclay formation is through a simple ion-exchange reaction and can be expressed as:

$R_1R_2R_3R_4N^+Cl^-$ + Na^+ -montmorillonite $\longrightarrow$ $R_1R_2R_3R_4N^+$ -montmorillonite + NaCl

Where "$R_1R_2R_3R_4$" = H, methyl or long chain alkyl (Wan, et. al.)

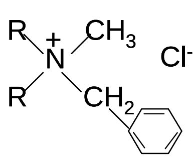
Many types of organic chemicals have been utilized for the modification of sodium bentonite clay. Most common of these are a family of quaternary ammonium cations also known as "quats". The positive charge of these amines allows for an effective bond to the negative charged surface area of the clay. Furthermore, there are several variations of these products that allow for the design of a media that will be more selective on certain organics based on their solubility. Three of the more common surfactants used and their applications are:

Di (hydrogenated tallow alkyl) dimethyl ammonium chloride



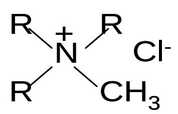
Application: Most commonly applied surfactant for surface modifying sodium bentonite clay, this organic cation is effective on a wide range of low soluble hydrocarbons.

Di (hydrogenated tallow alkyl) methyl benzyl ammonium chloride



Application: Selective on more soluble organic molecules such as: PAH, BTEX, TCE and PCE

Trihexadecylmethyl ammonium chloride



Application: More effective on grease, de-emulsified oils and other less soluble organic matter

As the organic surfactant is introduced to the negatively charged surface of the clay platelet an electrostatic attraction occurs and the hydrocarbon chain is extended away from the surface. This continues as more quat molecules are introduced to the platelet and results in a partition medium consisting of a uniform layer of organic cations oriented within the interlayer of the modified clay (figure 1). It is within this partition medium that the adsorption of the organic molecules occurs (Trauger et. al.).

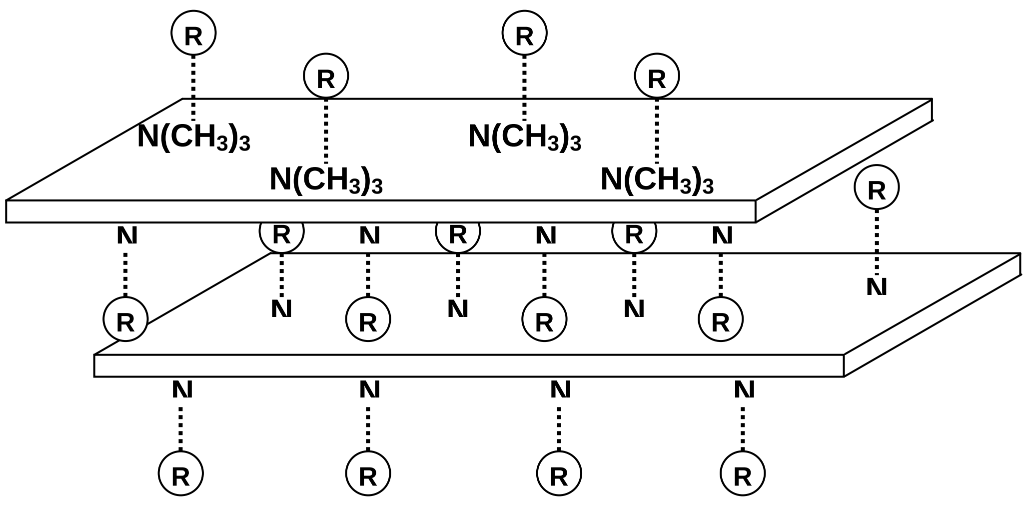


Figure 1. Schematic of typical organophilic clay platelet and the partition medium created when its reactive surfaces are modified with the selected organic amine

ADSORPTION MECHANISMS OF ORGANOCLAY

Unlike granular activated carbon (GAC), which adsorbs organic matter through a porous surface mechanism(2), Organoclays utilize the partition media created during the surface modification process. This layer between the platelets essentially becomes a reactive zone into which dissolves the less soluble organic contaminants present in the aqueous phase. (Trauger, et. al.) It is important to note that the removal efficiency of Organoclay is directly proportional to the solubility (in water) of the organic contaminants present. Less soluble organics will more likely prefer the partition medium of the

Organoclay. Typically, Organoclay is most effective in removing organic molecules whose aqueous solubility is 200 ppm or less (figure 2).

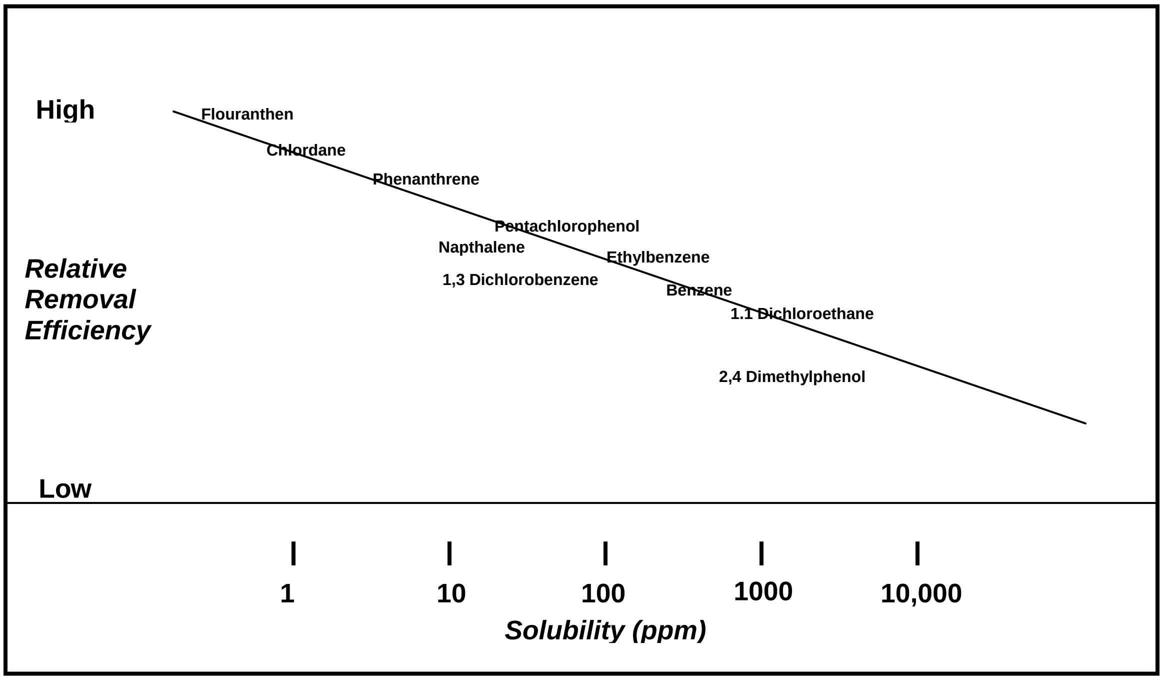


Figure 2. The relationship between solubility in water of the organic contaminant and its relative removal efficiency. Organoclay works best for organic matter whose solubilities are less than 200 ppm.

The reactions which occur with organoclays are adsorption and cation exchange. The primary adsorption mechanism is Van der Waals forces at the modified organophilic sites. However, hydrogen bonding will also occur at sites that were not completely reacted with the introduced organic cation since they remain hydrophilic. It has also been determined that a balance between the organophilic and hydrophilic clay sites optimizes the adsorption capacity of the clay.(3)

FUNCTIONAL USES OF ORGANOCLAY

Flow Through Filtration Media

Organoclay was initially developed as a filtration media to remove oil, grease and other high molecular weight hydrocarbons from water. Initial applications focused on inland and offshore drilling operations, which had traditionally utilized granular activated carbon (GAC) to treat process waters prior to discharge. While GAC has proven to be a very effective media for adsorbing organic matter, it is subject to blinding and premature exhaustion in the presence of petroleum based organic compounds and other high molecular weight contaminants.(4)

Organoclay can be placed in front of a GAC column to remove the longer-chain hydrocarbons and allow the GAC to capture more soluble organic matter and heavy metals, thus extending the life of the GAC considerably (figure 3).

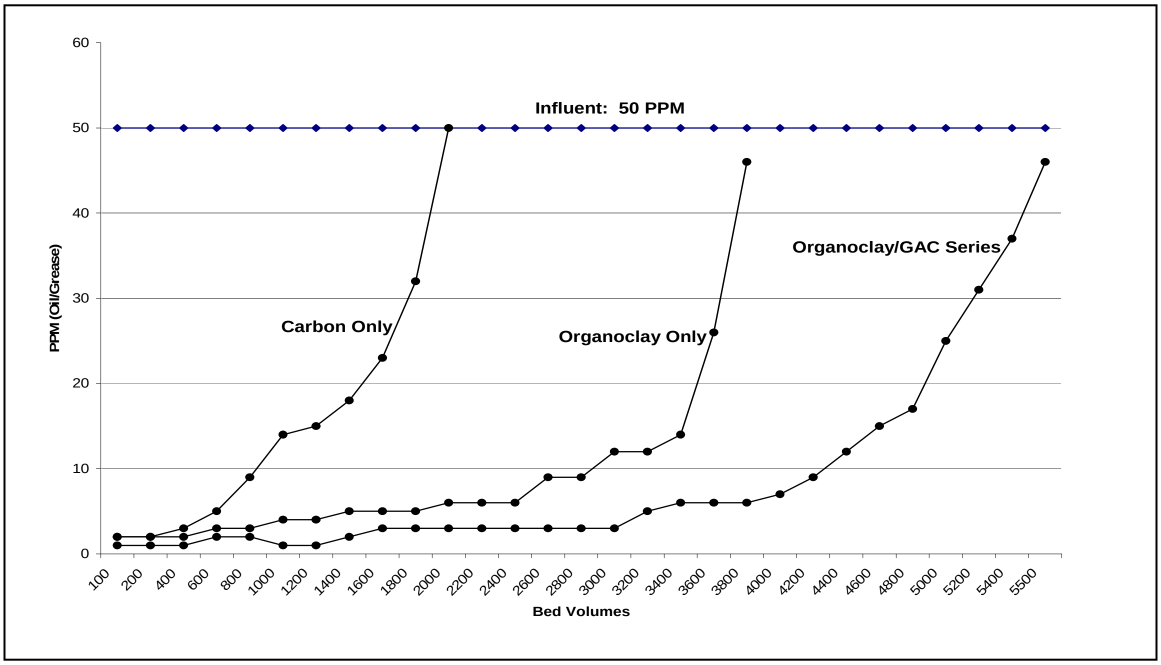


Figure 3. Efficiency of organoclay and organoclay/GAC in sequence over when treating oil, grease and similar high molecular weight organic compounds (Darlington, et.al.)

Case Study: Utilizing Organoclay For PCB Removal

A Superfund Site located in the Northeast United States was previously used for reclaiming and re-refining waste oils from 1945 – 1985, resulting in the presence of PCB's in seven lagoons containing over nine million gallons of water and oil. Due to heavy rains, the lagoons filled frequently, and several emergency removal actions were implemented to drain and treat the water and oil.

The primary treatment system consisted of an oil/water separator to remove free oil, a mix tank where the pH was adjusted with caustic soda and alum, and three clarifiers to settle out solids.

The clarified water was then passed through a sand filter prior being
passed through a column containing organoclay, finally followed by activated carbon polishing. The system operated at approximately 200 gpm. The influent water from the lagoons contained >1,000 mg/l of oil and grease, 1 to 6 mg/l volatile organics, 1 to 10 mg/l of heavy metals, and 100 mg/l of suspended solids.

The most expensive expendable material in the treatment system was the activated carbon and the costs associated with frequent change outs. By utilizing organoclay as a pre-treatment step to the GAC, the operating firm was able to significantly extend the lifetime of the material, resulting in a reduction of overall cost while maintaining effluent quality.

Permeable Reactive Barriers (PRB)

A permeable Reactive Barrier (PRB) is a reactive wall or trench constructed below grade to intercept and remediate contaminated groundwater (figure 4). This trench is filled with reactive media that sequesters pollutants migrating with the natural flow of the groundwater. Once backfilled with the selected media, the trench is then covered with native soils, plants and the area is returned to its natural state. Contaminants are contained within this treatment zone, mitigating the threat of down gradient contamination.

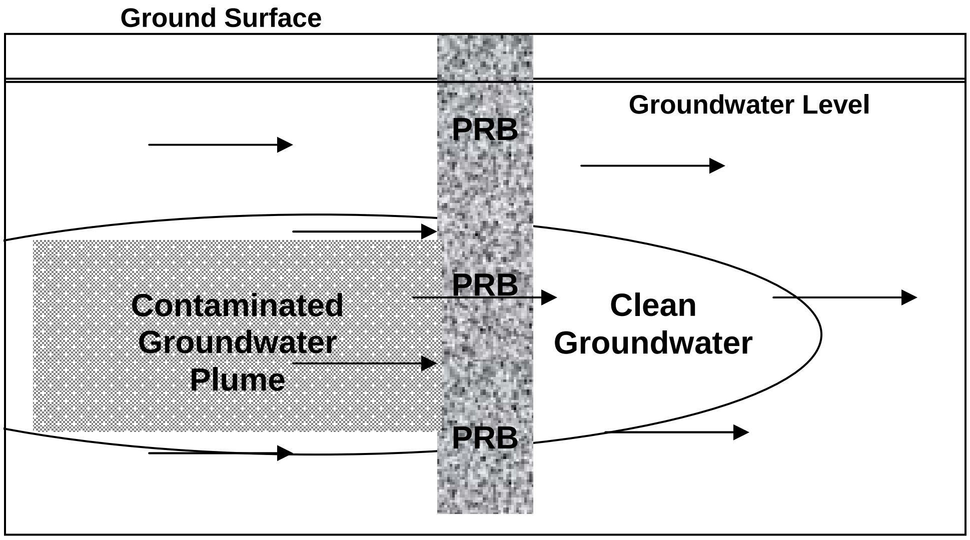


Figure 4. Permeable Reactive Barrier Configuration.

While some PRBs have been designed with selected media to precipitate heavy metals, the majority focus on applications which involve organic matter as the primary contaminant of concern. For example, zero valent iron is commonly used to remove solvents and similar chlorinated volatile organic compounds. This media acts a catalyst to breakdown the organic molecules through a chemical reaction called reductive dechlorination.

Because of their lower operating costs and ease of installation, PRBs are quickly gaining popularity as a viable option for many environmental remediation projects. As interest grows in this technology, so too will interest in the different types of reactive media which can be utilized. Organoclay has become an attractive alternative for these applications due its high adsorption capacity and its ability to remove a wide range of organic compounds. (Hornaday, et.al.).

Case Study: Utilizing Organoclay to remove non-aqueous phase liquids (NAPL)
Groundwater at a former creosote wood treatment site was contaminated with non-aqueous phase liquids (NAPL). The plume was migrating into a nearby fresh water bay and creating a sheen on the surface water, threatening local aquatic life and spreading toward open water.

It was determined that the best solution to stop further spreading was to install a PRB wall up-gradient of the beach head. Because of the low solubility of the contaminants of concern, Organoclay was selected due to its high capacity for these types of constituents.
Organoclay was mixed with 3 parts of pea gravel to maintain the desired hydraulic conductivity and optimal sorption capacity of the barrier. Visual observations showed that the sheen

completely dissipated soon after the PRB system was brought on line. Further field observations at the site confirmed no detrimental effects on the groundwater flow.

Sub Aqueous capping of contaminated sediments

Environmental remediation techniques have adapted to meet the demands of the growing brownfield redevelopment market, resulting in technological advances offering more cost effective alternatives for remediation of contaminated soils and sediments at these prospective sites.

The proper management of PCB and PAH contaminated sediments has proven to be a wide-spread, complex, and costly issue, and there are few viable cost-effective technologies to manage contaminated sediments (Lowry, et. al.). While dredging has traditionally been the preferred method of treatment, it requires deployment of heavy equipment and often has high costs associated with operations and solids disposal. Furthermore, contaminants may be mobilized during this process and potentially be dispersed over a larger area.

In-situ capping of contaminated sediments has long been considered an effective and economically viable alternative to dredging operations. In-situ sediment caps are typically designed to take into consideration stabilization and physical isolation of the sediments as well as contaminant transport mechanisms (Palermo, et al.). This process involves isolating and immobilizing contaminants of concern in the sediment with a cap design often consisting of several layers of natural inert materials including native sediments, sand and aggregate. These designs sometime also include the addition of geotextile fabrics to maintain the separation of the layers.

Regulatory and public acceptance of in-situ sediment capping technology has sometimes been difficult because contaminants are not removed or destroyed, and because the ability of a sand cap to isolate contaminants for long time periods depends upon site hydrogeology (e.g. groundwater seepage) and is uncertain. (Lowry, et.al.) However, studies and field tests have shown that adding a reactive or sorbent layer into a sediment cap design will enhance the overall performance to overcome these concerns (5).

Recently a Reactive Core Mat™ system has been devised that encapsulates reactive materials within a geotextile composite that can be easily deployed as an in-situ capping material over sediments. RCMs are permeable, allowing the passage of water and gasses while retaining organic and inorganic contaminants. These products ensure exact placement of reactive media and increase the sorption capacity of the overall cap, thus allowing a reduction in overallcap thickness.

Case Study: Utilizing Organoclay in a RCM as an active capping component

The McCormick and Baxter site in Portland, Oregon was added to the EPA's National Priorities List in 1994. This site is a former wood treatment facility where groundwater contaminated with NAPL was migrating into the Willamette River. Creosote and PCP contained within sediments began to transport through the water column with the release of methane gas bubbles. As the methane dispersed into the atmosphere, the remaining organics were deposited onto the water surface in nearby bays and low lying areas. This resulted in a visible sheen on the water.

A sediment cap was constructed in 2004 to isolate contaminated sediments adjacent to and downstream from the site. A portion of this cap included two layers of RCM containing Organoclay as the reactive media. RCM was selected because of its ease of installation and high permeability, allowing gasses to pass through the barrier while selecting and adsorbing the NAPL within the mat.

While methane gas continues to release at this site, the sheen created by the organic contaminants has disappeared. The RCM was exhumed for evaluation in October, 2006 and core samples of mat and sediment were taken. Visual observations showed that while the bottom mat appeared to contain organic matter, the top mat appeared free of contaminants. Initial conclusions are that the RCM is effectively removing the NAPL and has adequate capacity to continue adsorbing contaminants transporting through the sediment.

CONCLUSION

Organoclay is a high-efficiency media for the adsorption of low solubility organic compounds. The unique sorption mechanism and high surface area of this specialty media allow it to adsorb up to 60% of its own weight. While originally designed as a flow through media to offer a more effective alternative to GAC for removing oil, grease and other high molecular weight organics from water, this product has been adapted for use in sediment, groundwater and soils applications.

REFERENCES

(1) Newman, A.C.C., Mineralogical Society Monograph No. 6, *Chemistry of Clay Minerals*. John Wiley and Sons, New York (1987)

(2) McCrodden, B.A. *Treatment of Refinery Wastewater Using a Filtration Activated Carbon System*, NTIS Rep. No. PB-295 (1979)

(3) Cowen, C.T., and White, D. Adsorption *by Organoclay Complexes, I, Proceedings of the 9th National Clay Conference*, Pergamon Press, New York

(4) Freeman, H.M. *Standard Handbook of Hazardous Waste Treatment and Disposal.* McGraw Hill, New York (1989)

(5) Reible, D., Constant, D.W., Roberts, K., Zhu, Y., *Active Capping Demonstration Project In Anacostia DC*, Hazardous Substance Research Centers (HSRC), (2003)