Organoclays Trap PNAHs and Creosote in Permeable Barriers

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ABSTRACT: Permeable barriers at creosote containing sediments near wood treating plants, require a barrier which is permeable and, at the same time, traps creosote plumes which contain such organic hydrocarbons as PCP and other chlorinated phenolic compounds. Lab tests and actual field applications have shown that organically modified clays are an excellent medium to trap such compounds.

PNAHs are found in sediments at old MGP sites. These compounds include naphthalene, pyrene, fluorine, athrazene and others. Organoclays are very well suited to trap these compounds. PCB's are also retained very efficiently.

INTRODUCTION

Permeable barriers at creosote and PNAH containing sediments, require a barrier, which is permeable, and, at the same time, traps creosote and PNAH plumes. Such plumes can also include such organic hydrocarbons as PCP and other chlorinated phenolic compounds, PCB's and BTEX's. Lab tests and actual field applications have shown that organically modified clays are an excellent medium to trap such compounds in groundwater and in sediments at old MPG sites.

The PNAH compounds include naphthalene, pyrene, fluorine, anthrazene and others. Organoclays are very well suited to trap these compounds efficiently. Since pesticides are also a serious problem for groundwater and sediments, a brief literature review is included. This article reports on various laboratory tests and actual field results, which have been obtained over the years, showing the suitability of organoclays as a component of permeable barriers.

WHAT IS AN ORGANOCLAY?

Organoclays have become an important part of the treatment train to remove creosote and PNAH from contaminated groundwater at old wood treating facilities and MGP sites. Organoclays consist of bentonite that is modified with quaternary amines. Bentonite is a volcanic rock whose main constituent is the clay mineral montmorillonite. This gives the bentonite an ion exchange capacity of 70-90 meq/gram. By exchanging the nitrogen end of a quaternary amine onto the surface of the clay platelets, by cation exchange (Exchanging the sodium or calcium ion on the surface for the nitrogen which is positively charged), the bentonite now becomes organically modified and thus organophilic, which also means hydrophobic (Lagaly, 1984). The clay is arranged in a layered structure, platelets stacked on top of each other. When these platelets are placed into water, the amine chains are activated and stand up like dry hair, causing pillaring of the platelets, and allowing the end of the amine chains to stand or dangle into the water, reacting with organics that pass by (Mortland et al, 1986). The chains will then dissolve or partition into large organic compounds such as sparingly soluble chlorinated hydrocarbons. Oil is the most prominent of these (Smith et al, 1990). These same compounds, on the other hand, will blind the pores of activated carbon.

CASE HISTORY FROM CLEANING A SUMP SLUDGE.

A sump sludge contained a wastewater that required cleaning before it could be discharged. The water was passed through 300 lb of organoclay/anthracite and then discharged. The results are:

Contaminant	Inlet	Outlet	Solubility Mg/l
TOC	29%	65 mg/kg	
Oil	12 mg/kg	1 mg/l	
BOD	429 mg/kg	120 mg/kg	
COD	16,084 mg/l	202 mg/l	
Anthrazene	2,000 mg/kg	<10 mg/l	0.073
Benzo (A) Anthrazene	5,300	<10	0.014
Fluorene	10,000	<10	1.98
Indeno (1,2,3,C,D) Pyrene	200	<25	0.62
Naphtalene	29,000	< 10	34.4
Phenantrene	40,000	< 10	1.29
Pyrene	8,000	< 10	0.14
TPH	172,000	< 0.5 mg/l	

No change out of organoclay was required. The adsorber ran at 5 gpm.

Laboratory Test Results with 1,4 Dioxane. A batch test was conducted to determine the ability of a non-ionic organoclay to remove 1,4 dioxane from water. The testing method was:

Sorbent, 1,4 dioxane solution, and organic free, deionized (DI) water where combined in 10 ml glass tubes. The initial concentration of the contaminants was between 300-500 mg/l. The mass of sorbent used was between 0.5 and 1 grams. Tubes carrying the diluted contaminant, but no sorbent, where carried through the test and analyzed to determine losses due to reasons other than sorption to the sorbent. No significant losses where measured, and recovery in all tubes was determined to be greater than 95%. Tubes containing DI water and sorbent where carried through the test and analyzed to determine the possible presence of the contaminant on the sorbent. For each contaminant, negligible amounts where detected. The tubes where capped and shaken for one day at 23 degrees +/- C . After equilibration, the tubes where centrifuged at 2000 g and the supernatant was analyzed by gas chromatography with a flame ionized detector to quantify the concentration of the organic solute. The sorbed concentration of each solute was determined by difference assuming negligible losses of the solute. The results are:

Water was spiked with 958 mg/l 1,4 dioxane acqueous equilibrium concentration. The mass sorbed by 2 grams organoclay was 27.09 mg/l, or 2.709% of the organoclays weight. These results confirm the ability of non-polar organoclays to remove chlorinated organic hydrocarbons from water.

Laboratory Test Result with Two Nitrobenzenes. Nitro aromatic compounds are used by industry in pesticides, explosives, solvents, and intermediates in chemical synthesis (Boyd et al, 2001). These contaminants appear in soils and sediments and can be toxic to humans and animals. The ability of a powdered, non-polar organoclay to remove substituted nitrobenzenes from water was tested in the lab with the same method as 1,4 dioxane. The compounds tested for are 1,3-Dinitrobenzene and 1,3,5-Trinitrobenzene. The same testing method was used as for 1,4 dioxane (see above). The results are;

	Equilibrium Aqueous Concentration(mg/l)	**Mass Sorbed (mg/l)**	**% by Weight**
1,3-Dinitrobenzene	157.7	6.4	0.644
1,3,5-Trinitrobenzene	38.3	12.0	1.201

These results show that a regular organoclay can be used to fixate substituted nitrobenzene compounds, thus it is a viable component of permeable barriers.

Case History for Federal Creosote Superfund Site. The groundwater at this site showed the following data:

COD influent: 68 ppm, primarily PCP and other phenols.
10-20 ppm benzene.
COD effluent after organoclay tank: 19.5 ppm
After lead Granular activated carbon tank: Non detect.

TSS readings where 35 ppm after the lead carbon unit. When organoclay was included, the effluent after organoclay was 3 ppm. TSS where primarily iron 3. Carbon removed all of the benzene.

Flow rate: 170 gpm
Organoclay used: 20,000 lb; activated carbon used: 40,000 lb.

Non-ionic organoclays removal capacity of phenolic compounds as determined by batch tests (Alther, 1997).

Concentration	**25ppm in Water**	**Solubility**
Phenol	78.2% of organoclay weight.	86 g/l
2,4,6 Trichlorophenol	98.3% of organoclay weight.	800 mg/l
3 Chlorophenol	89.8% of organoclay weight.	27.7 g/l
*Pentachlorophenol (PCP)	87% of organoclay weight.	80 mg/l

**This means that 100 grams of organoclay can remove 87 grams of PCP (Alther, 1997).*

Literature Review of the Ability of Organoclays to Remove Pesticides. A comprehensive analysis of pesticide removal by organoclays, from water, is found in Sanchez-Martin, et al, 2006. The following pesticides where studied:

Common Name	Chemical Formula	Water Solubility
Penconazole	1-[2-(2,4-dichlorophenyl)pentyl]-1,2,4-triazole	73
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	81
Atrazine	2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	30
Alachlor	2-chloro-2',6'-dietyl-N-methoxymethylacetanilide	240
Metalaxyl	methyl N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-DL-alanite	8400
Lindane		10 ppm

(From Sanchez-Martin, et al, 2006)

Comparing these solubilities with organic hydrocarbons of known affinity to organoclays, we surmise that the first 4 and Lindane will be easily removed. Excellent results where also reported by Hermosin and Cornejo (1992) for adsorption of 2,4-D pesticide (2,4-dichlorophenoxy acetic acid) by standard organoclays. Tests conducted in our laboratory revealed good removal capacity by non-ionic organoclay for alachlor, diazinin, metalochlor, trifuralin, and 2,4,5-T.

The authors of the pesticide article used a different organoclay, but the results when compared to the quaternary amine (octadecyltrimethylammonium bromide) used in this study will not be markedly different (di-methyl di-hydroginated tallow ammonium chloride). Those authors concluded that soils containing organoclays provide barriers, which drastically decrease the mobility of these pesticides.

The lab results obtained from a mini-column test are (Alther, 2004, 2002):

	Solubility	% By Organoclay Weight Removed
Benzene	1800 mg/l	39
Toluene	535	44
o-Xylene	insoluble	44
Naphthalene	34.4	24.3
PCB 1260	insoluble	52 % by clay weight

Other case histories showed excellent removal capacity of organoclay for trichloroethene (sol. 1100 mg/l), and 1,1,1-dichloroethene (sol. 335 mg/l).

Isotherms for Three Compounds, Conducted by the ASTM Isotherm Method.

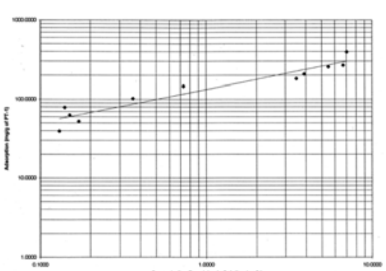

FIGURE 1. Organoclay Naphthalene Isotherm

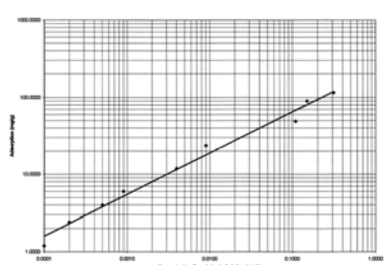

FIGURE 2. Organoclay Isotherm with PCB-1260 Adsorption = Concentration ^(0.5373441)*10^(2.352119)

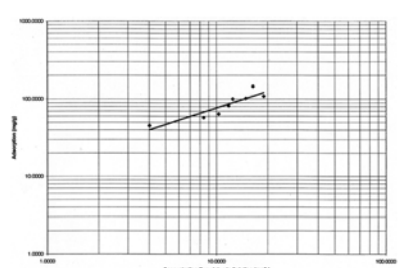

FIGURE 3. Organoclay Adsorption of Xylene (ortho) Adsorption = Concentration ^(0.708464989)*10^(1.178918)

CONCLUSIONS

These data show the ability of organoclays to remove or fixate a variety of recalcitrant compounds of low solubility from water and in soils. There is an industry in existence which manufactures and sells organoclays for such applications, with a successful track record of 20 years.

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