Group 1

Evaluation of an Organophilic Clay for Sorption of Dissolved Polycyclic Aromatic Hydrocarbon Compounds

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Background

For decades, active media have been successfully used to treat contaminated water and groundwater. In the past 15 years, contaminated sediment remediation projects have increasing utilized amendments for both capping and in-situ treatment. Per USEPA (2013), the appropriate use of these amendments for capping has the potential to limit contaminant exposure and reduce risk. Organophilic clays have been employed in sediment remediation as a means of absorbing coal tar, creosote or other nonaqueous phase liquids (NAPLs) in sediment caps serving as permeable absorptive barriers. Organophilic clays also sorbs dissolved phase organic contaminants, although less sorptive than activated carbon. But organophilic clays have the advantage that they show little tendency to foul or lose capacity in the presence of natural organic matter or non-targeted contaminants. In this study, the ability of Huesker, Inc. H-1 organophilic clay to sorb polynuclear aromatic hydrocarbons (PAHs) was investigated.

Test Material

Organophilic clay is a base clay (typically sodium bentonite) that undergoes an ion exchange process with a quaternary amine. This process changes the clay from hydrophilic to organophilic. Instead of absorbing water, the organo-clay absorbs both NAPL and dissolved organic compounds.

In order to determine whether sufficient ion exchange has occurred, it is critical to run manufacturing quality control tests on the organophilic clay. The lot of HUESKER H1 organophilic clay used in this study was first tested by the supplier. Two ASTM test methods were run for manufacturing quality control on the batch of organophilic clay.

ASTM D7626 is a set of *Standard Test Methods for Determining the Organic Treat Loading of Organophilic Clay*. This is a loss on ignition test that utilizes temperatures up to 750°C. The type of organophilic clay used in sediment remediation requires a minimum 25% organic treat loading. The lot of H1 organophilic clay had an organic treat loading of 32.4%.

ASTM D8106 is a set of *Standard Test Methods for Determining the Oil Sorption Capacity of Organophilic Clay*. This is an index test that uses an additive-free oil, either SAE 30 API SA grade motor oil or USP mineral oil with ISO 100 grade viscosity. Organophilic clay used in sediment remediation requires a minimum oil sorption capacity of 0.5 g oil/g organo-clay. The lot of H1 organophilic clay had an oil sorption capacity of 0.58 g oil/g organo-clay.

Batch Sorption Test Procedures

The water sorbent partitioning coefficient measurement was carried out in 250mL amber glass bottles with phenolic aluminum lined caps to minimize volatile loss during spiking. Amber bottles were filled with 250ml of artificial surface water which was prepared by mixing 350mg/L of instant ocean salt and 100mg/L of sodium azide (to inhibit bacterial degradation of the PAHs) to ultrapure water. The initial concentration of PAH was kept constant and the mass of the sorbent was varied (25mg-200mg) to get a range of 5 different final concentrations for the isotherm. Polydimethylsiloxane (PDMS)-coated fiber with a diameter of 2-cm was added to the amber bottle after cleaning it by soaking in hexane and acetone, then washing with de-ionized water and wiped clean with Kimwipes. Three replicates were prepared for each sorbent mass. Blanks with no sorbent and only initial PAH concentrations were also prepared as controls. The samples were left on a mechanical shaker for 21 days. After 21 days, the PDMS fiber was extracted, rinsed with de-ionized water and wiped clean with a Kimwipe to ensure that no sorbent was left clinging to the fiber's surface. The fiber was then immersed in 100µL of acetonitrile in a 2ml HPLC vial with a 250µL glass insert. Fibers were left immersed in solvent for at least 2 hours to ensure complete extraction. An Agilent 1260 HPLC with Fluorescence Detector was used to analyze the acetonitrile solution to measure the truly dissolved concentration of PAHs. The partition coefficient for five different water concentrations were measured.

The final PAH concentration on the PDMS (C_{PDMS}) was converted to water concentration (C_w, µg/L), with the PDMS-water partition coefficient using the equation below:

$$C_w = \frac{C_{PDMS}}{K_{PDMS}}$$

The PDMS water partition coefficient was estimated using the correlations of Ghosh et al. (2014). A material balance was used to estimate the mass of PAHs on the sorbent, and to estimate the partition coefficient at each concentration, as follows:

$$K_d = \frac{m_{PCB/PAH}}{C_w} = \frac{(m_o - C_w * V_w - C_{PDMS} * V_{PDMS})}{m_s * C_w}$$

where;

$m_{(PCB/PAH)}$ = the amount of PAH sorbed to solid phase with units of mass of contaminant per mass of sorbent.

V_w = Volume of water, and

V_{PDMS} = Volume of PDMS fiber.

Results

The best-fit partition coefficient between the organophilic clay and water was estimated from the slope of the least squares fitted curve of water concentration versus sorbed amount.. Figure 1 shows the plotted sorbed versus final water concentration.

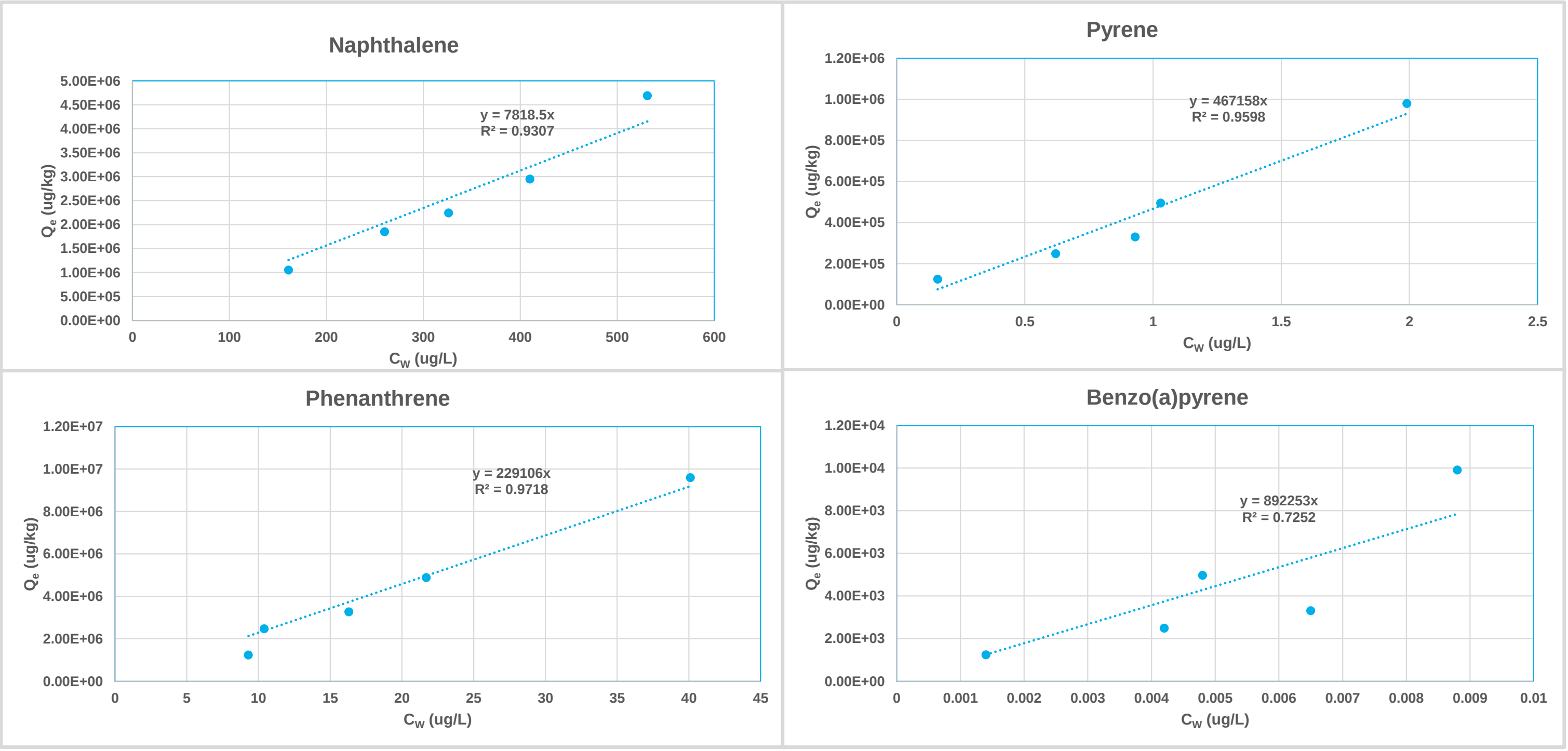

Figure 1. PAH isotherms of sorbed quantity versus concentration

As shown in Figure 1, the sorbed concentration is linear with the final concentration in the water. This is typically observed with contaminants on organophilic clays and suggests that the mechanism of sorption is absorption rather than a surface area related adsorption as is observed with activated carbon. As is also typical of absorption like phenomena, there is no observable competition effect with approximately the same partition coefficient being observed at low concentrations of co-contaminants as well as at higher concentrations (up to approximately 500 µg/L in naphthalene). For BaP, there is more variation around the best-fit linear curve possibly due to kinetic effects leading to only partial equilibration for the highly hydrophobic compound.

The H1 organophilic clay-water partition coefficient results are summarized and compared to the octanol-water partition coefficient in Table 1.

	K_d (L/kg)	Std Error	R^2	Log K_d	Log K_{Ow}
Naphthalene	**7,820**	449	0.93	**3.89**	3.41
Phenanthrene	**229,000**	10,700	0.97	**5.36**	4.74
Pyrene	**467,000**	26,400	0.96	**5.67**	5.25
Benzo(a)pyrene	**890,000**	138,000	0.72	**5.95**	6 to 6.54

Table 1. Estimated partition coefficients and standard error for each PAH.

Also included in Table 1 are the standard errors in the partition coefficient for each of the compounds in Figure 1 and the R^2. The organophilic clay-water partition coefficient data can also be correlated with the octanol-water partition coefficients of the PAH compounds.

Conclusion

Sorption of four PAH compounds; naphthalene (NAP), phenanthrene (PHE), pyrene (PYR) and benzo[a]pyrene (BaP), onto HUESKER H1 organo-clay were used to determine a correlation between dissolved contaminant sorption capacity of the organo-clay and the octanol-water partition coefficient, K_{ow}, of the PAH. The measured organophilic clay-water partition coefficient, K_d, for NAP, PHE and PYR averaged 2.8 times the octanol-water partition coefficient of the compound or **$\text{Log}K_d = 1.11 * \text{Log}K_{ow}$** ($R^2 = 0.97$). BaP deviated from this relationship although this may simply be due to lack of achievement of equilibrium in the short-term sorption tests due to slow sorption of this highly hydrophobic compound or uncertainty in Log K_{ow} of BaP which has values reported between 6.0 and 6.54 (SPARC estimate). With BaP, the best fit relationship between K_d and K_{ow} is given by **$\text{Log}K_d = 1.03 * \text{Log } K_{ow}$** ($R^2$=0.6) using the SPARC estimate of K_{ow} = 6.54 and **$\text{Log}K_d = 1.07 * \text{Log}K_{ow}$** ($R^2 = 0.85$) using $\text{Log}K_{ow} = 6$. These K_d values can be inserted into the CapSim model.

References

ASTM D7626, Standard Test Methods for Determining the Organic Treat Loading of Organophilic Clay, ASTM International, West Conshohocken, PA.

ASTM D8106, Standard Test Methods for Determining the Oil Sorption Capacity of Organophilic Clay, ASTM International, West Conshohocken, PA.

Ghosh, et al. 2014. **"**Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation", *Journal of Integrated Environmental Assessment and Management,* SETAC.

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