EVALUATION OF SORPTIVE AMMENDMENTS FOR USE IN EARTHEN LANDFILL LINERS

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ABSTRACT

Four materials with high sorptive capacities for organic compounds (granular activated carbon (GAC), shale, benzyltriethylammonium-bentonite, and hexadecyltrimethylammonium-bentonite) were evaluated for their use in compacted clay landfill liners by conducting laboratory sorption and permeability experiments with a 0.002 N $CaSO_4$ solution (to simulate the ionic strength of ground water). Results from equilibrium sorption experiments with 0.002 N $CaSO_4$ indicate that all four amendments have a very high sorptive capacity for the three organic solutes tested: benzene, trichloroethylene, and 1,2-dichlorobenzene. GAC exhibited the highest sorptive capacity for all three solutes, followed by BTEA-bentonite, HDTMA-bentonite and shale. Permeability tests conducted on specimens composed of Ottawa sand, untreated bentonite and either 3% or 9% amendment by weight were also performed. Results indicate that all amended specimens had a hydraulic conductivity less than or equal to 1×10^{-7} cm/s, with the exception of the specimen amended with 3% GAC, which had a measured conductivity value of 2×10^{-7} cm/s.

RÉSUMÉ

Quatre matériaux ayant des capacités sorbantes élevées pour les composés organiques (charbon actif granulaire (GAC), schiste, benzyltriethylammonium-bentonite, et hexadecyltrimethylammonium-bentonite) ont été évalués pour leur usage dans les recouvrements compacts d'argile (pour des centres d'enfouissement des déchets) en entreprenant des expériences de sorption et de perméabilité de laboratoire avec une 0.002 N solution de CacSo4 (pour simuler la concentration ionique des eaux souterraines). Les résultats des expériences de sorption d'équilibre avec 0.002 N CacSo4 indiquent que chacun des quatre amendements a une capacité sorbante très élevée pour les trois corps dissous organiques examinés : benzène, trichloréthylène, et 1,2-dichlorobenzene. GAC a montré la capacité sorbante la plus élevée pour chacun des trois, suivie du BTEA-bentonite, du HDTMA-bentonite et du schiste. Des essais de perméabilité effectués sur des spécimens composés de sable d'Ottawa, bentonite non traité et amendement de 3% ou de 9% en poids ont été également réalisés. Les résultats indiquent que tous les spécimens modifiés ont eu une conductivité inférieur ou égal à un 1×10^{-7} hydrauliques cm/s, excepté le spécimen modifié avec 3% GAC, qui a eu une valeur mesurée de conductivité de 2×10^{-7} cm/s.

1. INTRODUCTION

Leachates from municipal solid waste (MSW) and hazardous waste disposal facilities have been found to contain a wide range of potential environmental contaminants, including volatile organic compounds. A recent U.S. Environmental Protection Agency (EPA) report characterizing landfill leachates from over 200 MSW landfills found organic compounds such as benzene, toluene, ethylbenzene and methylene chloride in over 50% of the leachate samples tested (U.S. EPA 2000). In order to protect underlying ground-water resources from these and other pollutants, waste disposal sites are commonly lined with clay and geomembrane composite liners. For the most part, design of these liner systems has focused on minimizing the flow rate of leachate through the liner. However, even with hydraulic conductivities less than 10^{-7} cm/s, the mass flux of many organic pollutants across earthen and intact geomembrane liners by diffusion can be significant (Shackelford 1991; Mott and Weber 1992; Park and Nibras 1993; Gullick 1998). An additional contribution to pollutant mass flux across landfill liners is made as a result of regularly occurring defects in geomembranes, either within the geomembrane itself, or within the seams between geomembrane sections.

Due to the inability of composite landfill liners to impede diffusive transport, enhancement of the sorption capacity of earthen liner materials should be considered as a means to improve liner performance. The magnitude of organic pollutant sorption to natural soils and clays is related to the organic solute's aqueous solubility and the organic-carbon content of the sorbent (Smith 1988; DiCesare and Smith 1994; Chiou 1998). Because natural soils and clays typically have organic-carbon contents less than 0.5%, pollutants such as chlorinated solvents and gasoline-range hydrocarbons (with solubilities greater than a few mg/L) do not sorb appreciably. By contrast, strongly hydrophobic organic contaminants (e.g. polychlorinated biphenyls, polycyclic aromatic hydrocarbons, etc.) and many heavy metals bind strongly to natural soils and clays.

A method of enhancing organic pollutant sorption and thus minimizing the flux of leachate pollutants through earthen liners is to amend the liners with materials capable of strongly sorbing organic pollutants. Several proposed amendments include organophilic bentonites, activated carbon, and shale (Bierck and Chang 1994; Smith and Jaffé 1994; Gullick and Weber 2001). In some cases, sorption capacities are 4 or 5 orders of magnitude greater for these materials than for natural soils and clays. Increasing the sorption capacity of the earthen liner effectively reduces the pollutant advection velocity and the rate of solute diffusion during transient solute transport without requiring an increase in liner thickness. Although a sorbed pollutant will eventually desorb from the liner, the mass flux from the bottom of the liner should be significantly reduced when an organobentonite, shale, or activated carbon is a component of the liner. In order to evaluate the potential effectiveness of sorptive materials as amendments to clay liners, sorption and permeability testing was performed on four materials: benzyltriethylammonium-bentonite (BTEA-bentonite), hexadecyltrimethylammonium-bentonite (HDTMA-bentonite), shale, and granular activated carbon.

2. METHODS AND MATERIALS

2.1 Sorptive Materials and Solutes

The two organoclays evaluated for potential use in liner systems were hexadecyltrimethylammonium-bentonite (HDTMA-bentonite) and benzyltriethylammonium-bentonite (BTEA-bentonite). The HDTMA-bentonite was synthesized at an organic cation loading corresponding to 80% of the cation-exchange capacity of the base bentonite while the BTEA-bentonite was synthesized with a loading corresponding to 50% of the cation-exchange capacity. These percentages have been shown to result in the maximum sorptive capacity for a number of volatile organic compounds (Bartelt-Hunt et al. 2003). Details concerning the method used to synthesize the organoclays have been described previously (Bartelt-Hunt et al. 2003). The GAC used in this study was a granular reactivated carbon (GAC-840R) obtained from American Norit, Inc. with a mesh size of 8x40 and was used as received. The shale used in this study was carbonaceous shale obtained from Ward's Geology. The shale was ground and the portion passing a number 40 sieve was used in experimental testing.

Conventional liners materials were represented in this study by untreated bentonite and Ottawa sand. The bentonite clay was composed of 3.6% sand, 7.3% silt, and 89.1% clay. The exchangeable inorganic cation on the base bentonite clay was primarily sodium. The Ottawa sand (Grade F-25) was obtained from U.S. Silica Company and was used as received.

Sorption testing was performed for three relatively water-soluble organic pollutants: trichloroethylene (TCE), 1,2-dichlorobenzene (1,2-DCB), and benzene. These solutes were chosen because they are common ground-water pollutants and their solubilities make them relatively mobile in natural porous media.

Table 1. Composite soil samples used in permeability testing.

Sample	Ottawa Sand (percent)	Bentonite (percent)	Amendment type and percent
1	90	10	None
2	87	10	3% GAC
3	81	10	9% GAC
4	87	10	3% HDTMA-bentonite
5	81	10	9% HDTMA-bentonite
6	87	10	3% BTEA-bentonite
7	81	10	9% BTEA-bentonite
8	87	10	3% Shale
9	81	10	9% Shale

2.2 Sorption Isotherms

Sorption of TCE, 1,2-dichlorobenzene, and benzene to the four proposed amendments was quantified using a conventional batch equilibration technique that has been described previously (Smith and Jaffé 1994; Smith and Galan 1995).

Kinetic sorption experiments were performed to determine the time required for the three proposed solutes to reach equilibrium with the shale and activated carbon. 24 h is considered to be a sufficient time for the two organobentonites to reach equilibrium (Deitsch et al., 1998). Results of kinetic testing indicated that sorption to GAC reaches equilibrium in 24 hrs, with the majority of uptake occurring in the first 30 minutes. Equilibrium sorption to shale was determined to have occurred after 48 hrs of solute-sorbent contact.

2.3 Permeability Testing

Permeability tests were performed on specimens composed of Ottawa sand, untreated bentonite, and sorptive amendment at different weight percentages with a 0.002 N $CaSO_4$ solution. Permeability testing was also done on a core composed of Ottawa sand and untreated bentonite, which were used to represent conventional clay liner materials. Composition of all of the nine specimens tested is given in Table 1. The permeability of compacted soil specimens was measured with a changing-head permeability test using flexible-wall permeameters according to ASTM D5084.

3. RESULTS AND DISCUSSION

3.1 Equilibrium Sorption Isotherms

Results from sorption experiments with benzene, TCE, and 1,2-DCB as the solutes and 0.002 N $CaSO_4$ as the solvent phase can been seen in Figures 1-3. Recovery in all isotherm experiments was greater than 95%. In general, GAC had the highest sorptive capacity for all

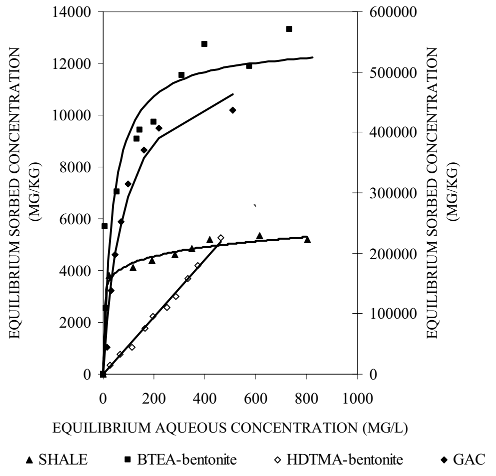

Figure 1. Equilibrium sorption isotherms for benzene for all four sorbents with 0.002 N $CaSO_4$ as the solvent phase. GAC data should be read using the secondary y-axis. Lines represent isotherm model fits.

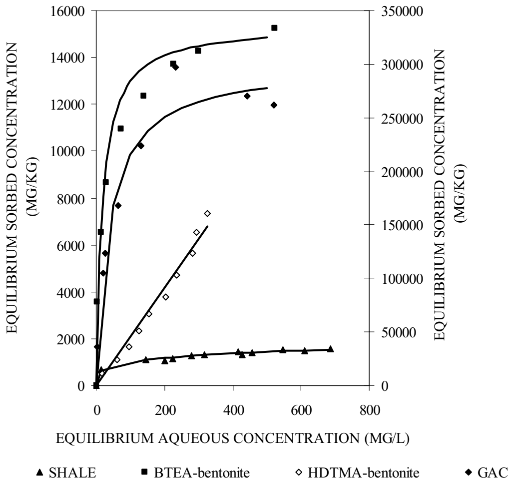

Figure 2. Equilibrium sorption isotherms for TCE for all four sorbents with 0.002 N $CaSO_4$ as the solvent phase. GAC data should be read using the secondary y-axis. Lines represent isotherm model fits.

solutes, followed by BTEA-bentonite, HDTMA-bentonite, and shale.

The mechanisms of sorption to each of the proposed amendments vary. Sorption to activated carbon is generally thought to occur by a physical adsorption process and is characterized by competitive, non-linear isotherms (Manes 1998). In this study, organic solute sorption to GAC was non-linear. Sorption of all three solutes to BTEA-bentonite was also non-linear. Previous research has shown that when an organoclay

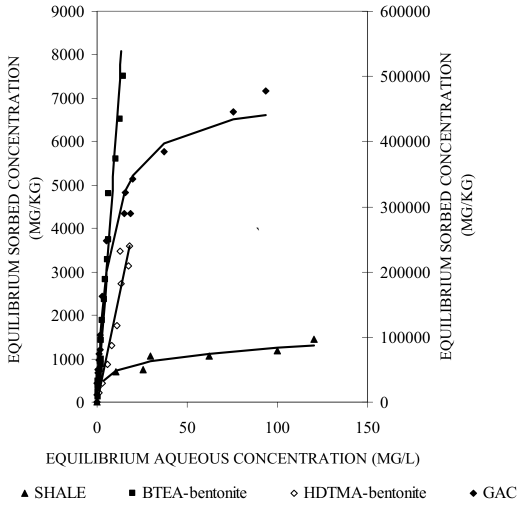

Figure 3. Equilibrium sorption isotherms for 1,2-DCB for all four sorbents with 0.002 N $CaSO_4$ as the solvent phase. GAC data should be read using the secondary y-axis. Lines represent isotherm model fits.

has an exchanged quaternary ammonium cation with benzyl, phenyl, and/or relatively short-chain alkyl functional groups (ethyl or methyl functional groups), sorption is characterized by competitive, nonlinear isotherms with no clear solubility dependence (Smith et al. 1990). Based on these observations, the mechanism of sorption has been attributed to a physical adsorption process.

Uptake of benzene and TCE by HDTMA-bentonite was linear. Isotherm data for sorption of 1,2-dichlorobenzene to HDTMA-bentonite were slightly concave up. All HDTMA-bentonite isotherms were linear or slightly concave up, supporting the theory that sorption to clays modified with cations with long alkyl chains like HDTMA occurs primarily by a partition process between the aqueous solution and the organic medium created by the alkyl chains (Smith et al. 1990). The slight upward concavity observed in some of the HDTMA-bentonite isotherm data has been observed by previous researchers and has been attributed to the formation of a discrete solute phase on the surface of the clay (Jaynes and Boyd 1991).

Sorption of benzene, TCE and 1,2-DCB to all amendments was much greater than for conventional liner materials. Sorption isotherms for the untreated bentonite and Ottawa sand had a slope of zero – indicating no measurable sorption occurred to these materials.

3.2 Permeability Testing

Results from permeability tests with 0.002 N $CaSO_4$ as the permeant fluid are given in Table 2. All amended specimens met or exceeded the hydraulic conductivity requirement of $1x10^{-7}$ cm/s stipulated by the U.S. EPA for materials used in landfill liners, with the exception of the specimen amended with 3% GAC which had a

Table 2. Results from permeability experiments with 0.002 N $CaSO_4$ as the permeant fluid.

Amendment Type	**Hydraulic Conductivity (cm/s)**		**Bulk Density (g/cm^3)**		**Dry Bulk Density (g/cm^3)**		**Porosity**		**Number of Replicates**
	ave.	std error	ave.	std error	ave.	std error	ave.	std error	
no amendment	$1x10^{-7}$	$2x10^{-8}$	2.20	0.02	1.73	0.01	0.47	0.01	5
3% GAC	$2x10^{-7}$	$8x10^{-8}$	2.09	0.01	1.62	0.01	0.48	0.01	3
9% GAC	$1x10^{-7}$	$7x10^{-8}$	2.15	0.07	1.62	0.05	0.53	0.02	3
3% HDTMA-bentonite	$4x10^{-8}$	$1x10^{-8}$	2.37	0.05	1.86	0.04	0.50	0.02	3
9% HDTMA-bentonite	$7x10^{-8}$	$3x10^{-8}$	2.13	0.01	1.74	0.01	0.39	0.01	3
3% BTEA-bentonite	$1x10^{-8}$	$2x10^{-9}$	2.15	0.03	1.76	0.01	0.40	0.01	3
9% BTEA-bentonite	$1x10^{-8}$	$2x10^{-9}$	2.13	0.01	1.74	0.01	0.38	0.01	3
3% shale	$2x10^{-8}$	$4x10^{-9}$	2.20	0.01	1.79	0.01	0.41	0.01	3
9% shale	$3x10^{-9}$	$8x10^{-10}$	2.14	0.02	1.76	0.01	0.37	0.01	3

measured conductivity of $2x10^{-7}$ cm/s. The specimens amended with shale had the lowest conductivity, followed by specimens amended with BTEA-bentonite and HDTMA-bentonite. Specimens amended with GAC had the highest and most variable conductivity. The total porosity of the specimens ranged from 0.37 to 0.53, and a general decrease in porosity was observed between the 3% and 9% amendment levels for all four amendments. An exception occurred for specimens amended with GAC, which had a measured porosity of 0.48 at the 3% amendment level and 0.53 at the 9% amendment level. This increase in porosity may be due to the high internal porosity of the GAC, resulting in a greater overall porosity for specimens composed of a larger weight percentage of this material.

Analysis of the permeability testing results conducted with 0.002 N $CaSO_4$ indicate that the incorporation of GAC, shale, or organoclay amendments will have no adverse effect on the overall permeability of compacted clay liners below landfills, and in fact, may actually serve to decrease the permeability of a liner system. The decrease in permeability associated with the amendments is due to the fact that the amendments have finer particle-size distributions than the Ottawa sand they replace.

4. CONCLUSIONS

The measured sorption capacity of all amendments was greater than for conventional soil materials (Ottawa sand and untreated bentonite clay). For all three solutes, GAC exhibited the highest sorptive capacity, followed by BTEA-bentonite, HDTMA-bentonite and then shale. Hydraulic conductivity of specimens amended with either 3% or 9% amendment by weight met or surpassed regulatory requirements of 1 x 10^{-7} cm/s, with the exception of 3% GAC, which had a measured K value of 2 x 10^{-7} cm/s. This study suggests that sorptive amendments may be useful additives to conventional earthen liners to reduce the rate of pollutant transport through the liner.

5. ACKNOWLEGEMENTS

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6. REFERENCES

Bartelt-Hunt, S.L., Burns, S.E. and Smith, J.A. 2003. “Sorption of nonionic organic solutes to two organobentonites as a function of organic-carbon content.” Journal of Colloid and Interface Science, v. 266, pp. 251-258.

Bierck, B.R. and Chang, W.C. 1994. “Innovative solutions for contaminated waste site management.” Water Environmental Federation Specialty Conference, Miami, FL, pp. 461-472.

Chiou, C.T. 1998. “Soil sorption of organic pollutants and pesticides.” Encyclopedia of environmental analysis and remediation. John Wiley and Sons, New York, pp. 4517-4554.

Deitsch, J.J., Smith, J.A., Arnold, M.B. and Bolus, J. 1998. “Sorption and desorption rates of carbon tetrachloride and 1,2-dichlorobenzene to three organobentonites and a natural peat soil." Environmental Science and Technology, v. 32, pp. 3169-3177.

DiCesare, D., and Smith, J.A. 1994. "Effects of surfactants on the desorption rate on nonionic organic compounds from soil to water." Reviews of Environmental Contamination and Toxicology, v. 134, pp. 1-29.

Gullick, R.W. 1998. "Effects of sorbent addition on the transport of inorganic and organic chemicals in soil-bentonite cutoff wall containment barriers." Doctoral Dissertation. University of Michigan, Ann Arbor, MI.

Gullick, R.W. and Weber, W.J. 2001. "Evaluation of shale and organoclays as sorbent additives for low-permeability soil containment barriers." Environmental Science and Technology, v. 35, pp. 1523-1530.

Jaynes, W.F. and Boyd, S.A. 1991. "Clay mineral type and organic compound sorption by hexadecyltrimethyl-ammonium-exchanged clays." Soil Science Society of American Journal, v. 55, pp. 43-48.

Manes, M. 1998. "Activated carbon adsorption fundamentals." Encyclopedia of environmental analysis and remediation, John Wiley and Sons, New York, pp. 26-68.

Mott, H.V. and Weber, W.J. 1992. "Sorption of low molecular weight organic contaminants by fly ash: considerations for the enhancement of cutoff barrier performance." Environmental Science and Technology, v. 26, pp. 1234-1242.

Park, J.K. and Nibras, M. 1993. "Mass flux of organic chemicals through polyethylene geomembranes." Water Environment Research, v. 65, pp. 227-237.

Shackelford, C.D. 1991. "Laboratory diffusion testing for waste disposal – a review." Journal of Contaminant Hydrology, v. 7, pp. 177-217.

Smith, J.A., Witkowski, P.J. and Chiou, C.T. 1988. "Partition of nonionic organic compounds in aquatic systems." Reviews of Environmental Contamination and Toxicology, v. 39, pp. 465-473.

Smith, J.A. and Jaffé, P.R. 1994. "Benzene transport through landfill liners containing organophillic bentonite." Journal of Environmental Engineering, v. 120, pp. 1559-1577.

Smith, J.A., P.R. Jaffé and Chiou, C.T. 1990. "Effect of ten quaternary ammonium Cations on tetrachloro-methane sorption to clay from water." Environmental Science and Technology, v. 24, pp. 1167-1172.

Smith, J.A. and Galan, A. 1995. "Sorption of nonionic organic contaminants to single and dual organic cation bentonites from water." Environmental Science and Technology, v. 29, pp. 685-692.

U.S. Environmental Protection Agency 2000. "Evaluation and characterization of landfill leachates." Draft report submitted by Science Applications International Corporation, Reston, VA.