USING ORGANO-SILICATE NANOCOMPOSITES FOR AQUEOUS LEAD SPECIES REMOVAL

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INTRODUCTION

Methods to reduce, control or eliminate the impact of soluble lead discharges from small arms range berms to the environment are varied and complex (1). Methods utilized to date include four fundamental processes: physical separation, erosion control, soil modifications and phyto-remediation. Physical separation techniques have been used by the chemical and mining industry for many years, while the others have been employed in varying situations and conditions. Generally these methods are expensive and time consuming to accomplish (2). With a reported 2,600 small arms ranges in use nation-wide the U.S. military would likely welcome innovative technologies to stabilize or adsorb aqueous lead run off.

The science of nanocomposites is rapidly developing with bright prospects in chemical, energy, electronics and space industries (3). Emerging nanocomposites could become this innovative technology, which heretofore has not been explored for such field applications as controlling soluble lead in small arms range storm water run-off. Total lead in storm water discharges of an active U.S. Air Force small arms range have routinely exceeded the base's storm water permit limit of 50 ppb. In this study we investigate the organo-silicate hexagonal meso-structure (HMS), MCM-41 and MCM-48 to absorb aqueous lead. Isotherm Langmuir and Freundlich models were also reviewed.

METHODS AND MATERIALS

Organo-silicate nanocomposites are crystalline lattice structures prepared from tetraethylorthosilicate (TEOS) and either an ionic (cetyltrimethylammonium) or neutral (dodecylamine) surfactant. As-synthesized nanoporous materials have orderly pore openings and specific crystalline phases: hexagonal and independent channels (HNS and MCM-41), cubic and interconnected channels (MCM-48) (4,5).

The isotherm study used different adsorbent masses of 0.050, 0.100, 0.150, and 0.300 g, added to 30.00 ml of solution (50 $\mu g l^{-1}$ Pb) as Pb $(NO_3)_2$. The bottles were hand shaken and ultrasonically exposed for 15 minutes in a Bransonic 321 (Branson Cleaning Equipment Co., Shelton, CN). Solutions were allowed to achieve equilibrium (72 h) at constant temperature (temperature (23.0 $\pm$ 1°C). A second set of solutions was prepared similarly, vigorously hand-shaken, not exposed to ultrasonic mixing, and were analyzed within 2hrs of preparation. Both sample sets were analyzed by Graphite Furnace Atomic Adsorption (Varian Australia Pty Ltd, Mulgrave, Australia). Comparison with Langmuir isotherm models were made.

RESULTS AND DISCUSSION

HMS, MCM41 and MCM48 demonstrated their strong adsorbent affinity for metal cations removing most of lead cation species at all masses attempted. The first set of adsorbents exposed to ultrasonic treatment removed on average 99.9% (SD = 0.003, n = 15) of Pb from the sample solution. The second sample set again demonstrated effective removal ability. HMS varied in it's performance with increasing adsorbent weights. Average HMS Pb adsortion was 99.9% (SD = 0.18, n = 3), while MCM-41 and MCM-48 averaged 88.5% (SD = 0.04, n = 6) removal (Figure 1).

Each adsorbent generally showed increased Pb removal with increased amount of adsorbent. The equilibrium removal of metal ions can be mathematically

expressed in terms of adsorption isotherms. A common model for adsorption isotherm data is the Langmuir model (eqn (1)):

$$qe = K_L Ce/(1 + aCe) \quad (1)$$

$$qe = K_F Ce^n \quad (2)$$

These models are rearranged to the linear form as follows:

$$Ce/qe = (1/K_L) + (a/K_L)Ce \quad (3)$$

$$\log qe = \log K_F + n \log Ce \quad (4)$$

Langmuir, the simplest type of isotherm, is based on the view that every adsorption site is equivalent and independent; the ability of a molecule to bind there is independent of whether or not neighboring sites are occupied. The molecular sieves Langmuir isotherms model is depicted in (Table 1). Adsorption on nonuniform sites, either pre-existing in the different adsorption sites or caused by repulsive forces between adsorbed atoms or molecules, is the basis of the Freundlich model. All adsorbents did not fit the Freundlich model.

CONCLUSIONS

Organo-silicate nanocomposites demonstrate promise as molecular sieves, which could improve absorbent options to field managers. Mechanical and structural stability of these composites require further study for application at small arms ranges where lead cations mobilize in colloidal and aqueous species.

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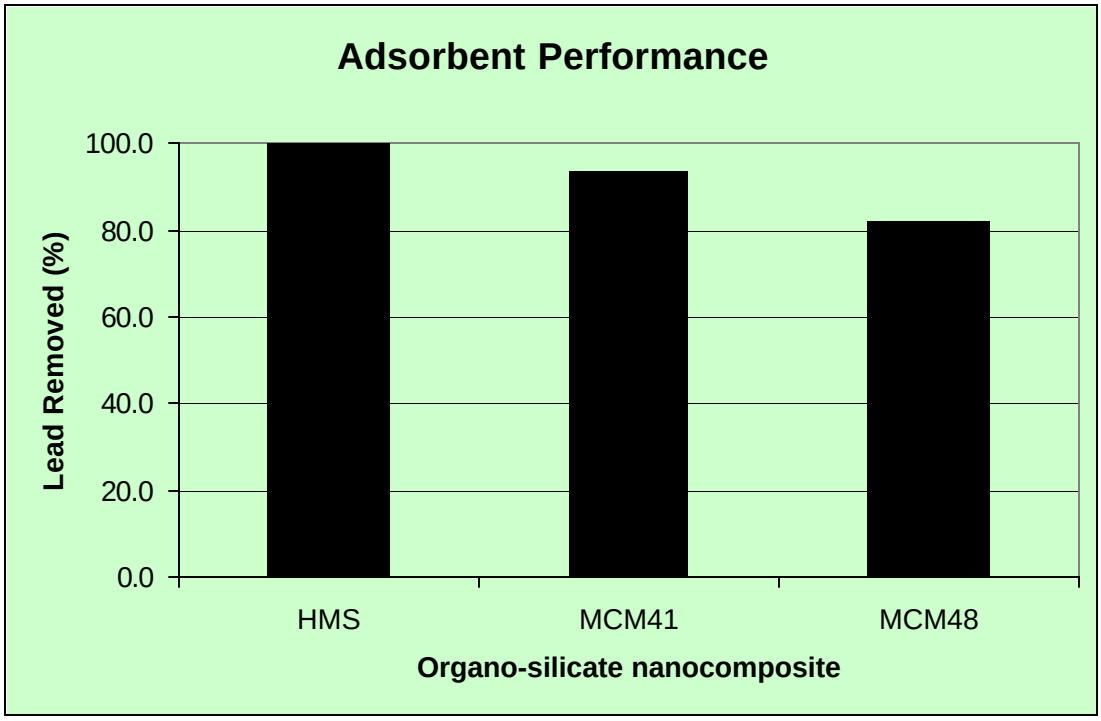

Figure 1 Organo-silicate nanocomposites performance for 50 mg of adsorbents in 30 ml of 50 µg L^{-1} Pb as $Pb(NO_3)_2$. Solutions were vigorously hand mixed an analyzed within 2hr of mixing.

Table 1 Langmuir parameters for various adsorbents.

Adsorbent	R^2	K_L	a
HMS	0.979	1250	320
MCM-41	0.932	5000	3230
MCM-48	0.930	1429	909