The influence of pH and temperature changes on the adsorption behavior of organophilic clays used in the stabilization/solidification of hazardous wastes

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Abstract: The effect of temperature, pH, and Na^+/Ca^{2+} concentration on the adsorptive behavior of organophilic clay used in the solidification/stabilization of hazardous wastes was addressed. The organophilic clay used was montmorillonite type clay modified by cation exchange with a mixed tallow amine as the sorbent. The contaminants used in this work were phenol, 2-chlorophenol, aniline, and chlorobenzene. 2-Butanone (also known as methyl ethyl ketone, MEK) was initially studied, but preliminary work showed that the organophilic clay poorly sorbed it and it was not studied further. A group of isothermal tests were performed to clarify specific sorption behaviors due to temperature effects, high pH, and concentration of the cations Na^+ and Ca^{2+}. The adsorption capacity of the organophilic clay decreased as follows: chlorobenzene > 2-chlorophenol > phenol > aniline. Desorption in high pH environments was seen for phenol and 2-chlorophenol. Changes in temperature, rise in the pH, or increases in Na^+/Ca^{2+} concentrations had no effect on the adsorption of either aniline or chlorobenzene.

Key words: organophilic clay, adsorption, hazardous wastes, solidification/stabilization, isotherm.

Résumé : Cet article traite de l'effet de la température, du pH et de la concentration Na^+/Ca^{2+} sur l'absorption de l'argile organophilique utilisée pour la solidification/stabilisation des déchets dangereux. L'argile organophilique utilisée était une argile du groupe de la montmorillonite, modifiée par échange cationique avec une amine mélangée de suif servant de sorbant. Les contaminants utilisés dans ce travail étaient le phénol, le 2-chlorophénol, l'aniline et le chlorobenzène. Le 2-butanone (également connu sous le nom de méthyléthylcétone) a été étudié au début, mais le travail préliminaire a démontré que l'argile organophilique l'absorbait mal et il n'a pas été étudié plus longtemps. Un groupe de tests isothermes ont été effectués de manière à comprendre les comportements de sorption spécifiques selon les effets de la température, du pH élevé et la concentration des cations Na^+ et Ca^{2+}. La capacité d'absorption de l'argile organophilique décroissait selon l'ordre suivant : chlorobenzène > 2-chlorophénol > phénol > aniline. La désorption dans les environnements à pH élevés a été remarquée pour le phénol et le 2-chlorophénol. Des changements dans la température, une augmentation du pH ou des augmentations dans les concentrations de Na^+/Ca^{2+} n'ont eu aucun effet sur l'absorption de l'aniline ou du chlorobenzène.

Mots clés : argile organophilique, déchets dangereux, solidification/stabilisation, isotherme.

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Introduction

Cement-based stabilization/solidification processes have been used for about two decades for the immobilization of heavy metals in hazardous wastes and contaminated soils. These processes usually work well for heavy metals, but they do not work well for toxic organic materials that are often present along with the heavy metals. A number of additives have been tried to improve the retention of these organics in the resulting waste form, with mixed results.

The effectiveness of an organophilic clay in the treatment of contaminated soils via stabilization/solidification (S/S) pro-

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cesses was studied in this research as part of a larger study to develop effective immobilization processes for organic contaminants. Organophilic clays are currently used in some S/S processes for this purpose. In our larger research program, we compared the efficacy of organophilic clays to other additives, such as activated carbons and catalytic carbons, for the immobilization of toxic organics in contaminated soils.

Clays are composed mainly of silica, alumina, and water, frequently with appreciable quantities of iron, alkalis, and alkali earths. The maximum size of particles in the clay fraction is usually considered to be 2 μm (Grim 1968).

Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygens or hydroxyls in which aluminum, iron, or magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygens or hydroxyls. The second unit is built of silica tetrahedrons (Fig. 1). The silica tetrahedrons are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$ (Grim 1968). These two structural units (phyllosilicates) condense with each other in two different ways. Condensation with a 1:1 proportion gives rise to two-sheet or dimorphic minerals with a general formula $M_{2-3}Si_2O_5(OH)_4$, of which kaolinite is perhaps the best known example. Similarly, the three-sheet or trimorphic clays are formed by a 2:1 condensation, the octahedral sheet being sandwiched between two sheets of inward-pointing tetrahedra (the mica type layer structure), giving a layer formula of $M_{2-3}Si_4O_{10}(OH)_2$. There is room in these structures for isomorphic substitution, which is for substitution of Si^{4+} and (or) $M^{2+/3+}$ by cations of similar size but different (usually lower) valencies. As a result of isomorphic substitution, the structure of many phyllosilicates is negatively charged. Electrical neutrality is usually maintained by sorption of extraneous cations, which may or may not be exchangeable (Theng 1974).

The hydration of metal exchanged cations imparts a hydrophilic nature to the mineral surface. In the presence of water such mineral surfaces are often not good adsorbents for poorly water-soluble organic species, which cannot compete with highly polar water for adsorption on the clay mineral surface. However, organic cations may enter into ion exchange reactions on the exchange sites of clay, forming an organophilic clay (Theng 1974). When the exchanging organic cations contain sizeable organophilic moieties, the surfaces of the clay may be greatly modified to become strongly organophilic. As a result, the organo-clay complex becomes an excellent sorbent for poorly water-soluble organic species. It is this property that is exploited in the use of organo-clays in stabilization/solidification of wastes.

Numerous studies have been made on the behavior of the exchanged, now organophilic, clay (Faschan et al. 1993; Montgomery et al. 1991; Conner 1990; Sheriff et al. 1989; Gibbons and Soundararajan 1988). In general, the type of organic cation chosen for the exchange is a surfactant in the form of any of the four types of alkyl amines (i.e., primary, secondary, tertiary, and quaternary). Gitipour (1993) used dimethyl dihydrogenated

amine as the cation in experiments involving removal of benzene, toluene, xylene, and ethylbenzene (BTEX substances); trimethylammonium was analyzed for the removal of 1,2,4-trichlorobenzene in the presence of tannic acid (Dentel et al. 1998), for benzene, toluene, and o-xylene (Cadena 1989), and in a Fourier transform infrared spectroscopy (FTIR) study of water adsorption (Stevens and Anderson 1996a). Polubesova et al. (1997) studied the adsorption of benzyltrimethylammonium (BTMA) and benzyltriethylammonium (BTEA) on montmorillonite. The use of BTMA-montmorillonite has also been analyzed for the case of reduction of photodegradation and volatilization of herbicides (El-Nahhal et al. 1999); similarly, the orientation of trimethylphenylammonium (TMPA) in montmorillonite, as well as its implications in the adsorption of aromatic compounds, has been studied (Stevens and Anderson 1996b). The most utilized ammonium salt for organo-clay formulations has been hexadecyltrimethylammonium (HDTMA) (Boyd et al. 1988; Jaynes and Boyd 1991; Guangyao et al. 1996; Zhao et al. 1996; Dentel et al. 1998; Zhao and Vance 1998). Some patented products include a tallow amine with alkyl chains ranging from 12 to 18 carbons as the exchange cation. Kramer (2000) and Uribe (2000) studied the adsorption behavior of this type of organo-clay.

Organo-clays have been used as stabilizing agents in the stabilization/solidification of hazardous wastes, but little information is available in the literature about this process. To assess if the organo-clay would be useful for such a task, three important questions must first be answered. First, is the capacity of the organo-clay for the contaminants of interest sufficient for economic S/S of the waste? Second, would the sharp increase in pH due to the formation of lime during cement hydration reactions have any effect on sorption? Finally, will the heat generated during the hydration reactions affect the ability of the system to retain sorbed organics? The present work was designed to provide information on these questions.

Materials and methods

Two sets of experiments were performed to evaluate the effect of pH and temperature variations independently of each other. The main variable observed was the adsorption capacity of the clay samples in response to variations of each parameter.

The chemical compounds used in these experiments were chosen to cover a range of different organic groups and chemical behaviors in the environment. Table 1 shows the list of compounds chosen, along with selected characteristics of each. Aldrich Chemicals supplied all chemicals at reagent grade. The adsorbent PT-1E organophilic clay, suggested by the manufacturer for this use and supplied by BIOMIN Inc., Ferndale, Mich., was chosen for this research. This organo-clay is a common bentonite (Na^+ montmorillonite) modified with a mixed tallow amine (RNH_2). Characteristics of the amine are shown in Table 2; properties of the clay provided by the manufacturer are presented in Table 3.

Fig. 1. General structure of calcium montmorillonite. Notice the 2:1 configuration of the silicate tetrahedra and the aluminate octahedra. Adapted from Theng (1974).
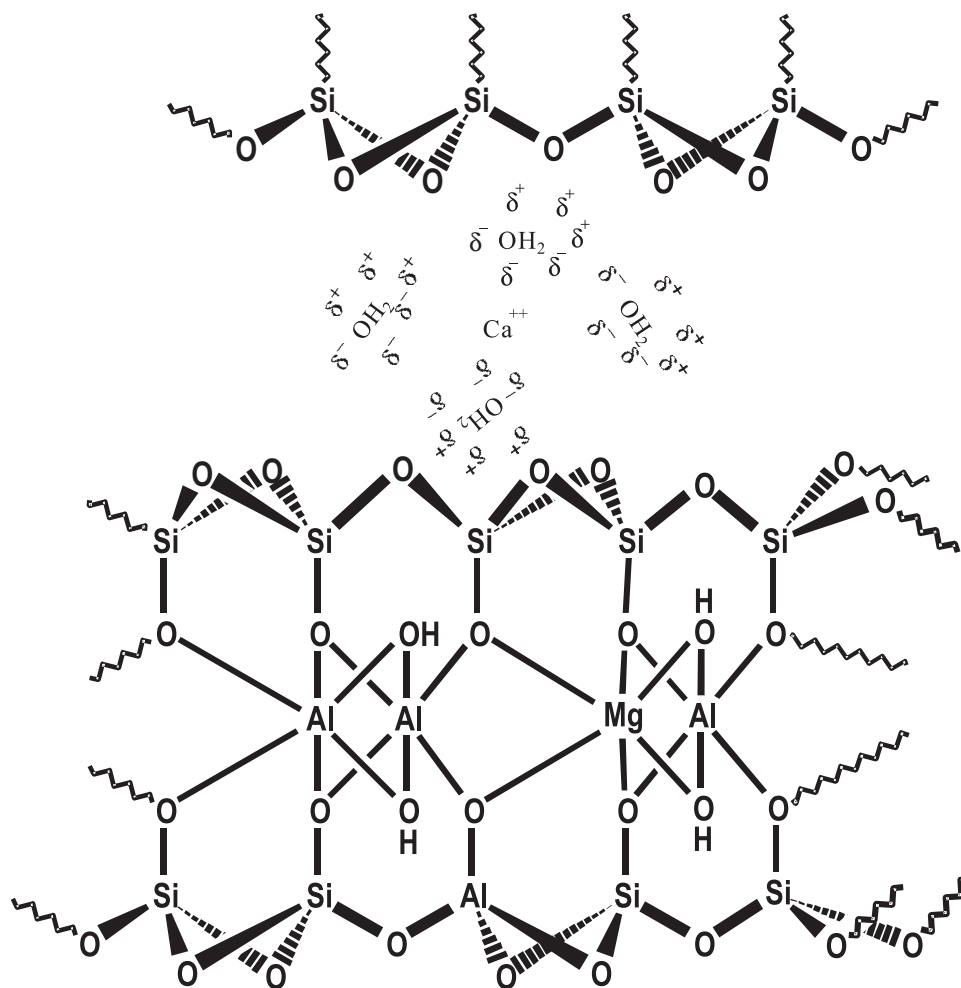

Table 1. Characteristics of the selected adsorbates.

Name	Formula	Molecular weight	Henry's constant (bar m^3/mol)†	Water solubility at 25°C (g/L)	Log K_{OW}	Observations
Phenol	C_6H_6O	94	4.0×10^{-7}	87	1.5	Aromatic semivolatile weak acid, $pK_a = 9.98$
Aniline	C_6H_7N	93	1.4×10^{-1}	36	0.9	Aromatic semivolatile weak base, $pK_b = 9.4$
2-Chlorophenol	C_6H_6OCl	129.5	5.7×10^{-7}	22	2.15	Aromatic semivolatile halogenated weak acid, $pK_a = 8.53$
Chlorobenzene	C_6H_5Cl	112.5	3.5×10^{-3}	0.49	2.84	Aromatic semivolatile halogenated cyclic hydrocarbon
2-Butanone (methyl ethyl ketone, MEK)	C_6H_8O	72	4.7×10^{-5}*	256	0.28*	Aliphatic, semivolatile, high solubility

Note: Adapted from Lide (1993). CRC handbook of chemistry and physics, 73rd ed. CRC Press, Boca Raton, FL.

*Watts (1998). Hazardous wastes: sources, pathways and receptors, Wiley, New York, NY.

†1 bar = 100 kPa.

Adsorption isotherm test measurements were made in 15-mL borosilicate glass test tubes, with Teflon coated threaded caps (Kimble Glass Inc). Five different amounts of adsorbent (organophilic clay) were measured into 15-mL test tubes; the tubes were then filled with 15 mL of stock solution containing the organic of interest (see Tables 4 and 5). The filled tubes were

Table 2. Characteristics of the mixed tallow amine.*

Appearance (at 25°C)	Typical alkyl composition (%)			Moisture (%)	Color (APHA)
	C_{14}	C_{16}	C_{18}		
Light yellow liquid	4	30	66	0.5 max	150 max

*Taken from KAO Corp. http://chemical.kao.co.jp/e/productspecification/catalog/amine(e)/E1amine.htm

Table 3. Characteristics of the organophilic clay PT-1E.

Appearance	Amine content	% C.E.C.	Specific surface area
White fine powder	156 mEq/100 g	~150	~400 m^2/g

transferred into a rotary tumbler and tumbled at approximately 30–50 rpm until equilibrium was reached (~24 h). Upon reaching equilibrium, the suspension was allowed to settle for 2 h. An aliquot of the supernatant was then extracted, filtered through a 0.45 μm filter, and analyzed. For the pH studies, a series of the tubes were spiked with either NaOH or Ca(OH)$_2$ and returned to the tumbler for another equilibration time period identical to that described above. Control samples were prepared by adding the solutions into test tubes in the absence of adsorbent. They were run along with the other samples to ensure that any removals detected were due to the sorbent. All experiments were performed in duplicate.

For the temperature effect studies, the tumbler was placed in an incubator room at the desired temperature for 24 ± 2 h prior to beginning the experiment to ensure that the temperature inside the tumbler chambers was the same as outside. The temperature range was selected to simulate conditions during the solidification/stabilization process. The lowest temperature used was the expected ambient temperature; the midpoint and the higher temperatures were selected to determine the effects, if any, of a temperature rise within the solidified sample due to the heat of hydration of the cement.

The effects of a high pH resulting from the production of calcium hydroxide during the hydration processes were studied by adding Ca(OH)$_2$; this reflects the alkaline material in a cement matrix. NaOH was also used as a control experiment aimed at discriminating the pH effect from that caused by cation interaction, although in both cases a reverse cation exchange might be produced (i.e., reversibly exchanging the tallow amine by the metal).

To spike the samples, two 5N stock solutions (one of NaOH and one of Ca(OH)$_2$) were made. The desired CEC factor (Table 5) was obtained by adding 0.2 mL of the stock solution to the 15- mL test tubes, yielding a total of 1 meq of the compound per tube. The minimum CEC factor was calculated in relation to the amount of equivalents and the amount of clay in the tubes. For example, for aniline the maximum amount of clay was 1000 mg (1 g). In that tube there was 1 meq of either NaOH or Ca(OH)$_2$. The ratio of these two quantities (1 meq/g) is equivalent to the nominal CEC of the clay (100 meq/100 g);

therefore, the minimum CEC factor for aniline is 1 (as expressed in Table 5).

Results and discussion

Effects of temperature

The experiments dealing with temperature effects had two specific purposes: (a) determine the effect of temperature on adsorption of the compounds onto the organophilic clay and (b) if possible, calculate the isosteric heat of adsorption for each compound.

Phenol

Figure 2 shows the sorption isotherms collected for phenol at 22, 40, and 44°C (see Table 4). The data obtained suggest that, over the range tested, the isotherms are linear (all $R^2 > 0.99$). Also, the adsorption capacity appears to be relatively insensitive to temperature. The isotherms are generally consistent with the data of Dentel et al. (1995).

No calculations for the heat of adsorption were made for this compound (or others in the study) because of the small differences between the equilibrium states of different temperature isotherms.

2-Chlorophenol

The isotherms for 2-chlorophenol run at different temperatures are shown in Fig. 3. For this case, type I isotherm behavior was observed. As for phenol, no significant temperature dependence was observed over the temperature range studied. The Freundlich adsorption isotherm can be used to model the data ($R^2 > 0.95$). 2-Cholorphenol is the only compound that showed an isothermal shape different from linear. Chlorobenzene (to be described later) showed a sharp linearity (and higher adsorption capacity) in its isotherms, principally due to its hydrophobicity. Phenol showed the same linear behavior but lesser affinity to the clay (shallower slope), suggesting that it might be at the lower end of a Freundlich type isotherm. 2-Chlorophenol showed an intermediate behavior between the two compounds, due probably to its being structurally intermediate between the two compounds.

Table 4. Experimental matrix for determining the effect of temperature.

Sample ID	Contaminant	Initial concentration (mg/L)	Amounts of clay (mg)	Test temperature (°C)
IsoPhe22	Phenol	279.76	500, 300, 200, 100, 50, Ctrl	22
IsoPhe40	Phenol	280.00	500, 300, 200, 100, 50, Ctrl	40
IsoPhe44	Phenol	277.97	500, 300, 200, 100, 50, Ctrl	44
IsoAni22	Aniline	212.23	1000, 500, 300, 200, 100, Ctrl	22
IsoAni40	Aniline	152.51	1000, 500, 300, 200, 100, Ctrl	40
IsoAni44	Aniline	205.27	1000, 500, 300, 200, 100, Ctrl	44
Iso2CP29	2-Chlorophenol	304.00	100, 60, 40, 30, 20, Ctrl	29
Iso2CP40	2-Chlorophenol	200.71	200, 100, 60, 40, 20, Ctrl	40
Iso2CP44	2-Chlorophenol	240.58	200, 100, 60, 40, 20, Ctrl	44
IsoChbz29	Chlorobenzene	406.92	100, 60, 40, 30, 20, Ctrl	29
IsoChbz40	Chlorobenzene	358.24	200, 100, 60, 40, 20, Ctrl	40
IsoChbz44	Chlorobenzene	328.24	200, 100, 60, 40, 20, Ctrl	44
IsoMEK29	MEK	240.90	100, 60, 40, 30, 20, Ctrl	29
IsoMEK29 II	MEK	217.50	1000, 500, 300, 200, 100, Ctrl	29
IsoMEK29 III	MEK	62.00	1000, 500, 300, 200, 100, Ctrl	29

Note: Results obtained for MEK suggested that the clay does not work well under the conditions tested; therefore no pH tests were performed with it.

Table 5. Experimental matrix for determining the influence of pH, Na^+, and Ca^{2+}.

Sample ID	Contaminant	Initial conc. (mg/L)	Amounts of clay (mg)	Compound spiked	Spiked normality (Eq/L)	pH	Min. CEC factor[†]	Temp. (°C)
IsoPheCtrbe	Phenol	279.76	500, 300, 200, 100, 50, Ctrl	—	—	7.18	—	
IsoPheNa	Phenol	279.71	500, 300, 200, 100, 50, Ctrl	NaOH	6.67×10^{-2}	>12	2	22
IsoPheCa	Phenol	273.27	500, 300, 200, 100, 50, Ctrl	Ca(OH)$_2$	6.67×10^{-2}*	>12	2	
IsoPheCtraf	Phenol	279.04	500, 300, 200, 100, 50, Ctrl	—	—	7.04	—	
IsoAniCtrbe	Aniline	212.23	1000, 500, 300, 200, 100, Ctrl	—	—	7.52	—	
IsoAniNa	Aniline	204.10	1000, 500, 300, 200, 100, Ctrl	NaOH	6.67×10^{-2}	>12	1	22
IsoAniCa	Aniline	206.34	1000, 500, 300, 200, 100, Ctrl	Ca(OH)$_2$	6.67×10^{-2}*	>12	1	
IsoAniCtraf	Aniline	207.44	1000, 500, 300, 200, 100, Ctrl	—	—	7.5	—	
Iso2CPCtrbe	2-Chlorophenol	244.04	200, 100, 60, 40, 20, Ctrl	—	—	6.8	—	
Iso2CPNa	2-Chlorophenol	243.50	200, 100, 60, 40, 20, Ctrl	NaOH	6.67×10^{-2}	>12	5	22
Iso2CPCa	2-Chlorophenol	244.57	200, 100, 60, 40, 20, Ctrl	Ca(OH)$_2$	6.67×10^{-2}*	>12	5	
Iso2CPCtraf	2-Chlorophenol	247.26	200, 100, 60, 40, 20, Ctrl	—	—	6.8	—	
IsoChbzCtrbe	Chlorobenzene	334.15	200, 100, 60, 40, 20, Ctrl	—	—	7.4	—	
IsoChbzNa	Chlorobenzene	317.94	200, 100, 60, 40, 20, Ctrl	NaOH	6.67×10^{-2}	>12	5	22
IsoChbzCa	Chlorobenzene	307.00	200, 100, 60, 40, 20, Ctrl	Ca(OH)$_2$	6.67×10^{-2}*	>12	5	
IsoChbzCtraf	Chlorobenzene	321.72	200, 100, 60, 40, 20, Ctrl	—	—	7.2	—	

*Ca(OH)$_2$ was in suspension; this normality exceeds the solubility of Ca(OH)$_2$.

†Indicates the minimum excess of the cation exchange capacity (CEC) from the 100 mEq/100 g for the clay.

The adsorption capacity observed for 2-chlorophenol in this experiment is higher than that reported in the literature by Lo (1996). It is important to note that the capacity of the organophilic clay for 2-chlorophenol in this research is 2.5 times that found for phenol and almost 7 times that found for aniline; only chlorobenzene showed better adsorption on the clay.

Aniline

Figure 4 shows the isotherms measured for aniline at the three different temperatures. In this case, the isotherms are linear ($R^2 > 0.98$) over the range of loadings tested. Also, there is no significant temperature dependence within the range of conditions studied.

No data could be found in the literature for the adsorption of aniline onto organically modified clays, but there are data available for adsorption onto non-modified clays (Homenauth and McBride 1994). Aniline is an amine, as is the tallow amine with which this organophilic clay has been modified. Comparing results from Homenauth and McBride (1994) with those reported

Fig. 2. Effect of temperature on organophilic clay – phenol isotherms. Lines represent linear isotherms.
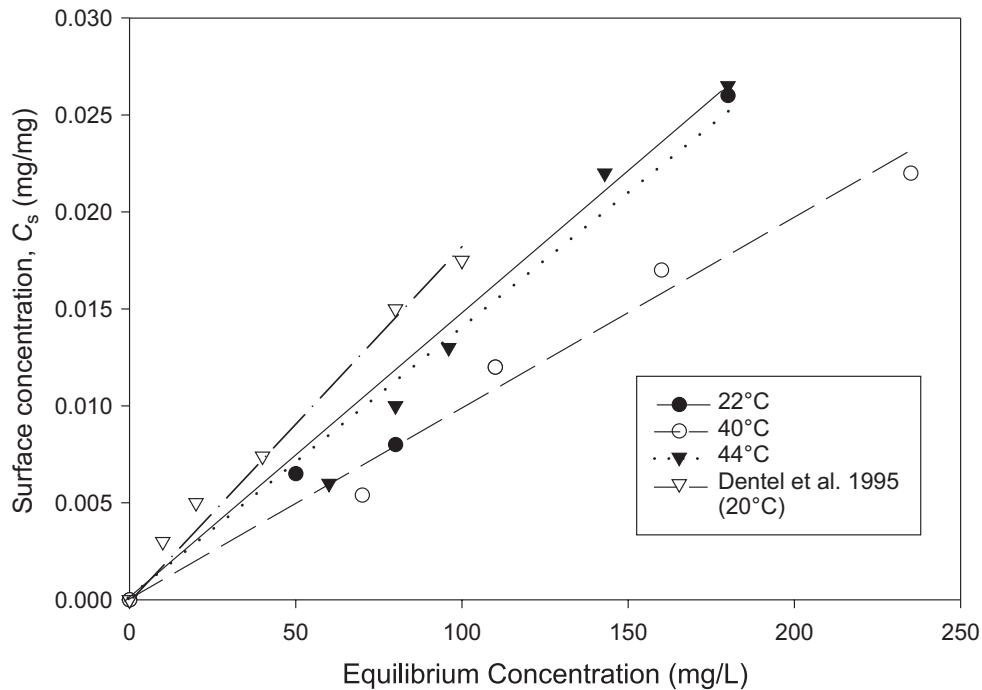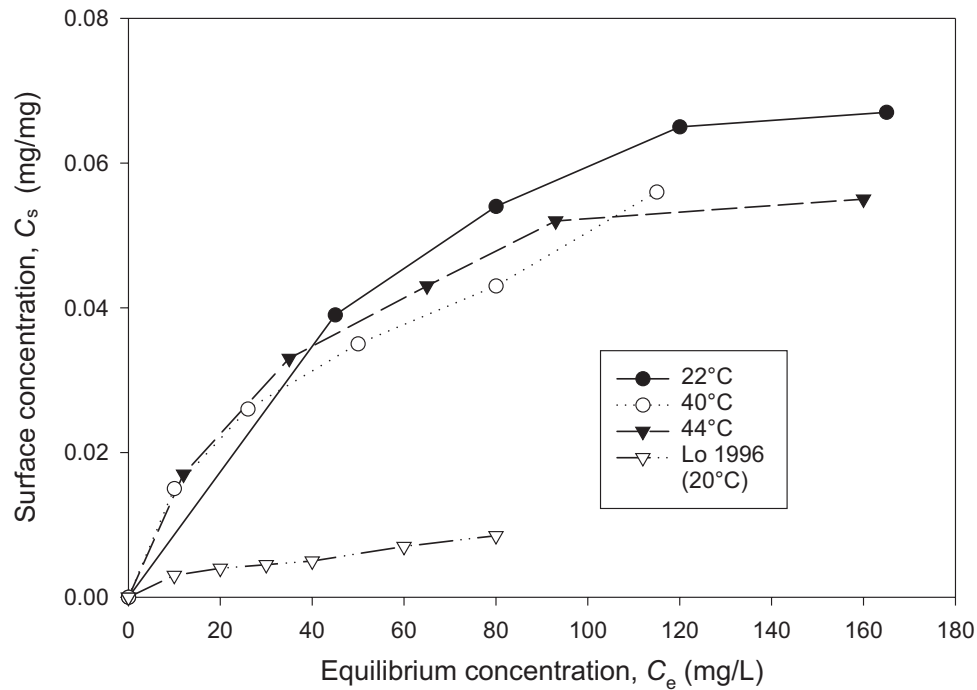

Fig. 3. Effect of temperature on organophilic clay – 2-chlorophenol isotherms.

here suggests that aniline will adsorb better onto a non-modified clay (i.e., calcium montmorillonite). This suggests that there is competitive adsorption between aniline and the tallow amine for the silicate lattice. Aniline might preferably adsorb onto the silicate lattice, rather than onto the organic phase of the organophilic clay. Ideally, all the available sites are already taken by the tallow amine, which could explain the very low capacity of the organophilic clay for aniline.

Chlorobenzene

Figure 5 illustrates the measured isotherms for chlorobenzene on the organophilic clay. Chlorobenzene is the only compound in which the resulting equilibrium concentrations approach the water solubility of the compound. Chlorobenzene is the most hydrophobic of the compounds tested and also showed the highest adsorption onto the organophilic clay. In a related study, chlorobenzene also had the least leachability from solid-

Fig. 4. Effect of temperature on organophilic clay – aniline isotherms. Lines represent linear isotherms.
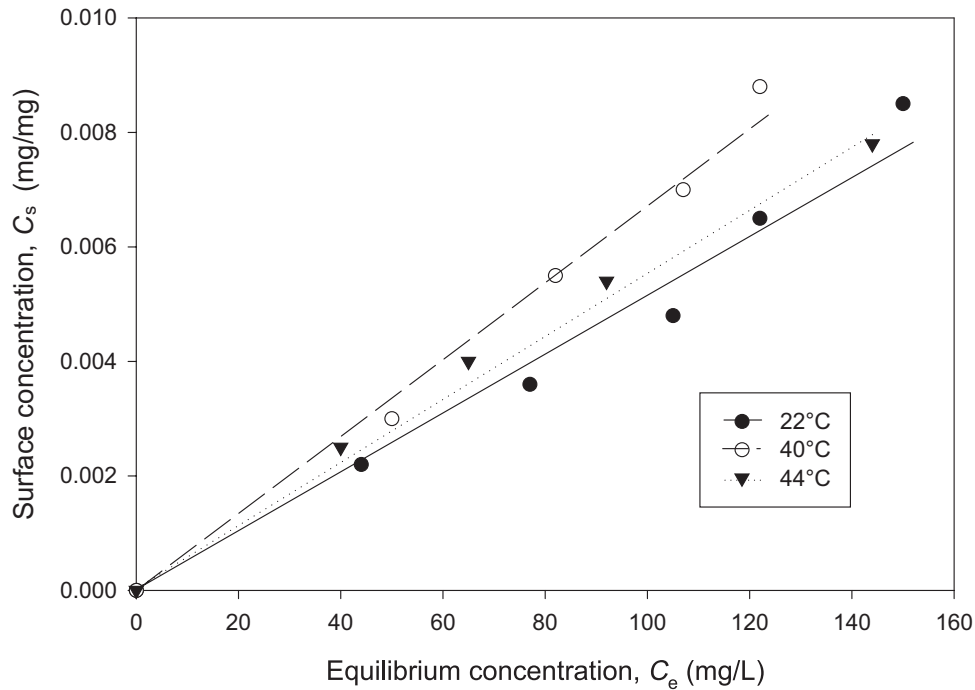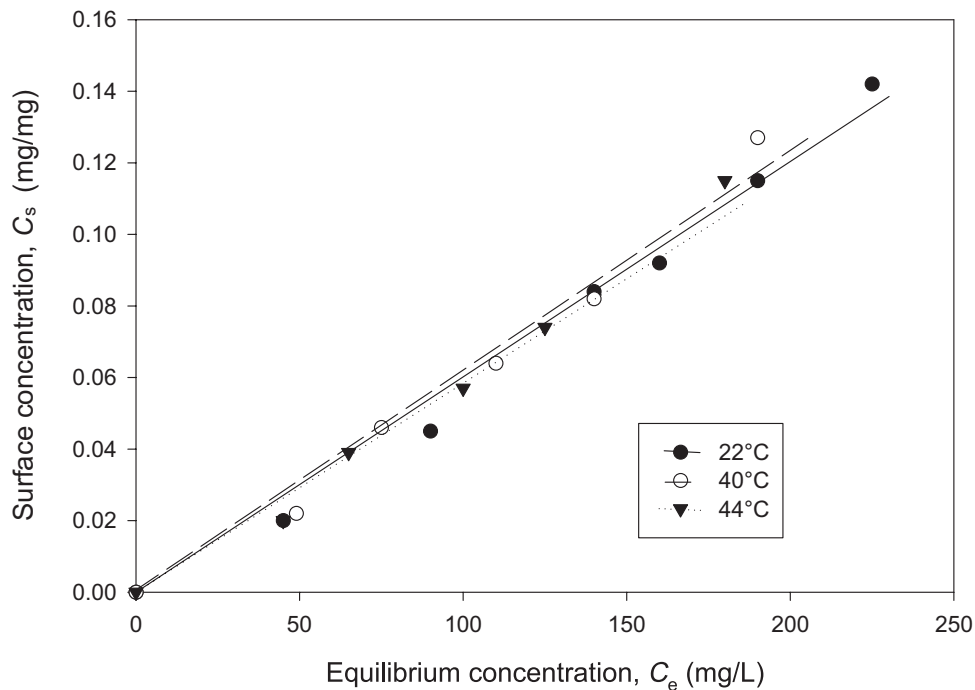

Fig. 5. Effect of temperature on organophilic clay – chlorobenzene isotherms. Lines represent linear isotherms.

ified/stabilized samples of soils contaminated with chloroben-zene (Hebatpuria et al. 1999). It is important to note that, de-spite the relatively high solution concentrations, the isotherms are linear ($R^2 > 0.99$) and the effect of temperature is minimal. The linearity of the isotherm might imply that another phe-nomenon, or one in conjunction with adsorption, is occurring. Several authors have suggested that solvation (or absorption) of the compound within the organic phase might be the primary

phenomenon occurring in this case (Boyd 1988; Dentel et al. 1995; Dentel et al. 1998).

Summary

In summary, it is observed that, with the exception of 2-chlorophenol, all the measured isotherms were linear. Further-more, within the temperature range of interest, increases in tem-perature did not cause a significant decrease in sorption. Thus,

any desorption due to heat release during solidification/stabiliz-ation is not likely to be significant. The relative capacities of the adsorbates were found to be, in decreasing order, chloro-benzene > 2-chlorophenol > phenol > aniline.

Effect of pH, Na$^+$, and Ca^{2+}

A set of isotherm experiments was performed to determine the effects that a sharp rise in the pH might have on adsorption of the compounds studied. Because of the formation of lime during cement hydration reactions, the pH of S/S waste forms is typically 11.0–12.5. To simulate the condition at which the adsorption might occur within the cement matrix, the pH was raised using Ca(OH)$_2$. To differentiate effects possibly caused by pH from those caused by the specific cation present, a set of isotherms was also performed using NaOH instead of Ca(OH)$_2$.

Phenol

Figure 6 presents the isotherms obtained for phenol, show-ing the effects of pH and cation present. For this experiment all three sample sets were first driven to equilibrium in the same way as for the temperature studies, at a pH of 7.18. After reach-ing equilibrium, one of the sets was measured for isotherm solution concentrations, a second set was spiked with NaOH as explained in the previous section, and the third set was spiked with Ca(OH)$_2$ in the same way as the second. Isotherm mea-surements were again made.

Adsorption was linear in all cases ($R^2 > 0.97$). It is observed from Fig. 6 that phenol desorbs from the clay when the solutions are spiked with alkali. The capacity dropped by a factor of approximately six when the pH increased from 7 to 12. It is also observed that there is an insignificant difference between the pH 12 isotherms with Ca(OH)$_2$ and with NaOH.

The effect of pH explains the behavior previously reported for solidified samples containing organophilic clay (Uribe 2000), in which phenol was almost completely leached out. Within a so-lidified sample, the pH is typically high (above 12), mainly due to the presence of Ca(OH)$_2$. At this pH, the phenol is completely ionized to phenolate ion. Since phenolate ion is negative, and the organophilic clay has a negative surface charge (isoelectric point at pH 9.34), a lower adsorption capacity is observed at pH 12 than at pH 7. It appears that the adsorption of ionizable molecules is strongly dependent on the pH.

2-Chlorophenol

Figure 7 illustrates the effect of pH on the isotherms for 2-chlorophenol. As for phenol, a significant drop in capacity was observed with increase in pH from 7 to 12. The resulting isotherms fit a Freundlich isotherm model, rather than a linear model. Once again, the isotherms in the presence of NaOH and Ca(OH)$_2$ are essentially identical.

Desorption of the compound from the clay might obey the same rule stated for phenol. As with phenol, 2-chlorophenol at high pH will be in its ionized negative form, and the interaction between the ion and the surface of the clay might force the molecule out.

Aniline

For the case of aniline (see Fig. 8), the results obtained sug-gest that neither the pH nor the cation in the solution had much effect on the adsorption capability of the clay. Again, the isotherms were linear ($R^2 > 0.98$).

Aniline is a weak base, and at a high pH the aniline remains in its neutral state (non-protinated). Surprisingly, little discernable difference could be found between the isotherms made under conditions in which the aniline might be present in its anilinium state and those in which aniline would more likely be present in its neutral form.

Chlorobenzene

The isotherm data collected for chlorobenzene are shown in Fig. 9. The isotherms are again linear ($R^2 > 0.93$), although there is more data scatter. It is apparent that adsorption of chloro-benzene is not affected significantly by the pH or the cation present.

Since chlorobenzene is a non-polar organic compound, the pH is not expected to affect the capacity, as was observed. The data also suggest that no cation exchange occurred, or if it oc-curred it was to a very limited extent. The fact that the isotherms are very similar implies that the active component of the clay (tallow amine) remained in place; otherwise the capacity for chlorobenzene adsorption would have been affected. A desorp-tion effect would be expected in this case, since the natural clay has a low affinity for chlorobenzene.

Summary and conclusions

The organophilic clay used in this research as a sorbent aid for the stabilization/solidification of hazardous organic contam-inants is not as effective as reactivated carbon, which was stud-ied previously by this group (Arafat et al. 1999; Hebatpuria et al. 1999a, 1999b; Rho et al. 2001). It is not likely that addi-tion of this particular organo-clay to a S/S formulation would be cost-effective for the immobilization of this group of toxic organics. A different organophilic clay, though, may give better results.

Based on the experimental results, the following character-istics were observed:

(1) The adsorption capacity of the organophilic clay decreased as follows: chlorobenzene > 2-chlorophenol > phenol > aniline.

(2) The maximum adsorptive capacities observed for the organo-clay were 0.15 mg/mg for chlorobenzene, 0.07 mg/mg for 2-chlorophenol, 0.03 mg/mg for phenol, and 0.01 mg/mg for aniline.

(3) There is a dramatic influence of pH on the adsorption ca-pacity of phenols by the organophilic clay. At high pH, the phenols are in their ionic state, decreasing the ability of the clay to adsorb them. The capacity of the clay for both phe-nol and chlorophenol decreased from the maximum stated

Fig. 6. Effect of pH and cations on organo-clay – phenol isotherms. Lines represent linear isotherms.
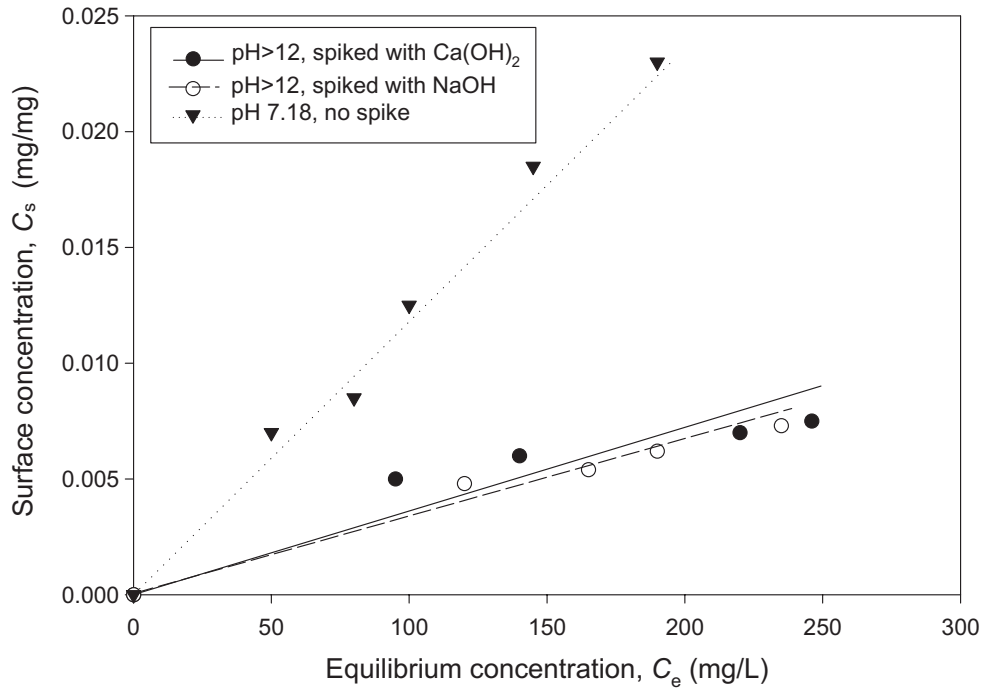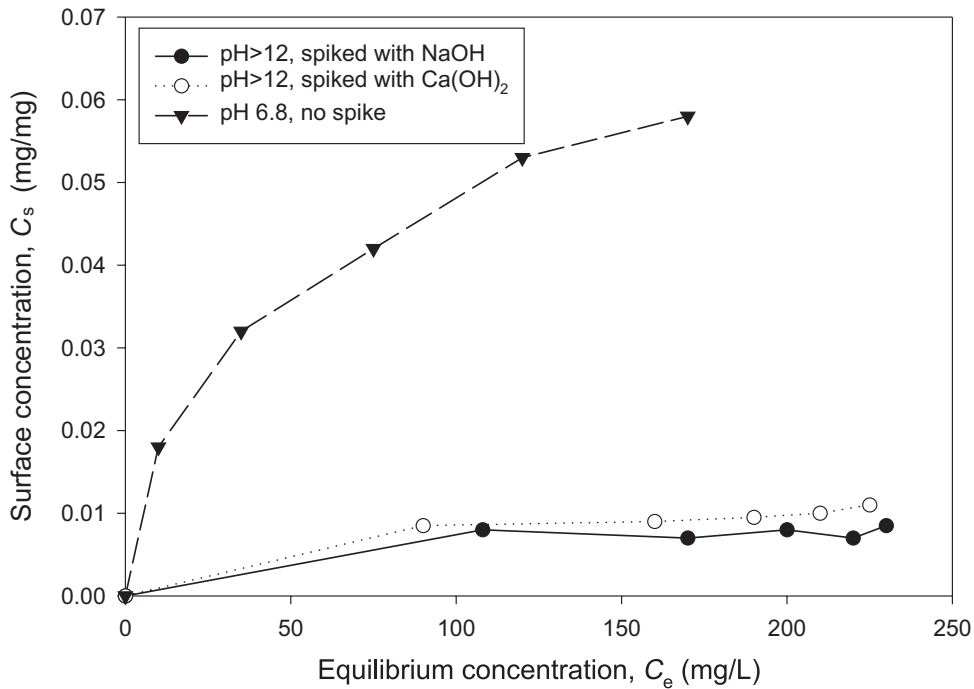

Fig. 7. Effect of pH and cations on organo-clay – 2-chlorophenol isotherms.

above to 0.01 mg/mg. This suggests that the pH conditions that would be present in the S/S process would make the organophilic clay tested in this study not appealing for stabilizing phenols.

(4) None of the compounds tested exhibited a significant temperature dependency in terms of adsorption onto the organophilic clay.

Further investigation of the interaction of the organophilic clay with the crystalline lattice in the cement matrix might prove it to be an important issue in the determination of the adsorptive behavior of organophilic clays subjected to a stabilization/solidification process. The results observed for the phenols, in terms of pH dependence, suggest that different interactions might be occurring on the surface of the organophilic clay. Adsorption of such compounds in high pH environments

Fig. 8. Effect of pH and cations on organo-clay – aniline isotherms. Lines represent linear isotherms.
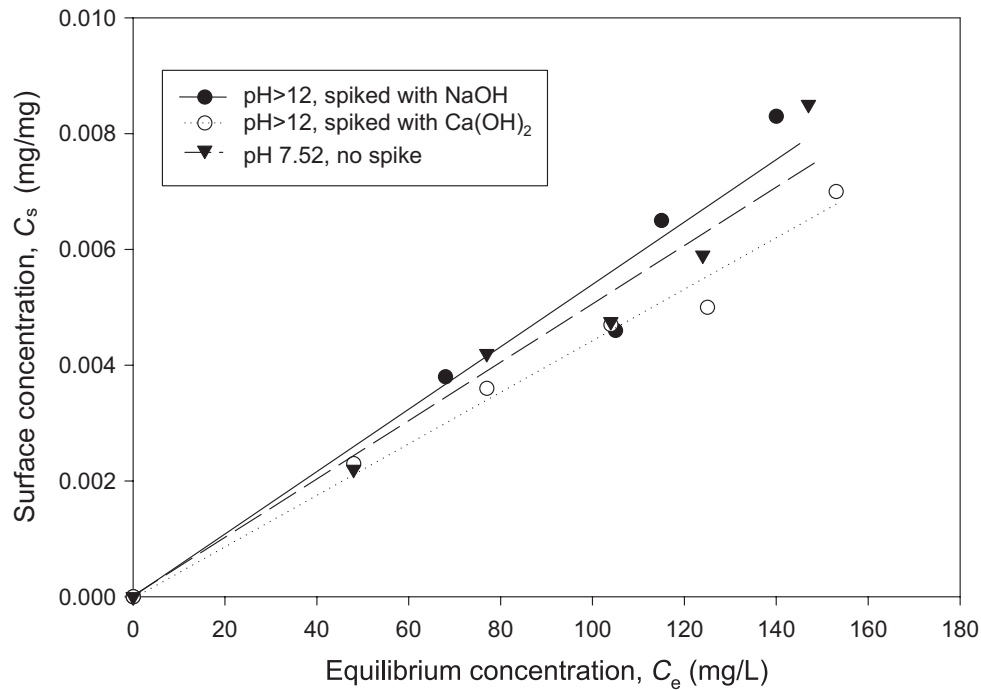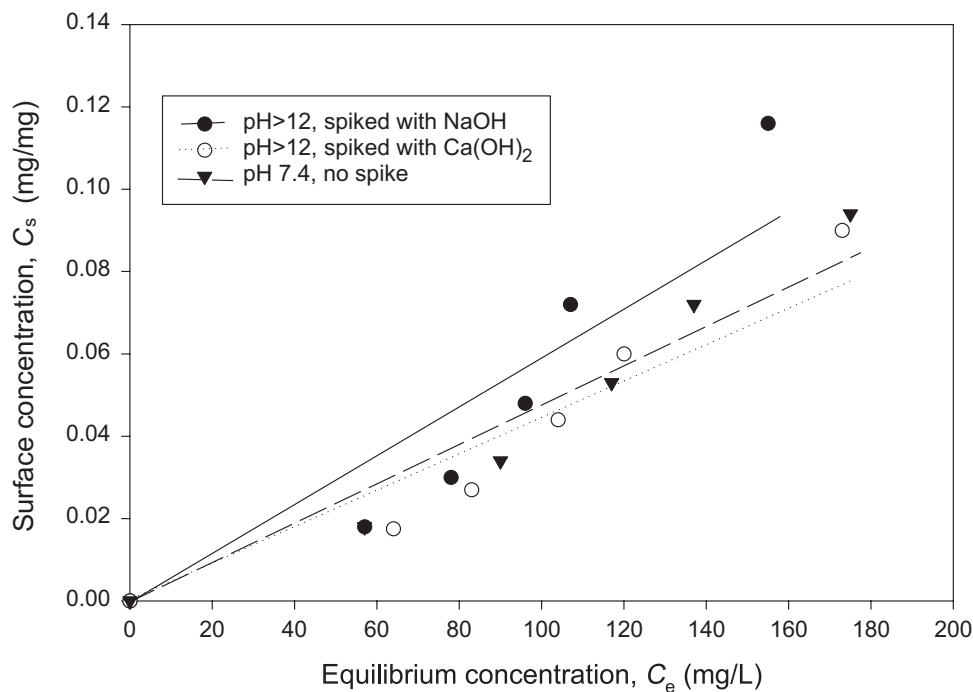

Fig. 9. Effect of pH and cations on organo-clay – chlorobenzene isotherms. Lines represent linear isotherms.

onto non-modified clays (i.e., naturally occurring montmoril-lonite) might prove important in the elucidation of whether or not these kinds of compounds interact more with the organic moieties or with the mineral structure of the clay.

Some researchers have suggested that organophilic clays could be tailored to adsorb specific compounds. Determination of these specificities and application of them into solidification/stab-

ilization processes might prove valuable for industry. Although addition of the organophilic clay tested in this work did not significantly improve the performance of the solidification/-stabilization treatment process, that does not mean that other types of organophilic clays, modified with different surfactants, could not work better. It has been suggested that the degree of saturation of the nitrogen in the surfactant used could have an

important effect in the strength of adsorption (i.e., a quaternary amine is better than a primary amine). This remains to be verified.

Acknowledgements

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