

ADSORPTION OF CHLORINATED PHENOLS FROM AQUEOUS SOLUTION BY SURFACTANT-MODIFIED PILLARED CLAYS

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Abstract—New pillared clay-based adsorbents have been prepared by incorporating a nonionic surfactant of general formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_3H$ (commercial name, Tergitol 15S-5), during the synthesis of the aluminum hydroxide pillaring reagent. Different loadings of surfactant have been examined. The presence of the surfactant enhanced the adsorption capacity of the clay toward 3-monochlorophenol from aqueous solution. On the basis of adsorption results for a series of clays with increasing surfactant loadings, the best adsorbent was obtained at a surfactant loading of 255 mg/g of clay. At this loading, the surfactant occupies the micropores, as well as the mesopores and the external surfaces of the pillared clay. Analysis of the adsorption isotherms for 3-monochlorophenol, 3,5-dichlorophenol, 3,4,5-trichlorophenol and pentachlorophenol at different pH shows that the most energetic adsorption sites are the surfactant-occupied micropores between pillars. Additional binding of chlorinated phenols occurs at surfactant sites on external surfaces and mesopores. Upon calcination at 500°C, the clay is converted to a conventional alumina-pillared clay with a basal spacing near 16 Å. This calcined product can be reused as an adsorbent for chlorinated phenols by re-adsorbing fresh surfactant. The recycled adsorbent exhibits performance properties comparable to the original adsorbent. These results demonstrate the feasibility of utilizing a surfactant-modified pillared clay as a recyclable adsorbent and combustion catalyst for environmental pollutants.

Key Words—Adsorption, Alumina-pillared clay, Chlorinated phenols, Tergitol.

INTRODUCTION

Activated carbons are among the most effective adsorbents known for the removal of organic toxicants from aqueous effluents and contaminated groundwater (Suffet and McGuire, 1980). Although these high surface area materials can be regenerated by thermally desorbing or combusting the toxicant in air, a substantial fraction of the carbon is lost with each oxidation cycle. This loss of adsorbent is a major economic consideration in any large-scale remediation application (Guymont, 1980).

In the past few years, there has been increasing interest in designing recyclable inorganic adsorbents, particularly smectite clay-based materials for the efficient removal of organic pollutants from aqueous solutions. Organic molecules can bind to smectite clay surfaces by a variety of mechanisms (Mortland, 1970, 1986; Theng, 1974; Chiou *et al.*, 1979, 1983). Owing to their hydrophilic nature, however, these clays are relatively poor adsorbents for the removal of neutral organics from aqueous environments. Thus, chemical modification of smectite clay surfaces is necessary in order to utilize their high internal surface area ($\approx 750 \text{ m}^2 \text{ g}^{-1}$) efficiently.

In one approach to the chemical modification of smectite clays, the inorganic exchange cations on the gallery surface of the pristine minerals were replaced with organic cations containing long-chain alkyl groups (McBride *et al.*, 1977; Garwood *et al.*, 1983; Wolf *et al.*, 1986; Boyd and Mortland, 1985, 1986; Mortland

et al., 1986; Boyd *et al.*, 1988). Boyd and his coworkers (Boyd and Mortland, 1985, 1986; Mortland *et al.*, 1986; Boyd *et al.*, 1988) have shown that these clay-organic complexes are exceptionally effective in adsorbing a variety of organic molecules from water through what has been called hydrophobic binding. Even chlorinated phenols, which represent one of the most challenging classes of priority pollutants to be removed from waste streams and ground waters (Chapman *et al.*, 1982), can be adsorbed onto organo-cation exchange forms of smectite clays (Boyd and Mikesell, 1989).

Recently, Srinivasan and Fogler (1990a, b) prepared clay adsorbents by adding cetyl pyridinium cations to a hydroxy-Al cation exchange form of montmorillonite. The resulting products, referred to as inorgano-organoclay, were effective adsorbents for removing pentachlorophenol and benzo(a)pyrene from aqueous solution.

We have proposed that microporous metal-oxide pillared clays and mesoporous delaminated smectite clays might be suitable as recyclable adsorbents for the adsorption of organic pollutants (Zielke and Pinnavaia, 1988). In pillared clays, the gallery surfaces of face-face aggregated layers are made accessible by the intercalation of metal-oxide aggregates formed by the dehydration and dehydroxylation of polycations such as the oligomeric $Al_{13}O_4(OH)_{24}(H_2O)_{7\frac{1}{2}}$ cation. Conversely, in delaminated clays cardhouse-like, face-edge layer aggregation competes with face-face aggregation. Although the basal surfaces are readily accessible for adsorption in both classes of materials, the hydrophilic

nature of these surfaces limits their affinity toward organic adsorbates in aqueous environments.

In the present study, we have prepared surfactant-modified pillared clays and have investigated their adsorption properties toward chlorinated phenols in aqueous solution. The initial pillaring agent was the oligomeric Al_{13} polycation. The nonionic surfactant, Tergitol® 15S-5, an alkyl polyethylene oxide, was used to modify the pillar surfaces. This surfactant has been used to improve the methane storage capacity of alumina pillared clays derived from the Al_{13} oligomer (Fahey *et al.*, 1989). The results reported here demonstrate that the surfactant facilitates the adsorption of chlorinated phenols. Also, the surfactant can be reabsorbed following the combustion of the adsorbed toxicant at elevated temperature. Thus, the clay functions as a recyclable surfactant support for the adsorption and subsequent combustion of organic toxicants.

EXPERIMENTAL

Surfactant-modified pillared clays

The clay used for this study was natural Wyoming sodium montmorillonite with an idealized unit cell formula of $Na_{0.86}(Al_{2.98}Fe_{0.41}Mg_{0.56})(Si_{7.85}Al_{0.15})O_{20}(OH)_4$. Prior to use, the clay was purified and sodium-saturated according to procedures described elsewhere (Landau, 1984). The procedures include: sedimentation for the removal of the particle fraction $>2 \mu m$, treatment with acetic acid in sodium acetate at pH 5 at $70^\circ C$ to dissolve the carbonates, three exchanges in 1.0 M NaCl, and final washing in deionized water until the solution is chloride-free as judged by the silver nitrate test.

The nonionic surfactant, Tergitol 15S-5 was provided by Union Carbide Corp. This surfactant is a derivative of a secondary alcohol containing 5 ethylene oxide units with the general chemical formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_5H$. The average molecular weight of the surfactant is 420 and the specific gravity is 0.961.

Pillaring solutions containing $[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]_{(7-x)}$ ions were prepared by slowly adding a 0.4 M solution of sodium hydroxide to a 0.4 M solution of aluminum chloride in order to obtain a final hydrolysis ratio $OH^-/Al^{3+} = 2.4$. This value of 2.4 was chosen because it has been shown (Bottero *et al.*, 1987) that for this particular ratio the Al_{13} ion exists principally as a monomeric form, whereas larger oligomers form at higher hydrolysis ratios.

The Tergitol-modified pillared clays were prepared by first adding known quantities of the surfactant to the pillaring solution in order to form a surfactant-pillar complex. The desired amounts of Tergitol solution (1.0 g/liter) were added to 300 ml of the Al_{13} solution. A 300-ml portion of a clay suspension (5.0 g/liter) was added dropwise under vigorous stirring to the pillaring solution. The ratio of aluminum to clay

was 20 mmoles/meq. The final suspensions were allowed to age overnight. The products were collected by centrifugation, washed with deionized water until free of chloride (as judged by the silver nitrate test), and finally, air-dried on a glass plate. The amounts of Tergitol used were in the range 17–620 mg/g of clay.

The adsorbent recyclability experiments were carried out using the following procedure. A quantity of the modified pillared clay was calcined at $500^\circ C$ for 12 hours in air in a programmable oven. The calcined product was then suspended in water and the pH was adjusted to 8.0 using potassium hydroxide. The purpose of adjusting the pH was to return the alumina pillar surface mainly to the $AlOH$ form (Rakotonarivo *et al.*, 1988). An excess amount of Tergitol 15S-5 (≈ 1 g/g of clay) was added to the suspension and the suspension was stirred for 4–5 hours. The product was then washed five times using deionized water and air dried. In the case where a third cycle was attempted, the product obtained from the second cycle was calcined at $500^\circ C$ and treated according to the same procedure with Tergitol 15S-5.

Characterization methods

X-ray diffraction patterns were obtained for oriented film samples using a Rigaku diffractometer with rotating anode and $CuK\alpha$ radiation. Surface area measurements were performed at 77 K on a Quantasorb Jr surface area analyzer using nitrogen as an adsorbate. The samples were outgassed at $130^\circ C$ under a vacuum of 10^{-2} torr. Surface areas were obtained using the BET method.

Adsorption isotherms

Chlorinated phenols for adsorption studies were obtained from Sigma Chemical Corporation and were used without further purification. Table 1 summarizes the relevant physical properties of these compounds. The solubility of 3,4,5-trichlorophenol was estimated to be ≈ 1.2 g/liter based on the amount of solid dissolved in aqueous solution after stirring a mixture containing 5.0 g of the phenol per liter of water for a period of three days at room temperature.

The adsorption isotherms were carried out using the batch equilibration technique. For each isotherm, 40-mg portions of the clay were weighed in glass flasks, and 40 ml of a chlorinated phenol solution at a known concentration were added. The suspensions were stirred overnight at $25^\circ C$ in a thermostated shaker. After centrifugation, the concentration of the supernatant was determined from the UV absorbance at λ_{max} of the phenol. An IBM Model 9430 UV-visible spectrophotometer was used for the absorbance measurements. The adsorbed quantities were then determined from the difference between the initial and final concentrations. Each adsorption isotherm was determined in duplicate using two independent samples.

Table 1. Physicochemical properties of chlorophenols.

Compound	Abbrev.	λ_{\max} (nm)	Water solubility (g/kg)	pK _a
Pentachlorophenol	PCP	302,320	0.014	4.70
3,4,5-Trichlorophenol	3,4,5-TCP	294	≈1.2	7.75
3,5-Dichlorophenol	3,5-DCP	277	4.5	8.15
3-Monochlorophenol	3-MCP	274	26	9.08

RESULTS AND DISCUSSION

Adsorbent synthesis

Although nonionic polyether surfactants have been reported in the patent literature (Fahey *et al.*, 1989) for the synthesis of modified pillared clays, relatively little is known concerning the nature of these pillared products. Therefore, it was necessary as a first step to characterize some of the physical properties of the complexes obtained by using increasing amounts of Tergitol 15S-5 in the synthesis. Moreover, each sample was characterized with regard to chlorophenol adsorptive properties in order to determine a representative surfactant loading for further study.

Table 2 presents the initial quantity of surfactant used in the synthesis, the final quantity of surfactant bound to the clay based on carbon analyses, the basal spacing, and the BET surface area of the samples used in this first part of the study. Carbon analysis of the loaded samples show that for reaction mixtures containing less than 67 mg of Tergitol/g of clay, about 85% of the surfactant is present in the final product. The samples with higher Tergitol loadings show somewhat lower surfactant uptake; approximately 75%. After having been calcined at 500°C, the samples contained little or no carbon, indicating that all the surfactant is eliminated from the clay.

The X-ray basal spacings in Table 2 show that pillaring did indeed occur. For Tergitol loadings ≤134 mg/g of clay, the basal spacings are nearly constant at approximately 18.5 Å. For higher loadings, the d-spacing increases to 23 Å at a Tergitol concentration of 470 mg/g of clay.

Surface area measurements show the following trends. For Tergitol loadings ≤56 mg/g, the BET surface area remains approximately constant at ≈220 m² g⁻¹ and the shape of the N₂ adsorption isotherms are typical of microporous materials. For higher loadings, the BET surface area decreases drastically from 220 to 80 m² g⁻¹ and the shape of the isotherm reflects little microporosity. This can be explained in terms of a filling of the micropores by surfactant molecules at high loadings. Furthermore, the decrease of the surface area is correlated with an increase of carbon content of the samples.

3-monochlorophenol adsorption

Figure 1 presents the adsorption isotherm of

3-monochlorophenol (3-MCP) for each surfactant-modified sample at ambient pH (≈6.5). For low surfactant loadings, ≤56 mg/g, there is very little or no effect of surfactant on the adsorption of monochlorophenol. In this range of surfactant loading, adsorption occurs only in the microporous interlayer region of the pillared clay. The adsorbed quantity corresponding to the microporous sites is nearly constant at Q_a ≈ 25 μmoles/g. For higher loadings, where the surfactant begins to fill the micropores, there is a dramatic effect on 3-MCP binding. For an equilibrium 3-MCP concentration of 9 × 10⁻⁴ moles/liter, the adsorbed quantity is more than doubled at a Tergitol loading of 255 mg/g of clay and is quadrupled at a loading of 470 mg/g. This suggests that the presence of surfactant in the microporous volume of the pillared clay does not greatly enhance the adsorptivity of the complex. However, when the micropores are filled, surfactant molecules adsorb on secondary sites at the external surfaces of the clay particles. The surfactant-modified external surfaces have a high affinity for 3-MCP.

For the secondary surfactant binding site at external surfaces, the adsorbed quantity of 3-MCP increases with the amount of bound Tergitol. Therefore, it was of interest to normalize the adsorbed quantity obtained for these samples to the quantity of clay-immobilized surfactant. The result is presented in Figure 2. It is apparent that the normalized isotherms are quite similar. We conclude, therefore, that the chlorophenol in

Table 2. Initial and final surfactant contents, basal spacings, and BET surface areas of surfactant-modified pillared clays.

Tergitol used in synthesis (mg/g of clay) ^a	Final Tergitol content (mg/g of clay) ^b	Basal spacing (Å)	BET surface area (m ² g ⁻¹) ^c
0	0	18.3	225
17	15	17.8	243
33	28	18.6	241
67	56	18.7	225
170	134	18.9	80
330	255	19.5	65
500	320	21	104
620	470	23	72

^a Quantity of Tergitol 15S-5 added to the pillaring solution, per gram of clay.

^b Quantity of Tergitol 15S-5 fixed to the clay based on the results of the carbon analyses.

^c Outgassing conditions: 150°C, 10⁻² torr, 15 hours.

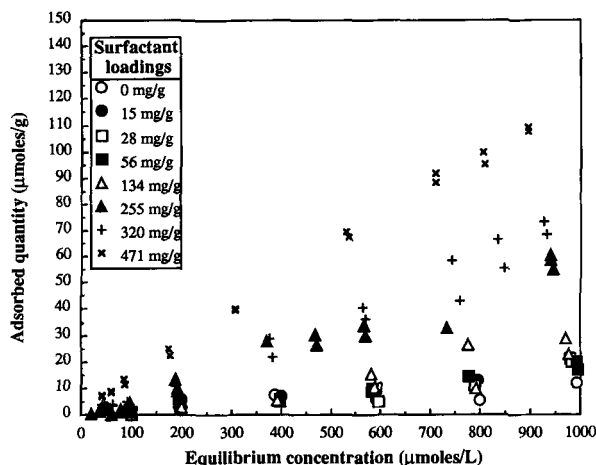


Figure 1. Adsorption of 3-monochlorophenol from water onto Al_{13} montmorillonites containing different amounts of Tergitol 15S-5.

this second adsorption stage is bound onto surfactant molecules.

In order to determine what effect the addition of surfactant has on the energetics of adsorption, it is necessary to replot the isotherms relative to the degree of undersaturation of the adsorbate in solution $\ln(C_e/C_s)$ (Cases and Mutaftshiev, 1968; Cases, 1979) where C_e is the equilibrium concentration and C_s the solubility limit of the adsorbate. The result of this transformation is presented in Figure 3. Some of the data for adsorbents with low Tergitol loadings have been omitted from this figure for clarity. Two distinct effects are evident from the curves in Figure 3. Firstly, the surfactant increases the affinity of the microporous interlayer sites towards the organic pollutant. The degree

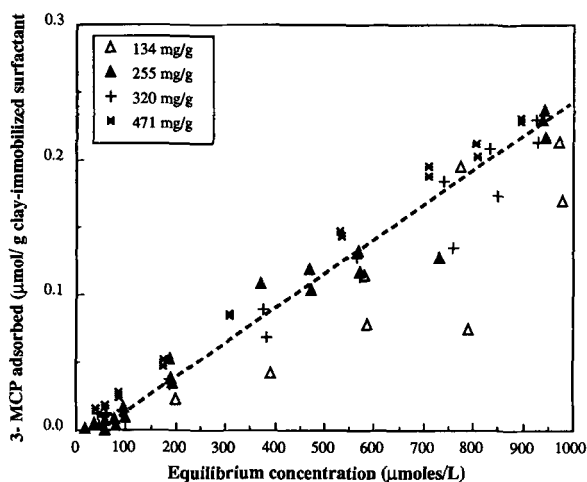


Figure 2. Normalized adsorption isotherm for 3-monochlorophenol on Al_{13} montmorillonites containing different amounts of Tergitol 15S-5.

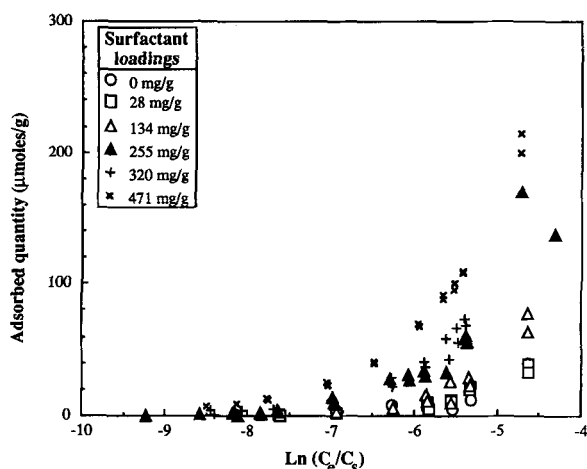


Figure 3. Adsorption of 3-monochlorophenol from water onto Al_{13} montmorillonites containing different amounts of Tergitol 15S-5. Replotted relative to the degree of undersaturation of the adsorbate.

of undersaturation needed to adsorb 25 μmoles of 3-MCP/g (which corresponds to the adsorption capacity of the interlayer sites) decreases with increasing surfactant loading. Each curve exhibits an inflection point corresponding to the filling of these microporous sites. On the other hand, once the interlayer adsorption sites were saturated, new surfactant adsorption sites, which increase linearly with surfactant loading, become available for adsorption.

These studies show that above a particular value of surfactant loading, corresponding to the amount of Tergitol needed for filling completely the microporous volume of the pillared clay, 3-MCP adsorption occurs by a single mechanism on the non-microporous surfaces. Hence, it is possible to select a loading of surfactant to study the adsorption of chlorinated phenols at the external surfaces of the surfactant-modified pillared clay. Accordingly, all subsequent studies were carried out at a surfactant loading of 255 mg/g of clay where all the micropores were filled by surfactant and where adsorption occurs mainly on the external surfaces of the surfactant-modified pillared clays.

Adsorption of 3-monochlorophenol, 3,5-dichlorophenol, 3,4,5-trichlorophenol and pentachlorophenol

As shown in Table 1, the pK_a values for 3-MCP, 3,5-DCP and 3,4,5-TCP are >7.5 . Thus, under natural pH conditions (≈ 6.5), they will all be present as the neutral phenol and not as the phenolate form. In the case of pentachlorophenol ($\text{pK}_a = 4.70$), the adsorption is carried out at pH 4 in order to limit phenolate formation in solution. The influence of the pH on the adsorption of PCP will be discussed later.

As revealed by the water solubility data (Table 1),

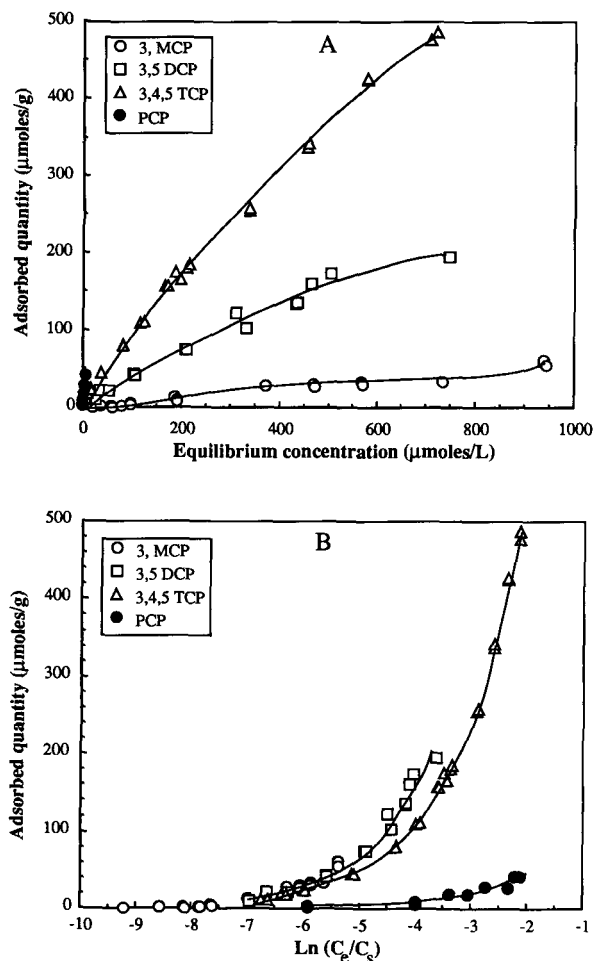


Figure 4. Adsorption of 3-monochlorophenol (pH 6.5), 3,5-dichlorophenol (pH 6.5), 3,4,5-trichlorophenol (pH 6.5), and pentachlorophenol (pH 4.0) onto Al₁₃ montmorillonite loaded with 255 mg/g of Tergitol 15S-5. (A) plotted relative to equilibrium concentration. (B) plotted relative to the degree of undersaturation of the adsorbate.

the polarity of these compounds, and thus their affinity towards the aqueous phase, decreases with increasing chlorine substitution. One may then expect that the amount adsorbed from water for a given equilibrium concentration should increase in the order 3-MCP < 3,5-DCP < 3,4,5-TCP < PCP. Figure 4A presents the adsorption isotherms at 25°C for these four adsorbates on an Al₁₃-pillared montmorillonite loaded with 255 mg of Tergitol 15S-5 per gram of clay.

As expected, the uptake of chlorinated phenol increases with the number of chlorines present. In order to compare the intrinsic affinity of the adsorbent towards the adsorbate, one needs to replot the isotherms with regard to the degree of undersaturation, $\ln(C_e/C_s)$, for reasons already mentioned. Figure 4B presents the results of such a treatment. It is then possible to draw the following conclusions from the results in Fig-

ure 4B. The affinity of the surface towards the pollutant increases in the order PCP < 3,4,5-TCP < 3,5-DCP < 3-MCP as the isotherms shift towards lower $\ln(C_e/C_s)$ values, in that order. It is interesting to notice that the isotherms are similar in shape and exhibit a small inflection point near an adsorbate loading of 25 μmoles/g. This suggests that the mechanism for adsorption is the same for these four compounds.

Influence of pH on pentachlorophenol adsorption

Figure 5A presents the adsorption isotherms for PCP at three different equilibrium values of pH. The greatest adsorption occurs at pH 4, where most of the PCP is present as the neutral phenol. Considerably less adsorption occurs at pH 7 and 10 where the phenolate form is present in solution. At pH 4, nearly all the PCP available in solution is adsorbed on the clay. The solid/liquid ratio used throughout this study limits the adsorption capacity. These results are similar to those

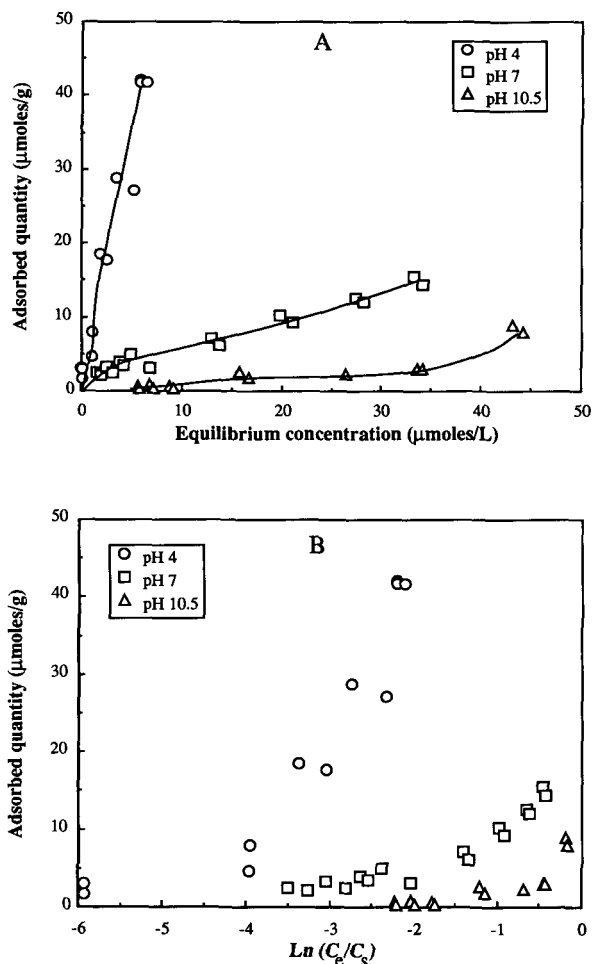


Figure 5. Adsorption of pentachlorophenol on Al₁₃ montmorillonite loaded with 255 mg/g of Tergitol 15S-5 at different pH. (A) plotted relative to equilibrium concentration. (B) plotted relative to the degree of undersaturation of the adsorbate.

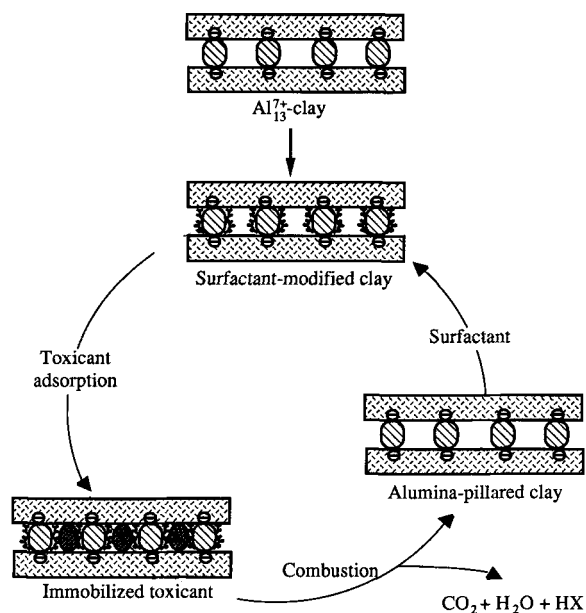


Figure 6. Scheme for the thermal recycling of a surfactant-modified pillared clay adsorbent. The surfactant is shown to occupy only microporous sites on the pillar surfaces. Surfactant on active external sites has been omitted for clarity.

obtained by Srinivasan and Fogler (1990b) for PCP adsorption on Al_{13} montmorillonite modified by coadsorption of a cationic surfactant.

In order to obtain a better understanding of the PCP adsorption mechanisms, it was necessary to replot the isotherms relative to the degree of undersaturation, as shown in Figure 5B. In a paper dealing with the adsorption of chlorinated phenols on pillared and delaminated clays, Zielke and Pinnavaia (1988) showed that pentachlorophenol adsorption was very much influenced by the equilibrium pH, with almost no measurable uptake for equilibrium pH > 7. In contrast, pentachlorophenol adsorption on organo-clays is also pH independent (Boyd *et al.*, 1988). Considering this fact, it is now possible to explain the PCP behavior displayed in Figure 5B. At pH 4, a limited number of metal-oxide surface sites of the clay are preferred for PCP adsorption. This can be deduced from the inflection point in the curve around $Q_a = 25 \mu\text{moles/g}$. For a value of $\ln(C_e/C_s)$ near -2 , surfactant sites become available for adsorption and the adsorbed quantity of

PCP increases again. For an equilibrium pH of 7, the metal-oxide sites, which may also be influenced by the pH, adsorb only very little PCP (inflection point for $Q_a \approx 5 \mu\text{moles/g}$). However, at a value of $\ln(C_e/C_s)$ near -2 , the surfactant sites become occupied and the adsorbed quantity again increases. At pH 10.5, neither of these two classes of sites is preferred by the phenolate anion. It is interesting to note that in the case of the adsorption of PCP on alumina pillared montmorillonite at acidic pH (Zielke and Pinnavaia, 1988), the adsorbed quantities were much smaller than those obtained for our surfactant-modified pillared clay. Clearly, chemical modification by coadsorption of nonionic surfactant increases the binding energy of the surfaces, thus dramatically improving PCP adsorption.

Recyclability experiments

One of the main objectives of the present study was to design adsorbents that could be recycled by simple combustion of the coadsorbed organic toxicant. The surfactant-modified Al_{13} montmorillonite would then be capable of thermal recycling by combustion of both the adsorbed toxicant and surfactant as illustrated schematically in Figure 6.

Table 3 presents the surface areas and the basal spacings for a Tergitol pillared clay that has been recycled by calcining at 500°C and re-adsorption of surfactant through three cycles. This table shows that, after calcination of the surfactant-modified pillared clay at 500°C , the product obtained is an alumina-pillared clay with a basal spacing near 15 \AA , and a surface area, mainly microporous, near $250 \text{ m}^2 \text{ g}^{-1}$. When Tergitol is re-adsorbed on this pillared clay, it is again fixed to the surface as evidenced by the low N_2 surface area. The d-spacing remains constant, indicating that the pillared structure remains intact. After a second calcination cycle, one obtains, once again, an alumina-pillared clay that can be re-treated in a similar way using Tergitol.

Figure 7A presents the adsorption isotherms for 3-MCP obtained at 25°C on four of the five products used in the thermal recycling experiments (cf. Table 3). The curves displayed in this figure show good reproducibility. For samples subjected to two and three thermal cycles (samples 3, 5; Table 3) the amount adsorbed is even slightly higher than the one obtained for the initial modified alumina-pillared montmoril-

Table 3. Surface areas and basal spacings of recycled samples.

Sample	Description	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Basal spacing (\AA)
1	Al_{13} montmorillonite loaded with 255 mg/g of Tergitol 15S-5	65	19.5
2	Sample 1 calcined at 500°C	240	15.2
3	Sample 2 after suspension in Tergitol 15S-5 (1 g/g of clay)	12	15.2
4	Sample 3 calcined at 500°C	220	n.d.
5	Sample 4 after suspension in Tergitol 15S-5 (1 g/g of clay)	17	n.d.

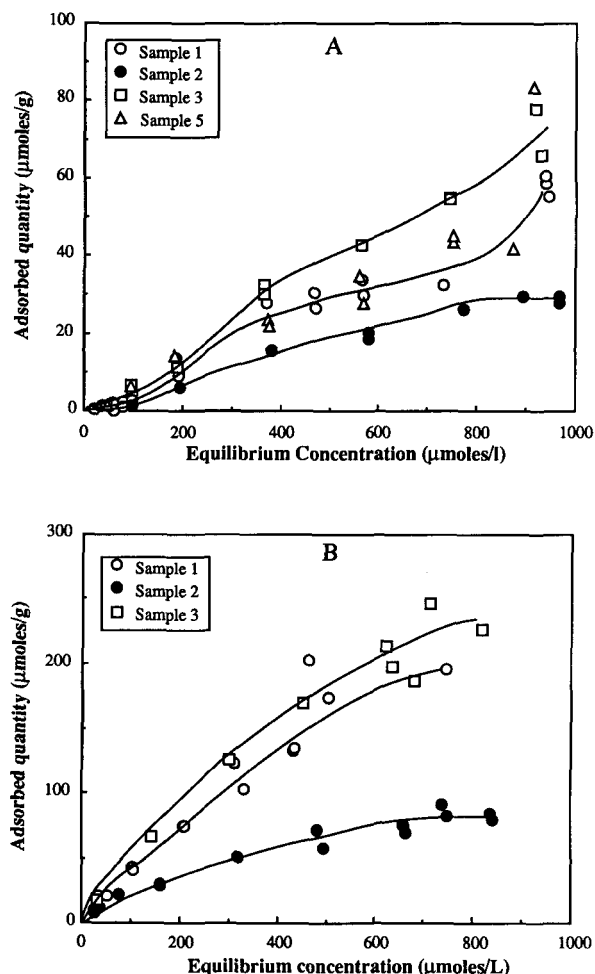


Figure 7. Adsorption on modified and recycled alumina-pillared montmorillonite. Samples described in Table 3. (A) 3-monochlorophenol adsorption. (B) 3,5-dichlorophenol adsorption.

lonite. The fact that the recycled samples exhibit slightly higher uptakes could very well be due to the dehydroxylation of the pillars during the thermal treatment.

The recyclability of the surfactant-modified pillared clay was also demonstrated with 3,5-DCP adsorption, as presented in Figure 7B. The trend exhibited for 3,5-DCP is very similar to that observed for 3-MCP. The recycled sample adsorbs somewhat more pollutant than the original product, perhaps due to pillar dehydroxylation during the calcining process.

CONCLUSIONS

It has been demonstrated here that aluminum-pillared clays modified by the addition of the nonionic surfactant, Tergitol 15S-5, exhibit interesting adsorption properties with regard to chlorinated phenols. The surfactant has a dual effect. First, it increases the affinity of the microporous interlayer adsorption sites. In the

case of pentachlorophenol adsorption, this improved affinity allows adsorption to occur much more efficiently than in the case of a conventional pillared clay. Second, surfactant molecules create new adsorption sites on the external surfaces of the clay layers. These surface chemical effects may be very useful in designing a viable adsorbent for future groundwater treatment applications.

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