

VAPOR-PHASE SORPTION AND POLYMERIZATION OF PHENOLS BY SMECTITE IN AIR AND NITROGEN

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Abstract—Reactions of smectite with phenols were investigated to understand the role of clay minerals in abating transport of these organic pollutants to ground water. Sorption of *o*-methylphenol, *o*-chlorophenol, and *m*-methylphenol by the clay with different exchange cations was accomplished by passing phenol vapors in a slow stream of air or nitrogen through the samples. The resulting products, extracted with methanol and analyzed by using mass spectrometry, included monomers, dimers, trimers, and tetramers of the parent phenol and of the corresponding quinones, the oxidation product of the phenols. In extracts from the Fe-clay-phenol complexes formed in air, traces of the phenolic pentamers were also detected. Both sorption and polymerization were much higher in air than in nitrogen. The greatly reduced polymerization in nitrogen suggests that anaerobic environment of the landfill sites may facilitate phenol transport to ground water. The degree of polymerization and its magnitude was in the order Fe- > Al- > Ca- > Na-clay.

Key Words—Adsorption, Mass spectrometry, Nitrogen, Phenols, Pollution, Polymerization, Smectite.

INTRODUCTION

Numerous investigations (Wauchope and Haque, 1971; Thompson and Moll, 1973; Saltzman and Yariv, 1975; Mortland and Halloran, 1976; Wang *et al.*, 1978; Larsen and Hufnal, 1980; Isaacson and Sawhney, 1983; Sawhney *et al.*, 1984) have shown that phenols are commonly polymerized on clay surfaces. Consequently, these compounds are strongly held by clays and soils. Sawhney and Kozloski (1984) recently reported, however, concentrations as high as 4 ppm in ground water underneath a landfill site. Artiola-Fortuny and Fuller (1982) also noted that under saturated conditions phenols move fairly rapidly through soil columns. Sawhney and Kozloski (1984) suggested that anaerobic conditions within the landfill may prevent sorption and polymerization of phenols on soil and clay surfaces, thus facilitating their transport to ground water. Indeed, the lack of polymerization of phenols in aqueous solution under nitrogen atmosphere has been observed in clays (Thompson and Moll, 1973) and in soils (Boyd, 1982). The vapor phase is important in the transport of phenols and constitutes a simpler system than the aqueous phase, where water competes with phenols, for studying clay-phenol interactions and their products.

This report describes the sorption and polymerization of phenols in the vapor phase in air and nitrogen atmospheres, and identifies the reaction products by mass spectrometry.

MATERIALS AND METHODS

Smectite (Wyoming bentonite, API No. 26) was obtained from Ward's Natural Science Establishment,

Rochester, N.Y. The <2- μ m clay obtained by sedimentation was used throughout. Three phenols *o*-methylphenol, *m*-methylphenol, and *o*-chlorophenol, of 99% purity were purchased from commercial sources.

Na-, Ca-, Al-, and Fe-saturated smectites were prepared by three centrifuge washings of the clay fraction with a 0.1 N chloride solution of the respective cation, followed by three centrifuge washings with distilled water. The colloid was then dried at 100°C and ground to a fine powder using an agate mortar and pestle. Portions of the powdered clays (0.4 g) were placed in 2 × 0.5-in. glass columns, prepared from disposable pipets, and held in place with glass wool inserted into both ends of the column. The clays in the columns were dried again at 100°C to remove any adsorbed moisture. The columns were weighed and inserted into outlets in a glass tube manifold placed in an oven maintained at 50°C. Vapors of the phenol in a U-tube also placed in the oven were passed through the columns in a slow stream of air or nitrogen. The entire arrangement is shown in Figure 1. The columns were periodically removed from the manifold and weighed; the increase in weight gave the amount of phenol sorbed by the sample. Any water retained by the clay at 100°C and replaced by the phenol would only have resulted in under-estimation of the phenol sorbed. At the end of the experiment, the samples were flushed with the carrier gas for several hours to determine the extent of desorption of the phenols from the clays. Flushing the clay-phenol complexes produced no weight loss, indicating that the phenols were tightly sorbed onto the clays.

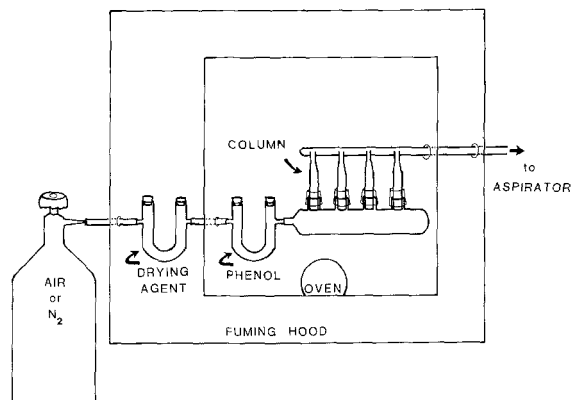


Figure 1. Diagrammatic sketch of the assembly used for vapor-phase sorption of phenols by clay samples contained in columns.

The clay-phenol complexes were analyzed by X-ray powder diffraction (XRD) using oriented specimens; a ~20-mg portion of the clay was suspended in 0.5 ml of water and air-dried on a glass slide. The basal spacing of the oriented clay was measured with a Norelco wide-angle goniometer using $\text{CuK}\alpha$ radiation.

The remaining portions of the clay-phenol complexes were then extracted with two, 5-ml centrifuge washings with methanol, and the methanol extracts were analyzed by mass spectrometry (MS) using a HP 5985 GC/MS system. Methanol washings remove essentially all the phenols from most clays. A 10- μl aliquot of the extract contained in a capillary tube was placed directly into the MS probe and heated from 30° to 300°C at a rate of 15°C/min. The total ion spectrum for 0–800 mass units (m/e) was obtained for each sample. Mass spectra of the individual peaks within the total ion spectra were then obtained. These spectra gave the masses and relative abundance of ionic components of each individual peak, which included the parent phenol as well as their polymerized products.

RESULTS AND DISCUSSION

Sorption of phenols

Figure 2 illustrates the sorption of *o*-methylphenol in air by smectite with Na, Ca, Al, and Fe on exchange sites. The shapes of the isotherms show that sorption was rapid initially and then appeared to level off for all samples after about 40 hr. Sorption was greatly influenced by the exchange cation and was much higher in air than in nitrogen. The Ca-saturated smectite sorbed the highest amount of the phenol, 17.2% by weight after 140 hr, whereas the Na-saturated smectite sorbed the lowest amount, 4.5%. The Fe- and Al-saturated samples sorbed intermediate amounts, 12.2% and 10.2%, respectively. Sorption of *m*-methylphenol and *o*-chlorophenol followed the same order, i.e., Ca >

Table 1. Phenols sorbed (%) in air and nitrogen by smectite saturated with different cations.

Saturating cation	<i>o</i> -methylphenol		<i>o</i> -chlorophenol		<i>m</i> -methylphenol
	Air	Nitrogen	Air	Nitrogen	Air
Na	4.5	0.08	N.D. ¹	0.20	3.2
Ca	17.2	0.05	17.3	0.40	11.6
Al	10.2	0.53	13.6	1.1	7.0
Fe	12.2	0.75	14.5	1.1	8.5

¹ N.D. = not determined.

Fe > Al > Na-saturated clay. The amounts of the phenols sorbed were in the order of their vapor pressures: *o*-chlorophenol > *o*-methylphenol > *m*-methylphenol. The greater sorption in air by the Ca-, than by the Al- and Fe-clays may be due to its larger interlayer spacings. XRD analysis showed a 15.5-Å *d*(001) spacing for the Ca-saturated clay and its phenol complex as compared to a 14-Å spacing for the Fe- and Al-saturated clays and their complexes. All clay-phenol complexes, however, resisted collapse on heating at 100°C. Thus, whereas greater interlayer sorption by Ca-clay was likely, neither the greater interlayer sorption nor the extent of this sorption in these complex systems could be established by XRD. Also, because sorption likely occurred in the interlayers as well as on the outer surfaces of clays, the basal diffraction peaks were broad and the higher order peaks were not well defined, possibly due to the formation of interstratified materials.

In contrast to vapor-phase sorption, sorption of phenols from aqueous solutions followed in the order Fe > Al > Ca > Na-saturated clay (Isaacson and Sawhney, 1983). The amounts of phenols sorbed from the vapor phase were also much higher than the amounts sorbed from the aqueous phase for two reasons: (1) because the sorptions in aqueous solutions were generally conducted at low concentrations which were limited by the solubility of the phenols; and (2) water competed with the phenols for the sorption surfaces on the clay.

The amounts of *o*-methylphenol and *o*-chlorophenol sorbed in the nitrogen atmosphere were much less than the amounts sorbed in air (Table 1). To illustrate the greatly reduced sorption in the nitrogen atmosphere, an isotherm for *o*-methylphenol sorption by Fe-saturated smectite in nitrogen is included in Figure 2. The data in Table 1 show that whereas Fe-smectite sorbed as much as 12.2% *o*-methylphenol by weight in air, it sorbed only 0.75% in nitrogen. Similarly, Al-smectite sorbed 10.2% *o*-methylphenol in air and only 0.53% in nitrogen. Ca- and Na-smectites sorbed only traces (<0.08%) of *o*-methylphenol in nitrogen. Just as in air, somewhat higher amounts of *o*-chlorophenol than *o*-methylphenol were sorbed in nitrogen (Table 1).

The sorption of phenols in nitrogen followed the

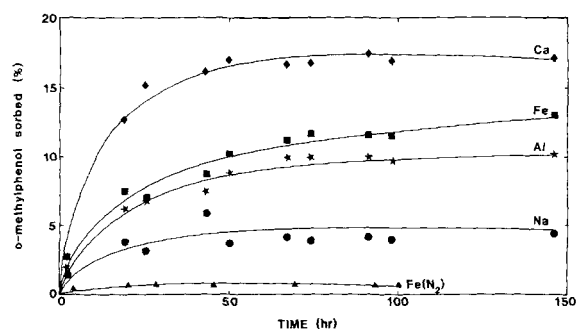


Figure 2. Vapor-phase sorption of *o*-methylphenol by smectite with Ca, Fe, Al, and Na as exchange cations (in air) and with Fe (in nitrogen).

same order, Fe- > Al- > Ca- > Na-clay, as the sorption in aqueous solutions (Isaacson and Sawhney, 1983). The higher sorption of phenols by Fe³⁺-clays than by the other clays may have been due to the fact that the exchange cation Fe³⁺ produced phenol polymerization (see Thompson and Moll, 1973; Morland and Halloran, 1976; and the results below).

Polymerization of phenols

Analyses of the methanol extracts of the clay-phenol complexes revealed that the products formed in the presence of air contained oligomers of phenols and of quinones, the oxidation products of phenols. Polymerization was inhibited or markedly reduced in the presence of nitrogen.

Based on the chromatograms and the mass spectra, showing abundance of ions of different mass (*m/e*) comprising each of the chromatographic peaks, esti-

mates of the various oligomers in the extracts from clay-phenol complexes were made (Table 2) as percentages of the total ions in the extract. The data (Table 2) show that the sorption of *o*-methylphenol in air by Na-smectite produced only the phenol dimer (*m/e* = 214), sorption by Ca-smectite produced both the phenol dimer (*m/e* = 214) and the respective quinone dimer (*m/e* = 212), as well as the phenol trimer (*m/e* = 320) and tetramer (*m/e* = 426). Fe-smectite produced di-, tri-, and tetramers of phenols as well as of the three respective quinones with *m/e* = 212, 318, and 424. Polymerization occurred to a lesser extent in the Al-smectite than in the Fe-smectite system. Traces of the pentamer of *o*-methylphenol were also detected in the extracts from Fe-clay system. Methanol extracts of the interaction products of *o*-chlorophenol with different clay preparations in air also showed that the degree of polymerization as well as the amounts of the polymerized products were the largest in Fe-clay system. Generally, the extent of polymerization of the phenols occurred in the order Fe- > Al- > Ca- > Na-clay.

In addition to the polymerized species shown in Table 2, the extracts contained the parent phenols. The proportions of these monomeric forms in the extracts were the largest and varied from 20 to 33% of total ions. The extracts also contained components with smaller *m/e*, possibly fragmentation products of the phenolic compound and of ubiquitous contaminant phthalates. No polymerization of *o*-methylphenol occurred in the nitrogen atmosphere, except for small amounts of phenolic dimers. In contrast, appreciable polymerization of *o*-chlorophenol occurred in Fe-clay, but not in other clay preparations in nitrogen.

Polymerization of phenols, being an oxidation process, is favored in the presence of air and inhibited or

Table 2. Polymerization of *o*-methylphenol and *o*-chlorophenol sorbed in air and nitrogen by Na-, Ca-, Al-, and Fe-saturated smectite.

Polymer type	Mass (<i>m/e</i>)	Air				Nitrogen			
		Na	Ca	Al	Fe	Na	Ca	Al	Fe
Percent polymer (<i>o</i> -methylphenol) ¹									
Quinone-dimer	212	—	0.34	0.15	0.24	—	—	—	—
Phenol-dimer	214	2.0	4.2	3.3	4.7	1.0	1.45	0.67	0.52
Quinone-trimer	318	—	—	0.35	0.67	—	—	—	—
Phenol-trimer	320	—	0.54	0.52	0.86	—	—	—	—
Quinone-tetramer	424	—	—	—	0.05	—	—	—	—
Phenol-tetramer	426	—	0.09	0.03	0.04	—	—	—	—
Percent polymer (<i>o</i> -chlorophenol)									
Quinone-dimer	252	N.D.	—	0.03	0.74	—	—	0.30	2.08
Phenol-dimer	254	N.D.	0.12	0.11	2.81	—	—	0.53	3.47
Quinone-trimer	378	N.D.	—	—	1.5	—	—	—	0.45
Phenol-trimer	380	N.D.	—	0.08	1.6	—	—	—	0.84
Quinone-tetramer	504	N.D.	—	—	—	—	—	—	—
Phenol-tetramer	506	N.D.	—	—	tr	—	—	—	—

¹ Percentage of total ion estimates in the mass chromatogram of methanol extracts. — = not detected; tr = trace (<0.002%); N.D. = not determined.

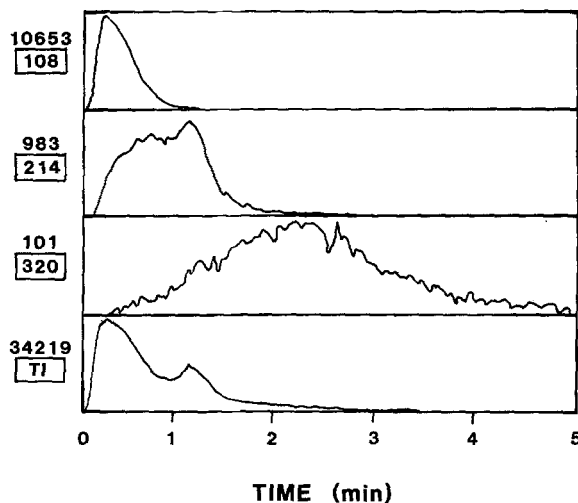


Figure 3. Total ion-mass chromatogram (TI) and mass spectra of methanol extract from Fe-clay-o-methylphenol complex, showing phenolic compounds of $m/e = 108, 214,$ and 320 . Numerical values above the boxes indicate relative abundance of the ions.

reduced in nitrogen; hence, the observed greater sorption and polymerization in air than in nitrogen. However, the amounts of phenols sorbed in air, as compared to N_2 , are in large excess of the amounts of the polymerized products. The mechanism for this large sorption is not yet clear. Nevertheless, one possibility is that the polymerized phenols may form an organophilic surface layer. Consequently, increased phenol sorption by partitioning into the organic layer on smectite surface would occur. Thus, the lack of polymerization and sorption of phenols under anaerobic conditions in landfills may facilitate their movement to ground water (Sawhney and Kozloski, 1984). The primary mechanism of polymerization involves radical species. Clay surfaces, for example, may contribute hydroperoxyl radicals (OOH) from surface adsorbed oxygen by transfer of an electron from the structural cations, such as Fe^{3+} (Larson and Hufnal, 1980). Exchange cations have been shown to influence this polymeri-

zation (Isaacson and Sawhney, 1983). In particular, transition metal cations, such as Fe^{3+} , on exchange sites can provide organic radical cations (Pinnavaia *et al.*, 1974; Mortland and Halloran, 1976) which can further enhance the degree of polymerization. Thus, Fe^{3+} -clay is more effective not only in the polymerization of phenols in the air but also in nitrogen.

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Резюме—Исследовались реакции смектита с фенолами для выяснения роли глинистых минералов в уменьшении переноса этих органических загрязняющих веществ в почвенную воду. Сорбция о-крезола, о-хлорфенола, и m-крезола глиной с различными обменными катионами достигалась путем прохождения паров фенола в медленном потоке воздуха или азота через образцы. Результирующие продукты, извлеченные метанолом и исследованные с помощью масс-спектрографа, включали мономеры, димеры, тримеры и тетрамеры исходного фенола и соответствующих хинонов, продуктов окисления фенолов. В экстрактах из Fe-глина-фенол комплексов, образованных в воздухе, были обнаружены следы фенольных пятизвенных полимеров. И сорбция и полимеризация были намного больше в воздухе, чем в азоте. Значительно уменьшенная полимеризация в азоте предполагает, что анаэробная среда почвенных насыпей может облегчать перенос фенола в почвенную воду. Последовательность степени полимеризации и ее величины была следующей: Fe- > Al- > Ca- > Na-глина. [E.G.]

Resümee—Es wurden die Reaktionen von Smektit mit Phenolen untersucht, um die Rolle der Tonminerale zu verstehen, die sie bei der Verhinderung des Transportes dieser organischen Verunreinigungen in das Grundwasser spielen. Die Sorption von o-Methylphenol, o-Chlorophenol, und m-Methylphenol durch Ton mit unterschiedlichen Kationen wurde erreicht, indem Phenoldämpfe in einem langsamen Luft- oder Stickstoffstrom durch die Proben geleitet wurden. Die entstehenden Produkte, die mit Methanol extrahiert und dann mittels Massenspektrometer analysiert wurden, beinhalteten Monomere, Dimere, Trimere, und Tetramere des Ausgangsphenols und der entsprechenden Quinone, die Oxidationsprodukte von Phenolen. In den Extrakten aus den Fe-Ton-Phenolkomplexen, die in Luft gebildet wurden, wurden auch Spuren des phenolischen Pentamers gefunden. Sowohl Sorption als auch Polymerisation waren in Luft viel ausgeprägter als in Stickstoff. Die stark reduzierte Polymerisation in Stickstoff deutet darauf hin, daß ein anaerobes Milieu der Landabfall-lage den Phenoltransport ins Grundwasser erleichtern könnte. Der Grad der Polymerisation und ihre Größenordnung verlief in der Reihenfolge Fe- > Al- > Ca- > Na-Ton. [U.W.]

Résumé—Les réactions de la smectite avec des phénols ont été investiguées pour comprendre le rôle des minéraux argileux dans la réduction du transport de ces polluants organiques aux nappes d'eau souterraines. La sorption par l'argile de méthylphénol-o, de chlorophénol-o, et de méthylphénol-m, avec différents cations d'échange, a été accomplie en passant des vapeurs de phénol dans un flot lent d'air ou de nitrogène à travers les échantillons. Les produits résultants, extraits à l'aide de méthanol et analysés en employant le spectrométrie de masse, ont inclu des monomères, dimères, trimères, et tétramères du phénol parent et des quinones correspondants, le produit d'oxidation des phénols. Dans des extraits des complexes Fe-argile-phenol formés dans l'air, des traces des pentamères phénoliques ont aussi été détectées. A la fois la sorption et la polymérisation étaient beaucoup plus élevées dans l'air que dans le nitrogène. La polymérisation fortement réduite dans le nitrogène suggère que l'environnement anaérobique des sites de remblais pourrait faciliter le transport de phénol aux nappes d'eau souterraines. Le degré de polymérisation et sa magnitude étaient de l'ordre de argile-Fe > -Al > -Ca > -Na. [D.J.]