Clays and Clay Minerals, Vol. 37, No. 5, 487–492, 1989.

DIOXON SORPTION BY HYDROXY-ALUMINUM-TREATED CLAYS

TIM NOLAN, KEERAN R. SRINIVASAN, AND H. SCOTT FOGLER
Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan 48109

Abstract—The treatment of smectites with a hydroxy-Al polymer produced chemically modified clays that had much greater affinities for chlorinated dioxins and biphenyls than untreated clays. For hydroxy-Al-treated kaolinite, the high affinity for chlorinated dioxins is thought to have arisen from an interaction between the hydroxy-Al polymer bound to the clay and the chlorinated dioxin in solution. Thus, the adsorption of dioxins from aqueous solution by hydroxy-Al-treated clays is similar to the adsorption of reactants from the gas phase by metals supported on mineral oxides during catalysis. In both systems, the essentially inert mineral oxide support effectively disperses the active adsorptive agent. At the concentrations of octachlorodioxin used in this study ($\leq$5 ppb), hydroxy-Al-montmorillonite had a distribution coefficient of 90,000 (ml/g), corresponding to about 95% removal efficiency of the dioxin from solution per batch. For hexachlorobiphenyl, the distribution coefficient was 30,000 (ml/g), and the removal efficiency was 85%.

Key Words—Adsorption, Biphenyl, Dioxin, Hydroxy-Al, Kaolinite, Pollutant, Smectite.

INTRODUCTION

The compound 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is one of the most toxic priority pollutants on the U.S. Environmental Protection Agency's list, and the development of remedial action for this toxic organic has been difficult (Rice, 1982). To destroy dioxin by biological, chemical, or thermal means will probably entail high costs, because it occurs in such low concentrations in the environment. Further, because of its extreme toxicity, there is no lower limit at which dioxin can be considered safe and would therefore require no remedial action. Thus, large amounts of environmentally neutral material must be treated along with dioxin in any treatment-destruction process. If the destruction step is preceded, however, by a matrix pretreatment operation to concentrate the pollutant, a significant reduction in cost can be realized.

One potential method of concentration involves adsorption of the dioxin from solution onto a solid. Such a physical separation could be used to remove dioxin from contaminated fluids or from solid waste leachate (Jackson *et al.*, 1986). The optimal solid sorbent for dioxin should have the following properties: low cost, ease of handling, environmental neutrality, high affinity, high selectivity, and the capability of being integrated into a dioxin-destruction process. Among the many candidate sorbents examined, clays meet the majority of the above criteria; however, clays in their natural state exhibit neither high affinity for nor removal selectivity of hydrophobic compounds, such as dioxin (Weber *et al.*, 1983; Karickhoff *et al.*, 1979). On the other hand, clays may be easily modified to adsorb dioxins selectively from solution. Further, the reported ability of Cu^{2+}-exchanged smectite to catalyze dioxin-dechlorination reactions raises the possibility of combining adsorption and subsequent destruction of dioxins on such modified clays (Boyd and Mortland, 1985).

Previous work in the authors' laboratory on the use of modified clays as sorbents for dioxin removal has resulted in the development of an inorgano-clay (e.g., hydroxy-Al-montmorillonite) and an organo-clay (e.g., humic acid-hydroxy-Al-montmorillonite) (Srinivasan and Fogler 1986a, 1986b; Srinivasan *et al.*, 1985). The high binding affinity of the former for dioxin was attributed to the clay's ability to function as a two-dimensional zeolite. It is well known that smectites intercalated with the hydroxy-Al moiety can entrap small molecules (Tzou, 1983; Pinnavaia, 1983); but, on the other hand, humic acid-hydroxy-Al-montmorillonite does not bind dioxins strongly even at a high organic carbon content of 8.6% (Srinivasan and Fogler, 1986b). A different kind of an organo-clay containing cationic surfactant as the source of surface organic carbon, however, was found to be as effective as hydroxy-Al-montmorillonite in binding dioxins (Fogler and Srinivasan, 1986). Even hydroxy-Al-kaolinite was found to be a potent adsorbent of dioxins (Nolan, 1988). Because kaolinite is not known to intercalate hydroxy-metal polymers, the hydroxy-Al itself may have been the active component mediating the strong affinity of the hydroxy-Al-modified clays for dioxins in solution. Thus, the hydroxy-Al clay can be envisioned as a composite consisting of a base clay and a hydroxy-Al polymer.

In the present paper, the strong affinity of modified smectites and other clay minerals for dioxins in aqueous media is described. Inasmuch as 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is extremely toxic, a structural analog of 2,3,7,8-TCDD, octachlorodibenzo-p-dioxin (OCDD) was chosen as the target sorbate, and the bulk of the work discussed in this paper is related to OCDD binding, with the caveat that such an analysis is also applicable to 2,3,7,8-TCDD. Data on the adsorption of structurally related polychlorinated biphenyls are also discussed.

Copyright © 1989, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1989.0370515 Published online by Cambridge University Press

MATERIALS AND METHODS

Preparation of sorbents

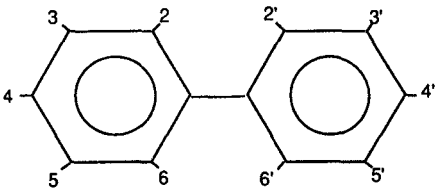
Montmorillonite (SWy-1) and kaolinite (KGa-1) were obtained from the Source Clays Repository of The Clay Minerals Society (van Olphen and Fripiat, 1979). Activated carbon (Filtrasorb 400) was obtained as a gift from Calgon Corporation. All materials were washed with water to remove soluble salts prior to use in the partitioning experiments. Pseudo-gibbsite (gelatinous aluminum trihydroxide) was prepared by titrating hydroxy-Al polymer solution obtained from Reheis Chemicals. The solution was first diluted to 0.3 M from a 6.1 M stock concentration and then titrated with 0.1 M NaOH. During titration an aluminum hydroxide gel formed; this gel was separated by centrifugation and dried in an oven at 80°C. The resultant solid was then ground to a powder.

The hydroxy-Al-montmorillonite composites were prepared by treating montmorillonite with Reheis hydroxy-Al polymer solutions (Srinivasan and Fogler, 1986a). An analogous procedure was followed for the preparation of hydroxy-Al-kaolinite. Additionally, fresh solutions of hydroxy-Al polymer (Tzou, 1983) were prepared from 0.3 M $AlCl_3$ solutions titrated with 0.1 M NaOH until an (OH/Al) ratio of 2:1 was obtained. Solutions were prepared at room temperature and at 95°C, with vigorous mixing. They were then mixed for 1 day to eliminate colloidal solids formed during the titration procedure. After this period, the prepared hydroxy-Al solutions were equilibrated with montmorillonite following the same procedure used for the equilibration of clay with the solutions prepared from the commerical hydroxy-Al polymer mixture.

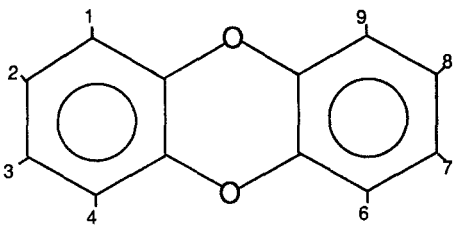
Partitioning experiments

All sorbates employed in the partitioning experiments were obtained from Pathfinders Laboratories in Saint Louis, Missouri, and were labeled with ^{14}C for liquid scintillation counting. The sorbates and their respective aqueous solubilities (20°C) are: octachlorodibenzo-p-dioxin, 0.2 ppb (Friesan *et al.,* 1985); 2,3,7,8-tetrachlorodibenzo-p-dioxin, 0.32 ppb (Schroy *et al.,* 1985); 1,3,6,8-tetrachlorodibenzo-p-dioxin, 0.32 ppb (Friesan *et al.,* 1985); 2,4,2′,4′-tetrachlorobiphenyl, 68 ppb (Hutzinger *et al.,* 1974); 3,4,3′,4-tetrachlorobiphenyl, 175 ppb (Hutzinger *et al.,* 1974), and 2,4,5,2′,4′,5′-hexachlorobiphenyl, 8.8 ppb (Hutzinger *et al.,* 1974). The generic structure and the nomenclature of dioxins and biphenyls are shown in Figure 1.

All adsorption experiments were performed in 20-ml glass scintillation vials. The sorbents were weighed and placed in the vials. The sorbent concentration used in this study was fixed at 5 mg/20 ml or 250 ppm. For 1,3,6,8-tetrachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin, the aqueous medium was spiked with 3000 ppm of tetrahydrofuran (THF). The presence of



Biphenyl Structure with Hydrogen Substitution Nomenclature



Dibenzo-p-dioxin Structure with Hydrogen Substitution Nomenclature

Figure 1. Biphenyl and dibenzo-p-dioxine structures.

THF as a co-solvent was necessitated by the low aqueous solubility of dioxins. In the absence of the co-solvent, the sensitivity of the ^{14}C radiometric assay was not sufficiently high to provide reliable data on the residual dioxin concentration in solution following adsorption. ^{3}H labeling, which would yield higher specific radioactivities, was not possible with OCDD, because it has no hydrogen atoms. With 3000 ppm by volume of THF in the medium, initial dioxin concentrations in ppb range (1–5 ppb) could be used. Previous work by Srinivasan and Fogler (1986b) established that a binary mixture of 3000 ppm THF-H_2O was a good solvent for dioxins at ppb levels, thus minimizing nonspecific adsorption of dioxins on walls of reaction vessels.

For 2,3,7,8-tetrachlorodibenzo-p-dioxin, the level of radiolabeling was sufficiently high to allow the sorption experiments to be performed at less than the reported solubility limit. Finally, because of the higher aqueous solubilities of polychlorinated biphenyl congeners, a co-solvent was unnecessary and was, therefore, not used.

Each of the experiments was performed in batches of six replicates. In each, the sorbate mass accounted for exceeded 95%, and less than 5% of the initial charge of sorbate was found to be associated with the glass vial. The concentrations of the sorbate in solution and on the sorbent surface were independently measured, as has been detailed elsewhere (Srinivasan and Fogler, 1986b). The extent of adsorption is quantified by the so-called partition coefficient or a phase transfer ratio. The phrases partition coefficient and distribution coefficient are used here interchangeably without specific implication with regard to the actual adsorption mech-

https://doi.org/10.1346/CCMN.1989.0370515 Published online by Cambridge University Press

Table 1. Binding of octachlorodioxin (OCDD) to different preparations of hydroxy-Al-montmorillonite.

Sorbent	$OCDD_{3000}$[1] distribution coefficient (ml soln/g)
Montmorillonite d-value = 9.8 Å BET surface area = 25 m^2/g	2,800 ± 800
Hydroxy-Al-montmorillonite	
Commercial hydroxy-Al solution 0.3 M Al, OH/Al = 2.5 d-value = 17.8 Å BET surface area = 200 m^2/g	94,000 ± 10,000
Hydroxy-Al solution from aluminum chloride titration 0.3 M Al, OH/Al = 2.0 d-value = 15.5 Å BET surface area = 250 m^2/g	37,000 ± 5,700
Hydroxy-Al solution from aluminum chloride titration 0.3 M Al, OH/Al = 2.0 Solution prepared at 95°C d-value = 15.4 Å BET surface area = 150 m^2/g	42,200 ± 4,300

[1] Same symbols as in Tables 2 and 3.

anism. Thus, the distribution coefficient (DC) is defined as:

$$(DC) = \frac{\text{Sorbate solid-phase concentration}}{\text{Sorbate solution-phase concentration}}.$$

The units of the distribution coefficients are ml of solution/g of sorbent. The mean distribution coefficients and their respective standard deviations were calculated from all the six experimental values. All sorption experiments were performed at 25°C.

The question is whether a single-point isotherm is a valid method of comparing the efficacy of different adsorbents. Previous work in this laboratory showed that for chemical modifications that result in significant enhancement of the phase distribution ratios or removal efficiencies, such a comparison is valid and provides for a qualitative understanding of the adsorption process. A full isotherm, however, is necessary to obtain the required adsorption parameters for use in the design of a large-scale treatment system.

Characterization of sorbents

The sorbents used in this study were analyzed by X-ray powder diffraction to determine basal spacings, and sorbent surface areas were determined by nitrogen adsorption and isotherm analysis by the BET equation. These studies demonstrated that the surface areas and basal spacings of the hydroxy-Al clays were comparable to those previously reported for hydroxy-Al-treated clays. Selected surface area and basal spacing results are listed in Table 1.

RESULTS AND DISCUSSION

Effect of hydroxy-Al treatment on dioxin adsorption

The increase in the partitioning due to hydroxy-Al treatment of montmorillonite for several chlorinated dioxins is presented in Table 2. As explained above, tetrahydrofuran (THF) was used as a co-solvent for 1,3,6,8-TCDD (30,000 ppm) and octachlorodioxin (3,000 ppm); however, no THF was present in the medium during adsorption experiments with 2,3,7,8-TCDD. For all three dioxin, the distribution coefficients increased significantly in comparison with the untreated montmorillonite. The distribution coefficient values reported in Table 2 correspond to 90–95% removal of the dioxin initially added to the vials. Results with different amounts of THF (Table 2) show that this co-solvent had no effect on the sorption process. Secondly, the similarity of distribution coefficients obtained with the three dioxins indicates that OCDD is an acceptable structural surrogate for all dioxins, especially for the higher chlorinated dioxins.

Effect of heat treatment on dioxin partitioning

Table 3 shows the partitioning of OCDD to hydroxy-Al clays that had been subjected to heat treatment. A sample of the hydroxy-Al sorbent was maintained at the indicated temperature for 24 hr, and then cooled in a desiccator until the partitioning experiment was performed to prevent rehydration of the heat-treated clay. The results presented in Table 3 reveal that the distribution coefficient of OCDD decreased sharply following heat treatment at temperatures >190°C. According to Tzou (1983) and Pinnavaia *et al.* (1984) at this temperature clay pillars do not collapse. The IR

Table 2. Partitioning of dioxins to hydroxy-Al-montmorillonite.

Sorbate[1]	Distribution coefficient (ml of soln/g)	
	Montmorillonite	Hydroxy-Al-montmorillonite
2,3,7,8-TCDD (no THF present)	2,800 ± 800	67,100 ± 6,000
1,3,6,8-TCDD (30,000 ppm THF)	9,700 ± 1,000	97,700 ± 12,000
Octachlorodibenzodioxin (3000 ppm THF)	2,800 ± 800	94,000 ± 10,000

[1] 2,3,7,8-TCDD = 2,3,7,8-tetrachlorodibenzo-p-dioxin; 1,3,6,8-TCDD = 1,3,6,8-tetrachlorodibenzo-p-dioxin; THF = tetrahydrofuran.

https://doi.org/10.1346/CCMN.1989.0370515 Published online by Cambridge University Press

Table 3. Effect of heat treatment of hydroxy-Al-montmorillonite upon octachlorodioxin (OCDD) partitioning.

Sorbent	$OCDD_{3000}$[1] distribution coefficient (ml of soln/g)
Montmorillonite	2,800 ± 800
Montmorillonite (heat treated at 550°C)	2,200 ± 400
Hydroxy-Al-montmorillonite	94,000 ± 10,000
Hydroxy-Al-montmorillonite (heat treated at 170°C)	1,100 ± 100
Hydroxy-Al-montmorillonite (heat treated at 550°C)	1,800 ± 200

[1] The subscript 3000 indicates that OCDD partitioning experiment was performed in presence of 3000 ppm of tetrahydrofuran.

measurements of Fogler and Srinivasan (1986) confirm this interpretation. Heat treatment at 550°C resulted in pillar collapse, and at this temperature OCDD partitioning was also greatly reduced. Thus, the hydroxy-Al pillars in the interlayer spaces of montmorillonite may not have been the key feature of the polymer-clay composite which strongly adsorbed dioxins. The observed changes in the pattern of OCDD partitioning were probably due to phase transitions on heating and dehydration of the gelatinous hydroxy-Al polymer associated with the montmorillonite-polymer composite. Gelatinous aluminum trihydroxide converts to η-alumina between 200° and 600°C (Misra, 1986) and apparently, at the onset of dehydration, the gelatinous trihydroxide began to lose its ability to partition. Therefore, experiments with precipitated hydroxy-Al polymer and hydroxy-Al-kaolinite were carried out.

The affinities of OCDD for the precipitated hydroxy-Al polymer (pseudo-gibbsite) and hydroxy-Al-treated kaolinite and the results for hydroxy-Al-treated montmorillonite are presented in Table 4. Chemically modified kaolinite and gibbsite showed marked improvements in dioxin adsorption compared with untreated clays. Because hydroxy-Al polymers do not intercalate kaolinite (Rengasamy and Oades, 1978), the high partitioning of hydroxy-Al-montmorillonite for dioxins may be attributed to the affinity of dioxin for the hydroxy-Al polymer bound to kaolinite. Similar considerations apply to precipitated hydroxy-Al wherein a base was used to neutralize the positive charge of the polymer instead of kaolinite or montmorillonite. The larger distribution coefficients seen with hydroxy-Al-montmorillonite compared with precipitated hydroxy-Al or hydroxy-Al-kaolinite suggest that montmorillonite was a much better dispersing medium or support. In other words, the clay may have improved the interaction of the hydroxy-Al polymer with dioxin in solution.

Table 4. Partitioning of octachlorodioxin (OCDD) on nonpillared hydroxy-Al-treated clays.

Sorbent	$OCDD_{3000}$[1] distribution coefficient (ml soln/g)
Untreated kaolinite (KGa-1)	380 ± 30
Hydroxy-Al-kaolinite	31,000 ± 400
Precipitated-hydroxy-Al (pseudo-gibbsite)	32,000 ± 6,000 (24 hr)
Hydroxy-Al-montmorillonite	94,000 ± 10,000

[1] The subscript refers to tetrahydrofuran concentration in ppm.

Table 5. Kinetics of octachlorodioxin (OCDD) adsorption to hydroxy-Al-derived sorbents.

Time (hr)	$OCDD_{3000}$[1] distribution coefficient (ml of soln/g)	
	Precipitated hydroxy-Al	Hydroxy-Al-montmorillonite
1	6,300 ± 400	29,500 ± 5,000
4	7,400 ± 400	37,200 ± 4,200
16	24,000 ± 4,000	87,200 ± 11,000
24	32,000 ± 6,000	94,000 ± 10,000
64	73,000 ± 12,000	90,000 ± 11,000
72	64,000 ± 10,000	88,000 ± 7,000
192	77,000 ± 11,000	87,000 ± 7,000

[1] Experimental conditions same as in Tables 2 and 3.

The rate of sorption of OCDD on precipitated hydroxy-Al and hydroxy-Al-montmorillonite is presented in Table 5. The attainment of stationary values of the distribution coefficients was much slower for the precipitated hydroxy-Al polymer, which could have arisen from mass transfer limitations on the surface of such a gelatinous material. Because the heat treatment results indicated that intercalation of hydroxy-Al in hydroxy-Al montmorillonite was not the decisive factor for improving dioxin adsorption, the faster kinetics observed for hydroxy-Al-montmorillonite may be attributed to preferential binding of dioxins to hydroxy-Al polymers on the external surfaces of montmorillonite; i.e., association of the polymer with the clay surface helped the polymer to contact OCDD more effectively, supporting again the concept of hydroxy-Al montmorillonite as a supported catalyst.

The partitioning behavior of octachlorodibenzo-p-dioxin in pure THF solutions is presented in Table 6. Because THF is a good solvent for dioxins, the solvophobic component of the adsorption free energy was essentially the same for all the adsorbents, i.e., treated and untreated clays. In other words, in aqueous solutions, the major impetus to the adsorption of dioxins

Table 6. Binding of octachlorodioxin (OCDD) to clay and modified clay from tetrahydrofuran solution.

Sorbent	OCDD distribution coefficient (ml of soln/g)
Montmorillonite	274 ± 27
Hydroxy-Al-montmorillonite	565 ± 28

https://doi.org/10.1346/CCMN.1989.0370515 Published online by Cambridge University Press

Table 7. Binding of chlorinated biphenyls[1] to treated clays.

Sorbent	Distribution coefficient (ml of soln/g)		
	2,4,2',4-TeCB	3,4,3',4'-TeCB	2,4,5,2',4',5'-HeCB
Kaolinite	1,350 ± 200	4,100 ± 500	1,500 ± 170
Montmorillonite	1,140 ± 200	5,200 ± 700	1,000 ± 150
Hydroxy-Al-kaolinite	2,200 ± 260	9,100 ± 1,000	7,920 ± 820
Hydroxy-Al-montmorillonite	3,000 ± 500	16,600 ± 3,400	30,500 ± 5,000

[1] 2,4,2',4-TeCB = 2,4,2',4-tetrachlorobiphenyl; 3,4,3',4'-TeCB = 3,4,3',4'-tetrachlorobiphenyl; 2,4,5,2',4',5'-HeCB = 2,4,5,2',4',5'-hexachlorobiphenyl.

was their extreme hydrophobicity. This driving force was augmented by specific interaction between the chlorine atoms of the dioxins and the Lewis acid sites of surface hydroxy-Al. Recent calculations of the electronic configuration of the ground state of dioxins have shown that chlorination at the carbon skeletal positions of 2, 3, 7, or 8 (Figure 1; bottom structure) leads to an increase in the localized electron density of 0.14 unit of charge per chlorine atom (Miller *et al.*, 1977). Thus, a charge-transfer type complex between chlorine atoms of dioxins and the Lewis acid sites of Al was possible. The existence of similar complexes between trichloroethylene and clay minerals was verified by infrared (IR) spectral shifts of C–Cl bonds, if the Cl atom was involved in surface complexation through intercalation. The IR band of C–Cl stretch showed a positive shift upon intercalation into the clay matrix. Gibbons and Soundararajan (1988) postulated that the coordination of Cl atom with the surface Al draws electron density from the carbon skeleton towards the C–Cl bonds, resulting in the observed positive shift. Such an induction effect resulted in the lone hydrogen atom of trichloroethylene being able to form a hydrogen bond to surface hydroxy groups.

Note, however, that chlorinated dioxins can also bind to electron donating sites, such as protein receptors, through the electropositive carbon skeleton, and that the electronegative Cl atoms on the molecule can help stabilize such complexes (Kende *et al.*, 1974). Thus, the exact mode of adsorption of dioxins on hydroxy-Al modified clay surfaces is not clear. Probably, desolvation (dehydration) of surface sites was the major inhibiting factor against dioxin adsorption. On the other hand, the extreme hydrophobicity of dioxins and their potential to form charge transfer complexes can compensate and help explain the affinity between dioxins and hydroxy-Al observed in this study. Because in neat THF, the solvophobic component of the adsorption free energy was very small, the adsorption efficiency was very low.

A comparison of different hydroxy-Al-montmorillonite samples prepared from various solutions of hydroxy-Al polymers is presented in Table 1 along with the relevant properties of these adsorbents. The lack of correlation between the observed physical properties of the adsorbents and their respective ability to bind dioxins is an indication of heterogeneity in the preparations. For all samples, however, a significant improvement in sorption efficiency was noted. The pillar heights of these treated clays were less than those obtained for the clay complexes derived from the commercially derived hydroxy-Al mixtures, in agreement with the observations of Oades (1984). Furthermore, the OCDD partitioning results also indicate that the height of the pillar was not the critical variable in determining the extent of dioxin sorption. The XRD results presented are in agreement with those reported by Pinnavaia *et al.* (1984), Lahav *et al.* (1978), and Oades (1984).

Chlorinated biphenyl results

Unlike dioxins, biphenyl rings have a tendency to bend out of the molecular plane, especially if a Cl atom is located at any one or more of the 2,2',6,6' positions of the two rings (Figure 1; top structure). Second, higher chlorinated biphenyls, such as hexachlorinated biphenyls, are less non-planar than the tetrachlorinated congeners. Third, the 2,2',4,4'-tetrachlorobiphenyl should be significantly non-planar and have a large dihedral angle (Rapaport and Eisenreich, 1984). The partitioning behavior of three different chlorinated biphenyls for untreated clays and hydroxy-Al-treated clays is presented in Table 7. As mentioned above, no cosolvent was present in the medium used for the sorption experiments. In all experiments hydroxy-Al treatment improved the sorption efficiency for all the biphenyls tested. The amount of increase, however, depended strongly upon the individual congener examined. Further, the partitioning values for hexachlorobiphenyl equaled or exceeded those previously reported for clays having various organic contents (Horzempa and DiToro 1983).

As pointed out above, 2,4,2',4'-tetrachlorobiphenyl may be significantly non-planar due to the overlapping of ortho-substituted chlorines relative to the phenyl inter-ring bridge. Second, the crowding of chlorines substituted on adjacent phenyl ring may also promote non-planarity of the ring system (Shaw and Connell, 1980). On the other hand, 3,3',4,4'-tetrachlorobiphenyl may be significantly less non-planar for the above

https://doi.org/10.1346/CCMN.1989.0370515 Published online by Cambridge University Press

mentioned reasons. Thus, the higher distribution coefficient for the 3,3′,4,4′-tetrachlorobiphenyl on hydroxy-Al-montmorillonite may have been related to the smaller dihedral angle for this congener. Inasmuch as the dioxins are rigid, planar molecules, the higher affinity of the 3,3′,4,4′-tetrachlorobiphenyl for hydroxy-Al surface supports the idea that hydroxy-Al modification may have promoted preferential adsorption of planar or near-planar hydrophobic molecules. This hypothesis is strengthened by the fact that this effect was observed for both kaolinite and montmorillonite. The observed variations in the partitioning of the chlorinated biphenyl congeners, however, may have stemmed from differences in the polarity or the aqueous solubility of the tetrachlorinated congeners.

Finally, the Cl atoms on polychlorinated biphenyls may have taken part in surface complexation reactions similar to the ones proposed for the chlorinated dioxins. Detailed calculations of the electron density distribution of the Cl atoms of chlorinated biphenyls are not available. Therefore, further consideration of such sorption mechanisms must await the availability of such data.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the U.S. Environmental Protection Agency (Grant No. CR 51255-02-0), the U.S. Department of Energy/Pittsburgh Technology Center (Grant No. DE-FG22-87PC79918), and the Jesse Noyes Foundation.

REFERENCES

Boyd, S. A. and Mortland, M. M. (1985) Dioxin radical formation and polymerization on Cu(II)-smectite: *Nature* **316,** 532–535.

Fogler, H. S. and Srinivasan, K. R. (1986) Use of clay-based adsorbents for the removal of chlorinated dioxins and biphenyls from industrial wastewaters: in *Proc. The Third World Congress of Chemical Engineering, Vol. 3, Tokyo, Japan,* Soc. Chem. Eng. Japan, Tokyo, 623–626.

Friesan, K. J., Sarna, L. P., and Webster, G. R. B. (1985) Aqueous solubility of polychlorinated dibenzo-p-dioxins determined by high pressure liquid chromatography: *Chemosphere* **14,** 1267–1274.

Gibbons, J. J. and Soundararajan, R. (1988) The nature of chemical bonding between modified clay minerals and organic waste materials: *American Laboratory* **20,** 38–46.

Horzempa, L. M. and DiToro, D. M. (1983) The extent of reversibility of polychlorinated biphenyl adsorption: *Water Res.* **17,** 851–859.

Hutzinger, S., Safe, S., and Zitko, V. (1974) *The Chemistry of PCB's:* CRC Press, Boca Raton, Florida, 269 pp.

Jackson, D. R., Roulier, M. H., Grotta, H. M., Rust, S. W., and Warner, J. S. (1986) Solubility of 2,3,7,8-TCDD in contaminated soils: in *Chlorinated Dioxins and Dibenzofurans in Perspective,* C. Rappe, G. Choudary, and I. H. Keith, eds., Lewis Publishers, Chelsea, Michigan, 185–200.

Karickhoff, S. W., Brown, D. S., and Scott, T. A. (1979) Sorption of hydrophobic pollutants on natural sediments: *Water Res.* **13,** 241–248.

Kende, A. S., Wade, J. J., Ridge, D., and Poland, A. (1974) Synthesis and fourier transform carbon-13 NMR spectroscopy of new toxic polyhalodibenzo-p-dioxins: *J. Org. Chem.* **39,** 931–937.

Lahav, N., Shani, U., and Shabtai, J. (1978) Cross-linked smectites. I. Synthesis and properties of hydroxy-aluminum-montmorillonite: *Clays & Clay Minerals* **26,** 107–115.

Miller, G., Sontum, S., and Crosby, D. G. (1977) Electron-acceptor properties of chlorinated dibenzo-p-dioxins: *Bull. Environ. Contamination & Toxicology* **18,** 611–616.

Misra, C. (1986) *Industrial Alumina Chemicals:* ACS Monograph 184, American Chemical Society, Washington, D.C., 73–95.

Nolan, T. (1988) Dioxin removal from aqueous solution by clays and hydroxy aluminum polymers: Ph.D. thesis, Univ. Michigan, Ann Arbor, Michigan, 187 pp.

Oades, J. M. (1984) Interaction of polycations of aluminum and iron with clay: *Clays & Clay Minerals* **32,** 49–57.

Pinnavaia, T. J. (1983) Intercalated clay catalysts: *Science* **220,** 366–371.

Pinnavaia, T. J., Tzou, M.-S., Landau, S. D., and Raythatha, R. H. (1984) On the pillaring and delamination of smectite clay catalysts by polyoxo cations of Al: *J. Mol. Catalysis* **27,** 195–212.

Rapaport, R. A. and Eisenreich, S. (1984) Chromatographic determination of octanol-water partition coefficients (K_{ow}'s) for 58 polychlorinated biphenyl congeners: *Environ. Sci. Technol.* **18,** 163–170.

Rengasamy, P. and Oades, J. M. (1978) Interaction of monomeric and polymeric species of metal ions with clay surfaces: III. Al(III) and Cr(III): *Aust. J. Soil Res.* **16,** 53–66.

Rice, A. P. (1982) Seveso accident: Dioxin: in *Hazardous Materials Spills Handbook,* G. F. Bennett, F. S. Feates, and I. Wilder, eds., McGraw-Hill, New York, 11–44.

Schroy, J. M., Hileman, F. D., and Cheng, S. C. (1985) Physical/chemical properties of 2,3,7,8-TCDD: *Chemosphere* **14,** 877–880.

Shaw, G. R. and Connell, D. W. (1980) Relationships between steric factors and bioconcentration of polychlorinated biphenyls (PCB's) by the sea mullet: *Chemosphere* **9,** 731–742.

Srinivasan, K. R. and Fogler, H. S. (1986a) Preparation and characterization of clay-based sorbents for the removal of trace levels of 2,3,7,8-TCDD from industrial wastewater: in *Chlorinated Dioxins and Dibenzofurans in Perspective,* C. Rappe, G. Choudary, and L. H. Keith, eds., Lewis Publishers, Chelsea, Michigan, 519–530.

Srinivasan, K. R. and Fogler, H. S. (1986b) Binding of OCDD, 2,3,7,8-TCDD, and HCB on clay-based sorbents: in *Chlorinated Dioxins and Dibenzofurans in Perspective,* C. Rappe, G. Choudary, and L. H. Keith, eds., Lewis Publishers, Chelsea, Michigan, 531–540.

Srinivasan, K. R., Fogler, H. S., Gulari, E., Nolan, T., and Schultz, J. S. (1985) The removal of trace levels of dioxins from water by sorption on modified clay: *Environmental Progress* **4,** 239–245.

Tzou, M.-S. (1983) Clay catalysts pillared by metal hydroxy polymers: Ph.D. thesis, Michigan State University, East Lansing, Michigan, 188 pp.

van Olphen, H. and Fripiat, J. J. (1979) *Data Handbook for Clay Materials and other Non-Metallic Minerals:* Pergamon Press, New York, 265 pp.

Weber, W. J., Jr., Voice, T. C., Pibazari, M., Hunt, G. E., and Ulanoff, D. M. (1983) Sorption of hydrophobic compounds by sediments, soils and suspended solids—II: *Water Res.* **10,** 1443–1452.

(Received 6 May 1988; accepted 25 February 1989; Ms. 1785)

https://doi.org/10.1346/CCMN.1989.0370515 Published online by Cambridge University Press