

Adsorption of Pentachlorophenol (PCP) on Clay Minerals from Hexane Solution

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崔 炅 : Hexane 溶液中에서 粘土鑛物에 의한 PCP 吸着

Summary

Adsorption experiments were carried out with several clay minerals and PCP hexane solution in order to clarify the status of adsorbed PCP on the clay surface.

The amount of PCP adsorption on clay minerals was much greater in the clay-hexane system than in the clay water system. Among the clay minerals, allophane and imogolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 1) were the most efficient adsorbents of PCP. The PCP adsorption from hexane solution was greatly hindered by the presence of water, suggesting the occurrence of adsorption by a dipole-dipole interaction.

PCP adsorption is dependent upon the nature of the clay surface and the exchangeable cations rather than the total surface area.

Introduction

Clay minerals have long been recognized as active components in soils because of their large specific surface area. Since most of the chemical and physical reactions which occur in soils are surface reactions. (6) Adsorption experiment using clay minerals is of fundamental importance to better understanding of mechanisms of adsorption in soils.

Although adsorption of many herbicides onto clays has been reported in many papers, there

are few data concerning PCP adsorption on clay minerals. Moreover, the data reported hitherto are so few that they can hardly explain the mechanism of PCP adsorption. The results reported by Choi and Aomine⁽⁵⁾ indicate that the PCP adsorption on allophanic soils ($\text{molar SiO}_2/\text{Al}_2\text{O}_3=1$) would mainly be due to coulombic force, while physical adsorption force would mainly contribute to the PCP adsorption on crystalline soils. In fact, the amounts of PCP adsorbed on the soils from aqueous solutions were so small that instrumental analysis such as infrared spectroscopy, X-ray diffraction and differential thermal analysis were inapplicable to study the interaction between clay and PCP. In the present study, PCP adsorption experiments on in various clay minerals were, therefore, undertaken in hexane solutions in order to clarify the mechanism of PCP adsorption on them and the status of adsorbed PCP.

Materials and methods

Preparation of PCP-hexane solution: PCP was prepared from a sodium pentachlorophenate (produced from Tokyo Kasei Co., Ltd.) solution by neutralizing it with HCl. PCP precipitate was thoroughly washed with deionized water, and then dissolved in benzene. PCP was recrystallized by evaporating the solvent. This purification procedure was repeated for three times. Eighty milligrams of purified PCP was dissolved in 100ml of normal hexane and the stock solution was stored in a cool dark place. Just before the adsorption experiment, the solution was diluted

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Table 1. Description of clay samples

Clay	pH*	Clay mineral §	Source	Reference
510	4.75	Allo>>Im (1.3)**	Andosol Choyo, Kumamoto	Yoshinaga and Aomine (15)
576	5.00	Allo>Im (1.2)**	Andosol Uemura, Kumamoto	Yoshinaga and Aomine (16)
PA	4.70	Allo (2)**	Weathered volcanic pumice Choyo, Kumamoto	Aomine and Wada (2)
VA	5.85	Allo (1.9)**	Weathered volcanic ash Choyo, Kumamoto	Aomine and Wada (2)
KiG	5.65	Im (1.1)**	Film gel material Kitakami, Iwate	Miyauchi and Aomine (9)
Gunma	—	Mt	Bentonite Yokogawa, Gunma	—

§ Allo : allophane, Im : imogolite, Mt : montmorillonite. * pH of clay suspensions (clay : water =1:10). ** Approximate molar SiO₂/Al₂O₃.

with normal hexane to a desired concentration.

Preparation of clay samples: Six clays separated from soils were used in this investigation. A brief description of the samples is given in Table 1.

Air-dried soil samples were treated three times with 6% H₂O₂ solution, washed with deionized water, and dispersed using NaOH as the dispersing reagent. Allophanic soils were subjected to ultrasonic agitation with 150W output for 10 minutes, and dispersed by adjusting the pH of their suspensions to 4 with HCl for soils Nos. 510 and 576 and to 10 with NaOH for Soils PA and VA. The fraction less than 2 μ in diameter was collected by sedimentation and flocculation by adding NaCl. The excess NaCl was removed by repeating washing with deionized water and by centrifugation. One additional washing was made after a chloride test with silver nitrate had been negative. These Na ion saturated clays (Na-clays) were lyophilized and stored in glass containers. A portion of the Na-clay was converted to H ion saturated clay (H-clay) with HCl and dialyzed against deionized water. H-clays were then lyophilized and stored in sealed glass containers to keep their moisture content constant. These clay samples were referred to H/Al clays in this investigation, since H-clay was known to partially Al-clay⁽³⁾. Total surface area and pHs of aqueous suspensions of these clay preparations were determined by ethylene glycol monoethyl ether

(EGME) method⁽⁴⁾ and glass electrode method, respectively. Clay minerals were identified by X-ray diffraction and the differential thermal and infrared spectroscopic methods.

Adsorption experiment:

Adsorption experiments were carried out as follows; fifty milligrams of clay and 8ml of PCP hexane solution (100ppm) were taken in a centrifuge tube. The tube was shaken at 300 strokes per minute for 3 hours at 30°C. The supernatant liquid was separated from the clay-hexane suspension by centrifugation for 15 minutes at 3,000rpm. The PCP concentration of the supernatant liquid was determined by the 4-aminoantipyrine method as slightly modified by Tsunoda⁽¹³⁾. This process was repeated for several times until no additional adsorption occurred.

Results and discussion

Effects of moisture on the PCP adsorption on clay: The water content of clays was known to be one of the principal factors in determining the nature of the interaction between organic molecules and clays⁽¹⁰⁾. Therefore, it is expected that the water content of clays also have some effects on the PCP adsorption. Adsorption experiments were carried out with the clay samples which had been stored in desiccators

containing H_2SO_4 solution of various concentration, or had been vacuum-dried over P_2O_5 . The procedure of these adsorption experiments was the same as described above. The results obtained are listed in Table 2. As shown in this table, the PCP adsorption capacity is a function of the water content of clays, and the lower the water content, the larger the PCP adsorption capacity. Also, there is an abrupt drop in the PCP adsorption capacity at some water content between 10 to 20%, which roughly corresponds to the amount of water covering the whole clay surface as monolayer.

Similar results were obtained by Spencer et al.^(11,12) for lindane (1, 2, 3, 4, 5, 6-hexachlorocyclohexane gamma isomer) and dieldrin (1, 2, 3, 4, 10, 10-hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8a-octahydro-1, 4-endo-exo-5, 8, -dimethanonaphthalene), and by Yaron and Saltzman⁽¹⁴⁾ for parathion (o, o-diethyl-o-p-nitrophenyl phosphorothioate) adsorption on soils. They found that partial vapor pressure of these insecticides in soil air was high when a monolayer of water was present in soil and decreased markedly when soil water content dropped below this value. On

the other hand, clay samples equilibrated with water saturated air exhibited a less PCP adsorption from hexane solution than from aqueous solution. In this particular situation it would be difficult for PCP to approach the adsorption site of clay surface, because PCP shows more affinity to hexane than water where the two liquids coexist. However, compared the clay-hexane system with the corresponding clay-water system in the case of clay No. 510, the PCP adsorption capacity was 7.67mg/g in the former system and 2.00mg/g in the latter system. In the clay-hexane system, PCP is preferentially adsorbed on the clay surface, because PCP has a dipole moment while hexane has not. Egashira and Aomine⁽⁶⁾ found that heat of immersion value of ethylene glycol was higher than that of ethanol for allophane. They ascribed this difference to the difference in the amount of adsorption, which would be resulted from the fact that ethylene glycol has a larger dipole moment than ethanol. In contrast to hexane, water is preferentially adsorbed on the clay surface by dipole-dipole interaction and/or hydrogen bonding, and relatively a small amount of PCP can approach to the clay surface.

Table 2. Effect of the moisture content of clays on the PCP adsorption capacity

510(H/Al)		510(Na)		VA(H/Al)		Gunma(H/Al)	
M. C* (%)	PCP AD** (mg/g)	M. C* (%)	PCP AD** (mg/g)	M. C* (%)	PCP AD** (mg/g)	M. C* (%)	PCP AD** (mg/g)
0	7.67	0	4.78	0	3.57	0	0.506
6.0	5.59	8.6	3.57	11.2	3.39	2.4	0.496
8.0	5.40	20.5	0.503	16.6	1.39	8.8	0.429
31.3	0.93	26.3	0.333	28.4	0.666	17.1	0.214
52.7	0.47	60.0	0.184	77.6	0.128	54.2	0.110

* M. C : Moisture content. **PCP AD. :PCP adsorbed. (H/Al) : H-saturated, (Na) : Na-saturated clay.

Distribution of PCP molecules on the clay surface: To investigate the distribution of PCP on the surface of clays, the adsorption capacity was determined on the water free clay-hexane system as described in adsorption experiment, and the ratio of the surface area of clay surface occupied

by PCP to the specific surface area of the clay was calculated. In calculation of the ratio, each PCP molecule was assumed to be a sphere of radius of 3.77Å. The results obtained are listed in Table 3. As shown in this table, the PCP adsorption capacity of H/Al clays varied from

Table 3. Relation between the PCP adsorption capacity and the specific surface area of clays

Clay*	Total surface area (T) (m ² /g)	PCP adsorption capacity		Area occupied by PCP (P) (m ²)	$\frac{P}{T} \times 100$ (%)
		(mg/g)	(mg/m ²)		
510(H/Al)	552	76.7	0.1389	76.7	13.9
510(Na)	500	47.8	0.0956	47.8	9.6
576(H/Al)	580	67.4	0.1162	67.4	11.6
KiG(H/Al)	700	65.6	0.0937	65.6	9.4
PA(H/Al)	560	33.9	0.0605	33.9	6.1
VA(H/Al)	575	35.7	0.0620	35.7	6.2
Gunma(H/Al)	638	5.1	0.0079	5.1	0.8

* (H/Al) : H-saturated and (Na) : Na-saturated clay.

about 77mg/g to 5mg/g. Taking into consideration of the content of allophane and imogolite in the clay samples, the decreasing order of the PCP adsorption capacity of clay minerals was inferred to be allophane and imogolite (molar SiO₂/Al₂O₃ ratio is near 1) > allophane (molar SiO₂/Al₂O₃ ratio is near 2) > montmorillonite. Though clay No. 510 has the greatest capacity of PCP adsorption, the PCP molecules adsorbed from hexane solution cover only about 14 percent of its total surface area. The result indicates that only a part of clay surface is accessible to the PCP molecules, probably because of the large size of PCP molecule.

In accordance with the result obtained by Greenland and Quirk⁽⁷⁾, Aomine and Otsuka⁽¹⁾ found that two thirds of the surface of allophanic clays was accessible to polar liquids such as EGME and water, but not to N₂ gas. This surface may be regarded as the internal surface, although its nature would be quite different from that of montmorillonite. An analogy of explanation might be possible for difference of adsorption capacity between EGME and PCP, if the difference is not in polarity but in size. There was a marked variation in the PCP adsorption capacities of the clay samples, irrespective of the specific surface area, suggesting a wide difference in the nature of clay surface between samples. The adsorption values are dependent upon the magnitude of the surface area available

to PCP adsorption, which varies with clay mineral species and saturated cations.

摘 要

Hexane 溶液中에서 粘土鑛物에 의한 PCP 吸着 실험을 행하여 粘土表面에서의 PCP의 狀態를 調査하였다. PCP는 水溶液中에서 보다 Hexane 溶液中에서 더욱 많은 量이 粘土에 吸着된다. 粘土鑛物 中에서도 珪礬比가 約 1 인 Allophane과 Imogolite 가 가장 많은 PCP를 吸着하며, 이 吸着現象은 PCP 와 粘土鑛物間의 dipole-dipole interaction에 依하여 일어난다. Hexane 溶液中에서 PCP가 粘土鑛物에 依하여 吸着될 때는 粘土鑛物의 全表面積보다 表面性質 및 交換性 陽 ion에 依하여 吸着量이 左右되었다.

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