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TOOLS, TECHNIQUES AND TECHNOLOGIES FOR POLLUTION PREVENTION, CONTROL AND RESOURCE RECOVERY

Effect of soil pH and organic matter on the adsorption and desorption of pentachlorophenol

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Abstract Various properties of soil affect the partition of organic contaminants within, and conversely, the properties of the organic contaminants also directly affect their partition behavior in soil. Therefore, understanding the effects of various properties of soil on the partition of organic contaminants favors subsequent assessment and provides soil remediation methods for policymakers. This study selected pentachlorophenol (PCP), a common hydrophobic ionizable organic compound in contaminated sites worldwide, as the target contaminant. The effects of pH, organic matter, and the combination of both, on PCP adsorption/desorption behavior in soil were investigated. Phosphoric acid and potassium hydroxide were used as buffer solutions to modify the soil pH by the batch and column extraction methods. A common retail organic fertilizer and fulvic acid were selected as additives to manipulate the soil organic content. Modifying the pH of the soil samples revealed that acidic soil exhibited a greater PCP adsorption rate than alkaline soil. The amount of PCP desorption increased regardless of pH of the in situ contaminated soil. The adsorption of PCP increased with increasing amount of organic additive. However, addition of fulvic acid yielded different results compared to the addition of organic fertilizer. Specifically, the organic fertilizer could not compete with the in situ contaminated soil in PCP adsorption, whereas fulvic acids increased the PCP dissolution to facilitate adsorbing contaminant adsorption. The combined effect of pH modification and organic matter addition provides additional PCP adsorption sites; therefore, adding the organic fertilizer to decrease the soil pH elevated the PCP adsorption rates of the laterite, alluvial, and in situ contaminated soil samples. The study results revealed that both pH and organic matter content are crucial to PCP adsorption/desorption in soil. Therefore, the effects of soil pH and organic matter should be considered in facilitating PCP treatment for soil remediation.

Keywords Pentachlorophenol (PCP) · Organic fertilizer · Fulvic acids · pH · Adsorption/desorption

Introduction

Chlorophenol compounds are a group of organic compounds not easily decomposed in a natural environment. Pentachlorophenol (PCP), being a precursor of dioxin, is a well-known contaminant. PCP is the most common hydrophobic ionizable organic compound in contaminated sites worldwide (Baker and Hites 2000). PCP is a synthetic compound synthesized by Otto Linné Erdmann in 1841 and originally marketed as a wood preservative by Dow Chemical and Monsanto in 1936 (Fisher 1991).

The characteristics (acidity, alkalinity, polarity, and polarization) of organic contaminants affect the adsorption of charged substances. For example, the target PCP contaminant in this study exhibits a weak acidity with a pK_a value of 4.75. Hamker and Thompsom (1972) emphasized that slightly acidic organic contaminants dissociate to form anionic substances repulsive to negative charges on soil surface in an alkaline environment resulting in the poor adsorption of the contaminants by

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soil. By contrast, contaminants in acidic soil exist as free acids and exhibit greater adsorption than do those in alkaline soil because of their positive charges and electrostatic attraction. Therefore, organic contaminants exhibit strong adsorbability when soil pH approaches pKa (Hamker and Thompsom 1972). The hydrophobic ionizable organic compounds (HIOCs) have relatively larger solubility and mobility in a water system, which usually implicates that it is easier to be taken by organisms. Adsorption of ionic PCP on soil/sediment is different from that of neutral PCP because it is not from micelles, exhibit strong amphiphilic characteristic or ionic exchange with soil/sediment (Cheng et al. 2014). Organic matter plays a critical role in soil and serves an essential indicator of soil quality (Wang et al. 1995). In the protonated form, PCP can behave similarly to other hydrophobic non-ionizable organic compounds (HNOCs) and partition into soil organic matter. In the ionized form, the charged functional group may result in a more specific surface adsorption reaction. The effects of adding residence time and pH on PCP sorption and desorption were examined (DiVincenzo and Sparks 2001). Additionally, studies have revealed that the strong adsorbability of organic matter on hydrophobic organic contaminants reduces the biodegradability of the contaminants (Ghosh et al. 2000; Ghosh et al. 2001). Furthermore, Ghosh et al. (2000) mentioned that hydrophobic organic contaminants exhibit a high affinity for organic matters. Their study results showed that coal- or wood-derived particles demonstrated substantially higher adsorbability on hydrophobic organic contaminants than did silica particles in soil. Moreover, the carbon/wood content in their soil sample was only approximately 5%, but could adsorb 62% of organic contaminants while the remaining 38% of the contaminants were adsorbed by the clay and silt (Ghosh et al. 2000). Peng et al. (2016) investigated the impacts of pH, inorganic fractions, and dissolved organic carbon on PCP adsorption on reed biochars. But, Diagboya et al. (2016) mentioned that PCP sorption was temperature and pH dependent, decreasing with increasing temperature and pH. Soil iron oxides played greater roles in PCP sorption than the organic matter content.

The present study was conducted to examine the adsorption and desorption of PCP by soil under different pH conditions. The main agricultural soils in Taiwan (laterite and alluvial soils) and the in situ contaminated soil in the China Petrochemical Development Corporation An-Shun site in Tainan City were selected. Phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) were used as buffer solutions to adjust the soil pH. In addition, two types of organic matter—the common retail GREENORCHIDS® organic matter and fulvic acid—were added to the soil samples, which were then extracted to analyze their organic contents through elemental analysis and Fourier transform infrared spectroscopy. The ingredients used in GREENORCHIDS® potting soil are peat, coconut shell powder, vermiculite, and small amounts of organic fertilizer (organic matter 52%, pH 5–6, electrical conductivity about 2.0 mS cm^{-1}). The results may enhance understanding the effects of the characteristics of these additives on the adsorption and desorption of PCP in soils.

Materials and methods

Soil sampling and treatment

Soil samples were collected from laterite soil dating back to the Pliocene epoch from the Dadu Plateau in Taichung City, sand-shale older alluvial soil which serves as topsoils in farmlands (0–20 cm), and the in situ PCP-contaminated soil from the China Petrochemical Development Corporation An-Shun site in Tainan City. Table 1 shows the Universal Transverse Mercator coordinates, locations, and soil sample types. The samples were air-dried and then sieved using a 2-mm sifter.

Soil preparation with various pH values

In this study, 0.2 M H_3PO_4 and 0.2 M KOH solutions were used to adjust the pH of soil samples to 3.00, 5.00, 7.00, and 9.00. The soil solutions were shaken and then left stationary until the soil pH stabilized; next, the samples were air-dried and sieved (2 mm). Two methods were used to observe the adsorption of PCP:

Method 1: After the pH values of soil samples were adjusted, the PCP contaminants were added to the soil samples to observe the PCP adsorption and desorption behaviors.

Method 2: Soil samples were first contaminated with PCP, followed by adjusting the soil pH values. Subsequently, the soils were analyzed 45 days after the treatment to examine the adsorption and desorption of PCP by soil.

Table 1 Soil excavate location and coordinates

	Laterite soil (Chen Cunliao series)	Alluvial soil (Dali series)	In situ contaminated soil
Location	Taichung City West District	Taichung City Nantun District	Tainan City An-shun site
Mercator coordinates	X: 206893 Y: 2672464	X: 215536 Y:2671358	X: 159978 Y: 2547815

Soil preparation with various organic matter

The organic additives of soil samples in this study were a common retail organic fertilizer and fulvic acid. Specifically, the ratios of soil to organic matter 100:1, 50:1, and 25:1 were prepared by 100 g soil in a glass beaker. Deionized water was used to adjust the water content of the additive-containing soil samples to 30%, and the wet-and-dry process was repeated at least three times. After 30 days, the soil samples were air-dried and sieved (2 mm), shook for 2 h to ensure even soil distribution, and thoroughly mixed.

Because the soil samples from the China Petrochemical Development Corporation An-Shun site had already been contaminated with PCP, the preparation process differed from that of the other soil samples. Specifically, the organic additives and deionized water were added to the An-Shun site soil samples, followed by air drying, sieving (2 mm), and shaking (2 h). A batched extraction test was conducted for 28 days, with each batch being initiated every 7 days. A control group was also prepared to examine the volatilization of PCP during the air-dry process.

Preparation of PCP-containing soil samples

The concentration of PCP in this study was configured to be 200 mg kg^{-1} in accordance with the regulated concentration of PCP in the Soil Pollution Monitoring Standard published by the Environmental Protection Administration of the Executive Yuan (2017). PCP-containing soil samples were prepared as follows: A 98% solid PCP standard was dissolved in acetone to prepare a stock solution with a PCP concentration of 200 mg L^{-1}. The stock solution was added in a 1:1 ratio (*w*/*v*) to the soil samples with different pH values. After the samples were evenly mixed for 2 h, they were placed in a fume hood to remove the solvent.

Extraction of PCP-containing soil samples

Batch test: The prepared soils and acetone were loaded into centrifuge tubes in a 1:10 ratio (*w*/*v*) and rested on a horizontal shaker, followed by shaking at 150 rpm (amplitude = 5 cm) for 2 h and then centrifuge at 150 rpm for 1 min. The supernatant solutions were extracted to analyze the PCP contents by using high-performance liquid chromatography (HPLC). Four trials were conducted to measure the PCP content of each sample.

Column test: A 0.83 cm^3 stainless steel column was initially weighed and recorded. The PCP-contaminated soil samples with previously modified pH values were tightly packed in the column, and weighed again. The weight of the soil inside the column was obtained by subtracting the initial weight of the column from the total weight, and served as a reference value for the subsequent calculation of PCP concentration. Figure 1 illustrates the device used in the column test. One side of the packed column was connected to a piston pump, and the test solution was injected into the column at 1 mL min^{-1}. The effluent was released from the other side of the column into a 2-mL brown vial. The PCP concentration was determined again with HPLC.

High-performance liquid chromatography and data analysis

The PCP concentration of the soil extract was determined using an HPLC equipped with ultraviolet detector at a wavelength of 254 nm, a flow rate of 0.9 mL min^{-1}, and an

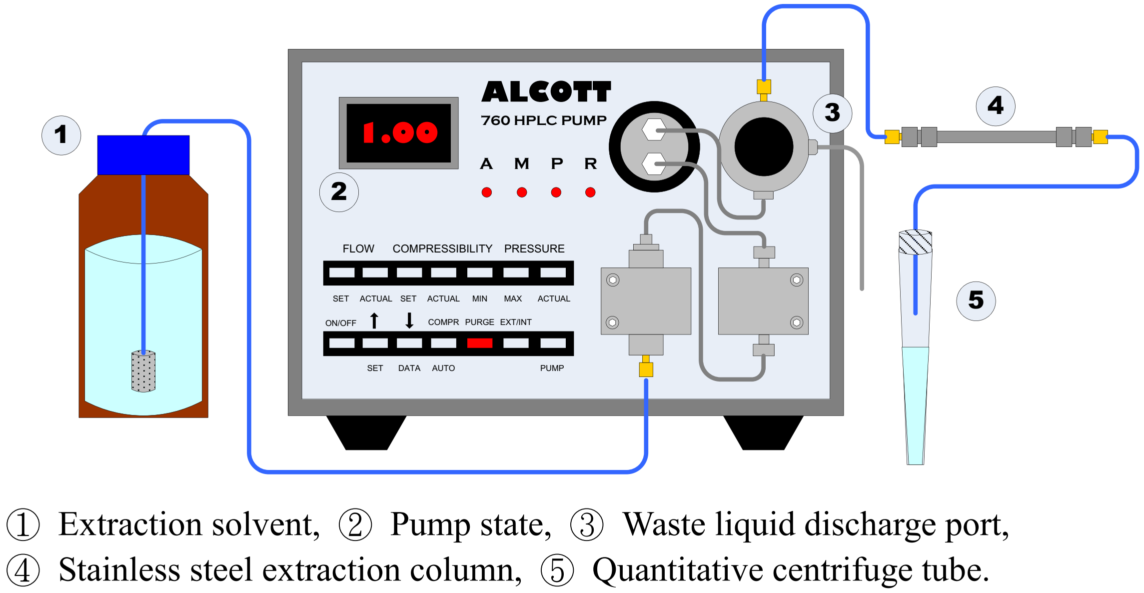


Fig. 1 The column extraction device. ① extraction solvent, ② pump state, ③ waste liquid discharge port, ④ stainless steel extraction column, and ⑤ quantitative centrifuge tube

Table 2 Soil physio-chemical properties

Soil species	pH	EC[a] (μS cm^{-1})	CEC[b] (cmol kg^{-1})	Organic carbon (%)	Particle size analysis			Texture
					Sand (%)	Silt (%)	Clay	
Laterite soil	4.8 ± 0.1	136 ± 20	6.7 ± 0.2	0.35 ± 0.02	17.0	36.0	47.0	Clay
Alluvial soil	5.4 ± 0.1	707 ± 61	14.2 ± 0.4	0.65 ± 0.02	9.50	61.7	47.0	Silty clay loam
Contaminated soil	7.0 ± 0.1	4889 ± 74	3.5 ± 0.2	1.43 ± 0.05	71.2	9.00	28.8	Sandy loam

[a] Electrical conductivity

[b] Cation exchange capacity

injection volume of 20 μL. A Mightysil RP-18 GP 250-4.6 chromatographic column was selected, and the mobile phase consisted of 90% methanol, 10% deionized water, and 0.1% H_3PO_4 solution. Through analysis of variance, Duncan's multiple-range test, and Fisher's LSD (least significant difference), the differences between the PCP adsorption rates of the samples were examined at a significance level of 0.05.

Results and discussion

Basic properties of the soils

This study analyzed the basic properties of the soil samples and attempted to relate them with the adsorption/desorption of PCP. Table 2 shows the physio-chemical properties of the soils. The laterite soil exhibited a lower pH value than the alluvial soil, but both were slightly acidic. By contrast, the contaminated soil from the An-Shun site demonstrated the highest pH value (7.0) among the three types of soil. In terms of soil texture, the laterite soil contained higher clay content than the alluvial soil. The contaminated soil, with a sandy loam texture and neutral pH, contained more organic carbon (1.43%) than the other two types of soil.

Changes in soil properties with additive materials

Table 3 lists the properties of the organic fertilizer and fulvic acid used as additive materials. The fulvic acid exhibited a lower pH value but contained 6% more organic carbon than the organic fertilizer. After the soil samples were mixed with different ratios of the fertilizer and fulvic acid, the organic carbon contents of the soil samples changed (Table 4). Specifically, the organic carbon contents of the soil samples increased notably and in proportion to the amount of organic materials added.

Table 3 The properties of organic fertilizer and fulvic acid

Material	pH	EC (mS cm^{-1})	Organic carbon (%)
Organic fertilizer	6.04 ± 0.05	0.85 ± 0.40	27.4 ± 0.08
Fulvic acid	3.80 ± 0.1	11.45 ± 1.02	33.64 ± 0.13

PCP adsorption/desorption of soils with different pH values

Batch and column tests

To analyze the adsorption rates of the soils after the addition of PCP, batch and column tests were conducted on the three types of soil sample and the control group (quartz sand). Subsequently, the effects of soil properties on the adsorption/desorption of PCP were examined. Quartz sand was selected as the control group because it is inert and not prone to the influence of pH or organic matter. Table 5 shows the results of the tests.

The PCP-acetone stock solution was prepared as an additive to the soil samples. The PCP concentration of the stock solution was determined to be 220 mg L^{-1}, which did not match the required concentration of 200 mg L^{-1} because acetone exerted an amplification effect during the HPLC process. Therefore, 220 mg L^{-1} was used as the denominator in subsequent concentration calculations.

The experimental results revealed that the batch extraction attained a slightly higher adsorption rate than the column extraction because of the substantial contact between the soils

Table 4 The soil organic carbon contents (%) after adding organic materials

Soil	Organic fertilizer				Fulvic acid			
	None	1%	2%	4%	None	1%	2%	4%
Quartz sand	0.00	0.27	0.46	0.71	0.00	0.36	0.61	1.29
Laterite soil	0.36	0.60	0.76	1.00	0.36	0.71	1.01	1.55
Alluvial soil	0.65	0.89	1.06	1.35	0.65	0.93	1.35	1.78
Contaminated soil	1.35	–	–	2.08	1.35	–	–	1.53

Table 5 PCP adsorption rates of batch and column tests in different soils

Extraction method	Contaminated soil mg kg^{-1}	Quartz sand	Laterite soil	Alluvial soil
		——% ——		
Batch	284.55 A[b]	85.12 A	64.88 A	81.90 A
Column	251.60 B	80.88 A	63.50 A	80.52 A
LSD[a]	22.05	15.68	6.70	8.51

[a] Values of least significant difference are for mean comparisons at 5% level, within treatment for each sampling time significant

[b] Means within a column (in capital letter) followed by Fisher's protected LSD test ($P < 0.05$)

and the solvent during the shaking process. The column extraction obtained results with higher variances than the batch extraction because the artificial soil columns with had varying soil pore densities.

After PCP was added to the soil samples, the alluvial soil extract showed a higher adsorption rate (approximately 80%) than the laterite soil (approximately 64%). This may be attributable to the higher clay content of the laterite soil (47%) compared with that of the alluvial soil (29%), indicating that soil texture affects the adsorption of PCP. Moreover, clay and silt particles in soil influence the adsorption/desorption of organic contaminants, and clay particles provide more adsorption sites for binding with PCP; thus, the laterite soil was observed to demonstrate a stronger adsorption on PCP than the alluvial soil. Additionally, past studies have used computational models to verify that sulfonamide compounds retained in the gaps of organic matters are critical to the adsorbability of soil (Schwarz et al. 2012; Thiele-Bruhn and Aust 2004). In the present study, a notable difference was observed between the adsorption rates of the control group obtained through the batch and column methods, which attained an adsorption rate of 85 and 81%, respectively. The batch extraction was more favorable than the column extraction for analyzing the control group because the solvent and the high-porosity quartz sand in the column could not be fully contacted during the column extraction, leading to a low adsorption rate. Regarding the contaminated soil from the An-Shun site, the extract concentrations through the batch and column methods were 284 and 252 mg kg^{-1}, respectively.

Changes in soil pH

One of the objectives of this study was to investigate the effects of soil pH on the adsorption of PCP. The soil samples were air-dried to reduce the effect of water content. Generally, the presence of water molecules in soil can compete for the adsorption sites on the soil surface and thereby lead to the desorption of some organic contaminants from the soil. Table 6 shows the changes in the pH values of the soil samples before and after adding PCP. Because the contaminated soil from the An-Shun site had already contained PCP, it was not suitable for preparation method 1 and only applied to preparation method 2. Since the samples of laterite soil and alluvial soil had the apparent difference in the amount of desorption at pH 3 and pH 9 by pre-experiment, the PCP dissolution was only observed under these two pH conditions in the contaminated soil experiments. The results (Table 6) displayed that the influence of long-term polluted soil was less apparent under the condition of adjusting the pH value.

PCP adsorption/desorption of soils with different pH values

Figure 2 presents the extraction rates when PCP was added after modification of the soil pH. The lowercase letters denote the significance levels of the differences between the adsorption rates obtained using the same extraction method and soils under the different pH values, whereas the capital letters compare the adsorption rates obtained using the different extraction methods under the same pH values. According to Fig. 2, the adsorption

Table 6 Changes in the pH values for different soil samples

	Preparation method 1[a]					Preparation method 2				
			pH					pH		
Soil	Original	3	5	7	9	Original	3	5	7	9
Quartz sand	5.83	2.97	4.89	7.23	9.35	5.83	2.56	4.87	7.83	9.42
Laterite soil	4.81	2.92	5.01	7.12	8.79	4.81	3.17	5.15	6.87	8.81
Alluvial soil	5.44	3.03	5.06	7.21	8.91	5.44	3.71	5.20	7.01	8.80
Contaminated soil	7.01	N.A	N.A	N.A	N.A	7.01	3.64	N.A	N.A	9.78

[a] Method 1, adjusting pH value of soil; method 2, after adding PCP in soil, the pH value of soil was adjusted supernatant

N.A not available

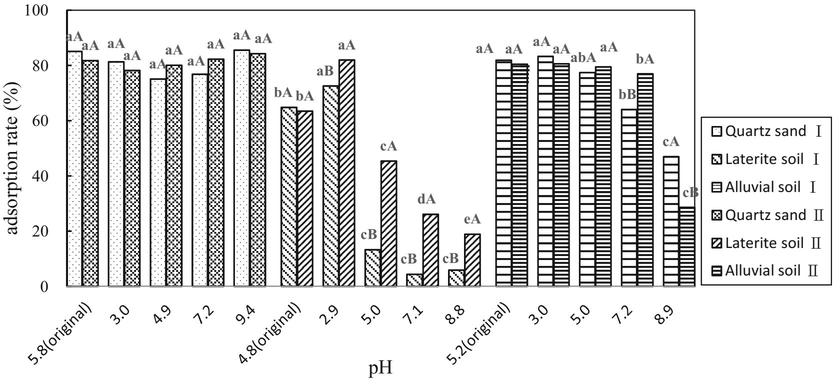


Fig. 2 PCP adsorption rate of three soils at different pH values (preparation method 1). *I* batch extraction. *II* column extraction. Means the adsorption rates within the batch extraction (in *lowercase letter*) and within the column extraction (in *capital letter*) followed by Fisher's protected LSD test ($P < 0.05$)

rate of the control group was approximately 75–85%. The quartz sand with unmodified pH exhibited the highest adsorption rate at 85%, and modifying the pH value did not significantly alter the adsorption rate of the quartz sand. By contrast, the adsorption/desorption capacity of PCP significantly varied by the pH value of the laterite and alluvial soils, with the pH value of 3 exhibiting the highest PCP adsorption rates at 73 and 83%, respectively. When the pH values of the laterite soil were modified to 5, 7, and 9, the adsorption rate differed significantly from that of the original laterite soil, with adsorption rates significantly reduced to 4–15%. When the pH values of the alluvial soil were modified to 7 and 9, the results differed significantly from that of the original alluvial soil, and the adsorption of PCP was also increased, with adsorption rates of 64 and 47%, respectively. The column test results revealed that the adsorption rate of PCP on the laterite soil with a pH value of 3 was 82%, and the desorption rate of PCP gradually increased as the soil pH value increased, with significant differences observed at pH values of 5, 7, and 9. Therefore, the adsorption and desorption of PCP were affected by the soil pH value. The adsorption rate of PCP on the alluvial soil with a pH value of 3 was 81%, but dropped to 49% when the pH value was modified to 9. Examining the differences in the adsorption rates between the batch and column extractions using preparation method 1 was mostly insignificant. Although in some instances the batch extraction exhibited significantly lower adsorption rates than the column extraction, this difference might be attributed to the inconsistent porosity of the packed soil in the column. Therefore, considering the required time and cost-efficiency of multiple extracting processes, the batch method was more preferable, but the column method could simulate the actual PCP adsorption/desorption more realistically.

In contrast to preparation method 1, preparation method 2 PCP was added to the soil before the soil pH was modified. As shown in Fig. 3, the adsorption rate of the control group ranged from 36 to 45%. The adsorption rate of the laterite soil was the highest, at 32%, when the pH value was 3. When the laterite soil was modified by the alkaline solution, the adsorption rate was merely 1–4%, significantly lower than that of the unmodified and acidified laterite soils. The adsorption rates of the alluvial soil with pH values of 3 (53%) and 5 (54%) differed insignificantly, whereas with pH values of 7 and 9 reduced to 20 and 12%, respectively. Similar results were observed in the column test. The adsorption rate of the laterite soil was the highest at 31% when the pH value was 3, whereas the lowest adsorption rate was at approximately 9% when the pH values were 7 and 9. The adsorption rate of the alluvial soil was the highest, at 54%, when the pH value was 3, whereas the lowest adsorption rate was 27%, when the pH value was 9.

The results from both batch and column recovery tests revealed that the adsorption rates of the soil samples were the highest when the pH value was 3, regardless of which preparation method was used. These results matched those in past studies, in which the adsorption capacity of chlorophenol contaminants in soil with pH value of 3 was significantly higher than that

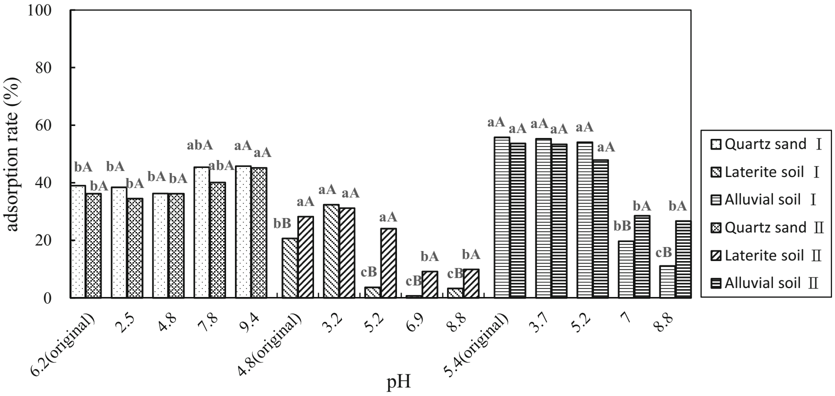


Fig. 3 PCP adsorption rate of three soils at different pH values (preparation method 2). *I* batch extraction. *II* column extraction. Means the adsorption rates within the batch extraction (in *lowercase letter*) and within the column extraction (in *capital letter*) followed by Fisher's protected LSD test ($P < 0.05$)

of other pH values. This is attributable to how a soil environment decisively affects the partition pattern of an adsorbate. When the soil pH is higher than the pK$_a$ of an adsorbate, the adsorbate is mostly in a dissociative state (i.e., dissolved in water). By contrast, when the soil pH is lower than the pK$_a$ of the adsorbate, the adsorbate mostly exhibits a crystalline state and becomes less soluble in water (Huang 2014). Under this condition, the amount of chlorophenol contaminants adsorbed by soil is increased. In the present study, adding the acidic and alkali buffer solutions dissolved the humic substances in the soil. When KOH was added, the adsorption of the dissolved humic substances on the hydrophobic organic contaminants decreased, thereby decreasing the subsequent extracted concentrations. Additionally, researchers have also stressed that when the pH value increases, the polarity of humic substances increases and their affinity on hydrophobic organic matters decreases (Ping and Luo 2005). Therefore, reducing the pH value favors the adsorption of organic contaminants on humic substances. The presence of other substances, such as soil minerals and suspended particulates in water, can reduce the pH value and change the structure of humic substances, thereby enhancing the adsorbability of humic substances. In addition, the low pH values favor the adsorption of hydrophobic organic contaminants onto mineral-humus complexes (Laor et al. 1999). Raber et al. (1998) argued that as the pH value decreases, the partition of hydrophobic organic contaminants in soluble organic contaminants increases.

Figures 2 and 3 demonstrate that the overall adsorption rate of the soil samples prepared in method 2 was significantly lower than that of method 1. A possible reason for this is because the soil samples must be placed in a fume hood to evaporate the test solutions after the pH values of the PCP-containing soil samples were adjusted. PCP is a semivolatile organic substance, and Huang (2014) revealed that under normal temperature and pressure, the weight of PCP gradually decreases over time. Therefore, PCP may have been partially lost by effusion during the preparation process. Additionally, the two preparation methods in the present study involved different preparation times. The PCP-containing soil samples in method 1 required 2 days to prepare, whereas the samples in method 2 required 45 days. This factor did not, however, affect the variation trends observed for the two methods. Specifically, in both method 1 and method 2, the desorption rate of PCP increased at low pH, and the adsorption rate decreased as the pH increased.

Figure 4 shows the test results of the contaminated soil from the An-Shun site. Comparing the test results revealed that both the acidified and alkalinized soil samples exhibited higher PCP desorption than the original soil sample after the pH value was modified using the method. However, the amount of PCP desorption was significantly different between the acidified and alkalinized soils. Because the contaminated soil from the An-Shun site had been polluted by PCP for a long period, the PCP adsorbability of the soil had become stable. Therefore, modifying the pH value of the in situ contaminated soil did not alter the adsorption/desorption of PCP as significantly as in the laterite and alluvial soil samples. According to the yearbooks edited by the Soil And Groundwater Pollution Remediation Funds (https://sgw.epa.gov.tw/Public/), the contaminated soil from the An-Shun site was polluted not only by PCP, but also by sodium pentachlorophenol (PCP-Na). However, the humic substances in the soil were dissolved in the alkaline solution after the in situ soil modified by KOH, and PCP-Na, was also partially dissolved. Consequently, the PCP concentration was increased in subsequent extractions.

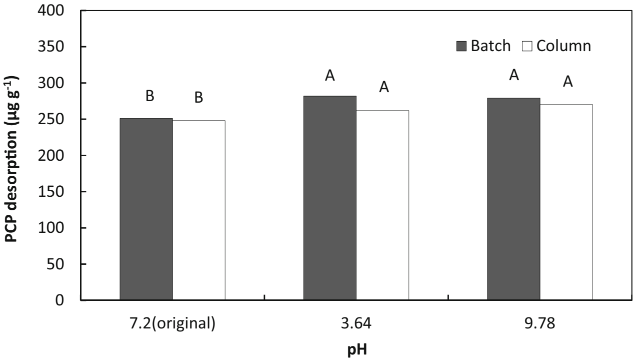


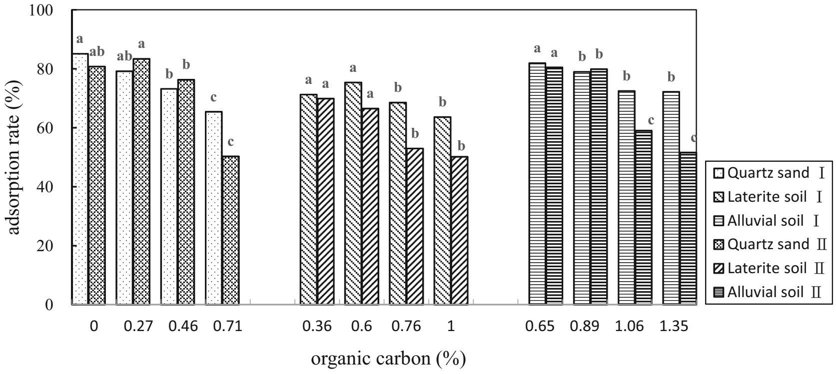
Fig. 4 The PCP desorption of contaminated soil after adjusted pH value. Means the PCP desorption within the extraction (in *capital letter*) followed by Fisher's protected LSD test ($P < 0.05$)

Experimental results of adsorption of PCP by organic matter

Adsorption test of PCP on soils by adding organic fertilizers

The effect of organic content on PCP adsorption was examined through an extraction test which an organic matter was added to the unmodified soil and quartz sand samples. Figure 5 presents the recovery test results of each soil type. The letters in the figure denote the significant levels of the differences between the adsorption rates obtained using the same soil samples and extraction methods under different organic contents. The results reveal that the PCP content increased as the organic matter content increased; i.e., there is significantly decreased desorption of PCP. Both the batch and column extractions yielded similar results. The PCP adsorption was the highest when the organic carbon content was the highest, and after organic matter was added, the alluvial soil exhibited significantly higher adsorption rates than both the laterite soil and quartz sand. Regardless of increasing or decreasing the pH of the in situ contaminated soil, the PCP desorption rate increased. These results verified that organic matter affected the adsorbability of PCP in the soils. Adding the organic fertilizer increased the soil organic matter content and provided extra space for PCP adsorption. This phenomenon concurs with the results of Hung (1996), who reported that organic matter in soil exhibited extremely large areas for both surface and inner adsorption of

Fig. 5 The adsorption rate of PCP from soils with added organic fertilizer. *I* batch extraction. *II* column extraction. Means the adsorption rates within the organic fertilizer (in *lowercase letter*) followed by Fisher's protected LSD test ($P < 0.05$)

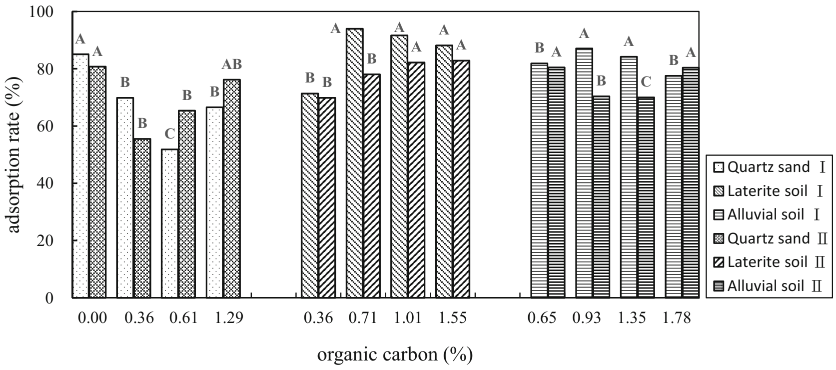


organic contaminants, thereby enhancing adsorbability of organic contaminants (Hung 1996). Richnow et al. (1994) revealed that organic matter contains numerous functional groups to facilitate binding with hydrophobic organic contaminants through noncovalent bonds (e.g., hydrophobic adsorption, charge transfer, and hydrogen bonds) and covalent bonds (e.g., ester, ether, and carbon-carbon bonds). During the binding process, the humic substances form more stable bonds with organic contaminants than with other inorganic contents; hence, humic substances are a crucial factor affecting the adsorption of organic contaminants. Additionally, some studies have argued that PCP adsorption in soil is mainly limited by soil organic matter (Johnson and Lamar 1997; Paaso et al. 2002; Peuravuori et al. 2002). Furthermore, some other studies have stated that organic matter in soil influences whether hydrophobic organic contaminants are retained in the soil-water system. Organic matter in soil is recognized as a crucial factor determining the allocation of hydrophobic organic contaminants in soil, and the adsorbability of such contaminants depends on their nonpolar and polar functional groups (e.g., −Cl functional group; Kile et al. 1995; Weber et al. 1998; Xia and Ball 1999; Xing and Pignatello 1997; Xia and Ball 1999). Recently, Ahmed et al. (2015) simulated the interaction of polar and nonpolar organic contaminants with organic matter in soil by using sorption experiments and molecular dynamics. The results revealed that the interaction depended on the chemical composition of the soil organic matter more than on the organic matter content, and the site-specific adsorption on the soil surfaces was explained by sorption hysteresis when the contaminants pass through the soil voids. Particularly, the hydrophobic hexachlorobenzene exhibited stronger adsorption than the hydrophilic sulfanilamide did (Ahmed et al. 2015). The PCP contaminant in the present study contained the −Cl functional group, which provided more opportunities for PCP adsorption when organic matter was added to the soil. In addition, the statistical results in Fig. 5 revealed that when the organic carbon content of the quartz sand and laterite soil was less than 0.6%, the PCP recovery (adsorption) rates differed insignificantly.

Adsorption test of PCP on soils by adding fulvic acids

Adding fulvic acid to the soil yielded different results than adding organic fertilizer. Figure 6 shows that after fulvic acid was added to the soil, the desorbability of PCP increased when the organic carbon content of the alluvial soil was increased to 0.93%. However, no significant difference was observed as the fulvic acid content increased, because the adsorption rate was maintained at approximately 75%. The PCP desorption increased when the organic carbon content of the laterite soil was increased to 0.71% by adding fulvic acid. However, no significant difference was observed as the fulvic acid content increased, because the adsorption rate was maintained at 80–90%. Esteves da Silva and Marques (2007) revealed that because PCP contains a benzene ring in its structure, the nonpolar capacity facilitates strong association with fulvic acid molecules. Johnson and Amy (1995)

Fig. 6 The adsorption rate of PCP from soils with added fulvic acid. *I* batch extraction. *II* column extraction. Means the adsorption rates within the fulvic acid (in *capital letter*) followed by Fisher's protected LSD test ($P < 0.05$)



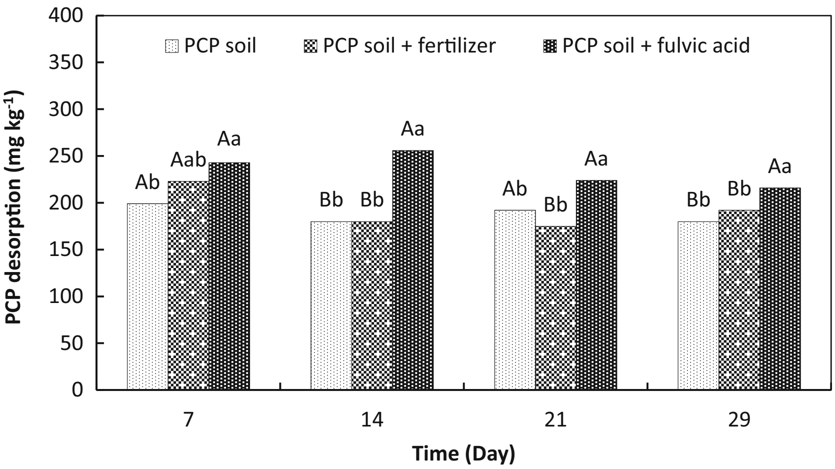


Fig. 7 PCP desorption from soils added organic materials (fertilizers and fulvic acid). Means the PCP desorption within the days (in *capital letter*) and within the organic materials (in *lowercase letter*) followed by Fisher's protected LSD test ($P < 0.05$).

found that humic acid and fulvic acid in soil and sediments can significantly increase the solubility of hydrophobic organic contaminants. Comparison of the present study results revealed that adding fulvic acid can effectively enhance the solubility of organic contaminants in favor of subsequent soil remediation.

Notably, the trend of the quartz sand differed from those of the laterite and alluvial soils. Presumably, the quartz sand could not be comprehensively mixed with fulvic acid during the experiment, and fulvic acid combined with water vapor in the air to forms precipitates as time increased, impeding the extraction of PCP. Consequently, the adsorption rate decreased as the fulvic acid content increased.

Adsorption test of the in situ contaminated soil by adding organic materials

Figure 7 shows the results of the in situ contaminated soil from the An-Shun site after the organic additives were added. On day 7 after the fertilizer and fulvic acid were added, the amount of PCP dissolution increased. On day 14, the dissolved PCP concentration of the contaminated soil with the fertilizer decreased; however, on days 21 and 28, no significant difference was observed in the amount of dissolution, indicating that the organic matter had been stabilized at this time. When fulvic acid was added to the in situ contaminated soil, no significant difference was found in the amount of dissolution on days 14, 21, and 28. Actually, observation of Fig. 7 reveals that the desorption of PCP from fulvic acid-added contaminated soil shows increased desorption on day 14 compared to day 7, and on days 21 and 28, the PCP desorption decreases insignificantly. These results demonstrated that adding the fertilizer did not significantly affect the contaminated soil from the An-Shun site. Because PCP had long been adsorbed to the organic matter and clay minerals in the contaminated soil, the added fertilizer could not increase the adsorption of PCP. The adsorption capacity of the soil itself was greater than that of the added organic matter; thus, the added organic matter could not significantly change the adsorption of PCP in the soil. The fulvic acid exerted a greater effect than the fertilizer did on reactions with PCP in the soil

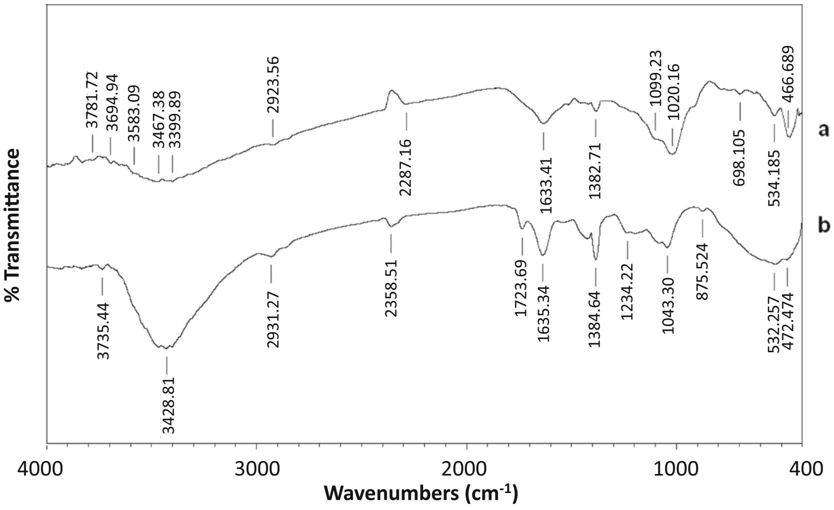


Fig. 8 The infrared spectrum of organic fertilizer (**a**) and fulvic acid (**b**)

and dissolving the PCP because fulvic acid contains smaller molecules that are highly soluble in water (Esteves da Silva and Marques 2007).

According to the test results with different organic additives, the PCP content in the soil increased as the fertilizer content increased, resulting in decreased desorption of PCP. However, when fulvic acid was added to the contaminated soil, the desorption of PCP increased as the fulvic acid content increased because of dissimilar properties of the materials. Figure 8 shows the infrared absorption spectrum of the organic fertilizer and fulvic acid. The main absorption peak of fulvic acid ranged 1725–1720 cm^{-1}, corresponding to the C=O bond in the COOH functional group; whereas the main absorption peak of the organic fertilizer ranged 1170–950 cm^{-1}, consisting of the C–C, C–OH, C–O–C, and impure Si–O bonds in typical carbohydrate links and the polysaccharide C–O bond. The carboxylic group was found in both the organic fertilizers and fulvic acid. Fulvic acid exhibited a more noticeable peak than the fertilizer, and the fertilizer demonstrated a shoulder-type weak absorption band. Thus, fulvic acid contained greater carboxylate content than the fertilizers. The carboxylic group is a hydrophilic functional group that reduces the adsorption of PCP in soil. Therefore, when fulvic acid was added to the soil, the PCP desorption increased.

Conclusion and suggestions

This study investigated the adsorption/desorption of PCP in the laterite, alluvial, and in situ contaminated soils through adjusting the soil pH and using a common retail organic fertilizer and fulvic acid as organic additives. The experimental results are listed as follows:

1. The adsorption rates between the column and batch tests differed insignificantly, but the column test yielded more noticeably different results in some instances because of the inconsistent porosity of the packed soil. Therefore, examining the required time and cost-efficiency of the two extracting processes revealed that the batch method was more preferable, but the column method could simulate the actual PCP adsorption/desorption in the soil more realistically.
2. The two prepared contaminated soils yielded significantly different adsorption rates after the pH values of the soils were modified. The acidified soils exhibited a greater PCP adsorption rate than the alkalinized soils. However, the PCP desorption rate of the in situ soil from the An-Shun site increased regardless of the in situ soil being acidified or alkalinized.
3. The PCP adsorption capacities of all three soil samples increased as the organic fertilizer content in the soils increased. The extra organic matter provided the soils with more opportunities for PCP adsorption. The organic fertilizer did not significantly alter the PCP adsorption of the in situ contaminated soil from the An-Shun site, indicating that the organic additives could not compete with the contaminated soil in PCP adsorption.
4. The PCP desorption of both the laterite and alluvial soils increased after fulvic acid was added to the soils mostly because the fulvic acid dissolved the PCP in the soils. Adding fulvic acid dissolved more PCP in the in situ contaminated soil from the An-Shun site than adding the organic fertilizer.
5. The aforementioned results suggest that effective utilization of the organic matter properties and its interaction with soil may facilitate implementation of soil remediation of PCP.

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