



## Interactive influence of Fe–Mn and organic matter on pentachlorophenol sorption under oxic and anoxic conditions



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### ABSTRACT

This study examined the adsorption of pentachlorophenol (PCP) on geosorbents (original bulk soil and soils treated to significantly remove organic carbon and oxides of Fe and Mn) under oxic and anoxic experimental conditions. pH effects on adsorption capacities were maximal at  $\text{pH} < \text{pK}_a$  of PCP (4.7). Decrease in redox potential and an increase in dissolve organic carbon inhibited PCP sorption. While contribution of Mn oxide to PCP sorption was negative due to decreasing charge interference, the study equally implied negligible role of surface area compared to organic matter contents and oxides of Fe with  $R^2 \leq 0.825$ . The rate of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  release under anoxic condition reduced interactions of phenolate with iron oxides and consequently, the distribution coefficients coupled with increased dissolve organic carbon. Pseudo second order and Langmuir isotherm provided the best kinetic and isotherm models respectively, although adsorption processes appeared to involve more than one kinetic stage based on intra-particle diffusion model ( $R^2 \leq 0.982$ ). The study suggests that soil treatment to remove Mn oxide may encourage transitory PCP sinks in some reductomorphic environments.

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## 1. Introduction

Several locations around the World, particularly where agriculture and timber preservation is being practiced, are contaminated with chlorinated organic compounds (COCs) such as pentachlorophenol (PCP) and trichloroethane [1,2]. Pentachlorophenol is persistent and toxic to all life forms, and is considered a high-priority pollutant [3]. More importantly, this class of COCs is of widespread environmental concern due to their recalcitrance to degradation, bioaccumulation and biomagnification in food chains, and potential toxicity to wildlife and humans [4,5]. The use and disposal of PCP has resulted in serious soil, leachates and groundwater contamination [6,7]. Levels of concern have been reported for surface water, soils, sediments and aquifers [8,9]. Adsorption is a major process controlling the distribution of pollutant between the solid phase and dissolved phase, and the

process is governed by both the physical and chemical properties of the solute, the sorbent, and the solvent.

Soil is heterogeneous and its characteristic nature has been shown to influence the fate and transport of PCP [10]. For instance, after reaching soil, PCP can be degraded by bacteria and sunlight and bacteria [11]. Through evaporation, it can leave the upper soil layer and leach into groundwater. Studies have shown that PCP degrades most rapidly in flooded or anaerobic (anoxic) soils especially at higher temperatures and in the presence of organic matter in the soil [12,13]. In a study, the sorption characteristic of PCP on surficial sediment was investigated using selective extraction procedures [14]. The study showed that the presence of Mn oxides retards PCP sorption while Fe oxides and organic materials both contributed significantly to sorption of PCP. Thus, contrary to previous report on the predominant nature of organic material on sorption of hydrophobic organic compounds (HOC) [15–17], the study further justified the significance of the mineral oxide phases, particularly the role of Fe oxide in the sorption of PCP. Recent studies on sorption of 2,4,6-trichlorobenzoic acid (2,4,6-TCB), 2,4-dichlorophenoxy acetic acid (2,4-D) and perfluorooctane

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sulphonate (PFOS) onto soil components revealed the significance of mineral phases in sorption of HOCs [18–20]. Some studies have shown that at typical environmental pH values (pH 7–8), several chlorophenols, including PCP are usually present in both molecular and phenolate form. Thus, their sorption is pH-dependent [21–26]. Correlation between sorbent organic matter contents and sorption capacity of ionized and neutral chlorophenols is well documented [21,27,28]. In addition, the presence of charged species in sorbent materials, ionic strength, and pH of the aqueous phase has also been noted to influence sorption capacity of chlorophenols [21–23,29,30]. All these studies and those not reported here were carried out under oxic condition. However, for field relevance, the condition of a contaminated system is mostly anoxic.

Anoxic condition in soil can develop during flooding [31], and therefore knowledge on both oxic and anoxic sorption in soil is important. A predominant anoxic condition may affect PCP mobilization. The chemically mediated oxidation–reduction potential may alter the chemical and physical characteristics of the soil including local pH increases, leading to increased dissolution of soil organic matter. Studies have shown that sorption is governed by competing sorbates as dissolved organic matter (DOM) in ligand exchange, as well as pH and ionic strength [18–20,32,33]. In addition, as redox potential decreases further, soils/sediments release manganese  $Mn^{2+}$  and iron  $Fe^{2+}$  via the microbiological and chemical reduction of metal oxides [18,19,34]. All these changes are expected to influence the sorption of PCP or any other ionizable organic compound (IOC).

Studies on soil components in PCP sorption under anoxic conditions are necessary to gain a better understanding of the fate and transport of PCP. Therefore, the objectives of the study were to determine the influence of oxic and anoxic processes on PCP sorption in a spectrum of soils. The soils were treated to remove some vital components, necessary to understand the kinetics involved. The influence of dissolved organic carbon (DOC) and redox potential ( $E_h$ ) were also investigated. It is hoped that knowledge of redox reaction of Fe and Mn oxides could substantially improve our understanding of surface chemical reaction during adsorption of PCP, particularly in dynamic, sub-oxic environments.

## 2. Materials and methods

### 2.1. Chemicals

PCP [ $C_6Cl_5OH$ , MW = 266.5 g/mol, 98%] was obtained from Sigma-Aldrich (USA) without further purification. PCP is a

hydrophobic organic compound with a log  $K_{ow}$  of 5.0 and an aqueous solubility of 14 mg/L at 25 °C [35]. All the other chemicals were of analytical grade and were obtained from Sigma-Aldrich.

### 2.2. Soil sampling and selective extraction

Surface soil (top 1–5 cm) was collected from Adekunle Ajasin University Campus, Ondo State, Nigeria with a clean methanol rinsed stainless steel trowel. The soil was air-dried, crushed, sieved through a 2 mm sieve, and stored at 4 °C in glass bottles for further use. In addition to the original untreated soil (UNTD), soil samples were also prepared with three different reagents to extract target components. Details have been published in our recent report on sorption of glyphosate, 2,4,6-TCB, 2,4-D and PFOS [17–20]. Briefly, 0.1 M  $NH_2OH \cdot HCl$  and 0.01 M  $HNO_3$  were used for 30 min to remove manganese oxides, and the product is denoted as  $S_{-Mn}$  [36]. In order to remove the soil organic matter (SOM), the bulk soil was repeatedly treated with 30% hot  $H_2O_2$  based on previous reports [37,38], and the product is designated as  $S_{-OM}$ . This was followed by washing the soil samples with deionized  $H_2O$ . This process was repeated until the electrical conductivity of the solution was  $<50 \mu S$ . 0.2 M of  $(NH_4)_2C_2O_4$  buffered with  $H_2C_2O_4$  at pH 3.0 and shaken in the dark for 4 h was employed to extract both Fe and Mn hydroxides, denoted as  $S_{-FeMn}$  [39]. All the samples were centrifuged at 3800 rpm for 30 min and the supernatants filtered (0.45  $\mu m$ ) into 50 mL polypropylene (PP) tube for the determination of Fe and Mn concentrations. The soil components were washed 3–4 times with distilled water, air-dried and stored in air-tight container.

### 2.3. Soil characterization

Soil samples were characterized by the following conventional Methods [40]. Briefly, the pH of the samples was measured in 1:10 solid to 0.01 M calcium chloride ( $CaCl_2$ ) ratio (as used in the sorption experiment). The cation exchange capacity (CEC) was determined following the silver thiourea method [41]. The specific surface area, organic carbon contents, total extractable and pseudo-total amounts of Fe and Mn in the samples were determined following standard procedures as reported recently [17–20]. The crystallinity of the samples was determined by X-ray diffraction, XRD (MD10) with  $Cu K\alpha$  radiation at 1.5406 Å. The X-ray diffractograms of the samples were recorded from 16° to 72° of  $2\theta$  at a scanning speed of 0.05° of  $2\theta s^{-1}$  and a divergent slit of 0.0625°. Operating conditions were;  $\lambda = 0.15406 \text{ \AA}$ ,  $V = 25 \text{ KV}$ ,  $I = 20 \text{ mA}$ . The XRD data was analyzed using a database supplied

**Table 1**  
Contents of metal oxides in the sediment particles pretreated by different procedures including sequential and selective extractions.

Samples	pH	$pH_{PZC}$	$E_h$ (mV)	SA ( $m^2/g$ )	CEC (cmol/kg)	OC (%)	OC-EE (%)	Fe		Mn	
								( $\mu mol Fe/g$ )	Fe-EE (%)	( $\mu mol Mn/g$ )	Mn-EE (%)
UNTD	6.4 (7.4) <sup>a</sup>	5.7	242 (−52) <sup>a</sup>	11.47	16.87	12.41		473.24 ± 8.94		121.34 ± 8.79	
$S_{-Mn}$	6.1 (6.9) <sup>a</sup>	6.3	247 (−81) <sup>a</sup>	31.23	11.23	10.26	17.32	397.42 ± 9.44	22.33	17.46 ± 3.92	90.81
$S_{-FeMn}$	5.6 (7.7) <sup>a</sup>	5.4	296 (−105) <sup>a</sup>	18.19	9.01	10.98	11.52	170.11 ± 8.92	89.34	16.84 ± 3.79	91.86
$S_{-OM}$	5.8 (7.9) <sup>a</sup>	6.7	334 (−55) <sup>a</sup>	38.24	7.71	0.92	92.52	428.33 ± 9.89	13.26	102.55 ± 8.94	16.43
TEM						12.41	100	339.42 ± 14.92		114.38 ± 7.21	

Dissolved organic carbon contents, DOC (mg/L) and percent OC corrected for DOC,  $OC_{doc}^{cor}$  (%)

	UNTD	$S_{-Mn}$	$S_{-FeMn}$	$S_{-OM}$
Oxic	8.12 (12.409) <sup>b</sup>	5.32 (10.259) <sup>b</sup>	6.74 (10.979) <sup>b</sup>	0.85 (0.9199) <sup>b</sup>
Anoxic	23.47 (12.407) <sup>b</sup>	15.44 (10.258) <sup>b</sup>	17.24 (10.978) <sup>b</sup>	3.15 (0.0197) <sup>b</sup>

<sup>a</sup> Data under anoxic condition. UNTD, untreated soil sample; STAOx, STHA and STHP are Soils treated to significantly remove Fe and Mn, Mn, and organic matter respectively. Average ( $n = 2$ ) ± standard deviation. The extraction efficiency (EE) was calculated by the following equation:  $EE = \frac{C_{ptc} - C_p}{C_{ptc}} \times 100\%$ , where  $C_{ptc}$  is pseudo-total content;  $C_p$  is contents of the metal oxides after extraction; TEM is total extractable amount from sequential extraction.

<sup>b</sup> Values in parentheses are %OC corrected for DOC  $\{OC_{doc}^{cor}(\%)\}$  under both experimental conditions.

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