

Adsorption behavior of 2,4-dichlorophenol and pentachlorophenol in an allophanic soil

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Abstract

The adsorption of 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) by a variable-charge soil from southern Chile was studied in a series of batch equilibration experiments. 2,4-DCP and PCP adsorption behavior was evaluated as a function of pH (pH values of 4.5, 6.0 and 7.5) in a 0.1 M KCl (25 °C) background solution for soil material collected at three different depths (0–20 cm, 20–40 cm, and 40–60 cm). 2,4-DCP and PCP adsorption decreased with increasing soil pH, suggesting that the undissociated species were adsorbed more readily and that electrostatic repulsion may inhibit partitioning as pH increases. The PCP adsorption was greater than observed for 2,4-DCP and decreased with soil depth. Multiple regression analysis between K_d and various soil properties indicated that the soil organic carbon content is a strong indicator of chlorophenol adsorption, and in addition to organic carbon, the soil pH is an important property controlling adsorption behavior.

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1. Introduction

Technologies for drinking water processing and advanced wastewater treatment have commonly used adsorption by activated carbon to remove toxic and mutagenic organic compounds. Previous studies have shown that chlorinated phenols are strongly adsorbed by activated carbon. However, due to the high cost of activated carbon, some researchers have proposed the use of novel sources of adsorbent materials, e.g. soil (Diez et al., 1999; Navia et al., 2003).

Some investigations have been conducted on the development of a new tertiary treatment for pulp mill wastewater

to remove phenolic compounds and humic substances that impart an unacceptable color due to the presence of high molecular weight phenolic compounds (Crooks and Sikes, 1990) and toxicity associated with wood resin and chlorinated phenols (Walden et al., 1986) to receiving surface waters and soils. These studies have demonstrated the effective remediation of the pulp mill effluents using volcanic ash soils (Andisols), which have a high adsorption capacity for these organic compounds (Diez et al., 1999; Vidal et al., 2001; Navia et al., 2003). The allophanic soils used in these studies are derived from volcanic ash and possess a highly pH-dependent variable surface charge. Allophane ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$), main component of the clay fraction of volcanic soils, has short to mid-range atomic ordering and a prevalence of Si–O–Al bonding. The surface area of allophane has been calculated to be about $1000 \text{ m}^2 \text{ g}^{-1}$, while values measured with ethylene glycol

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monoethyl ether range from 700 to 900 m² g⁻¹ (Wada, 1989). Furthermore, the allophane-ferrihydrite associations present in Chilean Andisols can alter the allophane surface reactivity and play a key role in determining the availability of nutrients and in controlling soil contaminant behavior (Mora and Canales, 1995).

The physical, chemical, and biological characteristics of the soil, as well as the chemical properties of the organic compounds will influence their fate and transport. The adsorption properties of chlorophenols are controlled largely by their degree of substitution and the resultant hydrophobicity. In the normal soil pH, most chlorophenols will be totally or partially ionized, affecting their solubility, adsorption, transport and their bioavailability (Kookana and Rogers, 1995). Several investigators have noted that pH plays an important role in the adsorption properties of compounds with acidic functional groups on activated carbon and soil because the neutral and ionic forms display very different adsorption behavior (Diez et al., 1999; DiVincenzo and Sparks, 2001; Hyun and Lee, 2004). In the absence of significant organic carbon (OC) content, the adsorption maximum for weak organic acids on hydrous Fe- and Al-oxide surfaces often occurs at or near their pK_a- due to the combined effects of pH on oxide surface charge and acid dissociation. The non-dissociated form of organic acids can both protonate uncharged surface sites to initiate an electrostatic interaction or neutralize the hydroxyls resulting from a ligand exchange at the oxide surface, thus enhancing the adsorption process (Schwertmann et al., 1986). However, chlorophenol adsorption in soil has been described assuming hydrophobic partitioning of the neutral species to soil organic matter (DiVincenzo and Sparks, 2001) or as described by He et al. (2006) as a hole-filling adsorption mechanism into the soil organic matter, facilitated by H-bonding (Xia and Pignatello, 2001).

The main objective of the present study was to evaluate the adsorption behavior of 2,4-DCP and PCP on an allophanic soil from southern Chile. The influence of various soil properties thought to regulate chlorophenol partitioning was evaluated by multiple regression analysis.

2. Material and methods

2.1. Soil

2,4-DCP and PCP adsorption behavior was studied on an Andisol collected from the Temuco Series, located in southern Chile (Table 1). A detailed description of Temuco Series was given by Mella and Kühne (1985). Three soil samples were collected representing depths of 0–20 cm, 20–40 cm and 40–60 cm within the soil profile. The materials were air dried at room temperature, and then passed through a 2 mm sieve prior to their use in this study. Various soil properties thought to impact chlorophenol adsorption were measured using the methods described by Sadzawka (1990).

Table 1
Physicochemical characteristics of the Allophanic soil

Parameter	Allophanic soil depth		
	0–20 cm	20–40 cm	40–60 cm
pH (H ₂ O)	5.90	6.39	6.80
Organic carbon (OC), %	8.50	4.60	2.60
Organic matter (OM), %	14.62	7.91	4.47
AEC, cmol(-)/kg	2.70	1.60	0.50
IEP	3.10	3.53	5.94
Sand, %	16.1	19.0	17.2
Silt, %	58.2	54.1	51.8
Clay, %	25.7	26.9	20.0
Al ₂ O ₃ , %	18.6	20.8	21.6
Fe ₂ O ₃ , %	10.5	11.7	12.4
SiO ₂ , %	41.6	43.7	45.0

AEC: anion exchange capacity; IEP: isoelectric point.

2.2. Chemicals

Pentachlorophenol (PCP) and 2,4-dichlorophenol (2,4-DCP) were purchased from Sigma Chemical Co. with reported purities of >95%. Relevant physical and chemical properties such as water solubility (*S_w*), octanol/water partition coefficient (log *K_{ow}*), and acid dissociation constant (p*K_a*), are presented in Table 2.

2.3. Equilibrium adsorption experiments

All equilibrium adsorption experiments were conducted in duplicate in 50-ml polycarbonate centrifuge tubes containing 0.5 and 0.1 g of soil for 2,4-DCP and PCP, respectively. The soil samples were equilibrated with 20 ml of 0.1 M KCl with range of PCP and 2,4-DCP concentrations at pH values of 4.5, 6.0 and 7.5 (adjusted as needed with 0.1 M HCl or 0.1 M KOH before equilibration) on a reciprocating shaker (Lab-Line) for 24 h in dark at 25 °C. An equilibration period of 24 h was chosen after preliminary experiments lasting up to 96 h indicated that such a duration was sufficient to achieve equilibrium with respect to 2,4-DCP and PCP adsorption. After equilibration, the sample tubes were centrifuged in a centrifuge Eppendorf 5804 R at 10000 rpm (11952g) for 10 min and passed through a PVDF membrane filter 0.45 μm pore size (Millipore). The 2,4-DCP and PCP concentration in the supernatant was determined by HPLC (high pressure liquid chromatography). The HPLC instrument equipped with a Merck-Hitachi L-7100 pump, a Rheodyne 7725 injector with a 20 μl loop, a Merck-Hitachi L-7455 diode array detector operating at 205 nm for 2,4-DCP and 215 nm

Table 2
Selected physicochemical properties of 2,4-DCP and PCP (Kookana and Rogers, 1995)

Compound	MW (g/mol)	Water solubility (mg/l) (25 °C)	log <i>K_{ow}</i>	p <i>K_a</i>
2,4-Dichlorophenol	163.1	4500	3.08	7.85
Pentachlorophenol	266.3	18	5.01	4.75

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