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Sorptive Behavior of Chlorophenols on River Volcanic Sediment

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PCP (Pentachlorophenol) and 2,4,6-TCP (2,4,6 Trichlorophenol) compounds are contained in bleaching-kraft pulp process effluents. In Chile, over half of the current total cellulose-production capacity (2 million tons/year) is located within the Biobio river basin (8th Region), which provides drinking water to more than 2 million inhabitants (González et al. 1999). The river-sediments have volcanic origin; yet despite the fact, PCP concentrations in sediment areas around kraft mill effluent discharges as high as 143.93 μg/kg have been reported (Parra et al. 1998). However, no sorptive capacity studies of this sediment have been performed to predict the PCP or 2,4,6-TCP mobility from the kraft mill effluents to the river volcanic-sediment (Fall et al. 2000).

The adsorption isotherms describe the features of interaction between river volcanic-sediment and PCP or 2,4,6-TCP compounds. Adsorption can be described by a Freundlich-type isotherm.

$$C_s = K_f \times C_e^{1/n} \tag{1}$$

Where C_s = mass of clorophenols adsorbed per mass of sediment (mg/kg); C_e = PCP or 2,4,6-TCP equilibrium concentration (mg/L); and K_f (L/kg) and n = Freundlich constants.

When 1/n = 1, the adsorption isotherm is linear, and K_d (L/kg) is the quotient between C_s and C_e. Equation 1 can be re-written as follows:

$$K_d = \frac{C_S}{C_e} \tag{2}$$

In aquatics systems, a linear relationship is often assumed (Gao et al. 1998a). However, Cristodoulatos and Mohiuddin (1996) proposed a generalized nonlinear empirical model (equation 3). This equation expresses the effects of the river volcanic-sediment and PCP or 2,4,6-TCP properties in function of the: a) cation exchange capacity (CEC); b) the organic carbon fraction (f_{oc}); c) the percent of fine grains in the sediment (f); d) the sediment-chlorophenol ratio (SS); and e) the pH of the PCP or 2,4,6-TCP.

$$K_d = \frac{213.80(SS)^{0.09}(CEC)^{1.09}(f)^{-0.60}(f_{oc})^{0.47}}{1+10^{pH-4.75}} \tag{3}$$

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According to equation 3, the pH dominates the distribution ratio and it is inversely correlated to K_d (Sabbah and Rebhun 1997; You and Liu 1996). Also, the chlorophenol sorption capacity for the sediments is a direct function of CEC. Furthermore, Cristodoulatos and Mohiuddin (1996) can correlate CEC with the f and f_{oc} coefficients: they obtained high positive correlations in mineral materials. If the content of organic matter in the sediment is less than 0.01 % (w/w), clay and silt are mainly responsible for adsorption. However, if the content of organic matter is up to 6-8% (w/w) then both organic and mineral surfaces are involved in adsorption (Gao et al. 1998a). Chlorophenols can be present in the dissociated form (phenolate ion) or undissociated form in the river. The distribution between the phenolate and undissociated phenol is a function of pH. In this way, the fraction of undissociated chlorophenol could be expressed as (Sabbah and Rebhun, 1997):

$$\alpha = \frac{CP^0}{CP_t} = \frac{1}{1+10^{pH-pKa}} \qquad (4)$$

Where: CP^o is the maximal soluble concentration of undissociated chlorophenol and CP_t is the chlorophenol total solubility.

Since PCP and 2,4,6-TCP are weak acids (pK_a: 4.75 and 6.2, respectively), their solubility increases drastically with increasing pH. When chlorophenols dissolve in water, two forms are normally present: (CP^0) and a dissociated anionic form, (CP^-) (Arcand et al. 1995). In this way, PCP and 2,4,6-TCP adsorbability of phenolate form should not be neglected, since at neutral pH values these compounds are present predominantly in the ionized form.

The goal of this study is to investigate the sorption behavior of 2,4,6-TCP and PCP in river volcanic-sediment.

MATERIALS AND METHODS

Sediment from the Biobío river (Southern Chile) was collected with a Petite Ponar dredge (225 cm^2 dredge area). The granulometric sediment classification was done by particle-size fractionation (2-mm sieve) following Folk (1980).

The effect of the clorophenols/sediment (SS) ratio and the log K_{ow} coefficient, representing partitioning, were evaluated. Batch assays (50 mL of volume) with 0.01 N $CaCl_2$ and different concentrations of PCP or 2,4,6-TCP (5, 10, 20 and 25 mg/L) were considered according to guideline 106 (OECD, 1981). Two different SS ratios were studied (0.2 and 0.042). The inhibition of microbiological activity was achieved with a NaN_3 solution (150 mg NaN_3/L). Each trial was conducted at 22 ± 0.1°C, pH = 7.0, shaken (150 r.p.m.) and in dark environment.

Chlorophenol concentration in the liquid phase was monitored at different times during a 24-hour period (2, 4, 6, 10, 12 and 24 h) (PCP and 2,4,6-TCP purity: 98%, Aldrich Chemical Company, Inc.). Each experiment was carried out in triplicate. Control samples were included under the same methodology, but without chlorophenol or sediment. At the end of the assays, solid-liquid separation was achieved by centrifugation at 7000 r.p.m. for 20 minutes (Centrifuge 5415 C Eppendorf).

Table 1. Main parameters affecting medium and coarse sand sorption of PCP and 2,4,6-TCP.

K_d	CEC	Solution pH	SS	f (%)	f_{oc} (%)	Reference
0.86	0.12	5.32	0.2	---	0.05	Fall et al. (2001)
0.89	0.57	7	0.16	0.3	0.07	Cristodoulatos and
0.69	0.57	7	0.016	0.3	0.07	Moihuddin (1996)
0.673	2.45	6.67	0.042	0.12	0.22	This study
0.852	2.45	6.67	0.2	0.12	0.22	This study
0.663	2.45	6.67	0.042	0.12	0.22	This study
0.579	2.45	6.67	0.2	0.12	0.22	This study

In the desorption study (after the adsorption experiment), the supernatants were replaced by a similar volume of 0.01 N $CaCl_2$ solution without chlorophenol. The centrifugation tubes were shaken at 150 r.p.m. The chlorophenol concentration in the solution was measured after each desorption step (at 0, 24, 48, 72 and 96 h). After the sorption experiments, a mass balance was done to determine the amount of chlorophenol adsorbed in the sediment as described in Cristodoulatos et al. (1994).

Adsorption and desorption isotherms were obtained for PCP or 2,4,6-TCP considering the different SS relationships in accordance with the classification system of Giles et al. (1960) and equation 1 as well as the linear form (equation 2). After equilibration, the sediment was separated from the liquid, placed in 25 mL of ethanol and mixed for 1 hour. Approximately 2 mL of the ethanol extract was centrifuged to separate the solids and were analyzed for PCP (Christodoulatos et al. 1994). Mass balances were performed on sorption vials, using measured concentrations in the liquid phase.

The concentration of organic matter was determined in accordance with Mills (1978). Sediment pH (in 0.01 N $CaCl_2$ solution, sediment:solution = 1:2) was measured with a glass electrode (Sentix 41, Wissensaftlich Technische Werkstätten, Germany). The concentrations of 2,4,6-TCP and PCP in the equilibrium condition were determined by reverse-phase high performance liquid chromatography (HPLC) as described by Domínguez et al. (2002).

RESULTS AND DISCUSSION

The granulometric distribution of the sediment samples shows uniformity. Physical and chemical characteristics of the sediment are: CEC of 2.25, pH = 6.67 (solid), pH = 7 (solution) and 0.22% of organic carbon content and 0.0078 mm of particles size. The classification of all of the samples corresponds to coarse sand in the Wentworth size class (McManus 1988). In fact, its origin is basaltic and there are no studies related to the sorption phenomena.

Figure 1 shows the kinetics of the PCP or 2,4,6 adsorption (μg) over time (h). Each point shows the minimum, maximum and average of the three replicates.

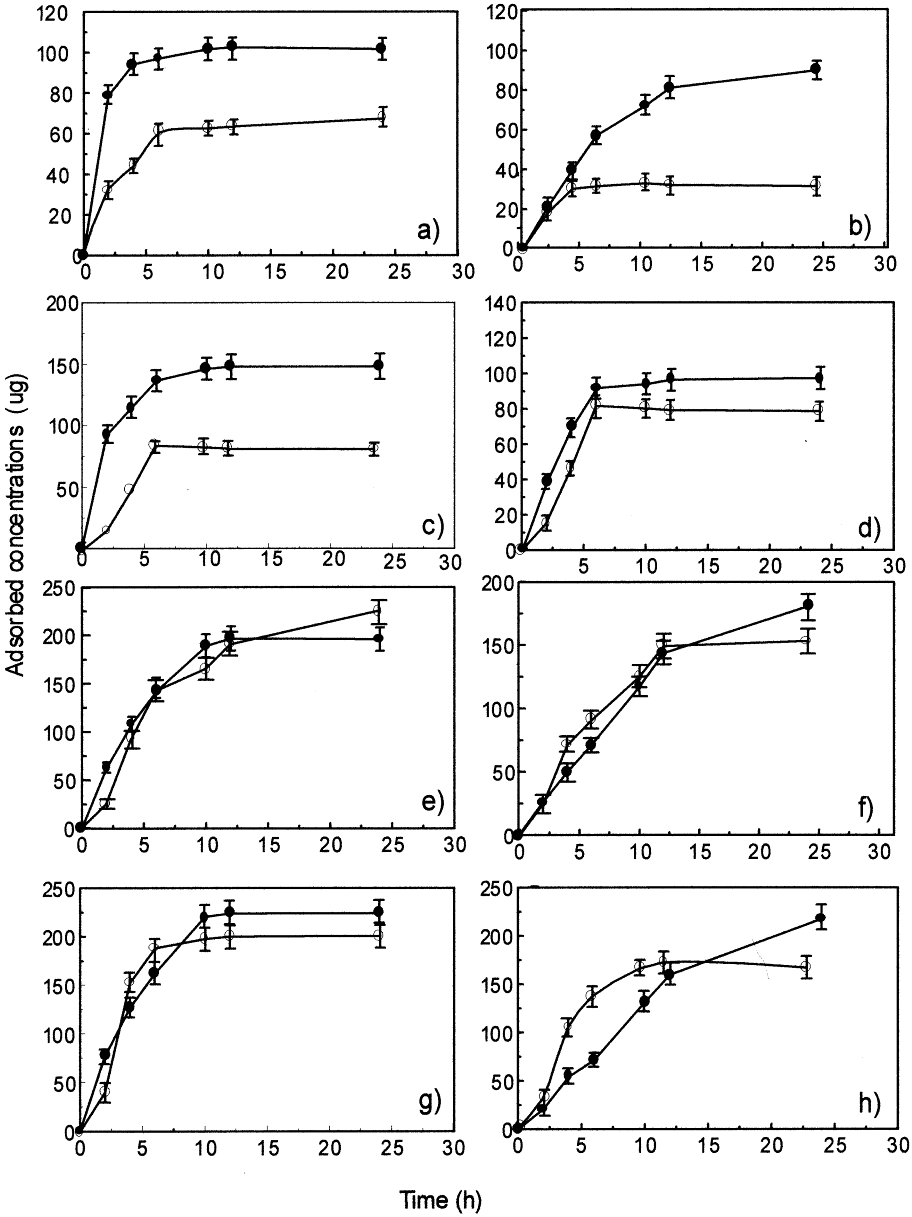

Figure 1. Adsorption kinetics of PCP (O) and 2,4,6-TCP (●) at: a) initial concentrations of 5 mg/L, SS = 0.2; b) initial concentrations 5 mg/L, SS = 0.042; c) initial concentration of 10 mg/L, SS= 0.2; d) initial concentrations of 10 mg/L, SS = 0.042; e) initial concentration of 20 mg/L, SS = 0.2; f) initial concentration of 20 mg/L, SS = 0.2; g) initial concentrations of 25 mg/L, SS = 0.2; h) initial concentrations of 25 mg/L, SS = 0.042.

Table 2. Adsorption constants and coefficients of 2,4,6-TCP and PCP into river volcanic sediment

		Freundlich isotherm			Lineal isotherm	
Chlorophenols	SS	K_f (L/kg)	1/n	r^2	K_d (L/kg)	r^2
2,4,6-TCP	0.200	7.254	0.373	0.998	0.579	0.982
2,4,6-TCP	0.042	4.926	0.437	0.846	0.663	0.963
PCP	0.200	2.26	0.712	0.817	0.852	0.799
PCP	0.042	0.806	0.974	0.983	0.673	0.964

The adsorption kinetics corresponds to the L type in the classification proposed by Giles et al. (1960). The adsorption stationary state was obtained by all the assays between 7 h (Figure 1: a,b,c,d) to 11 h (Figure 1: e,f,g,h). The mass balance has indicated that the 85% of chlorophenol content in each assay or upper has been adsorbed in this period of time. The initial chlorophenol adsorption rate, calculated as the quotient between the amount of chlorophenols/time, indicated that the main effect is produced by the SS parameter. Therefore, the 2,4,6-TCP compound at SS = 0.2 indicates the faster initial adsorption rate (see Figure 1: a,c,e and g). On the other hand, the initial chlorophenol concentration does not show influence on the initial adsorption rate.

Adsorption isotherm results are described in Table 2. The worst linear-model r^2 was 0.799, observed for PCP. This result is similar to the findings observed by Fall et al. (2001) whose least precise result corresponded to soils containing sand with a smaller adsorption capacity.

The higher values of K_f (7.254 and 4.926 L/kg) for 2,4,6-TCP when compared to those of PCP (2.260 and 0.806 L/kg) could be explained as an initially quicker adsorption (Figures 1: a,b,c,d). Both are weak acids: PCP pKa=4.75) (Christodulatos and Moihuddin 1996) and 2,4,6-TCP (pKa=6.2) (Arcand et al. 1995; Sabbah and Rebhun 1997). In fact at neutral or high pH values, the phenolate ion of PCP and 2,4,6-TCP is present. From equation (4) in this case when pH=7 and using the CP_t values proposed by Arcand et al. (1995), the 2,4,6-TCP^0 is 6,64 g/L and for PCP^0 is 2,5 g/L. The PCP solubility in this pH range (nearly 7) is higher at 480 mg/L at 20°C, while 2,4,6-TCP solubility is 420 mg/L (Sabbah and Rebhun 1997), which might explain why the higher values of K_f and the K_d values for 2,4,6-TCP (0.579 and 0.663 L/kg) and for PCP (0.852 and 0.673 L/kg) are not similar. The K_d in the volcanic sediments are consistent with the results of You and Liu (1996), Fall et al. (2001) and others indicating that adsorption decreases, when the pH increase.

Additionally, PCP and 2,4,6-TCP K_d values indicate an inverse relationship with the solubility property; similar results were found by Gao et al. (1998a) and You and Liu (1996). On the other hand, the low values of the adsorption constant (1/n < 1) indicate that sorption appears to approach a limit, which is also due to the lower values of f_{oc} and f. In the case of PCP, the 1/n values are higher (0.712 and 0.972) than 2,4,6-TCP (0.373 and 0.437).

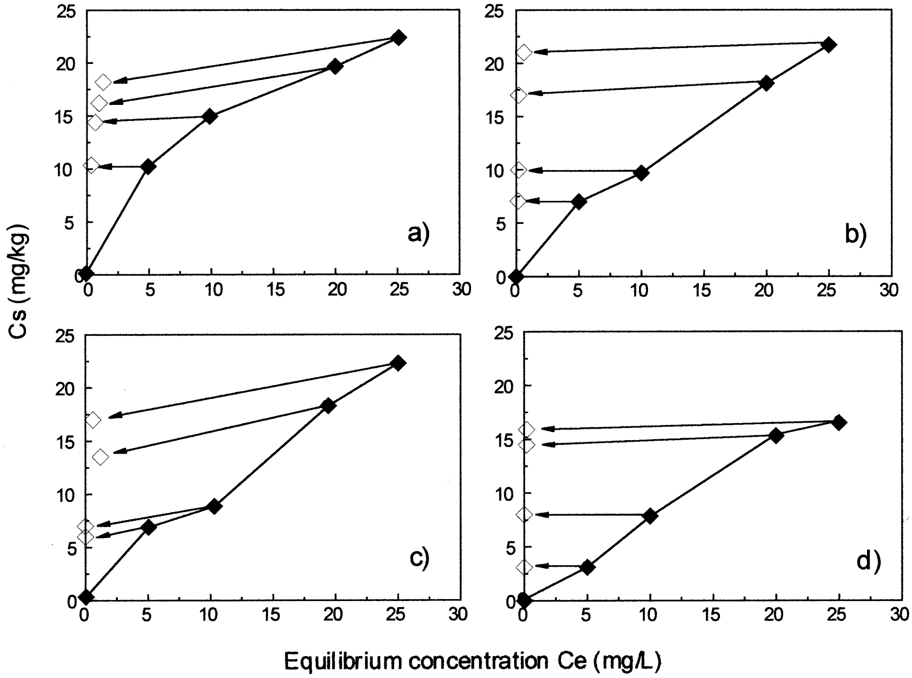

Figure 2. Desorption of a) 2,4,6-TCP (SS = 0.2) b) 2,4,6-TCP (SS = 0.042) c) PCP (SS = 0.2) and d) PCP (SS = 0.042). Adsorption (♦), desorption (◇).

Results of the adsorption-desorption experiments for 2,4,6-TCP and PCP are summarized in Figure 2. Parts a and b show the irreversible behavior of 2,4,6-TCP for SS of the 0.2 and 0.042. In the last case (Figure 2b), the slope of the desorption isotherms is practically 0, which can be explained by a complete irreversibility of the adsorption phenomena. A similar effect is observed in Figure 2d for the PCP case. Indeed, Fall et al. (2000) demonstrated that PCP desorption from contaminated soils can lead to three different behavior types: complete reversibility, partial reversibility, or total irreversibility. Moreover, Kan et al. (1997) identified several new unique features of sorption irreversibility, such as the additive nature of the filling of the irreversible adsorption compartment. They reported a stepwise increase in the irreversibly sorbed contaminant mass when soil is submitted to repeated cycles of adsorption-desorption.

Finally, the most cited factors for controlling the extent of irreversibility are organic matter and pH in the sediment (Fall et al. 2000; Gao et al. 1998b). Burgos et al. (1996) reported that phenols and chlorophenols undergo chemical interaction by oxidative coupling, resulting in irreversible adsorption. In fine and coarse sediment fractions, phenolic compounds desorption is slower than adsorption and might be favorable environments for reactions resulting in irreversibility of adsorption (Isaacson and Frink 1984).

In the specific case of this type of volcanic sediment where the fine content and f_{oc} are very low and the solution pH is nearly 7, the sorption of chlorophenols seems to be an irreversible phenomenon controlled by chemical adsorption.

2,4,6-TCP shows a higher initial adsorption, due to the pH value of 7 were the undissociated form is one order of magnitude higher when compared to PCP. On the other hand, bleach kraft mill effluent contains many other chlorophenols and resin-acid compounds that may affect sorption of PCP and 2,4,6-TCP in aquatic environments. Further studies will be needed to develop a better understanding the extent to which synergistic interactions affect sorption behavior.

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