Bull. Environm. Contam. Toxicol. 28, 605–610 (1982)

Sorption of Pentachlorophenol by Unbleached Wood Pulp Fibers

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Pentachlorophenol (PCP) has been an ingredient of slimicides used in the pulp and paper industry. Following inclusion of PCP on the EPA priority pollutant list and the detection of PCP in some mill effluents (BALL et al. 1978), its use by the pulp and paper industry was discontinued.

Determination of PCP in an effluent involves acidification of the sample to <pH 2, extraction with methylene chloride, and analysis of the extracts by GC or GC/MS (FEDERAL REGISTER 1979). Incomplete recovery of PCP added to aqueous samples containing wood pulp fibers suggested that sorption of the PCP by the fibers might have hindered the analysis. In addition to affecting its determination, sorption of PCP onto suspended solids in an effluent might influence its removal in waste treatment processes, its availability to aquatic life, and its ultimate fate in the environment.

This study documents the sorption of PCP by wood pulp fibers. The amount of PCP sorbed and the conditions under which sorption occurs are described.

MATERIALS AND METHODS

Pentachlorophenol (Eastman Kodak) was purified by recrystallization from hexane. Saturated aqueous stock solutions were prepared by the method of CHIOU et al. (1977); concentrations were determined by acidification, extraction with benzene (Burdick and Jackson), and analysis by GC. Unbleached softwood kraft pulp (Domtar Pulp Ltd.) was beaten in a Valley laboratory beater, classified in a Bauer-McNett classifier, and the on-14 mesh fraction was used in this study.

Sorption studies were conducted by placing a pulp suspension in a sample jar, adjusting the pH, and pipetting in the desired amount of aqueous PCP solution. Initial PCP concentrations ranged from 54 to 540 µg/L, with pulp consistencies from 0.6 to 0.8%. A few studies were also performed at 0.25% consistency. Samples were shaken overnight on a Dubnoff Shaker (Precision Scientific). In orienting studies pulp fibers and water were then separated by filtration using a coarse sintered glass filter funnel. PCP in the aqueous phase was determined by the procedure of MURIN and SNOEYINK (1979) involving acidification

0007-4861/82/0028-0605 $01.20
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to pH 2, triple extraction with benzene, drying of the benzene extract by passage through a column of anhydrous sodium sulfate, and analysis by GC. Determination of PCP sorbed by the wood pulp required extraction of the fibers with 4% NaOH, as described by LODE (1964). The alkaline extract was then acidified and extracted with benzene as described above for analysis of the aqueous phase. PCP in the benzene extract was determined on a Varian 1440 GC with a tritium foil electron capture detector and a 1/4-inch by 3-feet-long glass column packed with 1% SP-1240DA on 100/120 Supelcoport. Column temperature was 180°C, and N_2 flow rate was 40 mL/min.

The average total recovery of PCP from water plus fibers in orienting studies was 93.8 $\pm$ 2.0% for 32 samples. In subsequent studies only the PCP in the aqueous phase separated from the fibers by decantation was determined.

RESULTS AND DISCUSSION

Sorption of PCP by unbleached kraft pulp fibers was studied at pH 2 and 5. Figure 1 shows log-log plots of the results. Although the data obtained at pH 2 may be described with the empirical Freundlich adsorption equation, the pH 5 data form a curved isotherm. Curved isotherms have also been observed in studies of adsorption of chlorophenols on activated carbon (SNOEYINK et al. 1977, MURIN and SNOEYINK 1979). The finding of more extensive sorption of PCP at pH 2 than at pH 5 is consistent with the pK_a of PCP (4.86) and with the lower water solubility of PCP than of its sodium salt.

Using the method of CHIOU et al. (1977) gave PCP solubilities at pH 2 and 5 of 4.6 and 9.8 ppm, respectively. After a procedure devised by HANSEN and CRAIG (1954) the sorbed PCP concentration was plotted against a reduced concentration C_{eq}/C_s, where C_s is the solubility limit at a given pH. The improved correspondence of the lines in a reduced concentration plot, Fig. 2, suggests that sorbate-surface interactions are similar for PCP sorption at pH 2 and 5. The pH dependence of PCP sorption onto unbleached kraft pulp can be largely attributed to changes in the PCP itself with pH.

Values for the equilibrium concentration of PCP in solution at pH 5 originally shown in Fig. 1 have been recalculated to indicate only the concentration of PCP in the molecular form. A replot of these data shows an approximate correspondence of the pH 2 and pH 5 isotherms which is almost identical with Fig. 2. These plots provide a strong indication that it was predominantly the molecular form of PCP which was sorbed onto unbleached kraft pulp fibers. This is supported by results of earlier orienting studies conducted over a wider pH range, shown in Table 1, which reveal that there was only slight sorption of the dissociated form of PCP.

These results differ significantly from work on sorption of di-

and trichlorophenol on activated carbon in which maximum sorption occurred at pH levels near the compound's pK_a (SNOEYINK et al. 1977, MURIN and SNOEYINK 1979). In that work, however, the high specific surface area of the carbon permitted sorption of chlorophenols in their molecular and ionic forms to give surface concentrations about four orders of magnitude greater than observed on wood pulp fibers in the current study. Pulp fibers used in the current work had a hydrodynamic specific surface area of about 1 m^2/g, compared with a typical activated carbon specific surface area of 10^3 m^2/g (BET-N_2 method).

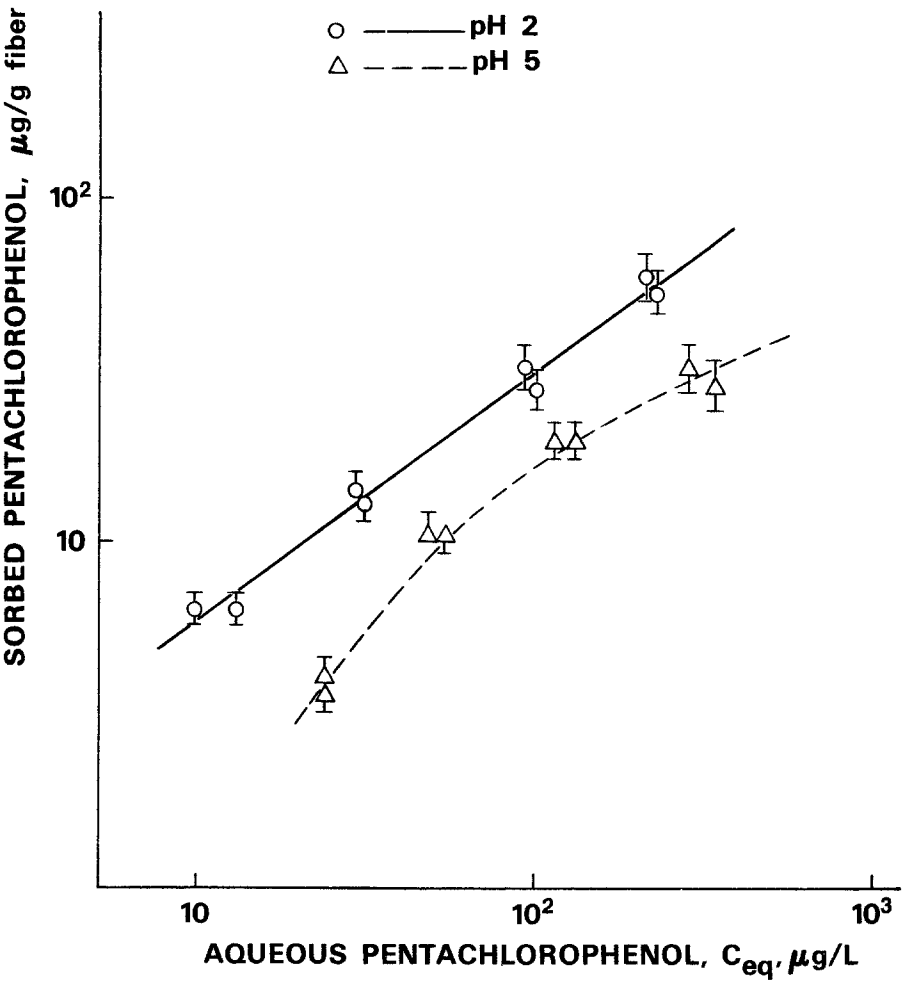

Figure 1. Sorption isotherms for pentachlorophenol on unbleached wood pulp at pH 2 and pH 5.

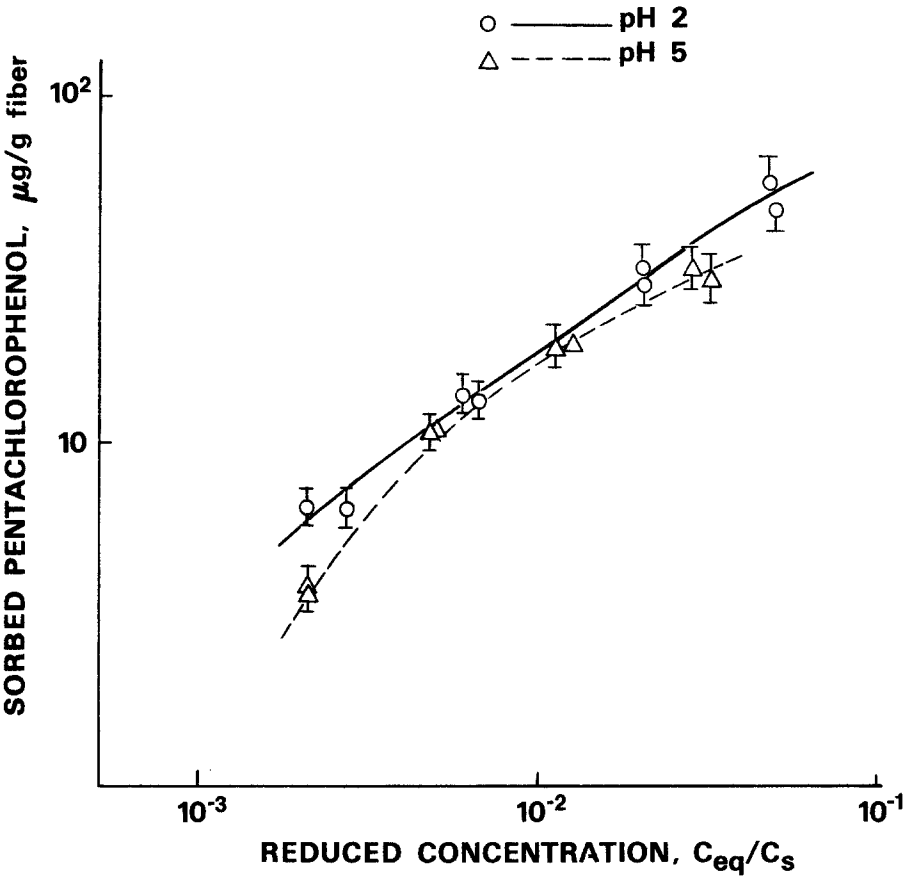

Figure 2. Sorbed pentachlorophenol as a function of reduced concentration.

TABLE 1

Effect of pH on Sorption of Pentachlorophenol by Unbleached Wood Pulp Fibers

pH	PCP Recovered from Fibers, % of PCP Added to Suspension
2	84.2
5	27.0
7	7.0
11	5.8

As shown in Table 2, sorption equilibrium was achieved within 10 minutes after unbleached pulp fibers were placed in an acidic (pH 2) aqueous solution of PCP. A week-long exposure of pulp to aqueous PCP did not result in additional sorption beyond that which the same fibers experienced overnight. Table 3 indicates that desorption of PCP from a separate unbleached pulp sample occurred promptly after the pH was raised.

TABLE 2

PCP Sorption Time Dependence

Exposure Time	Sorbed PCP, µg/g
One minute	9
Ten minutes	11
16 hours	11

TABLE 3

Desorption of PCP after Raising pH

Condition	Sorbed PCP, µg/g
Before pH raised, pH 2	5
One minute after pH raised, pH 8-9	0.7, 0.8
One hour after pH raised, pH 8-9	0.3
Equilibrium at pH 9 (not acidified)	0.1

Results of this investigation indicate that the PCP in an acidic process stream containing unbleached wood pulp will be sorbed by the pulp fibers. The PCP will be promptly desorbed from the fibers if the process stream is neutralized upon entry into a waste treatment system. Knowledge of the sorption behavior of PCP also provides the basis for an improved method for PCP determination in wood pulp-containing samples: the sample is made alkaline; the fibers are removed; and the aqueous phase is then acidified and extracted in the normal manner.

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