Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Nyssen, G. A. , Lovell, G. S. , Simon, A. A. , Smith, J. G. , Tolar, B. K. and Wilson, D. J.(1987) 'Removal of Trace Levels off Phenols from Aqueous Solution by Foam Flotation', Separation Science and Technology, 22: 11, 2127 — 2141

To link to this Article: DOI: 10.1080/01496398708068604

URL: http://dx.doi.org/10.1080/01496398708068604

SEPARATION SCIENCE AND TECHNOLOGY, **22**(11), pp. 2127-2141, 1987

Removal of Trace Levels of Phenols from Aqueous Solution by Foam Flotation

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Abstract

Pentachlorophenol (PCP) was removed from water by foam flotation with the cationic surfactant cetyltrimethylammonium bromide (CTAB). With initial PCP concentrations of 20 ppm or less, residual PCP concentrations of less than 0.05 ppm were obtained after 5 min flotation. The CTAB concentration and flotation time are directly related to the amount of PCP removed. PCP removal is most efficient at neutral to basic pH and at low ionic strength. PCP removal is less effective with sodium dodecyl sulfate. As much as 80% of the CTAB can be replaced by dodecylamine without inhibiting PCP removal. Alcohols up to 10% by volume do not affect PCP removal. Other phenols can also be removed equally well by foam flotation if the phenol is in the anionic form during flotation.

INTRODUCTION

Pentachlorophenol (PCP) is a highly toxic organic chemical which has been widely used as a wood preservative; it is quite persistent in the environment and has been found to occur in sewage (*1-3*). Its persistence, high toxicity and strong odor to humans, and detrimental effects to aquatic organisms, have led the EPA to set water quality criteria for it of 3.2 μg/L for protection of aquatic life and 30 μg/L for drinking water (*4*). EPA has published a report on the removal of phenolic compounds from wood-preserving wastewaters, from which one concludes that rapid, cheap separation techniques capable of attaining effluent standards consistent with the water quality criteria which have been set for this compound are not yet available (*5*).

An early study of the removal of phenolics by adsorptive bubble separation techniques was carried out by Grieves and coworkers, who investigated the removal of phenol itself by solvent sublation, solvent extraction, and foam fractionation techniques (*6*). The methods were effective but relatively slow and costly; they are also of dubious applicability to PCP, which is much more acidic than phenol, and also much less soluble in water. Quite recently Valsaraj and Springer completed a study of PCP removal by solvent extraction and solvent sublation (*7*). They found that the high acidity of PCP does indeed change its separation characteristics rather drastically as compared to those of phenol; a pH of about 2.5 is necessary in order to obtain effective removal. The processes are relatively slow.

The p*K* of PCP is 5.0, and its solubility in water over the 20–30°C temperature range is 14–19 mg/L. The solubility of the sodium salt of PCP is 79 mg/L at pH 5.0 and 4000 at pH 8.0 (*7*).

We found that PCP cannot be effectively precipitated as a calcium or zinc salt or coprecipitated with flocculating agents such as iron(III) or aluminum hydroxide. From flotation with a cationic surfactant does remove PCP effectively and is reported here.

The foam flotation removal of several other halogenated phenols from aqueous solution was also studied. Many of them have industrial uses and are potential water pollutants. The 2- and 4-monochlorophenols are intermediates in the manufacture of certain organic chemicals; 2,4-dichlorophenol and 2,4,5-trichlorophenol are the precursers for the herbicides 2,4-D and 2,4,5-T, respectively (*8*). Some bromophenols, including 2,4,6-tribromophenol, tetrabromobisphenol, and tetrabromobisphenol A, are used in the manufacture of fire retardants. The fire retardant decabromodiphenyl oxide might be expected to hydrolyze to pentabromophenol (*9*). The removal of these other halogenated phenols from water by foam flotation was therefore also attempted.

EXPERIMENTAL PROCEDURES

Chemicals

Reagents used include: CTAB (cetyltrimethylammonium bromide) surfactant (Eastman); deionized water; PCP (Aldrich, 99%); sodium dodecyl sulfate (SDS) (Sigma, 99%); reagent grade NaCl, NaOH, and HCl (all from Fisher).

Foam Flotation Procedure

Samples for foam flotation were prepared by diluting the proper amounts of 1000 mg/L phenol and surfactant stock solutions to 500 mL with deionized water. pH adjustment was done with HCl or NaOH using a Sargent-Welch Model LSX pH meter.

The foam flotation apparatus is similar to that used by Gannon and Wilson (*10*) and consists of a 3.5 cm diameter × 87 cm high Pyrex column fitted with a large stopper and a bottom consisting of a fine fritted glass disk. The column has a sampling stopcock and drain for obtaining PCP solution samples during foaming and fast drainage at the end of a run, respectively. House air was passed through a water saturator and a glass wool filter before going through the gas dispersion disk. Air flow rates were measured with a soap bubble flowmeter; a pressure of 2 psig was used for optimum results.

The air was passed through the fine fritted glass dispersion disk and into the solution. The air passing through the solution created a foam which, after rising further up the Pyrex column, passed through an outlet tube at the top of the column into a container for disposal. At suitable intervals the sampling stopcock was purged by the removal of 5 mL of liquid, and a 10–15 mL sample of liquid taken for analysis.

Analytical Procedure

Phenol concentrations were measured by observation of characteristic UV absorption peaks (e.g., 2500 Å for PCP) and comparing the absorbance of the sample with that of a standard solution. Ultraviolet absorbance measurements were done on a Cary 14 spectrophotometer, and the samples were made alkaline with NaOH to increase their absorbances if the run being made was not alkaline. (The anionic form of PCP absorbs more intensely than the neutral molecule.)

RESULTS

A study of the effect of CTAB concentration on PCP removal is summarized in Table 1. With an initial PCP concentration of 10 ppm, the initial CTAB concentration apparently should be at least 20 ppm for effective PCP removal. The removal of PCP is complete within 5 min.

Figure 1 indicates that PCP in higher concentrations than 10 ppm can be removed if the CTAB concentration is greater than the PCP concentration.

A study of the rate of PCP removal is shown in Fig. 2, which also confirms that optimum PCP removal occurs when the CTAB concentration is about 50 ppm. CTAB concentrations greater than 50 ppm cause excessive foaming.

The effect of pH on PCP removal is summarized in Fig. 3. Solutions with initial concentrations of 10 ppm PCP and 50 ppm CTAB were foam floated at initial pH values of 3.1, 5.0, and 9.2. These data show that PCP is removed most effectively at neutral or basic pH values, where PCP is

TABLE 1
Study of PCP Removal at Different Initial CTAB Concentrations[a]

Initial CTAB concentration (ppm)	Minutes of flotation	Final PCP (ppm)
10	5	0.0
10	10	0.5
10	15	1.0
20	5	0.3
20	10	0.3
20	15	0.5
20	25	0.3
30	5	0.3
30	10	0.2
40	5	0.0
50	10	0.0
50	15	0.0
50	25	0.0
75	5	0.0

[a] All initial PCP concentrations were 10 ppm and all initial pH values were 9.

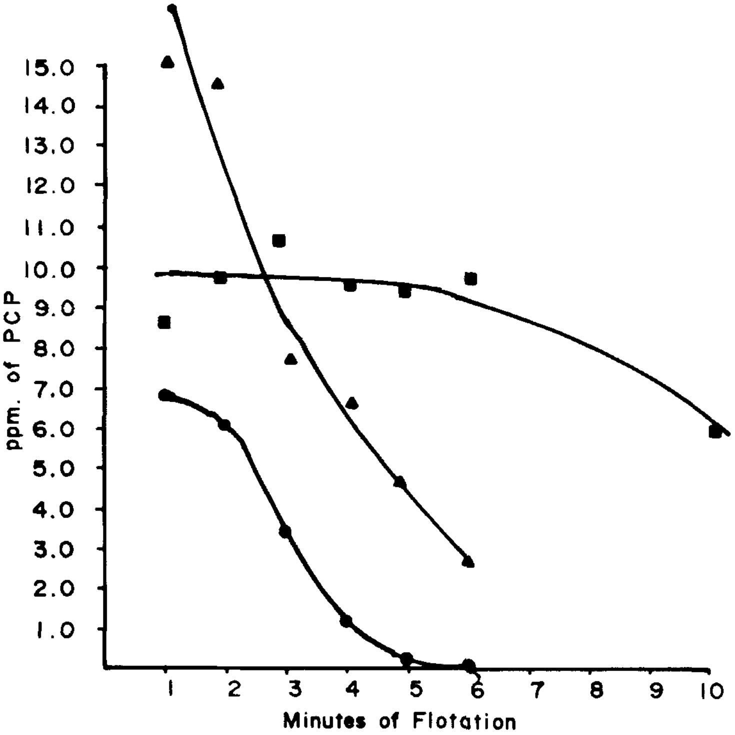

FIG. 1. Study of removal of higher concentrations of PCP. (●) Initial [PCP] = 20 ppm, (▲) initial [PCP] = 30 ppm, (■) initial [PCP] = 40 ppm. Initial conditions: [CTAB] = 50 ppm, pH = 9.

mostly in the anionic form. PCP is still removed, but less effectively, from acid solution, where PCP is in the uncharged, acidic form.

The results of an ionic strength study are shown in Fig. 4. Ionic strength was varied with NaCl, and the other parameters were kept constant. The data indicate that PCP removal is only slightly inhibited at higher ionic strength.

Straight-chain alkylamines like dodecylamine are protonated in neutral and acidic aqueous solutions and have structures similar to that of CTAB. Since dodecylamine is less expensive than CTAB and is expected to be more biodegradable, PCP removal was studied with partial and total replacement of CTAB with dodecylamine. The results are shown in Fig. 5. Although PCP removal is not very good when

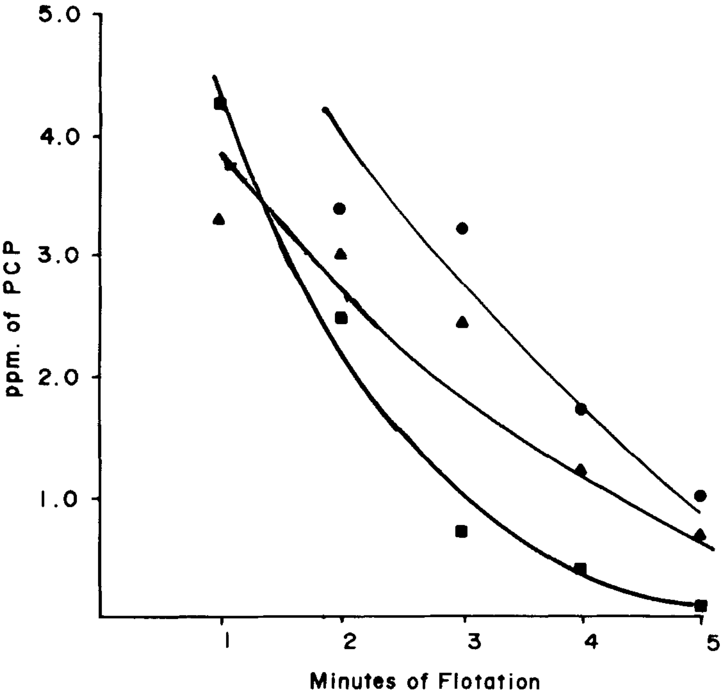

FIG. 2. Study of CTAB concentration effect on PCP removal. (●) Initial [CTAB] = 30 ppm, (▲) initial [CTAB] = 40 ppm, (■) initial [CTAB] = 50 ppm. Initial conditions: [PCP] = 10 ppm, pH = 9.

dodecylamine is the only surfactant, very good PCP removal occurs when as much as 80% of the CTAB is replaced with dodecylamine.

The data in Figs. 6, 7, and 8 indicate that the presence of as much as 10% by volume of methanol and ethanol and up to 5% by volume of acetone or methyl ethyl ketone slightly improves PCP removal.

The removal of halophenols other than PCP was also studied by UV spectrophotometry, using a wavelength at which strong absorbance occurs. The results for some chlorophenols are shown in Fig. 9. Several bromophenols related to fire retardants were studied and the results for these are shown in Fig. 10. Pentafluorophenol (PFP) can also be removed by foam flotation, but the removal is apparently slower and less effective than that of PCP. A relatively weak UV absorbance for PFP makes its measurement by UV spectrophotometry less accurate than those for the other halophenols. In general, a halophenol can be effectively removed

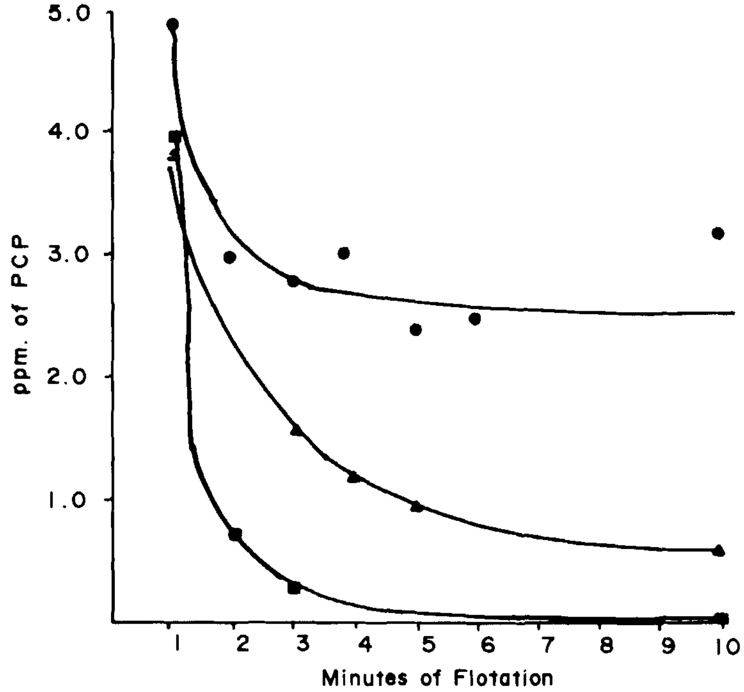

FIG. 3. PCP removal pH study. (●) pH 3.1, (▲) pH 5.0, (■) pH 9.2. Initial conditions: [CTAB] = 50 ppm, [PCP] = 10 ppm.

from aqueous solution by foam flotation if the phenol is predominantly in the anionic form during foam flotation with cationic surfactants. Phenols much less acidic than PCP must therefore be foam floated in basic solution.

Sodium dodecyl sulfate (SDS) is an anionic detergent whereas CTAB is cationic. A study of SDS as a surfactant in the removal of PCP gives additional insight into the mechanism of PCP removal. The data in Fig. 11 show that although foam flotation with SDS does remove PCP, the residual PCP concentration is greater than it is with the CTAB surfactant. The pH in this case is 4.0, sufficiently low to insure that PCP is primarily in the nonionic form.

DISCUSSION

CTAB, a cationic surfactant, is an effective surfactant for the removal of halogenated phenols. CTAB has an affinity for phenols as a result of

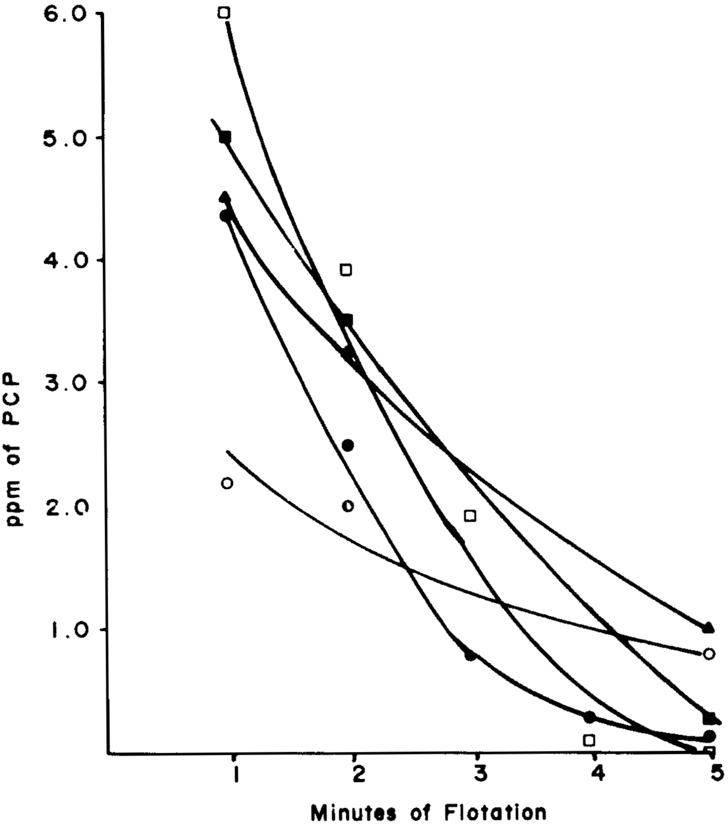

FIG. 4. PCP removal ionic strength study. (●) $I = 0.00$, (○) $I = 0.05$ (NaCl), (■) $I = 0.10$, (□) $I = 0.20$, (▲) $I = 0.30$. Initial conditions: [PCP] = 10 ppm, [CTAB] = 50 ppm, pH = 9.

electrostatic attraction to the phenolate anion and possibly ion-dipole attraction to the neutral phenol molecule. Its attractions for the phenol and for air make it possible for CTAB to form an ion pair with the phenol, and then, as air passes through the solution, the hydrophobic surfactant-phenol complex is carried up out of solution on the bubble surface.

The primary mechanism of phenol removal is believed to be an electrostatic ion-pair mechanism, since the most complete phenol removal by CTAB occurs at pH values where the phenol is an anion.

A secondary ion-dipole mechanism must also exist because of the less effective but still noticeable phenol removal by CTAB at lower pH values

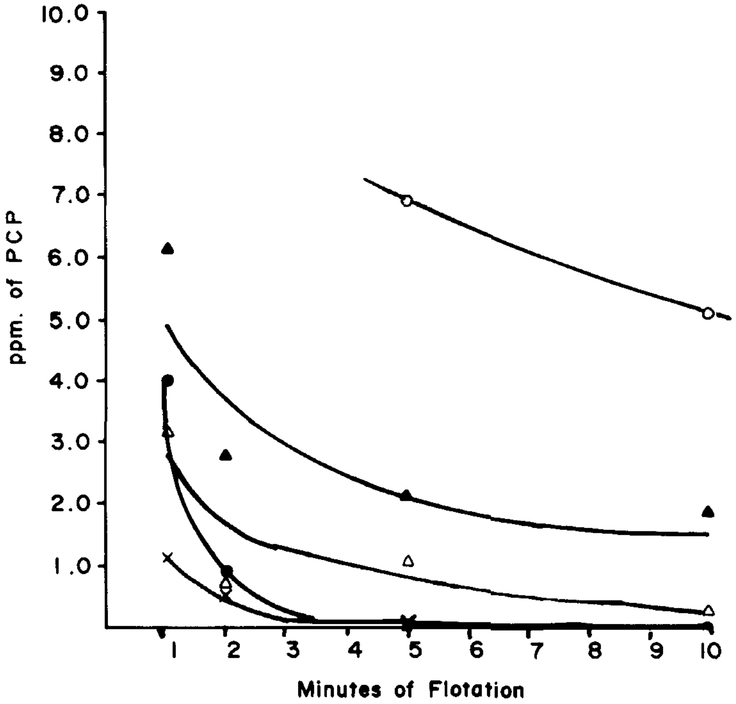

FIG. 5. Replacement of CTAB with dodecylamine. (●) 50 ppm CTAB, no dodecylamine, initial pH = 9.0; (×) 20 ppm CTAB, 30 ppm dodecylamine; (△) 10 ppm CTAB, 40 ppm dodecylamine; (▲) 5 ppm CTAB, 45 ppm dodecylamine. (○) no CTAB, 50 ppm dodecylamine. Initial conditions: [PCP] = 10 ppm, pH = 7.0 for all runs containing dodecylamine.

where the phenol is not ionized. The removal of un-ionized PCP with anionic SDS surfactant is also evidence of this ion-dipole attraction.

Foam flotation shows real promise as a means of removing PCP and other acidic phenols from wastewater, sludges, and soils.

Acknowledgments

The authors wish to thank the National Science Foundation for supporting the research with a grant. We are also grateful to Frank McConnell for helping with the artwork.

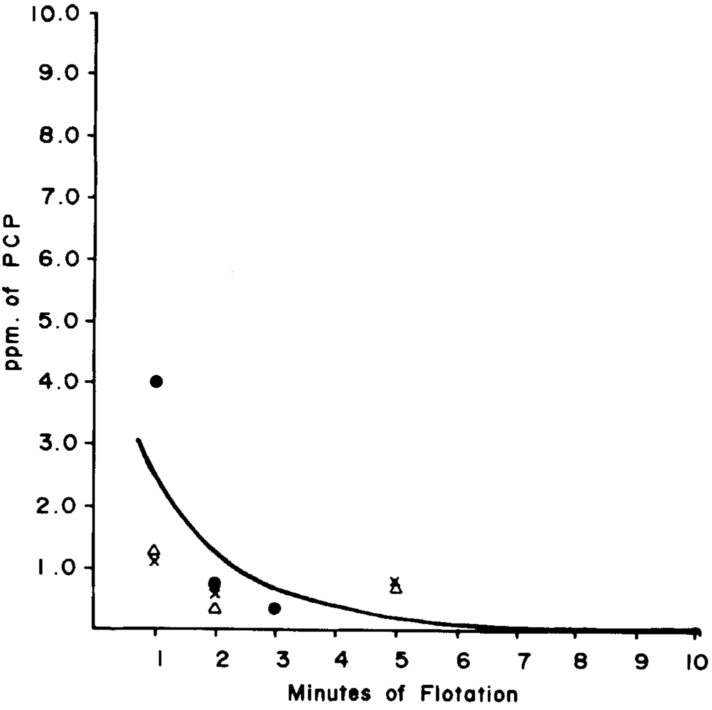

FIG. 6. Study of methanol effect on PCP removal. (●) No methanol, (Δ) 5% v/v methanol, (X) 10% v/v methanol. Initial conditions: [PCP] = 10 ppm, [CTAB] = 50 ppm, pH = 9.

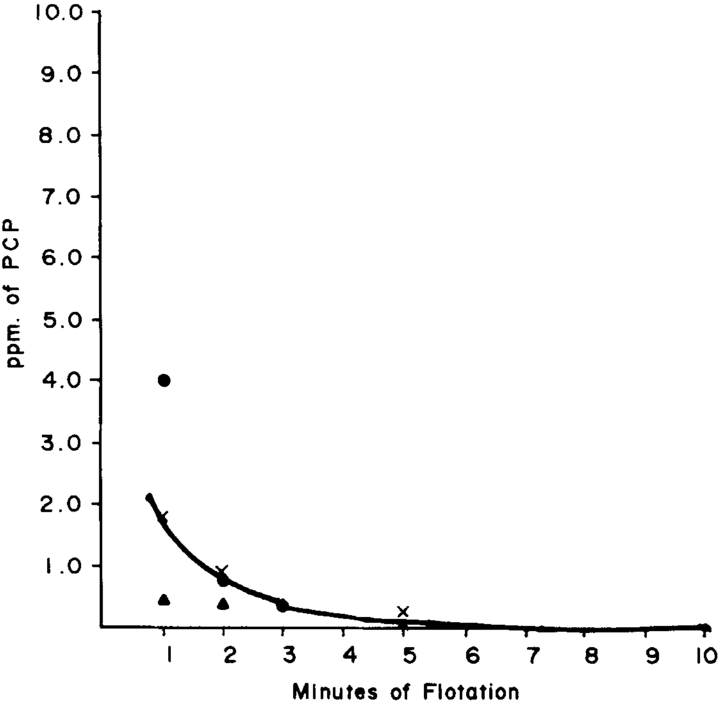

FIG. 7. Study of ethanol effect on PCP removal. (●) No ethanol, (▲) 5% v/v ethanol, (×) 10% v/v ethanol. Initial conditions: Same as in Fig. 6.

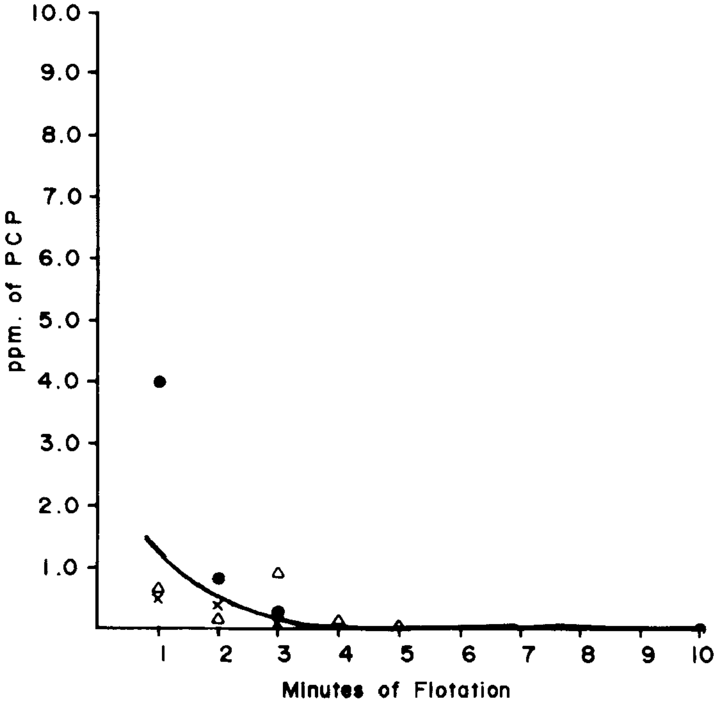

FIG. 8. Study of ketone effect on PCP removal. (●) No ketone, (×) 5% v/v acetone, (△) 5% v/v methyl ethyl ketone. Initial conditions: Same as in Fig. 6.

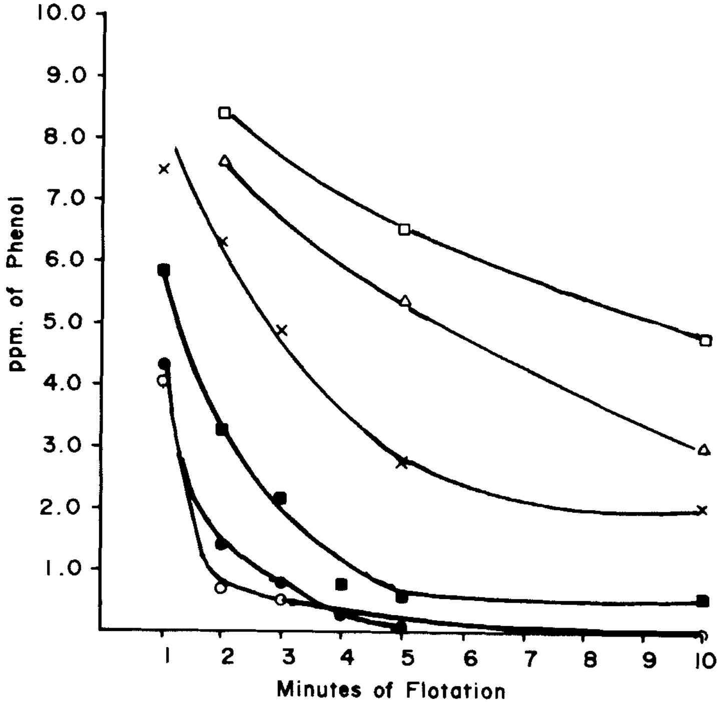

FIG. 9. Graph of chlorophenol concentration versus flotation time. (●) Pentachlorophenol, initial pH = 9; (■) 2,4,5-trichlorophenol, initial pH = 9; (○) 2,4,6-trichlorophenol, initial pH = 9; (×) 2,4-dichlorophenol, initial pH = 9; (△) *o*-chlorophenol, initial pH = 10; (□) *p*-chlorophenol, initial pH = 11. Other initial conditions: [chlorophenol] = 10 ppm, [CTAB] = 50 ppm.

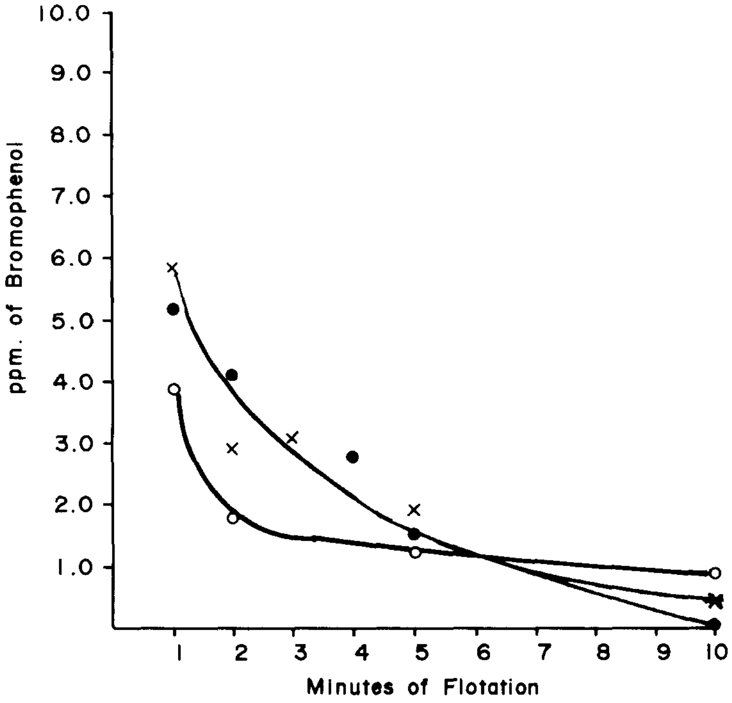

FIG. 10. Graph of bromophenol concentration versus flotation time. (●) Pentabromophenol; (O) 2,4,6-tribromophenol; (X) tetrabromobisphenol A. Initial conditions: [bromophenol] = 10 ppm, [CTAB] = 50 ppm, pH = 9.

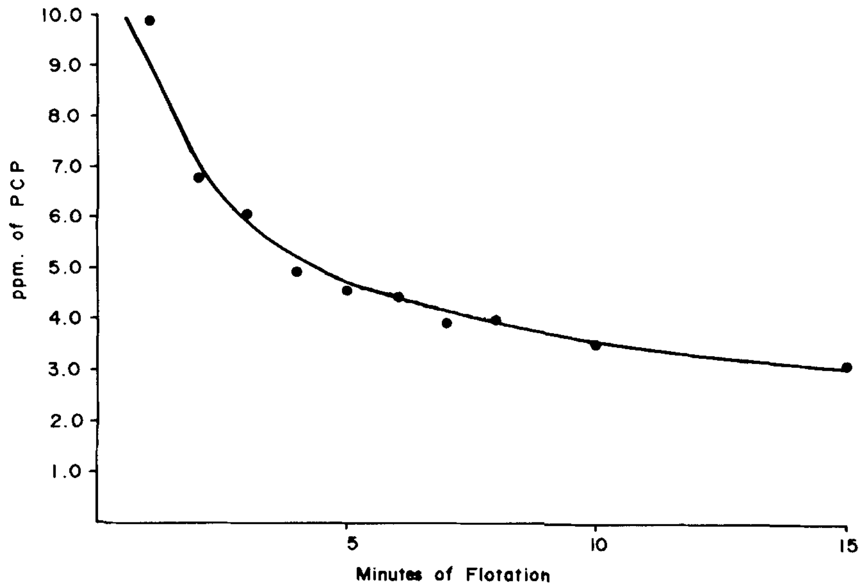

FIG. 11. Graph of PCP concentrations during flotation with sodium dodecyl sulfate. Initial conditions: [PCP] = 20 ppm, [SDS] = 200 ppm, pH = 4.0.

REFERENCES

1. D. R. Buhler, M. E. Rasmussen, and H. S. Nakau, *Environ. Sci. Technol.*, *7*, 929 (1974).
2. R. D. Arsenault, *Pentachlorophenol and Contained Chlorinated Dibenzodioxins in the Environment: A Study of Environmental Fate, Stability, and Significance When Used in Wood Preservation*, Annual Meeting, Wood Preservers Association, Atlanta, Georgia, April 25–28, 1976, p. 1.
3. A. Bevenue and H. Heckman, *Residue Rev.*, *19*, 83 (1976).
4. U.S. EPA, *Ambient Water Quality Criteria for Pentachlorophenol*, EPA 440/5-80-065, 1980.
5. B. K. Wallin, A. J. Cundren, and R. L. Walden, *Removal of Phenolic Compounds from Wood Preserving Wastewaters*, U.S. EPA 600/52-81-043, 1981.
6. R. B. Grieves, W. Charewics, and S. M. Brien, *Anal. Chim. Acta*, *73*, 293 (1974).
7. K. T. Valsaraj and C. Springer, *Removal of Traces of Pentachlorophenol from Aqueous Acidic Solutions by Solvent Extraction and Solvent Sublation*, Unpublished.
8. *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 5 (M. Grayson, ed.), Wiley, New York, 1979, pp. 864–872.
9. *Ibid.*, Vol. 10, pp. 385–395.
10. K. Gannon and D. J. Wilson, *Sep. Sci. Technol.*, *21*, 475 (1986).

Received by editor November 10, 1986