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, Gerard A. , White, Jonathan S. , Bibring, Peter and Wilson, David J.(1990) 'Removal of Trace Levels of Aromatic Amines from Aqueous Solution by Foam Flotation', Separation Science and Technology, 25: 7, 809 — 824

To link to this Article: DOI: 10.1080/01496399008050368

URL: http://dx.doi.org/10.1080/01496399008050368

SEPARATION SCIENCE AND TECHNOLOGY, 25(7 & 8), 809-824, 1990

Removal of Trace Levels of Aromatic Amines from Aqueous Solution by Foam Flotation

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Abstract

Aromatic amines, including 4-(*t*-butyl)pyridine, 4-(*n*-butyl)aniline, benzylamine, 4-aminobiphenyl, 1- and 2-aminonaphthalene, and 2,6-xylidine, were effectively removed from water by foam flotation with the anionic surfactant sodium dodecylsufate (SDS). With initial amine concentrations of 10 mg/L or less, residual amine concentrations of less than 0.1 mg/L were generally obtained after 10–30 min of flotation. The SDS concentration and flotation time are directly related to the amount of amine removed. Amine removal is most efficient at pH values low enough so that the amine is protonated (usually about 3), and at low ionic strength. Alcohols up to 10% by volume do not appreciably affect amine removal. The mechanism of removal is dominated by ion-ion attraction between the surfactant and the protonated amine; there is also apparently some contribution from ion-dipole attraction. Benzidine is not removed effectively; evidently it is insufficiently hydrophobic.

INTRODUCTION

Earlier work in this laboratory has shown that trace levels of pentachlorophenol and other acidic phenols (which exist in aqueous solution as anions) can be removed from water by foam flotation with a cationic surfactant (*1*). Earlier Grieves and coworkers (*2*) carried out a study of the removal of phenols by adsorptive bubble separation techniques; they investigated the removal of phenol by solvent sublation, foam fractionation, and solvent extraction. More recently Valsaraj and Springer (*3*) studied the removal of pentachlorophenol by solvent extraction and solvent sublation. We have studied the removal of 2,4-dinitrophenol and 2,4,6-trinitrophenol by solvent sublation with hexadecyltrimethylammonium bromide (*4*).

Aromatic amines in general have a rather bad reputation in terms of their toxicity and carcinogenicity (*5*, *6*). Benzidine, 4-aminobiphenyl, and the naphthylamines are all regarded as carcinogens. The naphthylamines and 4-aminobiphenyl are present in coal products and are designated as priority pollutants by the U.S. EPA (*7*). Methods for the removal of these compounds from aqueous wastes are therefore of some practical interest. 4-(*n*-Butyl)aniline and 4-(*t*-butyl)pyridine were selected as model compounds for basic pollutants in coal products.

Pyridines and aromatic amines have relatively small K_b values (*8*), typically around 10^{-10}; they are therefore present mostly in protonated form in aqueous solutions having pH values less than about 4. Since we wished to take advantage of ion-ion interactions with the anionic surfactant sodium dodecylsulfate (SDS), most of our work was carried out at

TABLE 1
pK_b Values for Some Organic Bases

Compound	pK_b	Reference
Aniline	9.42	*8*
p-Toluidine	8.92	*8*
4-(*n*-Butyl)aniline	9.26	Present work
2,6-Xylidine	10.15	Present work
1-Aminonaphthalene	10.08	*8*
2-Aminonaphthalene	9.89	*8*
Pyridine	8.77	*8*
4-(*t*-Butyl)pyridine	8.33	Present work
4-Aminobiphenyl	9.73	*10*
Benzidine	9.03	*8*
	10.25	*8*
Benzylamine	4.63	*8*

fairly low pH values. Table 1 lists the pK_b values of a number of aromatic amines, of benzidine, and of benzylamine.

EXPERIMENTAL PROCEDURES

Reagents used included: SDS (sodium dodecylsulfate), 99+% pure surfactant (Fluka); CTAB (cetyltrimethylammonium bromide) surfactant (Eastman); deionized water; 2-aminonaphthalene, 4-(*n*-butyl)aniline and 4-(*t*-butyl)pyridine (Aldrich); 2,6-xylidine (Columbia); 1-aminonaphthalene (MCB); benzylamine (Eastman); ethanol (AAPER Alcohol and Chemical Co.); reagent grade NaCl, NaOH, HCl, and methanol (all from Fisher).

The foam flotation procedure used was as follows. Samples for foam flotation were prepared by diluting the proper amounts of 1000 mg/L amine and surfactant stock solutions to 500 mL with deionized water. pH adjustment was done with HCl or NaOH; a Sargent-Welch Model LSX or a Lazar pH meter was used after calibration with Fisher buffers.

The foam flotation apparatus is similar to that used by Gannon and Wilson (*9*). It consists of a 3.5 cm diameter × 87 cm high Pyrex column fitted with a large stopper on top and with a fine grade fritted glass disk fused into the bottom for air dispersion. The column has at the bottom a sampling stopcock for obtaining amine solution samples during foaming and a drain for rapid draining of the column at the end of a run. House air or air from an air pump is passed through a water saturator and a glass wool filter before going through the gas dispersion disk and into the column. Air flow rates are controlled by means of a micrometer valve and measured with a stopwatch and a soap film flowmeter; an air pressure of about 2 psig was generally used.

The air is passed through the fitted glass dispersion disk and into the column. The foam formed by its passage through the surfactant solution rises up through a drainage section of the column and then passes through an outlet tube in the stopper at the top of the column and into a container for disposal. At suitable intervals the sampling stopcock is purged by the removal of 5 mL liquid, and a 10–20 mL sample of liquid is taken for analysis.

Amine concentrations were measured by observation of the characteristic UV absorption peaks [e.g., 285 nm for 4-(*n*-butyl)aniline] and comparing the absorbance of the sample with those of standard solutions. Beer's law is well obeyed by these solutions. Ultraviolet absorbance measurements were done on a Cary 14 or a Cary 2300 spectrophotometer, and the samples were made alkaline with NaOH to increase their absorbances. (The free base form of aromatic amines generally absorbs more intensely than the protonated form.)

RESULTS

A study of the effect of SDS concentration of 4-(*n*-butyl)aniline removal is summarized in Fig. 1, and the results of a study of the effect of initial amine concentration on this system are given in Fig. 2. Evidently the removal of the amine is most effective when the initial surfactant concentration is several times that of the amine. Similar behavior was observed in the removal of pentachlorophenol anion with the cationic surfactant cetyltrimethylammonium bromide (CTAB) (*1*).

The effect of pH on 4-(*n*-butyl)aniline removal is shown in Fig. 3. Since a pH titration curve indicates that the pK_b of this amine is about 9.26, the

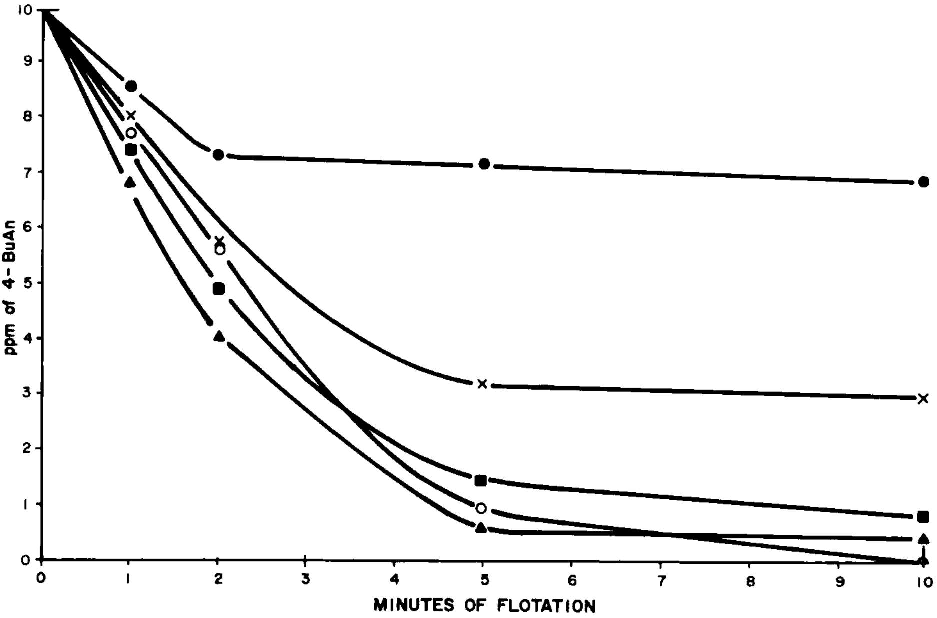

FIG. 1. 4-(*n*-Butyl)aniline removal at various SDS concentrations. Initial SDS concentration = 10 (●), 20 (×), 30 (■), 40 (▲), and 50 mg/L (O). Initial 4-(*n*-butyl)aniline concentration = 10 mg/L, pH = 3.75, air flow rate = 5 mL/s.

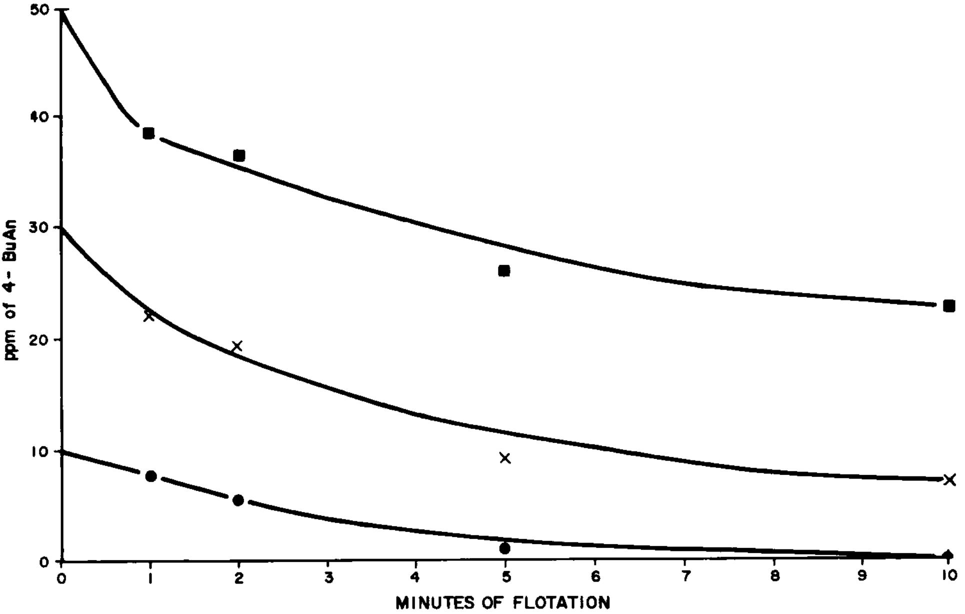

FIG. 2. 4-(*n*-Butyl)aniline removal at various initial amine concentrations. Initial base concentration = 50 (■), 30 (×), 10 mg/L (●). Initial SDS concentration = 50 mg/L, pH = 3.75, air flow rate = 5 mL/s.

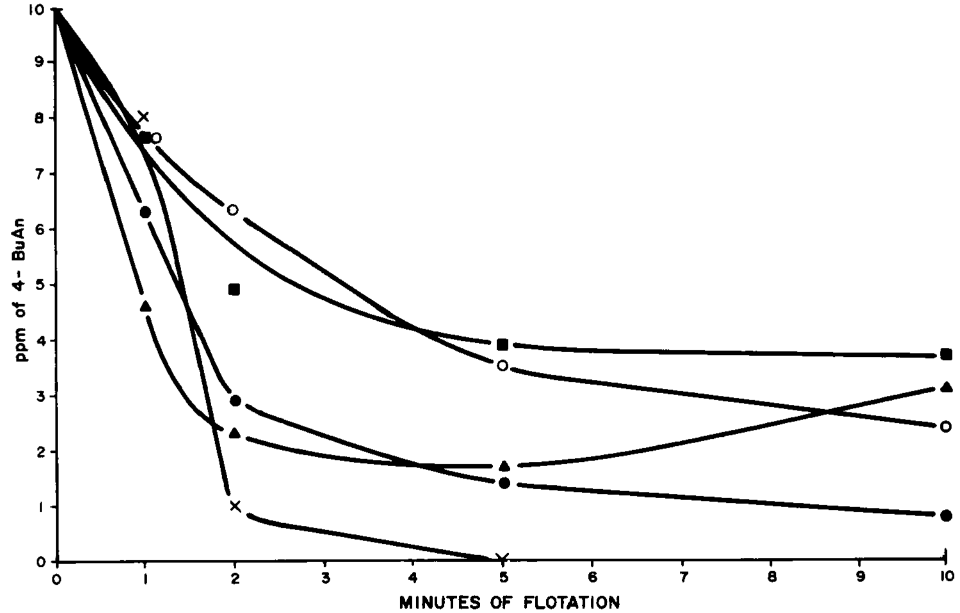

FIG. 3. Effect of pH on 4-(*n*-butyl)aniline removal. pH = 1.90 (●), 3.75 (×), 8.83 (○), 9.52 (▲), 11.45 (■). Initial SDS concentration = 50 mg/L, initial base concentration = 10 mg/L, air flow rate = 5 mL/s.

amine is predominantly in the protonated form when the pH is less than 14 − 9.26 = 4.74. The fact that the best removals occur at pH values of 1.90 and 3.75 leads one to conclude that the protonated form of the amine is more readily removed than the free base. Foam flotation of 4-(*n*-butyl)aniline is apparently not affected greatly by ionic strength, since Fig. 4 shows little change in the degree of removal at inert salt concentrations as high as 0.3 *M* NaCl.

An experiment was done at a relatively high pH (7.9), where 4-(*n*-butyl)aniline exists as the free base, with the cationic surfactant CTAB. We see in Fig. 5 that only slight removal of 4(*n*-butyl)aniline occurs; evidently the ion-dipole interaction which is present here is insufficient to yield a good separation. The presence of as much as 10% v/v methanol or ethanol appears to have little or no effect on the foam flotation removal of 4(*n*-butyl)aniline with SDS at low pH, as seen in Figs. 6 and 7.

Aeration at flow rates of about 5 mL/s caused somewhat excessive amounts of foam formation, inadequate foam drainage, and sometimes

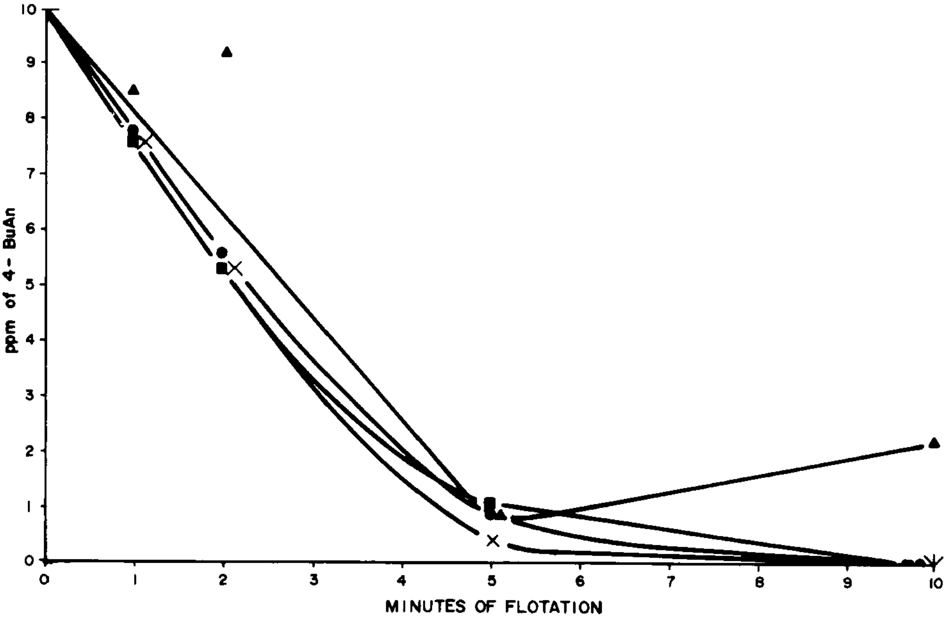

FIG. 4. Effect of ionic strength on the removal of 4-(*n*-butyl)aniline by flotation. Added NaCl: none (●), 0.10 *M* (▲), 0.20 *M* (■), 0.30 *M* (×). Air flow rate = 5 mL/s. Initial conditions: pH = 3.75, SDS concentration = 50 mg/L, base concentration = 10 mg/L.

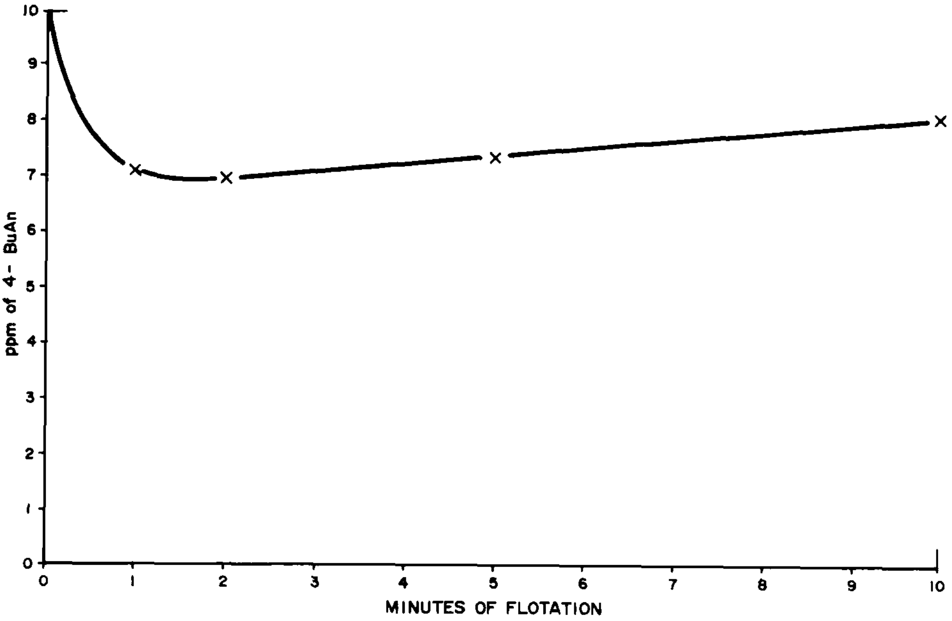

FIG. 5 Flotation of 4-(*n*-butyl)aniline with cetyltrimethylammonium bromide (CTAB). Initial conditions: pH = 7.9, base concentration = 10 mg/L, CTAB concentration = 50 mg/L, air flow rate = 4.5 mL/s.

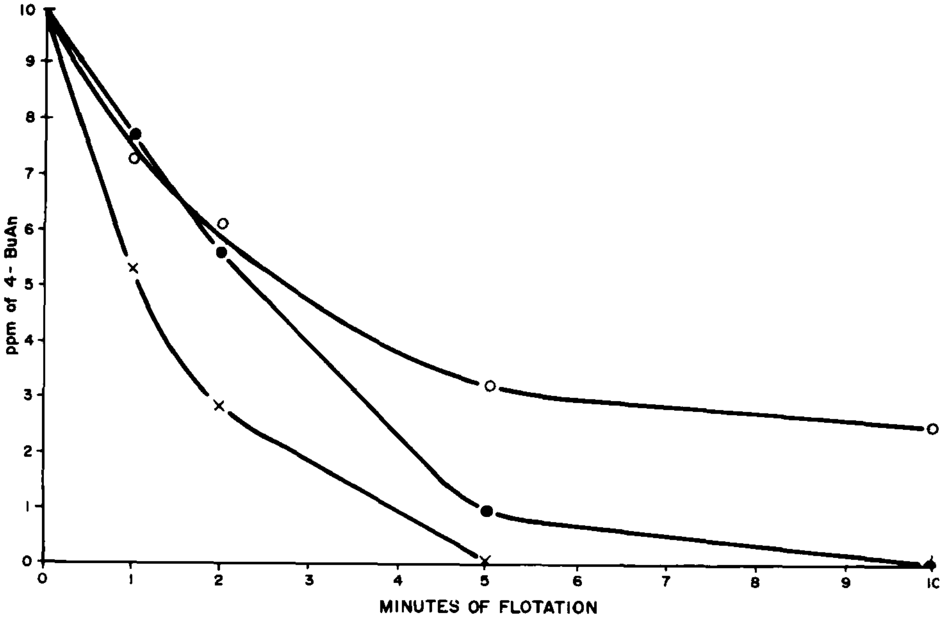

FIG. 6. Effect of methanol on the flotation of 4-(*n*-butyl)aniline. Added methanol: none (●), 5 (X), 10% (v/v) (O). Initial conditions: same as in Fig. 5.

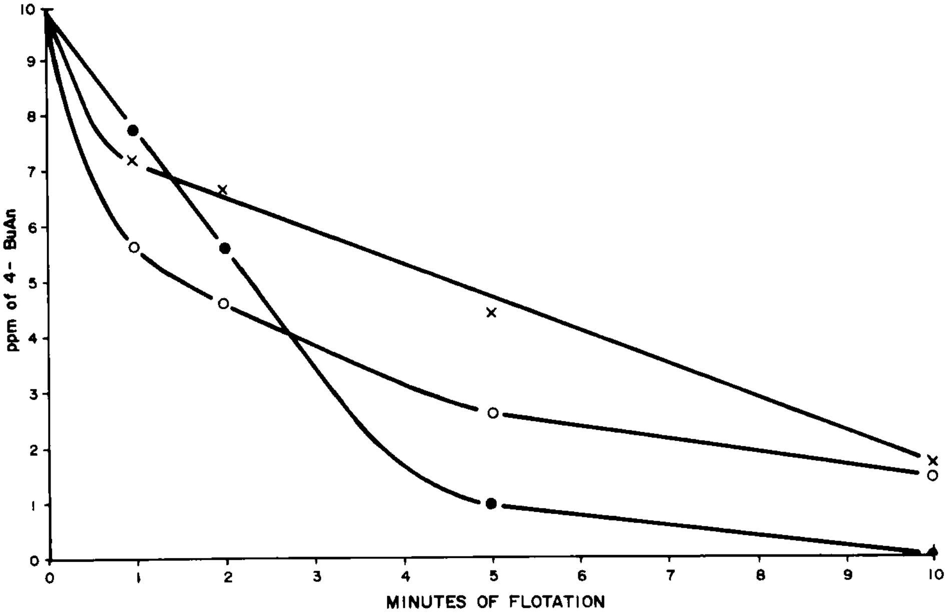

FIG. 7. Effect of ethanol on the flotation of 4-(*n*-butyl)aniline. Added ethanol: none (●), 5 (×), 10% (v/v) (○). Initial conditions: same as in Fig. 5.

resulted in the carry-over of more than 30% of the liquid being treated. Slower aeration rates allow better foam drainage and decrease the amount of liquid carried over as foamate; of course, they also decrease the rate of amine removal, as shown in Fig. 8. The results shown here also demonstrate that the extent of contaminant removal can be improved somewhat by a second addition of SDS after 10–20 min of flotation.

The heterocyclic organic base 4(*t*-butyl)pyridine behaves similarly to 4-(*n*-butyl)aniline. Its pK_b was determined by running a titration curve and found to be 8.33; in solutions having pH less than $14 - 8.33 = 5.67$, it is therefore present mostly in protonated form. The data presented in Fig. 9 indicate that the foam flotation of this compound is most efficient in the pH range in which the compound is protonated.

Figures 10 and 11 show that 4-(*t*-butyl)pyridine is most effectively removed when the initial SDS concentration is several times as large as that of the base, just as was the case with 4-(*n*-butyl)aniline. As with 4-(*n*-butyl)aniline, excessive carry-over of liquid into the foamate is prevented

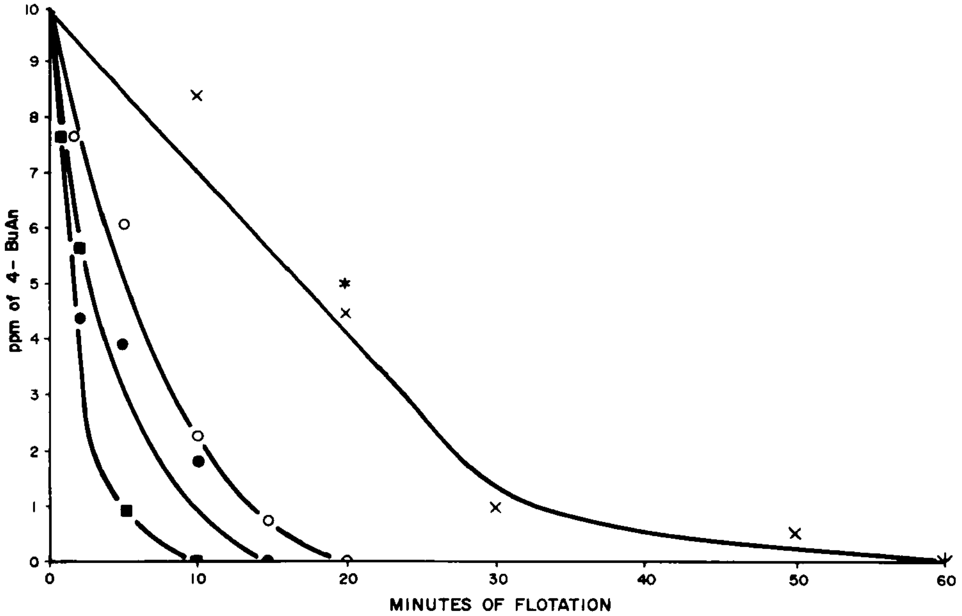

FIG. 8. Effect of air flow rate on the flotation of 4-(*n*-butyl)aniline. Asterisk (*) shows point at which a second 50 mg/L addition of SDS was made. Air flow rate: 0.48 (×), 0.89 (○), 2.0 (●), 5.0 mL/s (■). Initial conditions: pH = 3.75, SDS concentration = 50 mg/L, organic base concentration = 10 mg/L.

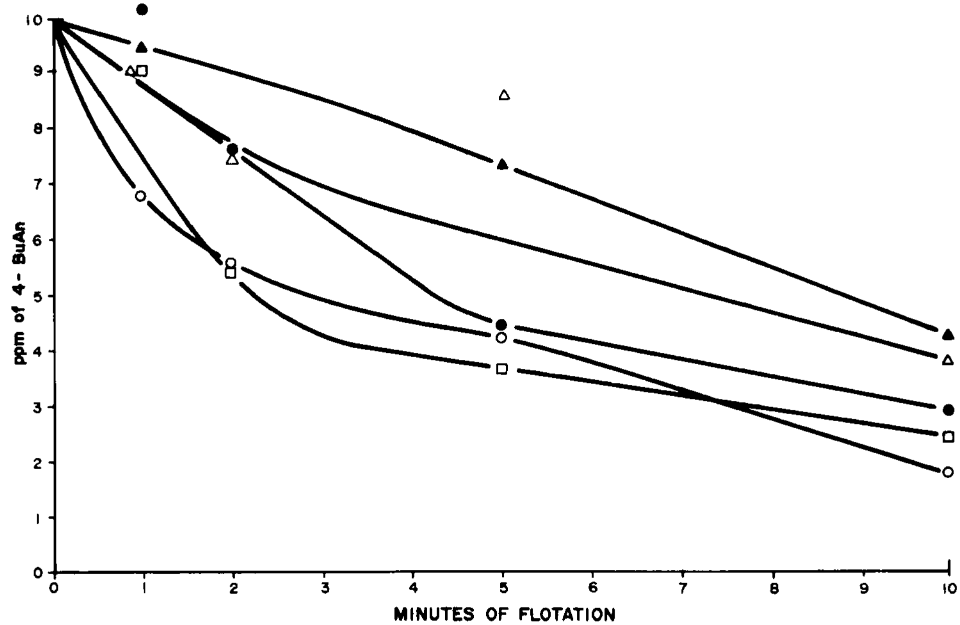

FIG. 9. Effect of pH on the flotation of 4-(*t*-butyl)pyridine. pH = 2.96 (○), 4.00 (□), 5.00 (●), 7.20 (△), 9.19 (▲). Initial conditions: SDS concentration = 50 mg/L, organic base concentration = 10 mg/L, air flow rate = 4.4–5.0 mL/s.

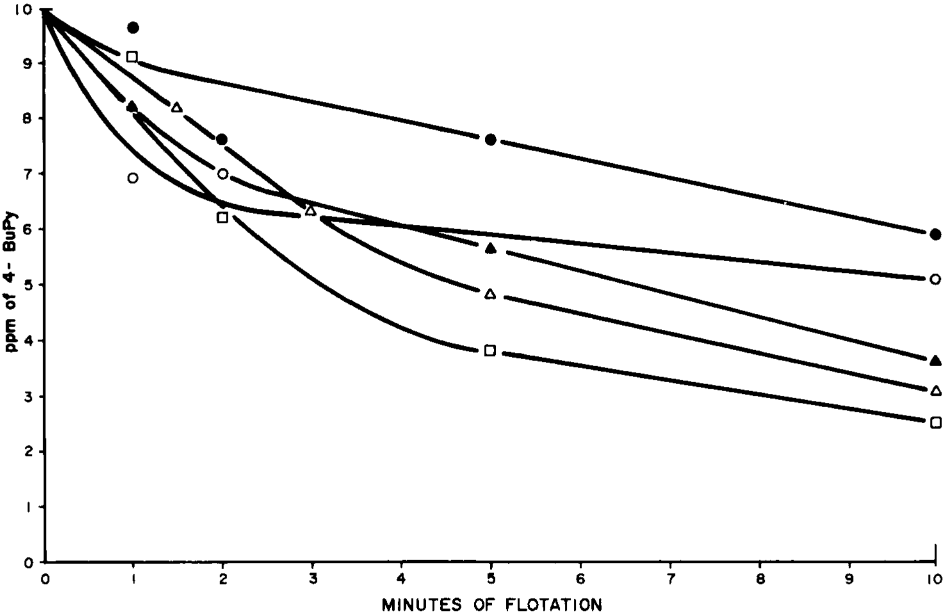

FIG. 10. Effect of SDS concentration on the flotation of 4-(*t*-butyl)pyridine. SDS concentration: 10 (●), 20 (○), 30 (▲), 40 (△), 50 mg/L (□). Initial conditions: pH = 5.00, organic base concentration = 10 mg/L, air flow rate = 4.3-5.0 mL/s.

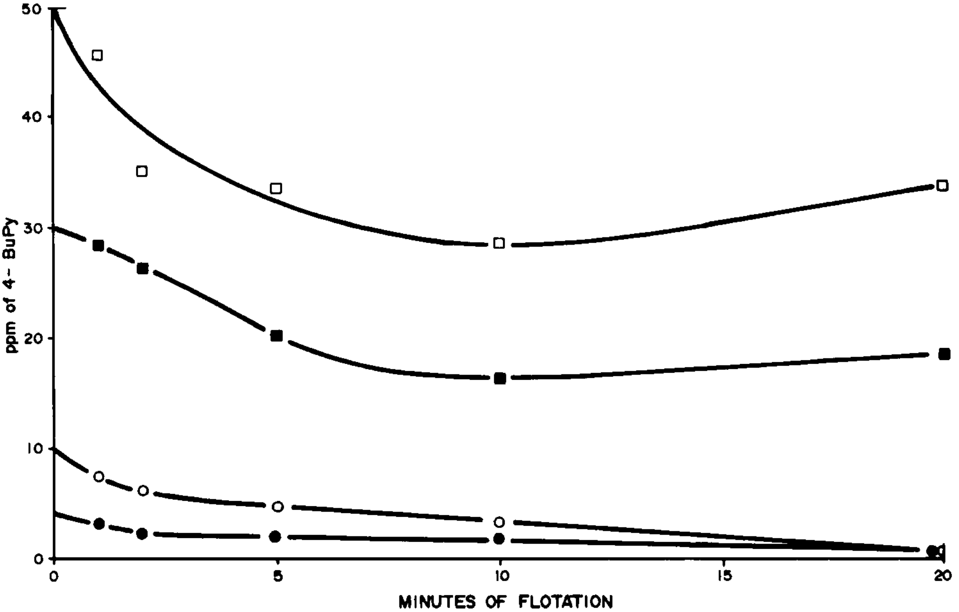

FIG. 11. Effect of initial 4-(*t*-butyl)pyridine concentration on its flotation with SDS. Initial organic base concentration = 4 (●), 10 (○), 30 (■), and 50 mg/L (□). Initial conditions: SDS concentration = 50 mg/L, pH = 5.0, air flow rate = 4.2–4.3 mL/s.

by reducing the air flow rate to about 1.0 mL/s, although this does reduce the rate of contaminant removal; see Fig. 12. A second addition of SDS allows one to remove nearly all of the contaminant in about 30 min of treatment.

2,6-Xylidine (and presumably other dialkylanilines) can also be removed from aqueous solution by foam flotation. The pK_b of 2,6-xylidine was determined to be 10.15, so this molecule is mostly protonated when the pH is less than 3.85. Figure 13 shows that its removal is most efficient in this pH range, and that a second addition of SDS can effect almost complete removal.

Figure 14 shows that benzylamine can be removed by flotation with SDS, and that a second addition of surfactant permits its virtually complete removal. Benzylamine has a K_b several orders of magnitude larger than the aromatic amines and pyridines, since its amine group is attached to a methylene group rather than to an aromatic ring. Its pK_b is 4.63 (see

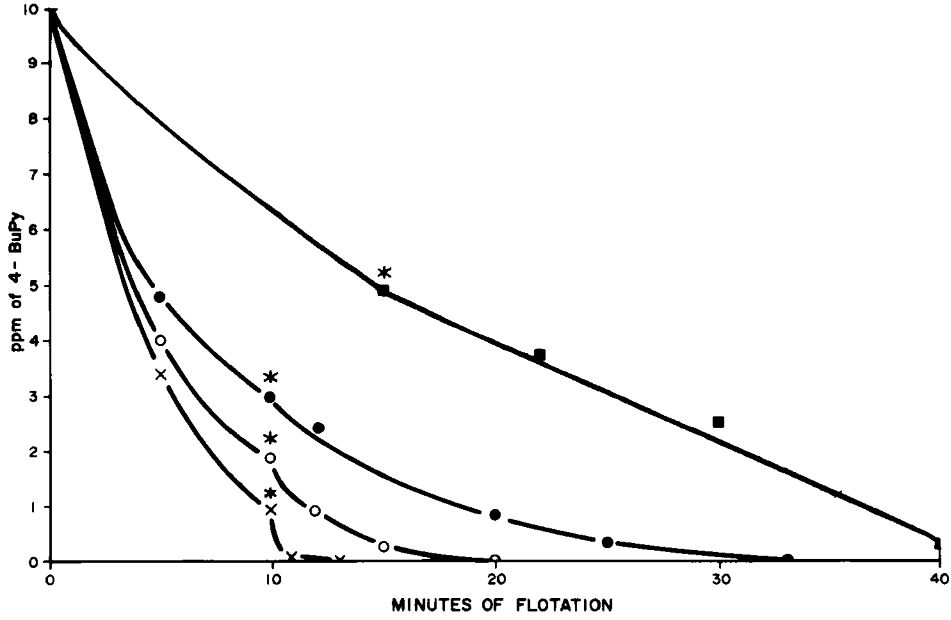

FIG. 12. Effect of air flow rate on the flotation of 4-(*t*-butyl)pyridine with SDS. Asterisks (*) show points at which a second 50 mg/L addition of SDS was made. Air flow rate: 4.7 (×), 2.1 (○), 1.0 (●), 0.54 mL/s (□). Initial conditions: pH 3.75, organic base concentrations = 10 mg/L, SDS concentration = 50 mg/L.

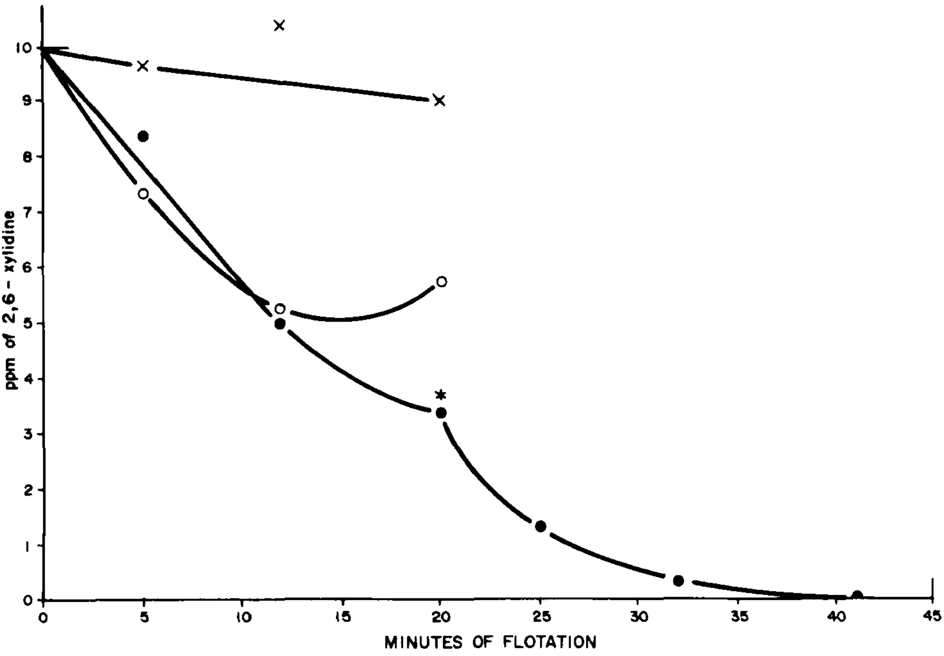

FIG. 13. Effect of pH on the flotation of 2,6-xylidine with SDS. The asterisk (*) shows where a second 50 mg/L addition of SDS was made. pH = 6.00 (X), 3.82 (O), 2.60 (●). Initial conditions: organic base concentration = 10 mg/L, air flow rate = 0.95 mL/s.

Table 1), so it is present in protonated form at pH values below 9.37. Thus the pH need not be acidic in order to protonate and effectively remove benzylamine by flotation with SDS.

Carcinogens like 4-aminobiphenyl and the naphthylamines can be removed by this process, but we were unable to develop a flotation method for benzidine. The benzidine molecule, having two amino groups, may be too hydrophilic to permit the formation of a sufficiently hydrophobic ion pair with the surfactant. Work with these carcinogens was carried out with rubber gloves in a fume hood. 4-Aminobiphenyl is most effectively removed at a pH of about 5, and Fig. 15 shows that a procedure in which multiple additions of SDS are used can result in virtually complete removal.

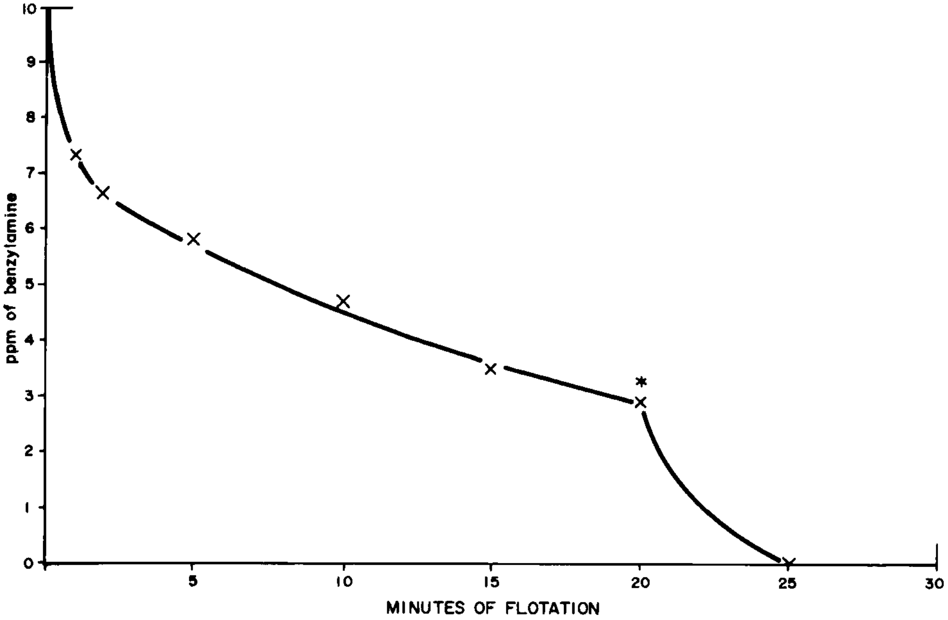

FIG. 14. Removal of benzylamine by flotation with SDS. Initial conditions: pH = 7.0, organic base concentration = 10 mg/L, SDS concentration = 50 mg/L, air flow rate = 1.2 mL/s. The asterisk (*) shows where a second 50 mg/L addition of SDS was made.

1-Aminonaphthalene, with a pK_b value of 10.08, is mostly protonated at pH values less than 3.92. Somewhat surprisingly, foam flotation with SDS was just as effective at a pH of 4 as at a pH of 2. Use of two additional portions of SDS solution resulted in essentiallly complete removal of the amine. These results are shown in Fig. 16, which also gives the results of a run made with 2-aminonaphthalene.

DISCUSSION

SDS, an anionic surfactant, is effective for the removal of aromatic amines and other organic bases by foam flotation. SDS has an affinity for these compounds as a result of electrostatic attraction to their protonated

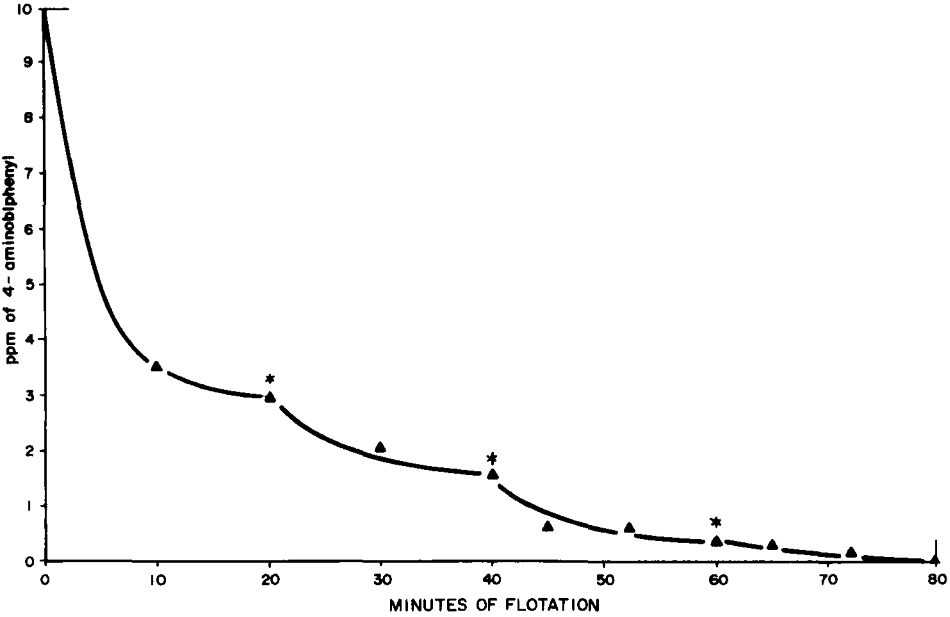

FIG. 15. Removal of 4-aminobipenyl by flotation with SDS. Initial conditions: pH = 5.0, 4-aminobiphenyl concentration = 10 mg/L, SDS concentration = 175 mg/L, air flow rate = 0.9 mL/s. Asterisks (*) show where additional 100 mg/L additions of SDS were made.

forms and also, possibly, ion-dipoie attraction between the surfactant and the neutral organic base molecule. The electrostatically bound base-surfactant ion pair is sufficiently hydrophobic that it is readily removed from the solution on the air-water interfaces of bubbles. Benzidine, unfortunately, is apparently insufficiently hydrophobic to permit its effective removal by this technique.

We believe this electrostatic ion pair mechanism to be the primary mechanism of organic base removal since the most complete organic base removals by SDS occur at pH values where the organic bases are present predominantly as cations. A secondary ion-dipole mechanism must also be operative because of the less effective but still noticeable base removal at higher pH values where the organic base is not protonated. The slight removal of un-ionized 4-(*n*-butyl)aniline with the cationic surfactant CTAB is also evidence for this ion-dipole attraction.

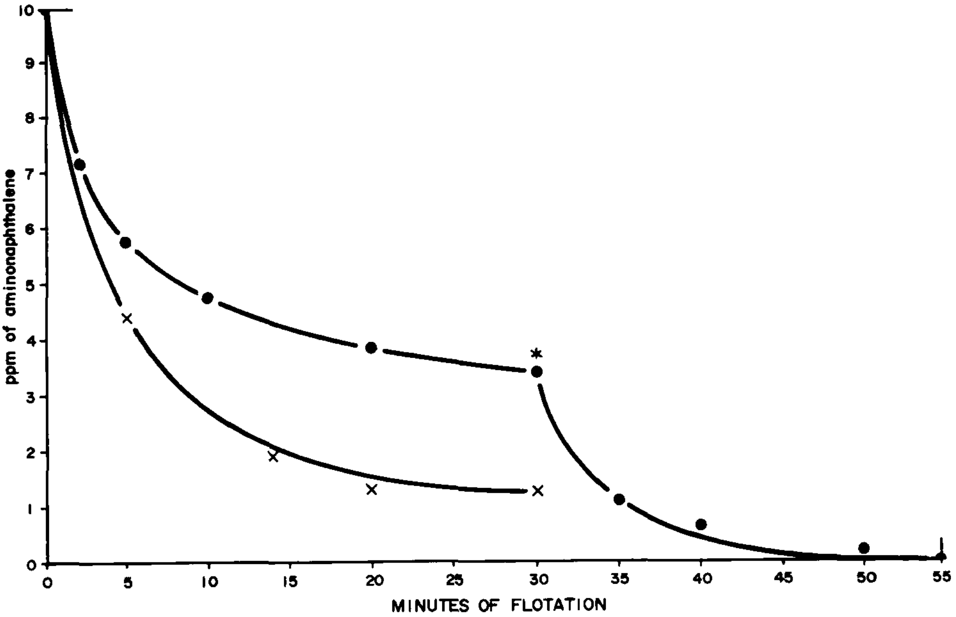

FIG. 16. Removal of 1- and 2-aminonaphthalenes by flotation with SDS. 1-Aminonaphthalene (●), 2-aminonaphthalene (×). The asterisk indicates where a second 50 μg/L addition of SDS was made. Initial conditions: pH = 4.0, organic base concentration = 10 mg/L, SDS concentration = 5 mg/L, air flow rate = 0.9 mL/s.

Foam flotation appears to be a promising technique for the removal of aromatic amines and other organic bases from wastewater; it may prove adaptable to the treatment of sludges and soils as well.

Acknowledgments

The authors wish to thank the Water Resources Research Institute of the University of Tennessee and Trevecca Nazarene College for financial support of this research. We are also indebted to Joyce B. Wilson, who did the preliminary work on 4-(*n*-butyl)aniline.

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Received by editor September 22, 1989