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The Continuous Foam Fractionation of Phenol

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Abstract

The continuous foam fractionation of phenol using a quaternary ammonium salt, ethylhexadecyldimethylammonium bromide, has been investigated. Experiments were conducted to determine the effects of pH and percentage reflux on the phenol removal. It was found that approximately 80% removal of phenol was obtained at a pH of 11.9 with 70% reflux. Poor removal occurred in the slightly basic region of 8.0 to 10.0; while adequate removal was obtained with no pH adjustment. Maximum removal occurred at 70 to 80% reflux. Sodium hydroxide was used to adjust the pH in most cases. Although similar effects were found using ammonium hydroxide, the percent removal of phenol was, in general, lower.

INTRODUCTION

A considerable amount of work has been reported in the past decade on the use of foam fractionation for removing both organic and inorganic solutes from water including such substances as dichromate, orthophosphate, phenol, alkyl benzene sulfates, and quaternary ammonium salts (1–7). Phenol, however, has been of particular interest due to its corrosiveness and high toxicity. Phenol is harmful to both aquatic and human life and is frequently found in industrial wastewaters.

Grieves and co-workers (3, 4) have investigated the separation of phenol by addition of a cationic surfactant. They reported limited success using

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batch foam fractionation and found that a pH of 11.0 to 12.0 was needed for adequate phenol removal.

The purposes of the present study were to determine the effects of reflux on the continuous foam fractionation of phenol and to determine if the use of reflux can eliminate the requirement of a high pH for the effective removal of phenol from wastewaters.

Experimental

The foam column, as shown in Fig. 1, was a Plexiglas tube 4 in. in diameter and 31.5 in. in height. The foam collector, a section of Plexiglas tubing 7-7/8 in. in diameter, encased the top of the column and was mounted on a Plexiglas sheet at an angle of 18.5°. A foam delivery tube extended from the foam collector to the foam breaker. The top of the foam collector was capped and the foam was thus forced to flow into the foam breaker. The foam was collapsed by putting it through a spinning wire basket. The foamate could be returned to the column as reflux or collected as product.

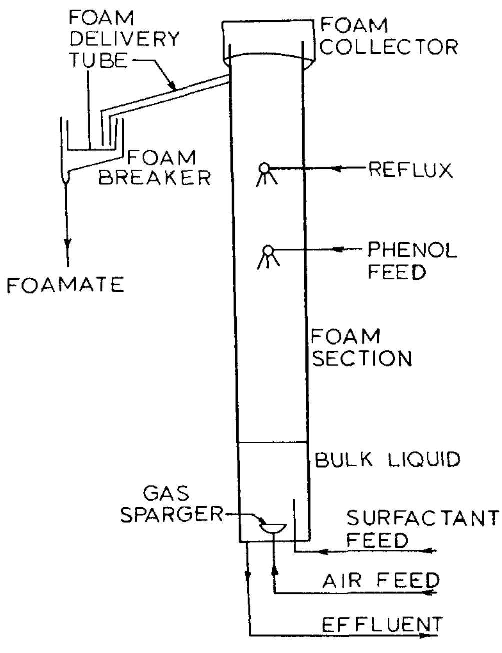

FIG. 1. Schematic diagram of the foam fractionation column.

Laboratory-compressed air was filtered, passed through a water saturator, and entered the base of the column through a 10–20 μ sintered glass disk. The air flow rate was held constant at 350 cc/min. Feed and reflux inlets were provided at heights of 18.5 and 24 in., respectively. These liquid streams entered the column through distributors which were made by inserting a number of pieces of hypodermic tubing in a rubber stopper. Phenol feed concentrations were held constant at 5 ppm with a feed rate of 12.7 ml/min, while the amount of collapsed foam returned to the column as reflux was varied from 0 to 100%. A concentrated surfactant solution of ethylhexadecyldimethylammonium bromide (EHDA-Br) was fed into the bulk solution at the base of the column at a feed concentration of 487 ppm.

Sodium hydroxide was used to adjust the pH in the majority of the experiments in which the pH was varied. In several runs, however, the effects of ammonium hydroxide as a pH adjuster were examined.

Phenol concentrations in the feed and effluent streams were determined by the 4-amino-antipyrine method (*8*). Surfactant concentrations were determined by use of the two-phase titration method (*9*).

RESULTS AND DISCUSSION

The results of the initial studies concerning the effect of pH on the removal of phenol are shown in Fig. 2. This series of experiments was made at 42% reflux using either sodium hydroxide or ammonium hydroxide to adjust the pH. The best removal was obtained in the pH range of 11.0 to 12.0 with both pH adjusters. A maximum removal of 84.5% was obtained at a pH of 11.9 using sodium hydroxide. It is apparent that this maximum removal is significantly better than was obtained using ammonium hydroxide. There is some difference in removal at a low pH although the two curves do intermingle at the intermediate pH values. The reasons for the differences in the two curves and the sharp minimums found are not known. However, it is clear that the effect of the base is more complex than simply providing an excess of OH^- ions.

Probably the most important aspect of Fig. 2 is the nature of the results obtained below a pH of 8.5. It can be seen that significant removal was obtained at a pH of 6.2, that is, with no base added; and that the removal then decreased sharply up to a pH of 8.4. The relative importance of this data may be better realized when compared to the results of Grieves and Aronica (*4*) using batch operation. Although the phenol and surfactant feed rates used in these studies are different, the differences in the general trends of these results are significant. Grieves and Aronica found a removal

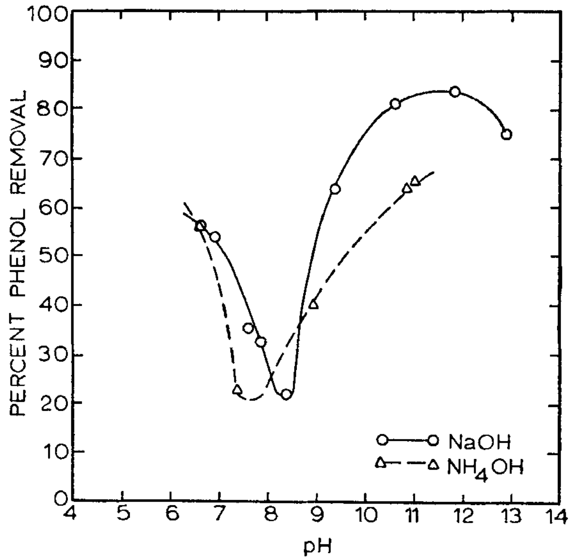

FIG. 2. Effect of pH on removal of phenol at 42% reflux. pH adjusted with either sodium hydroxide or ammonium hydroxide.

ratio approaching 1.0 at a pH of 6.0 (a removal ratio of 1.0 indicates no removal of phenol) with a gradual increase in removal up to a pH of approximately 9.0. The removal then increased considerably up to a maximum at a pH of about 11.8. In this research, however, relatively high removal was found at a pH of 6.2 with a sharp decrease in removal up to a pH of 8.4. Above this value an increase in the removal, similar to that of Grieves, occurred. The reason for the discrepancy between these two works is not clearly understood. Better removal was expected at a low pH as a result of the use of reflux but the sharp decrease in removal with the initial increase in pH certainly cannot be explained on the basis of reflux. It is believed that this system is much more complicated than it originally appeared, and that this phenomena must be attributed in some manner to the formation of the phenol–surfactant complex. There was no evidence that the surfactant removal was affected in this region. It is suspected, therefore, that the small amounts of base affect the phenol–surfactant complex such that the removal of phenol is limited. Since the sodium hydroxide and ammonium hydroxide runs were affected similarly, this decrease in removal must not be characteristic of any particular base.

Efforts were also directed at investigating the effect of reflux on the

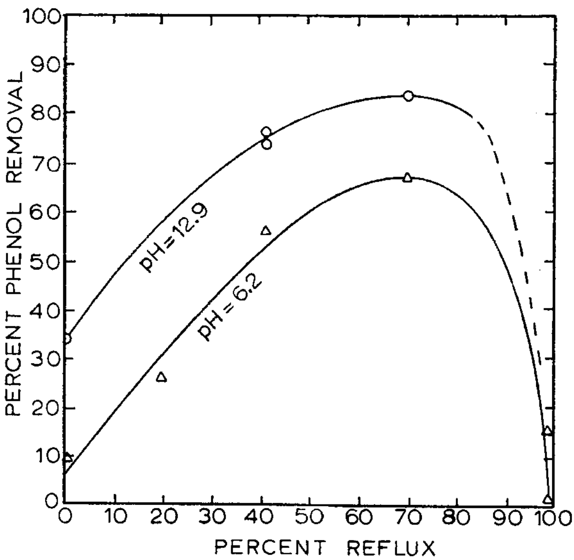

FIG. 3. Effect of reflux on phenol removal.

removal of phenol. Two series of experiments were made to determine if similar results could be expected at different pH levels using sodium hydroxide to adjust the pH. The results of these runs are shown in Fig. 3. The use of reflux greatly enhances the separation of phenol at pH values of 6.2 and 12.9. In both cases the removal increased steadily as the percent reflux was increased up to a maximum at approximately 70% reflux. The removal then decreased sharply to the limiting value at 100% reflux, where no removal can occur.

A few preliminary runs were then made to determine the effect of pH at 70% reflux, since maximum removal was obtained at this value. Only four data points were obtained at this level of reflux, using sodium hydroxide in each case to adjust the pH. However, the intent of these runs was not to determine the exact shape of the curve, but to confirm the general trends found at 42% reflux. Again, good removal was obtained at a high pH with a maximum of 84.5% at a pH of 11.7 to 12.9. The same reduction in removal occurred at a pH of 9.4, corroborating the results shown in Fig. 2. With 70% reflux almost 70% removal was obtained with no pH adjustment. This is very important in terms of the practicability of the foam fractionation process. These results indicate that the use of reflux does eliminate the high pH requirement. Although a removal of 70%

would probably not be adequate in most practical applications, by use of multicolumn operation and perhaps by selection of a more efficient surfactant, the removal of the phenol could be increased significantly without the requirement of a high pH.

CONCLUSIONS

The results of this study have shown that reflux can significantly increase the removal of phenol from water in the pH range of 6.2 to 12.9. Maximum removal can be expected at approximately 70% reflux.

The results also indicate that the severe requirement of a high pH for effective phenol removal is not justified for a continuous foam fractionation column. With no pH adjustment, almost 70% of the phenol can be removed using 70% reflux. However, maximum removal can be obtained by increasing the pH to within the range of 11.5 to 12.0.

It is evident from the sharp minimums of phenol removal found in the pH range of 8.0 to 9.0 that the effect of the base is far more complex than simply increasing the ratio of phenolate ion to phenol. Further study of the formation of the phenol–surfactant complex may lead to the identification of a more efficient surfactant for this process.

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