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Recovery of Chloroform from Effluent with Solvent Extraction–Distillation Process

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ABSTRACT

A solvent extraction–distillation process for recovery of chloroform in aqueous effluent was developed. Sulfonated kerosene was used for extraction of chloroform. When the flow ratio of organic phase to aqueous phase is 0.1, the chloroform concentration in the aqueous effluent can be decreased from 10 g/L to about 100 mg/L by 3-stage countercurrent extraction. The distribution ratio of chloroform between sulfonated kerosene and water is about 50. Sodium sulfate in the aqueous effluent will enhance the distribution. A small amount of water was added to the distillation column for stripping chloroform in sulfonated kerosene. RPC was used as a commercial extractor. Scale-up from the data of the pilot test was based on the Karr correlation. Recovery of chloroform was over 90%, and residual kerosene in the aqueous effluent from the extraction was lower than 70 mg/L. It is expected that the technique can be used for the recovery of other organic solvents miscible with kerosene.

Key Words. Solvent extraction; Recovery; Chloroform; Distillation

INTRODUCTION

Chloroform is a volatile, toxic solvent. Some research indicates that chloroform is a carcinogenic halohydrocarbon (1). Still, chloroform is adapted for the extraction process of pharmaceutical and other organic industry because of its high distribution, low viscosity, middle interfacial tension, and high density difference to an aqueous solution. The solubility of chloroform in water is 0.815 g for 100 g water at 20°C, and entrainment in phase separation will increase the amount of chloroform in an aqueous effluent. As a result, chloroform concentration in an aqueous effluent from solvent extraction is about 1 wt%. For example, in the caffeine synthesis industry process for an aqueous capacity of 5 t/h, the loss of chloroform is as high as 300 t/y. The high amount of chloroform is not only very expensive, but is also a serious environmental pollutant. Therefore, the recovery of chloroform becomes an important problem before the final treatment of the effluent. For recovery of the low concentration chloroform it would be difficult to directly distill before enriching. Chloroform is miscible with many organic solvents, so solvent extraction is an available technique for separation and enrichment. In order to choose the extractant, beside good distribution, the following factors should also be considered: 1) an acceptable boiling point difference between extractant and chloroform to make separation by distillation easy; 2) lower solubility in an aqueous effluent without subpollution; 3) toxicity and cost of operation. It was found experimentally that sulfonated kerosene is a good choice for the recovery of chloroform.

EXPERIMENTAL

Materials

Sulfonated kerosene was presented by Beijing Chemical Corp. It is a refined industry kerosene employing sulfonation to remove unsaturated aliphatic hydrocarbons and other impurities. The sulfonation process includes sulfonation with 98% H_2SO_4, water washing, and distillation. Kerosene's boiling point is in the 150 to 260°C range.

Chloroform, sodium sulfate, and other chemicals used in this work were reagent grade.

The aqueous effluent used in our pilot test for the recovery of chloroform was the raffinate after extraction by chloroform in a caffeine synthesis plant.

Apparatus

The RPC (reciprocating plate column) used in our pilot test was made of glass pipe with a flanged connection. Both the top and the bottom sections were 30 cm in height and 10 cm in diameter. The I.D. 38 mm plate stack section was 2.3 m in length. The parameters of the RPC used are shown in Table 1.

TABLE 1
The Parameters of RPC in the Pilot Test

Internal diameter of column	38 mm
Height of internals	2.3 m
Plate diameter	36 mm
Plate thickness	3 mm
Plate spacing	50 mm
Number of plates	42
Diameter of holes	10.8 mm
Arrangement of holes	Equilateral triangle
Triangular pitch	17 mm
Free area	0.366
Material	Teflon

The reciprocating plate stack was driven by a variable speed motor and an adjustable yoke. The sulfonated kerosene and aqueous effluent were fed by pumps from tanks to the column.

The distillation column for the pilot test was made of 38 mm I.D. stainless steel pipe. Both the rectifying section and the stripping section were 75 cm in height and packed with Rasching rings.

Procedures

In the experiment of extraction phase equilibrium for the preparation of an aqueous solution of chloroform, 5 mL chloroform was added to 1000 mL deionized water and stirred until it was completely dissolved. The solution was extracted by sulfonated kerosene in different volume ratios. The equilibrium chloroform concentration was measured by the pyridine colorimetric method (2) and a 752C spectrophotometer. In the study on the effect of sodium sulfate concentration on distribution, a chloroform–deionized water solution of 7.4 g/L was first prepared, then 0, 0.1, 0.2, 0.3, and 0.4 g dehydrated sodium sulfate were respectively added to 10 mL portions of the solution. Each sample was then extracted by 5 mL sulfonated kerosene.

To determine the vapor–liquid equilibrium of the sulfonated kerosene–chloroform–water system the phase composition was determined by a SP-2305 gas chromatograph.

In our pilot test to determine the throughput of the pilot column for sulfonated kerosene–aqueous effluent saturated with chloroform, the column was filled with sulfonated kerosene and then the aqueous phase was fed into the inlet located at the top of the plate stack. After the flow ratio of the two phases was fixed at a given amplitude and frequency of pulsation, the flow rates of the two phases were increased gradually until flooding occurred. For mass transfer, the concentration–time relationships of the two phases at the outlets were determined from starting to steady state. The extraction efficiency was calculated from the inlet and the outlet chloroform concentration of the aqueous effluent at steady state.

RESULTS AND DISCUSSION

Distribution of Chloroform between Sulfonated Kerosene and Water

Properties of Sulfonated Kerosene

Sulfonated kerosene is composed of alkanes which are nonreactive with strong acids, alkalies, and oxidants, and it has high chemical stability. The solubility of sulfonated kerosene in water is 7 mg for 100 g water at 20°C. Sulfonated kerosene is transparent and without color or odor. Typical composition and physical properties of sulfonated kerosene are shown in Tables 2 and 3.

Sulfonated kerosene is miscible with chloroform, and it has a high distribution and capability for the extraction of chloroform. In addition, the high boiling point difference between sulfonated kerosene and chloroform is favorable separation by distillation.

Distribution of Chloroform between Sulfonated Kerosene and Water

The distribution of chloroform between sulfonated kerosene and water was studied experimentally in Fig. 1 where *x* is the equilibrium chloroform

TABLE 2
The Typical Composition of Sulfonated Kerosene

Alkane	Content (wt%)	Boiling point at atmospheric pressure (°C)
C9	0.82	150.80
C10	8.71	174.12
C11	28.33	195.89
C12	38.63	216.28
C13	20.58	235.43
C14	2.93	253.52

TABLE 3
Physical Properties of Sulfonated Kerosene, at 25°C

Density (g/cm^3)	Viscosity (cP)	Interfacial tension with water (dynes/cm)
0.7910	1.4011	17.02

concentration in water (g/L) and y is that in sulfonated kerosene (g/L). It is shown that beyond 150 g/L the distribution decreases with an increasing chloroform concentration in water. Therefore, a concentration of chloroform in the aqueous phase lower than 100 g/L is controlled in the extraction process design.

The Effect of Sodium Sulfate Concentration on Distribution

The aqueous effluent usually contains sodium sulfate. The effect of sodium sulfate concentration on the distribution of chloroform for a given initial chloroform concentration in water was studied. As shown in Fig.

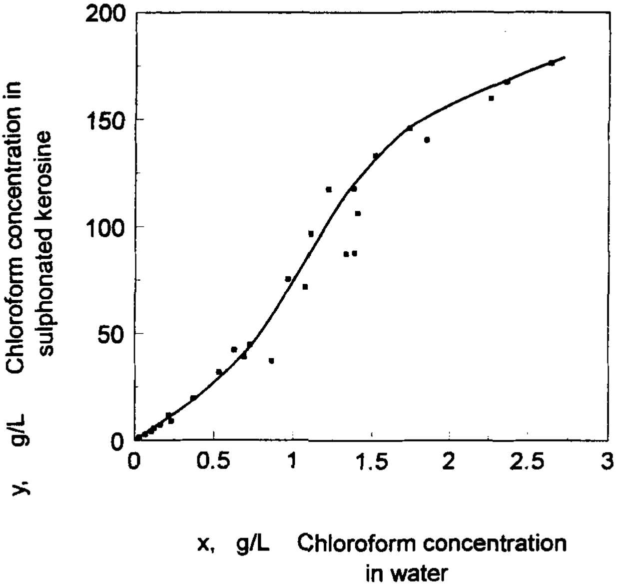

FIG. 1 Distribution of chloroform between sulfonated kerosene and water, 25°C.

2 sodium sulfate enhances the distribution of chloroform remarkably and also phase separation because of the salting-out effect.

Vapor–Liquid Equilibrium of Sulfonated Kerosene–Chloroform–Water System

The distillation temperature range of sulfonated kerosene is from 150 to 260°C and the boiling point of chloroform is 61.3°C at atmospheric pressure. It is very easy to separate the two because of their large boiling point difference. A little water is added to drop the boiling temperature of the system, and the chloroform can be easily distilled out by middle pressure steam stripping.

The vapor–liquid equilibrium of chloroform–sulfonated kerosene was determined. For simplicity, the mixture can be considered as a chloroform–kerosene pseudo-binary system. A small amount of water is an inert component whose role is to decrease the boiling point. The results are shown in Fig. 3, where X and Y are the weight fraction of chloroform in the liquid phase and in the vapor phase, respectively.

Recovery Process

The recovery process is composed of two units: solvent extraction and distillation (Fig. 4). The aqueous effluent is extracted by sulfonated kero-

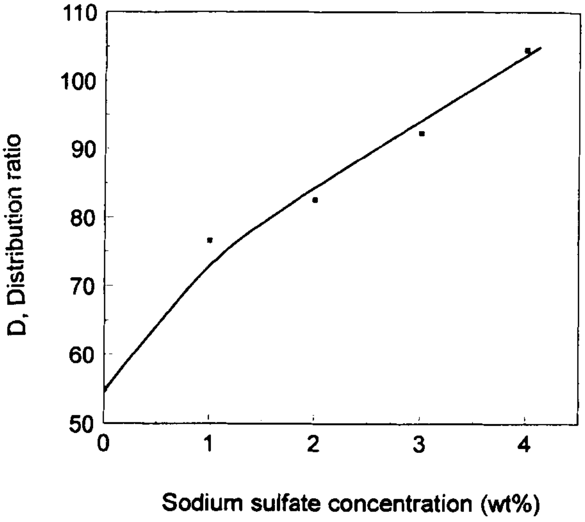

FIG. 2 The effect of sodium sulfate concentration on distribution ratio, 25°C.

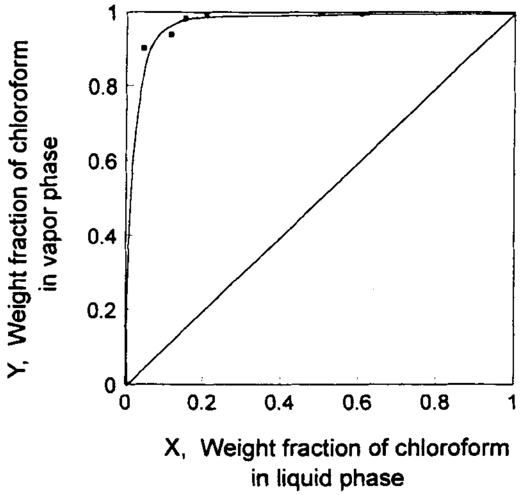

FIG. 3 Vapor–liquid equilibrium of chloroform–sulfonated kerosene system.

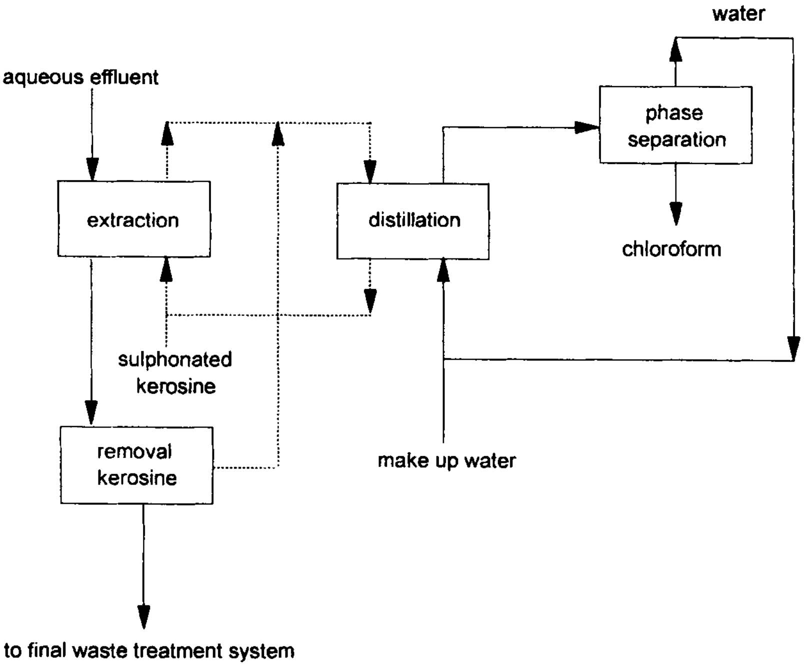

FIG. 4 Recovery process.

sene. Then the residual sulfonated kerosene in the aqueous effluent is removed by a polypropylene fiber bed. Finally, the effluent is pumped into a waste treatment system.

The loaded sulfonated kerosene is pumped into a distillation column for recovery of the chloroform. The unloaded sulfonated kerosene is cycled to the extraction unit.

Pilot Test

Solvent Extraction by RPC

The RPC (reciprocating plate column) has been used extensively for effluent treatment. It has high efficiency and capacity, flexibility, and stability (3, 4). In this work the continuous phase is the sulfonated kerosene and the dispersed phase is the aqueous effluent. The interface is located at the bottom of the column.

The flooding velocities, $V_c + V_d$ (cm/s), were determined at different flow ratios and pulse frequencies in the pilot test RPC. V_c is the superficial velocity of the continuous phase and V_d is that of the dispersed phase. In the experiment the variation of the flow ratio (sulfonated kerosene/aqueous effluent) ranged from 1/6 to 1/20, the pulse frequency ranged from 260 to 360/min, and the pulsation amplitude was 13 mm. The experimental results are presented in Fig. 5 which shows that the hydromechanics char-

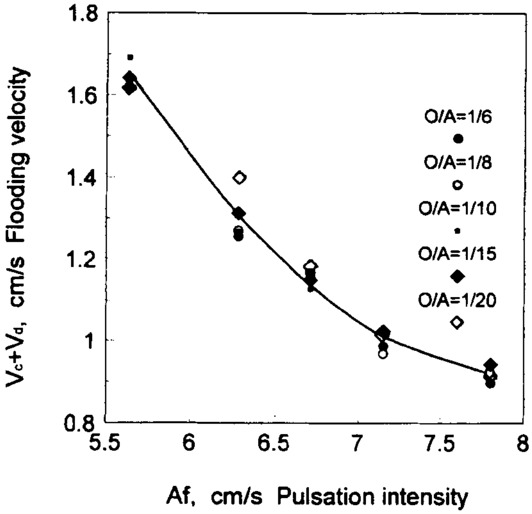

FIG. 5 Flooding velocity of RPC.

acteristic of the sulfonated kerosene–aqueous effluent system operated in the RPC is flexible, i.e. the effect of the flow ratio on the flooding velocity is not remarkable in the flow ratio range. Therefore, the RPC has good stability in operation.

Mass transfer of chloroform in RPC was studied with the aqueous effluent and sulfonated kerosene. The flow ratio was varied from 1/6 to 1/20 at a pulsation of 300/min frequency and 1.3 cm amplitude. The results are listed in Table 4.

It is shown that the RPC is suitable for the extraction of chloroform. The extraction efficiency of chloroform is 0.959 at a 1/10 flow ratio, a pulsation of 1.3 cm amplitude, and 300/min frequency.

Distillation

A small amount of water was added to the still to depress the boiling point of the sulfonated kerosene. The chloroform concentration of the feed was from 9 to 30 wt%. The boiling temperature of the chloroform–water azeotrope is 56.1°C. Therefore, the temperature at the top of the distillation column should be kept at 56°C. The experimental results are listed in Table 5.

The distillate was quite pure, suitable for use in the process industry. The chloroform concentration in sulfonated kerosene from the bottoms was from 42 to 2540 mg/L, and it can be cycled for extraction.

Scale-up Design and Commercial Application

An RPC of 600 mm diameter was successfully used in the extraction unit. A distillation column packed with Pall rings was matched to the RPC. The scale-up design of the commercial extraction column was based on data from the pilot test and the Karr correlation (3). For the 600-mm diameter column, plate spacing and total throughout per unit area of column section and amplitude were kept the same as in the pilot column.

TABLE 4
Mass Transfer in RPC

Flow ratio (sulfonated kerosene/aqueous effluent)	Two-phase velocity (cm/s)	Inlet concentration (mg/L)	Outlet concentration (mg/L)	Efficiency (%)	HETS (m)
1/6	0.72	2557	177	93.1	1.58
1/10	0.85	5116	211	95.9	1.21
1/20	0.80	3267	355	89.1	1.26

TABLE 5
Pilot Test for Distillation of Chloroform

Reflux ratio	Top temperature (°C)	Bottoms temperature (°C)	Pressure drop (Pa)	Distillate concentration (wt%)	Bottoms concentration (mg/L)
Total	56	102	490	99.97	42
Total	56	102	2750	99.99	1370
Total	56	102	3240	98.93	2540
1.0	56	102	2060	99.99	2130
0.5	70	102	490	89.84	2000
0.5	57	102	1080	99.96	1930

A Teflon plate stack was used in the pilot test, so the wettability effect should be considered in the scale-up design. Because the Teflon plate stack is wetted by kerosene as a continuous phase, mass transfer from the dispersed phase to the continuous phase will be less effective and the column capacity will be increased due to enhanced coalescence of dispersed phase drops (5). Due to the wettability effect and the occurrence of crud in the industry process, the free area of the stainless steel plate for a 600-mm diameter column was made slightly larger than in the pilot column.

In order to simplify the stack construction, doughnut-type baffles were not used in the 600-mm diameter extraction column. The free area was smaller than in the usual design in order to keep the plate rigidity (6).

The internals parameters for a 600-mm diameter column are listed in Table 6.

TABLE 6
Geometry of 600 mm Diameter Column

Height of internals	8 m
Plate diameter	580 mm
Plate thickness	3 mm
Plate spacing	50 mm
Number of plates	160
Number of holes per plate	1008
Diameter of holes	12 mm
Triangular pitch	17 mm
Free area	0.431
Material	Stainless steel

Although a slightly lower reciprocating speed than the calculated value from the Karr scale-up relation was used in operation, the extraction efficiency was still satisfactory. Many research results show that axial dispersion is strongly dependent on the reciprocating speed and amplitude (7). Therefore, a lower reciprocating speed may be favorable for not only decreasing the axial dispersion but also for decreasing phase entrainment and energy consumption.

The extraction–distillation system has been used to recover chloroform from the aqueous effluent of pharmaceutical plants (8). Devices of 5 t/h capacity with a 1/10 flow ratio of sulfonated kerosene to effluent can recover over 1000 kg/d chloroform. The sulfonated kerosene in the raffinate of a chloroform extraction column was removed by a polypropylene fiber bed. Finally, the raffinate was pumped to a final waste treatment system. The sulfonated kerosene concentration in the outlet of the fiber bed was about 70 mg/L.

CONCLUSIONS

1. An extraction–distillation system using sulfonated kerosene as the extractant can be used to recover soluble and entrained chloroform in the effluent. When the flow ratio of sulfonated kerosene to aqueous effluent is 1/10, over 90% of the chloroform can be recovered with 3-stage countercurrent extraction. Sodium sulfate in the aqueous effluent enhances the recovery process due to the salting-out effect.
2. RPC is an effective extractor to recover chloroform in the aqueous effluent for commercial application. Sulfonated kerosene is the continuous phase and aqueous effluent is the dispersed phase. The RPC is flexible at flow ratios of 1/6 to 1/20 with matching pulsation.
3. Sulfonated kerosene can be extended to extract other organic components in other aqueous effluents which are miscible with sulfonated kerosene. Therefore, it is expected that the extraction–distillation process can be used to recover other organic solvents soluble in an aqueous effluent with a modified extraction–distillation system.

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