THE NICOTINE EXTRACTION FROM TOBACCO WASTES

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ABSTRACT

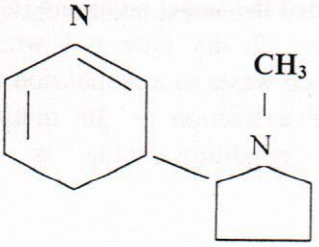
The extraction of nicotine from tobacco waste involves two main stages: Separation of total alkaloids from tobacco with ethanol-water mixture by leaching and the recovery of the nicotine from aqueous phase using solvent mixture such as hexane-chloroform by mixer-settler extraction process. Preliminary experiments were carried out first to study the effects of volume of solvents and the technique of separation.

The effect of the V/V solvent to organic phase ratio in the range of 0.75-1.25, volumetric percentage of chloroform to solvent ratio in the range of 0-10 %, and temperature (20-40 °C) on the extraction efficiency (E%) were studied using the Box-Wilson technique of designing the experiments. Useful relationship between the three controllable variables and the E% could be established. The experimental data collected by this design are successively fitted to a second order polynomial model.

The optimum conditions are: volumetric ratio of the solvent to aqueous phase (1:1), volumetric percentage of chloroform to solvent (7.5%), and the operating temperature (40 °C). At these conditions the nicotine extraction efficiency is 87.9 %.

INTRODUCTION

Nicotine is 1-methyl-2-(3-pyridyl) pyrrolidine. The structural formula shows the combination of pyridine and pyrrolidine ring[1,2].



Nicotine, a liquid alkaloid, is obtained from certain plants, such as Nicotiana tabaccum, which contains small quantities of other alkaloids, but its physiological action was largely due to the nicotine content[3]. Total alkaloid is usually expressed as nicotine, which amounts to 95 % or more than 98 % of the total alkaloid content in normal tobacco samples[4,5]. Commercial nicotine is entirely a byproduct of tobacco industry [1,6].

The primary objective in extraction is to affect a net transfer of solute molecules from the raffinate phase to extract phase. The transfer process assumes that two resistances in series impede the movement of solute from one phase to the other; a third resistance at the interface could also be considered [7].

The solvent is the key to a successful separation by liquid-liquid extraction and much of the process research effort is directed toward the evaluation of possible solvent. The solvent selection criteria is based upon the following[7]: selectivity, density and viscosity, insolubility in water, recoverability, interfacial tension, availability, cost, and[8] the K value (the distribution coefficient).

The distribution coefficient of nicotine between water and kerosene and petroleum fractions was studied[9, 10]. Temperature was the most important variable. Millen *et al.* [11] studied the influence of initial nicotine concentration, temperature and pH on the distribution coefficients of nicotine between hexane and water. They found that the coefficient was independent of initial concentration over the studied range; but was temperature and pH dependent. Their investigation was carried out over the concentration range of 1-8.5 g/l, temperature range of 5-20 °C and two pH values of 11 and 13.

Leslie *et al.* [12] employed counter-current extraction for winning nicotine out from tobacco juice. Several organic solvents such kerosene, petroleum, distillates, undecanol, chlorobenzenes, ethylene chloride, chloroform, hexane and methyl tert-butyl ether, have been used to extract nicotine from aqueous solutions [8 –13].

Supercritical extraction method was successfully applied for the extraction of nicotine from tobacco, caffeine from green tee [14]. Rincon *et al.*[15] studied the extraction of nicotine from tobacco waste by supercritical carbon dioxide at 50-70 °C and 15-30 MPa.

Recovery by an ion exchange of nicotine from tobacco drier gases is practiced by passing them through a scrubbing tower, the water being recirculated to build up the concentration of nicotine. The solution was then passed through a cation - exchanger bed to remove nicotine. The nicotine was then extracted by a one-step recovery process that was used directly as [Nicotine Zeo-Karb], an insecticide [16].

The aim of the present work is at the recovery of nicotine from tobacco waste and selection of the best solvent for this process. The main approach is to study the effect of different operating conditions on the extraction by applying the Central Composite Rotatable Design (Box-Wilson Design) to reach the optimum operating conditions in liquid - liquid extraction.

EXPERIMENTAL WORK

Apparatus

1. Mechanical stirrer: supplied by Karl Kolb.
2. Rotary evaporator: a 1-liter capacity supplied by Heidolph equipped with vacuum pump from Robinir and chiller from MGW Lauda, Germany.
3. Centrifuge: for separating the phases, T_5 Janetzki.
4. pH meter was from Metrohm model 3010 and calibrated with buffer solutions of pH = 9.2 and7.0.

Chemicals

1. Tobacco dust was a by-product of the State Company for Tobacco and Cigarette-Baghdad. The composition is indicated in Table 1. The tobacco dust was screened to be ≤ 200 □m. The dust was dried overnight in an oven at a temperature range (50-60 °C).
2. Standard tobacco juice was obtained from the Murphy Chemical Company Ltd.
3. Hexane was supplied by the State Company of Gas / North of Baghdad. (C_6 content > 92 %).
4. Chloroform and sodium sulfate were products of BDH.
5. Ethanol was supplied by the National Company for Food Industries at a concentration of 95 % by volume.
6. Calcium hydroxide, $Ca(OH)_2$, is G.P.R.) from ICI.
7. Perchloric acid, (Analar) from Fluka AG, Switzerland.
8. Glacial acetic acid, (analar), crystal violet indicator were supplied by Reidel-de Haen, Germany.
9. Toluene was supplied by The Arab Company for Detergent Chemicals with purity 99.9%.

Preliminary Experiments

Eleven experiments were carried out to reach the optimum soaking, filtration and extraction condition of nicotine. The soaking time was (24 h.) except when boiling water was used (2 h). The solvents were mixtures of benzene, toluene or hexane/ chloroform mixtures at a ratio of (9:1) by volume, respectively, and in contact with equal volume of aqueous phase. The other conditions were maintained the same, including (temperature = 25°C, pH = 12, dry lime = 1 wt. % to the original tobacco waste as a suspension of 7 wt.%, and time of extraction = 30 minutes). The experimental condition setup is given in Table 2.

Application of Box-Wilson design

The experiments were designed according to the central composite rotatable design (CCRD) for three variables in a solvent-liquid system. The operating ranges of the variables (X_j) were first specified in order to design the experiments as follows:

X_1 = Organic to aqueous phase ratio (S/A): 0.75-1.25.

X_2 = Organic solvent composition ($CHCl_3$/S): 0-10 %.

X_3 = Temperature (T): 20-40 °C.

The response function (Y) is the percentage of nicotine extraction efficiency (E %) as determined by non-aqueous titration of the hexane extract with perchloric acid in acetic acid medium employing crystal violet as indicator [4,18]:

Pipet, 20-ml aliquot of the solvent containing nicotine into 125-ml flask adding 2 drops of 0.02 wt./vol. % of crystal violet indicator solution in glacial acetic acid and titrate to the green end point with standardized 0.1 N perchloric acid in glacial acetic acid. All analyses were performed in triplicate. Calculate the extraction efficiency (E%):

Nic. in sol. wt% = [(Vol. $HClO_4$ x 0.1N x 32.45)/100 g] x 100%

E% = [(wt%)/ 1.4] x 100%

1.4 = Nicotine wt% in tobacco dust (Done in the Company)

then, 32.45 is the factor of calculation from ref. 18.

A preliminary step is to set-up the relationships between coded levels X_j (where j = 1, 2, and 3) and the corresponding real levels. According to CCRD of three variables, 17 tests were carried out as listed in Table 3.

Procedure

In a round bottom flask, distilled water was added to the tobacco dust for wetting. After 12 h., ethanol was added. The mixture was the mixed and left for 12 h. The soaking liquid was separated by press filtration, where the soaked material was placed in a cotton cloth between two iron plates (2 cm thick) and forced towards each other. The liquid was collected in a glass container. The mother liquor was then concentrated in a rotary evaporator under reduced pressure.

The solvent mixture, hexane-chloroform, was added to the concentrated aqueous solution together with dry lime suspension to keep the PH value at 12. The mixture was then heated to enhance liberation of nicotine to be received by the solvent. The time of extraction was kept constant at 30 min.

The resultant solution was separated into two layers, organic and aqueous layer, by centrifugation at a speed of 3000 rpm for 10 minutes. The organic layer was then transferred into a volumetric flask and 3 g of anhydrous sodium sulfate were added for overnight dehydration.

RESULTS AND DISCUSSION

The preliminary experiments gave the following results:

1. A weight ratio of water to tobacco of 3:1 was chosen, because at lower ratios (2:1) water is not sufficient to disintegrate the tobacco fibers and extract the nicotine from it. While, the high ratio (4:1) may cause partial oxidation [19].
2. Instead of using water alone in the soaking stage, alcohol was added to aid in nicotine extraction. Alcohol has comparable solubilizing ability to water for nicotine. Thus, the combined effect of water and ethanol improves leaching of nicotine from the dust. Besides, it has less polarity than water; therefore, it lowers the possibility of decomposition of nicotine in the aqueous solution [20]. Experiments showed that the optimum ratio of alcohol to water is 2:1.
3. Among the juice separation and purification methods used, press filter is the best technique.
4. Although, the mixture of benzene-chloroform gives relatively high extraction efficiency, we emphasize the use of the hexane-chloroform, because hexane is cheap, locally available and currently used for vegetable oil extraction. This mixture gives (E %) approximate to the result when the benzene-chloroform was used.

Analysis of Box-Wilson Experimental Results

The response of experiments conducted according to Box-Wilson method is fitted to a second order polynomial mathematical model and the optimum response is calculated from this model. The effect of each variable on the response is also determined by using the F-test. By using a uniform precision (CCRD) for nicotine extraction from aqueous phase, the arrangement of the three parameters studied in the solvent-liquid system are shown in Table (3) with the responses accomplished by the experimental work.

The statistical analysis system (SAS) software was used for estimating the mathematical model representing the second order response surface fitted to the design points and responses. The statistical analysis of the model gave values of 99.07% for the correlation coefficient, 98.16% for the variance explained and an average absolute error of 3.15. The second order response mathematical model can be written as follows:

$$\begin{aligned} y = {} & 80.1563 - 5.2105X_1 + 9.4644X_2 + 2.4833X_3 - 14.1589X_1^2 \\ & - 6.7416X_2^2 + 0.9013X_3^2 + 1.2498X_1X_2 + 0.8213X_1X_3 \\ & - 1.64263X_2X_3 \end{aligned} \qquad (1)$$

The optimization process was applied to equation (1) to find the optimum operating conditions for the extraction by using a computer program namely "Optimization Techniques". The results of optimization are: X_1: (S/A) = 1:1 by vol, X_2: (Chlor./S) = 7.5(vol. %), and X_3: temperature = 40 °C.

At these optimum conditions, the optimum extraction efficiency (E%) according to equation (1) is 87.9 % and the experimental efficiency of extraction at the same condition is 87.15 %.

Effect of Phase Ratio (S/A)

Fig.1 shows the effect of the volumetric solvent to the aqueous solution ratio on the E% at different temperatures of the system and at the optimum composition of chloroform. The E% increases with increasing S/A and attains maximum value at a ratio of about 1:1 by volume, beyond this ratio, the efficiency decreases. The temperature rises in favor of increasing the efficiency, so that maximum E% value at 20 °C can be obtained at 40 °C using lower phase ratio (e.g. 0.8). This can be explained as follows: as the amount of the solvent increases, the equilibrium is attained at a shorter time [19]. Longer time may cause a back extraction (nicotine transfer) from the organic solvent into the aqueous phase.

Fig.2 shows the effect of phase ratio on the E% at different chloroform content in the solvent mixture and at the optimum temperature. The increase in chloroform content from 0 to 5 vol.% causes improvement in E%. Further increase in the chloroform content causes no appreciable increase in the values of E%. This should emphasize that chloroform in the organic phase not to exceed 5%.

Effect of Chloroform Content in the Solvent Mixture

Figure 3 shows the effect of percentage volume ratio of chloroform to solvent mixture on the E% for different temperatures at optimum phase ratio (S/A). It can be seen that E% increases when chloroform to solvent volumetric ratio increases up to 7.5 % where the efficiency is almost constant. For chloroform percentage higher than 7.5 vol.%, chloroform contributes to the increase of the solvent polarity [19] and hence improves the tendency of accepting nicotine. The E% increases as the content of chloroform in solvent increases to about 7.5 vol. % at different phase ratio and at optimum temperature (Fig. 4). Again E % is maximum at phase ratio of about 1:1 by volume.

Effect of Temperature

Figure 5 shows the effect of temperature on the E% at different compositions of chloroform in solvent and at the optimum phase ratio. It is clear that E% increases as temperature increases. This effect is markedly noticed by working at high temperature because the increase in temperature can increase the solvent power and selectivity of solvent towards a certain solute [21]. These results are in agreement with those of previous works [9, 18]. It is clear that the increase in the chloroform content from 0 to 5 vol.% causes improvement in the E%. No further improvement could be attained at higher chloroform contents.

Figure 6 shows the effect of temperature on the E% at different values of phase ratio and at optimum composition of chloroform to solvent. The values of E% increases with increasing temperature and phase ratio up to 1:1 and that further increase in phase ratio results in a decrease in E%, the decrease may be associated with back extraction noticed above.

CONCLUSIONS

The optimum operating conditions for the recovery of nicotine from tobacco wastes are:

Soaking step: liquid mixture / tobacco = 3:1 v/w; alcohol / water = 1:1 v/v and soaking time 24 h.

Liquid- liquid extraction: solvent/ aqueous phase (S/A) =1:1 v/v; chloroform / solvent = 7.5% by volume and temperature = 40°C.

The efficiency of liquid-liquid extraction is related with the three variables by a second order polynomial model.

The three variables affect the extraction efficiency in the order: ($CHCl_3$/S) > (S/A) > T.

Beyond 1:1 by volume of the (S/A), the extraction efficiency decreases. The extraction efficiency increases by increasing the temperature from 20 to 40 °C. The increase in the chloroform content from 0 to 5% improves the efficiency, but further increase in the chloroform content caused no appreciable improvement in the extraction efficiency.

REFERENCES

1. Budavari S., "The Merck Index", Merck and Co. Inc., Rahway , U.S.A , 11th ed. , 1989.
2. Berichte D.D., "What is Nicotine", From Internet, Pcp's Home, 1999.
3. Badger G.M., "The Chemistry of Heterocyclic Compounds", New York and London , 6th ed , 1961, p 135.
4. Faster D.S. and E.S. Leslie "The Encyclopedie of Industrial Chemical Analysis", Canada and U.S.A , 1974, Vol. 19, p. 134 ,
5. Yong S.S. and I. Smetena , Chromatographia , 40 (1995) 375-8.
6. Sherve R.N ; A. Joseph ; J.R. Brink , " Chemical Process Industries" 4th ed. , MC Graw-Hill , Inc. New York , 1975, p. 424 .
7. Jimmy L. ; J. Humphrey ; R. Antonio and R. Fair , " The Essentials of Extraction" , Chemical Engineering , 1984, Vol. 17.
8. Badgett, C. O., "Solvent for extracting nicotine frm aqueous solutions" Ind. Eng. Chem., Dec., 1950.
9. Claffey J.B. ; C.O. Badgett ; J.J. Skalamera and G.W. Phillip , "Nicotine extraction from water with kerosene", Ind. Eng. Chem., 42 166.
10. Askew H.O. , "Determination of nicotine in commercial tobacco products", J. Sci. Technol., New Zealand , 24B (1942) 39.
11. Millen C. and W. Raymond , "Distribution coefficient of nicotine between hexane and water", Ind. Eng. Chem. Res., 33 (1994) 3238.
12. Leslie D.C. ;Millen ; W.R. Murphy , " Counter-current Extraction of Nicotine from tobacco Juice" , Ind. Eng. Chem. Res., 32 (1993) 12.
13. MMWR HTML , " Determination of Nicotine , PH and Moisture Content of Six U.S. Commercial moist Snuff Products" , Univ. of Florida Publ., 21 , 48 (19) , 1999.
14. Eshtiaghi M. , " Supercrtical Co_2" , Tuberlin Bulletine, 2000.
15. Rincon J.A. ; M.A.Garcia ; A. Garcia ; A. Delucas and A. Carnicer , Separation Science and Technology , 33 (1998) 411.
16. Kingsbury A.W. ; A.B. Mindler and M.E. Gilwood , "Recovery of nicotine by ion exchange",Chem. Eng. Prog., Vol. 44 , No. 7, 1948.
17. Montgomery, D.C.,"Design and Analysis of Experiments", John Wiley, London, 1976.
18. Millen D.L.C., Ph.D. Thesis, The Queen's Univ., Belfast, 1988.
19. Danials F. and R.A. Alberty, " Physical Chemistry", 4th ed., Wiley, New York, 1975.
20. Coluson J.M.; J.F. Richardson and R.K. Sinnotti, " Chemical Engineering", Vol. 6, Pergamon Press, 1983
21. Salem A.B; G.V. Jeffreys, "Find optimum temperature for counter- current ion exchange extraction", Hydrocarbon Process., 5(1982)61.

Table 1: The Composition of Tobacco dust

Constituent	Formula	Wt.%
Moisture	H_2O	5 %
Nicotine	$C_{10}H_{14}N_2$	1-1.8 %
Total Nitrogenous	-	2 %
Total Sugars	-	10-15 %

Table (2) The design of preliminary experiments

Exp. No.	Liquid / Dust (V/W)	Alcohol/ Water (Vol.)	Type of Filtration[A]	Solvent Mixture (9:1)
1	2:1	0:1	Buchner	Benzene-chloroform
2	3:1	0:1	Buchner	Benzene-chloroform
3	4:1	0:1	Buchner	Benzene-chloroform
4[B]	3:1	0:1	Buchner	Benzene-chloroform
5[C]	3:1	0:1	Buchner	Benzene-chloroform
6	3:1	1:1	Buchner	Benzene-chloroform
7	3:1	1:1	Centrifugal	Benzene-chloroform
8	3:1	1:1	Press-filter	Benzene-chloroform
9	3:1	1:1	Press-filter	Toluene-chloroform
10	3:1	1:1	Press-filter	Hexane-chloroform
11	3:1	2:1	Press-filter	Hexane-chloroform

[A] *Buchner filtration at 0.5 bar using Wattman No. 2 filter paper.*
[B] *The ratio of solvent mixture to aqueous phase was 3:1 v/v.*
[C] *Boiling tobacco dust with water for 2 hours.*

Table (3) Results of experimental planned according to central composite rotatable design

Exp. No.	Coded variables			Real variables			Efficiency (E %)
	X_1	X_2	X_3	S / A (vol.)	$CHCl_3/S$ (vol.)%	T (°C)	
1	-1	-1	-1	0.86	2	24	50.200
2	1	-1	-1	1.14	2	24	36.571
3	-1	1	-1	0.86	8	24	70.428
4	1	1	-1	1.14	8	24	61.642
5	-1	-1	1	0.86	2	36	59.285
6	1	-1	1	1.14	2	36	48.642
7	-1	1	1	0.86	8	36	72.857
8	1	1	1	1.14	8	36	67.428
9	-1.732	0	0	0.75	5	30	49.700
10	1.732	0	0	1.25	5	30	30.071
11	0	-1.732	0	1	0	30	46.429
12	0	-1.732	0	1	10	30	78.143
13	0	0	-1.732	1	5	20	83.714
14	0	0	1.732	1	5	40	86.713
15	0	0	0	1	5	30	80.161
16	0	0	0	1	5	30	80.078
17	0	0	0	1	5	30	80.000

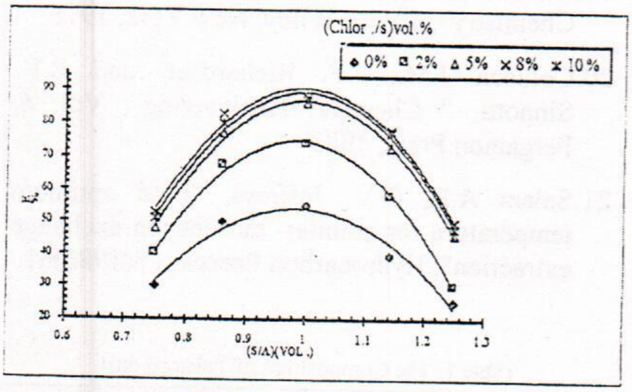


Fig. (1) Extraction efficiency of nicotine vs. phase ratio at different temperature and ($CHCl_3/S$) vol.%=7.5%

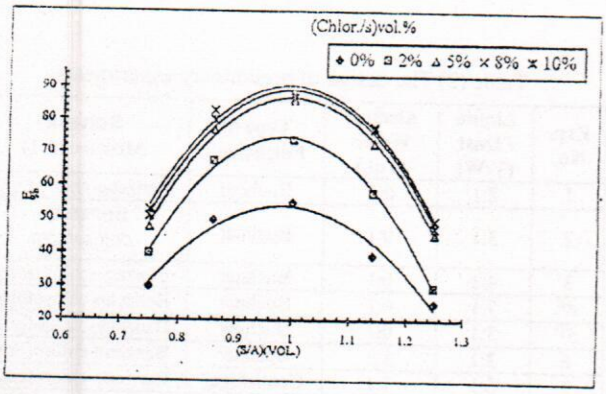


Fig. (2) Extraction efficiency of nicotine vs. phase ratio at different temperature and ($CHCl_3/S$) vol.% and temp. =40°C

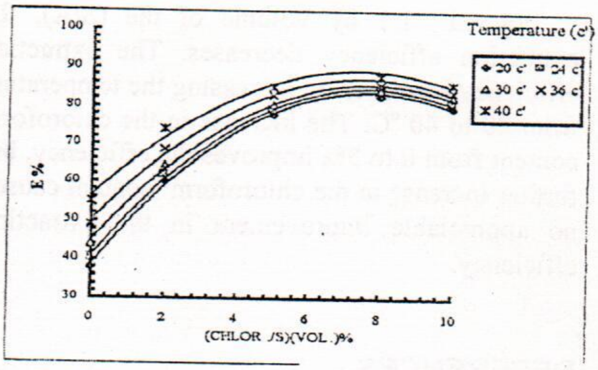


Fig. (3) Extraction efficiency of nicotine vs. composition of chloroform in solvent at different temp. and phase ratio = 1:1 (vol.)

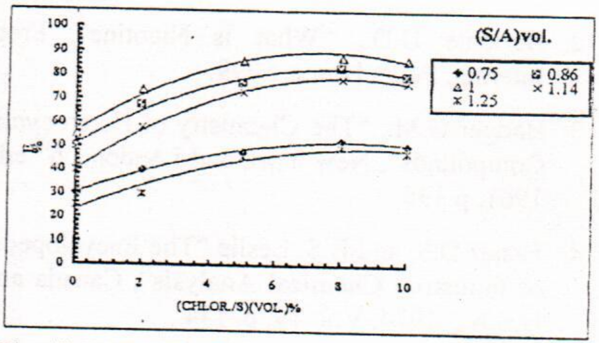


Fig. (4) Extraction efficiency of nicotine vs. composition of chloroform in solvent at and temp, = 40°C

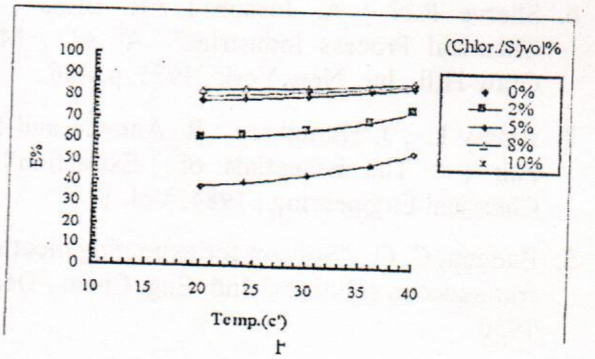


Fig. (5) Extraction efficiency of nicotine vs. temp. at different ($CHCl_3/S$) vol% and phase ratio 1:1 (vol)

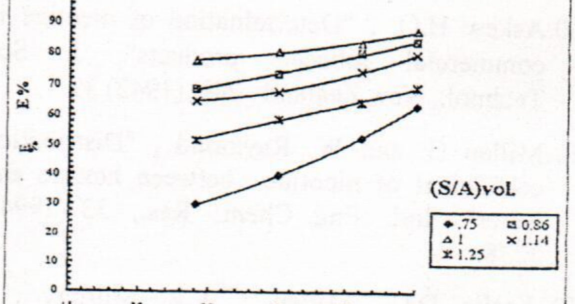


Fig. (6) Extraction efficiency of nicotine vs. temp. at different phase ratio and ($CHCl_3/S$) Vol% = 7.5%