Asian Journal of Chemistry Vol. 10, No. 4 (1998), 834–839

Ion Exchange Column Studies with Phenol: Choice of Solvent and Flow Rate

C.V. BHAT* and JITENDRA VARDIA*
Department of Chemistry
College of Science, Sukhadia University, Udaipur-313 002, India

The field of ion exchange has wide applications both in industry and laboratory. Most of the practical applications of ion exchange involve dynamic studies. This paper describes dynamic column studies of phenol with resin Dowex 1×4 in OH^- form, variation in flow rate as solvent medium both during exchange and elution of phenol were studied to optimize the column parameters and choice of the solvent medium.

INTRODUCTION

Synthetic organic ion exchangers are widely used both in industries and laboratories for various purposes such as concentration, identification, separation and extraction of compounds of plant origin from raw materials.[1–4] Phenols[5, 6] and substituted phenols have considerable physiological activity. They are powerful insecticides, fungicides, bactericides and herbicides. Recovery and concentration of these compounds from the industrial waste will not only help the economy of the industry but also will decrease the environmental pollution. Anderson and Hansen[7] had studied the adsorption of phenol and organic acids from waste waters by strongly basic anion exchange resins. Nelson and Kraus[8] and Robinson and Mills[9] also reported the solid solution binding of phenol to the resin. Saki[10] had carried out extensive work on the adsorption of phenol, *p*-cresol, *p*-tert-butylphenol and various nitrophenols on polystyrene type of anion exchangers and effected their separation by fractional elution. Seki[11], Sherma and Rieman[12] have separated some phenols by partition chromatography. Wheaton and Bauman[13] had studied the distribution of phenol between water and anion exchange resin and between water and cation exchange resins. Chasanov and coworkers[14] have shown that phenols and many phenol derivatives are strongly sorbed by resins with aromatic groups. Akeroyd, *et al.*[15] have shown that strongly basic anion exchange resins in hydroxyl form would absorb weak acids such as phenol. Industrial and analytical applications of rapid ion exchange separation of weak organic acids including phenol was studied by Skelly and Crummett.[16] Rehana and co-workers[17, 18] have made some extensive ion exchange studies on phenol, chlorophenol and nitrophenols in aqueous, non-aqueous and mixed media.

Earlier, column studies of nicotine[19] and aniline[20] were studied in this laboratory. The present study has been carried out to establish the dynamic conditions suitable for the concentration and recovery of phenol in aqueous

solution. It is hoped that such a study will enable to establish the conditions for the treatment of effluents of the industries which make use of phenol.

EXPERIMENTAL

Weighed amounts of air dry resin DOWEX 1 × 4 (mesh size – 20, + 50) in OH^- form (capacity = 1.22 meq/g and % moisture = 21.23) were slurried with distilled water and transferred to coming glass column fitted with zero porosity sintered glass discs. The resins in the column were back washed with distilled water, allowed to settle under gravity and the column data were determined; bed length = 14.5 cms, bed volume = 21.1 cm^3, column capacity = 10.9 meq and void volume = 7.0 cm^3.

In this study a total 39 runs were carried out. Each run consisted of two parts; part A includes exchange of phenol from various solvent media at different flow rates (the concentration of phenol in the influent was always *ca.* 2 meq dm^3) and part B describes the elution of exchange phenol from the column by various eluents at different flow rates. On the completion of part A of each run, the resin column was washed with two bed volumes of distilled water and then only part B was commenced. After the conclusion of each run, fresh resins were taken from the same stock for the next run.

In runs 1, 2 and 3 the solvent used in part A and the eluent in part B was distilled water. The flow rates were the same in both the parts, *i.e.* 10 cm^3, 20 cm^3 and 30 cm^3 per min. The per cent exchange of phenol per sample (P_x), the per cent of phenol eluted per sample (P_l), the milliequivalent of phenol exchanged (W_x) and phenol eluted (W_l) per sample were calculated by measuring the UV absorption at wavelength of maximum absorption ($\lambda_x = 269$ nm). The total amount (in m_{eq}) of phenol taken up (TW_x) and phenol eluted (TW_l) from the column was also calculated.

In runs 4, 5 and 6 part A were the repetition of part A of runs 1, 2 and 3 respectively except that the medium of influent was 0.1 N HCl. Part B of these runs were not carried out since the total exchange (TW_x) was found to be very small. In runs 7 to 15 parts 7A, 10A and 13A were the repetition of parts 1A, parts 8A, 11A and 14A were repetition of 2A; and parts 9A, 12A and 15A were repetition of 3A. Parts 7B, 10B and 13B were repetition of 1B except that in these runs eluents were 0.1N HCl, 0.5N HCl and 1N HCl respectively. Parts 8B, 11B and 14B were repetition of 2B except that in these runs the eluents were 0.1N HCl, 0.5N HCl and 1N HCl. Parts 9B, 12B and 15B were repetition of 3B except that the eluents were 0.1N HCl, 0.5N HCl and 1N HCl respectively and the sample volumes in 10B, 11B, 12B, 13B, 14B and 15B was 250 cm^3. Runs 16 to 24 were the exact replica of runs 7 to 15 except that in part B the eluents were 0.1N aqueous ammonia, 0.5N aqueous ammonia and 1N aqueous ammonia in place of aqueous HCl of corresponding strength and the sample volume in part B of the runs was 250 cm^3. In runs 25 to 36 part A of these runs were repetition of part A of runs 1, 2 and 3. The part B of these runs were the repetition of runs 1B, 2B and 3B except that 10 per cent aqueous ethyl alcohol was used in 25B, 26B and 27B; 30 per cent aqueous ethyl alcohol was used in 28B, 29B and 30B; 50 per cent aqueous ethyl alcohol was used in 31B, 32B and 33B and 80 per cent aqueous ethyl alcohol was used in 34B, 35B and 36B as eluent. The sample volume in part B of all these runs was 250 cm^3. Lastly, in runs 37, 38 and

39 part A of these runs were the repetition of 1A, 2A and 3A. In part B of these three runs 0.1N ammonia in 10 per cent aqueous ethyl alcohol was used at speeds of 10 cm^3, 20 cm^3 and 30 cm^3 per min. The sample volume in part B of all these three runs was 100 cm^3.

RESULTS AND DISCUSSION

Table-1 and Table-2 serve as typical example for recording the data of exchange and elution. Table-3 gives the absorption efficiency (A_r) at different flow rates. Here the absorption efficiency is defined as hundred times the amount of phenol absorbed per unit column capacity (100 TW_x/column capacity). It can be seen that the absorption efficiency of the resin column for phenol depends on the flow rate of the influent and it decreases with increase in the flow rate in both water and aqueous hydrochloric acid media. The absorption efficiency is considerably less when the phenol is in aqueous hydrochloric acid medium compared

TABLE-1
UPTAKE OF PHENOL BY A COLUMN OF RESIN 1 × 4 IN HYDROXYL FORM

Medium: Water; Sample volume: 500 cm^3; [Influent]: 2.1 m-moles dm^{-3}

Run flow rate (cm^3 min^{-1})	1A 10		2A 20		3A 30	
Sample No.	P_x	$10W_x$	P_x	$10W_x$	P_x	$10W_x$
1.	61.90	6.5	59.05	6.2	56.19	5.9
2.	59.05	6.2	58.10	6.1	51.43	5.4
3.	57.14	6.0	58.10	6.1	48.57	5.1
4.	57.14	6.0	57.14	6.0	45.71	4.8
5.	57.14	6.0	57.14	6.0	43.81	4.6
6.	57.14	6.0	55.24	5.8	39.05	4.1
7.	56.19	5.9	51.43	5.4	36.19	3.8
8.	51.43	5.4	51.43	5.4	28.57	3.0
9.	49.52	5.2	49.52	5.2	28.57	3.0
10.	49.52	5.2	49.52	5.2	26.67	2.8
11.	48.57	5.1	47.62	5.0	24.76	2.6
12.	47.62	5.0	47.62	5.0	24.76	2.6
13.	47.62	5.0	46.67	4.9	23.81	2.5
14.	45.71	4.8	45.71	4.8	22.86	2.4
15.	43.81	4.6	43.81	4.6	21.90	2.3
16.	41.90	4.4	41.90	4.4	20.95	2.2
17.	40.00	4.2	39.05	4.1	19.05	2.0
18.	36.19	3.8	35.24	3.7	17.14	1.8
19.	34.29	3.6	31.43	3.3	15.24	1.6
20.	30.48	3.2	28.57	3.0	15.24	1.6
TW_x		10.21		10.02		6.41

to the absorption efficiency in water medium. Therefore water is the better solvent medium for the absorption of phenol on resin 1 × 4. In water medium absorption efficiency at the flow rate of 30 cm^3 min^{-1} is considerably less ($A_{30} < 60$) compared to the absorption efficiency at 10 cm^3 min^{-1} and 20 cm^3 min^{-1} flow rates ($A_{10} > 90$ and $A_{20} > 90$). This indicates that for the absorption of phenol from aqueous medium influent flow rates of 10 and 20 cm^3 per minute are equally good. However, since the absorption efficiency at 10 cm^3 min^{-1} is only marginally greater than the absorption efficiency at 20 cm^3 min^{-1} ($A_{10} = 93.7$ and $A_{20} = 91.9$), that is, the difference is less than two per cent, influent flow rate of 20 cm^3 min^{-1} is better suited. Therefore, it can be concluded that, for the absorption of phenol from the industrial effluents on a column of resin 1 × 4 the effluent if acidic should be neutralized before passing through the column and a flow rate of not more than 20 cm^3 min^{-1} must be maintained.

TABLE-2
ELUTION OF PHENOL ABSORBED IN RUNS 1A, 2A AND 3A FROM A COLUMN OF RESIN 1 × 4

Eluent; Water; Sample volume: 500 cm^3

Run	1B		2B		3B	
Flow rate (cm^3 min^{-1})	10		20		30	
Sample No.	P_1	$10W_1$	P_1	$10W_1$	P_1	$10W_1$
1.	173.33	18.2	169.52	17.8	93.33	9.8
2.	172.38	18.1	158.10	16.6	84.76	8.9
3.	154.29	16.2	154.29	16.2	68.57	7.2
4.	116.19	12.2	119.05	12.5	59.05	6.2
5.	77.14	8.1	81.90	8.6	42.86	4.5
6.	58.10	6.1	59.05	6.2	30.48	3.2
7.	49.52	5.2	40.00	4.2	29.52	3.1
8.	32.38	3.4	26.67	2.8	20.95	2.2
9.	20.95	2.2	20.00	2.1	20.00	2.1
10.	17.14	1.8	19.05	2.0	17.14	1.8
11.	15.24	1.6	19.05	2.0	15.24	1.6
12.	14.29	1.5	17.14	1.8	14.29	1.5
13.	11.43	1.2	15.24	1.6	11.43	1.2
14.	9.52	1.0	11.43	1.2	10.48	1.1
15.	9.52	1.0	10.48	1.1	7.62	0.8
16.	8.57	0.9	7.62	0.8	5.71	0.6
17.	8.57	0.9	7.62	0.8	6.67	0.7
18.	7.62	0.8	3.81	0.4	4.76	0.5
19.	1.90	0.2	1.90	0.2	4.76	0.5
TW_x		10.06		9.89		5.75

TABLE-3
PHENOL ABSORPTION EFFICIENCY (A_r) OF THE COLUMN OF RESIN 1 × 4 in OH^- FORM FROM WATER AND 0.1N AQUEOUS HYDROCHLORIC ACID MEDIA AT DIFFERENT FLOW RATES

Solvent	Flow Rate (cm^3 min^{-1})		
	10	20	30
Water	93.7	91.9	58.8
0.1N HCl	62.7	61.4	31.2

Table-4 records the elution efficiency (E_r) defined as hundred times the ratio of the total amount of phenol eluted to the total amount of phenol absorbed (100 TW_1/TW_x), time efficiency (t_r) defined as the amount of phenol eluted per unit time (TW_1/time required for complete elution) and volume efficiency (V_r), defined as the amount of phenol eluted per unit volume (TW_1/volume required for complete elution of the eluent); at different flow rates. Examination of the elution efficiency data indicates that all the twelve eluents have nearly hundred per cent elution efficency at all the three flow rates with the exception of water at 30 cm^3 min^{-1} and aqueous 0.1N HCl at 20 cm^3 min^{-1} and 30 cm^3 min^{-1}. However from the economic point of view consumption of the eluent and the time required for complete elution are equally important. It is quite evident from the data that, in general, time efficiency increases and volume efficiency decreases when the flow rate increases from 10 to 30 cm^3 min^{-1} for all the twelve eluents. One has to make a proper choice of the flow rate also. Therefore if one chooses water, the least expensive of the 12 eluents (only distillation cost is involved) a flow rate of 20 cm^3 min^{-1} must be maintained because 30 cm^3 min^{-1} rate has

TABLE-4
ELUTION EFFICIENCY (E_r), TIME EFFICIENCY (t_r) AND VOLUME EFFICIENCY (V_r) AT DIFFERENT FLOW RATES

Eluent	E_{10}	E_{20}	E_{30}	t_{10}	t_{20}	t_{30}	V_{10}	V_{20}	V_{30}
				($\times 10^2$)			($\times 10^3$)		
Water	98.5	98.7	89.7	1.06	2.08	1.82	1.06	1.04	0.61
0.1N HCl	98.6	92.8	70.9	1.52	2.34	2.46	1.52	1.17	0.82
0.5N HCl	100.6	99.2	92.1	2.85	5.40	6.02	2.85	2.70	2.01
1.0 N HCl	100.9	100.2	98.6	3.13	5.89	8.72	3.13	2.94	2.91
0.1N aqu. NH_3	99.4	100.6	98.6	3.05	6.30	8.54	3.05	3.15	2.85
0.5N aqu. NH_3	99.0	95.2	90.7	4.45	7.78	8.24	4.45	3.89	2.75
1.0 N aqu. NH_3	99.8	101.1	99.8	5.09	10.19	12.12	5.09	5.10	4.04
10% aqu. ethanol	100.2	100.7	101.1	5.78	10.18	13.52	5.78	5.09	4.51
30% aqu. ethanol	99.7	99.3	100.8	4.41	7.94	12.28	4.41	3.97	4.09
50% aqu. ethanol	99.9	100.7	100.3	4.40	8.04	10.85	4.40	4.02	3.62
80% aqu. ethanol	99.7	99.2	96.9	2.85	5.70	8.38	2.85	2.85	2.79
0.1N NH_3 in 10% aqu. ethanol	99.7	99.5	98.8	9.17	20.20	24.70	9.15	10.10	8.23

very low volume efficiency. Among the aqueous hydrochloric acid eluents, 0.1N HCl at a flow rate of 20 cm^3 min^{-1} may be chosen for elution since it will consume the least amount of hydrochloric acid, that is, the cost involved will be the least. Among the aqueous ammonia eluents one would find 0.1N aqueous ammonia is better suited for elution of phenol when E_r, t_r and V_r for all of them are compared. For the same reasons, among aqueous ethanols, ten per cent aqueous ethanol is better suited considering E_r, t_r, V_r and cost of the chemical involved. Among the twelve eluents, 0.1N ammonia in ten per cent aqueous ethanol has the highest t_r and V_r with the same E_r. The difference in the t_r and V_r is so high that it would compensate the small cost of the chemicals involved in its preparation. Comparing the E_r, t_r and V_r of 0.1N ammonia in 10 per cent aqueous ethanol at different flow rates, the flow rate of 30 cm^3 min^{-1} is the best choice.

REFERENCES

1. K. Dorfener, Ion Exchangers, De Gruyter, New York (1991).
2. F. Helfferich, Ion Exchange, McGraw-Hill Book Co. Inc., New York (1962).
3. K. Dorfener, Ion Exchangers: Properties and Applications, Ann Arbor Sc. Publishers, Inc., Michigan (1972).
4. W. Rieman and H.F. Walton, Ion Exchangers in Analytical Chemistry, Pergamon Press, Inc., New York (1970).
5. N.N. Melnikov, Chemistry of Pesticides, Springer-Verlag, New York-Heidelberg-Berlin, pp. 92–107 (1971).
6. D. Logie, *Analyst*, **82**, 563 (1957).
7. R.E. Anderson and R.D. Hansen, *Ind. Eng. Chem.*, **47**, 71 (1955).
8. F. Nelson and K.A. Kraus, *J. Am. Chem. Soc.*, **77**, *Soc.*, 329 (1955).
9. D.A. Robinson and G.F. Mills, *Ind. Eng. Chem.*, **41**, 2221 (1949).
10. T. Saki, *J. Chem. Soc. Japan*, (*Pure Chem. Sect.*),**75**, 1297 (1954); through *Anal. Abstracts*, **2**, 1839 (1955).
11. T. Seki, *J. Chromatog.*, **4**, 6 (1960).
12. J. Sherma and W. Rieman III, *Anal. Chim. Acta*, **18**, 214 (1957); **19**, 134 (1978) ; **20** , 357 (1959).
13. R.M. Wheaton and W.C. Bauman, *Ind. Eng. Chem.*, **45**, 228 (1953); *Ann. N.Y. Acad. Sci.*, **57**, 159 (1953).
14. M.G. Chasanov, R. Kunin and F. McGarvey, *Ind. Eng. Chem.*, **48**, 305 (1956).
15. E.I. Akeroyd, T.R.E. Kressman and A.T. Cooper, *Mfg. Chem.*, **19**, 394 (1948).
16. N.E. Skelly and W.B. Crummett, *J. Chromatog.*, **55**, 309 (1971).
17. R. Sanwari, Studies on exchange resins on phenolic compounds. Ph.D. thesis, Sukhadia University, Udaipur (1986).
18. C.V. Bhat, B.S. Bhat, N.C. Bhargava, S. Singh and R. Sanwari, *Oriental J. Chem.*, **4**, 275 (1988).
19. P.C. Sindhi, Ion exchange studies of nicotine and related organic compounds Ph.D. thesis, Sukhadia University, Udaipur (1982).
20. K. Intodia, Physico-chemical investigation of ion exchange resin-organic base systems, Ph.D. thesis, Sukhadia University, Udaipur (1992).

(*Received:* 10 February 1998; *Accepted*: 28 May 1998) AJC-1495