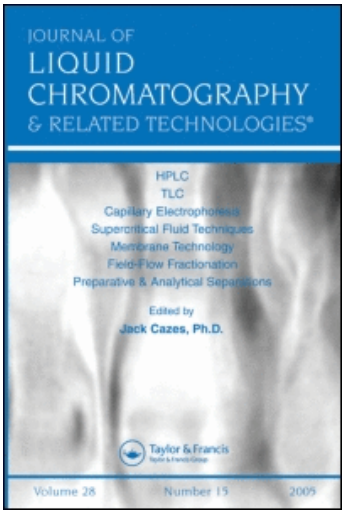

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Iron(III) Diethanolamine as a Ne Adsorbent for Chromatographic Separations of Phenols

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To cite this Article Singh, D. K. and Mehrotra, Pallavi(1988) 'Iron(III) Diethanolamine as a Ne Adsorbent for Chromatographic Separations of Phenols', Journal of Liquid Chromatography & Related Technologies, 11: 7, 1415 — 1432
To link to this Article: DOI: 10.1080/01483918808067183
URL: http://dx.doi.org/10.1080/01483918808067183

JOURNAL OF LIQUID CHROMATOGRAPHY, 11(7), 1415-1432 (1988)

IRON(III) DIETHANOLAMINE AS A NEW ADSORBENT FOR CHROMATOGRAPHIC SEPARATIONS OF PHENOLS

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ABSTRACT

A new adsorbent iron(III) diethanolamine has been utilized for the chromatographic separations of phenols. R_F values of 31 phenols in ethanol and ammonia solution of four different concentrations have been studied. On the basis of difference in R_F values various analytically important qualitative separations of phenols on impregnated papers and quantitative separations on columns of iron(III) diethanolamine have been achieved.

INTRODUCTION

Interest in adsorbents for the separation of different phenols has increased greatly in recent years (1-4). Clark suggested the use of ion exchange papers for the sepa-

ration of phenols (5). The inorganic ion exchangers stannic molybdate (6) and zinc silicate (2) have been utilized for the separation of phenols.

Chelating resin in Fe(III) form has been utilized for separation of phenols (7). A difficulty with ligand exchange chromatography is that a fraction of metal ions bound to the resin is removed when an eluent with a free cation is used.

Recently, zinc-silicate in Fe(III) form has been employed for ligand exchange chromatographic separations of some phenolic compounds (8). However, iron(III) based inorganic ion exchanger has not been reported for the separation of phenols. Iron(III) diethanolamine is superior due to its chemical stability and high affinity for phenols. The material is fairly stable in hydrochloric acid upto 2 M and in ammonia upto 4 M (9). In our present studies we have used iron(III) diethanolamine as a potential adsorbent for the phenols. The phenols have been separated qualitatively on impregnated papers and quantitatively on columns of iron(III) diethanolamine.

MATERIALS AND METHODS

Reagents. Iron(III) nitrate (BDH, India) and diethanolamine (BDH, India) were used. The phenolic solutions were prepared by dissolving them either in water or in ethanol depending on their solubilities. The Follins reagent was prepared following the standard method (10) for the spectrophotometric determination of phenols.

Apparatus. Chromatography was performed on impregnated Whatman No.3 paper strips (15x3 cms) using 20x5 cms glass jars. Ultraviolet-visible spectrophotometer, Perkin Elmer model-552 was used for spectrophotometric measurements.

Preparation of impregnated papers. Whatman No.3 paper strips of required size were dipped in 0.1 M iron(III) nitrate for 15-20 seconds and dried at room temperature. They were then dipped in 0.4 M diethanolamine for 40-45 seconds, the excess of the reagent was drained off and finally the strips were dried at room temperature.

Preparation of Adsorbent. Iron(III) diethanolamine (IDA) was prepared by mixing 0.1 M solution of iron(III) nitrate and 0.4 M solution of diethanolamine in the ratio of 1:1 (9). The mixture was allowed to stand at room temperature for 24 hours. The precipitate was filtered, washed and dried in an oven at 40°C. The product broke into small particles when immersed in distilled water. Iron(III) diethanolamine was finally ground and sized by sieving to 60-100 mesh.

RESULTS AND DISCUSSION

Sorption capacity. To determine sorption capacity 1 g iron (III) diethanolamine was supported on a glass wool in a column. 10 ml fractions of predetermined amounts of phenols were then passed through the column and the phenol collected in the effluent was determined. The amount initially taken minus the amount found after the passage through the column

gave the amount of phenol retained by the adsorbent. The process was continued until the amount of phenol in the fraction remained the same before and after passing through the column. The results presented in Table 1 reveal that sorption capacity varies from 23.16 to 83.10 mg/g. The affinity of iron(III) diethanolamine for phenols is by virtue of the ability to form complexes of varying stability with iron(III).

Break-through capacity. The break-through behaviour (11) of resorcinol and pyrogallol was studied by passing 1 mg ml^{-1} solution of each phenol through a glass column, 30 cm x 0.39 cm^2 cross-sectional area packed with 1 g iron(III) diethanolamine. The flow rate was maintained 0.5 ml min^{-1}. The results are plotted in figure 1. This study revealed that 1 bed volume of resorcinol (corresponding to 10 mg retention) can be passed through the adsorbent column without any trace being detected in the effluent. For pyrogallol break-through occurs after 6 bed volumes (corresponding to 60 mg retention). The order of break-through curves obtained for these phenols is similar to the order of their elution in the mixture (figure 2d).

R_F values. One or two spots of phenol solution were placed with a fine capillary on the impregnated paper strip. The chromatography of 31 phenols was achieved in ethanol and ammonia solution of four different concentrations. The R_F values are summarized in Table 2. In alcoholic system only bromocresol green and phenolphthalein were detected with

TABLE 1

Sorption capacity on iron(III) diethanolamine

Sl. No.	Substance	Sorption capacity, mg/g
1	Resorcinol	23.16
2	Quinol	24.00
3	α-Naphthol	32.25
4	Catechol	51.18
5	Pyrogallol	83.10

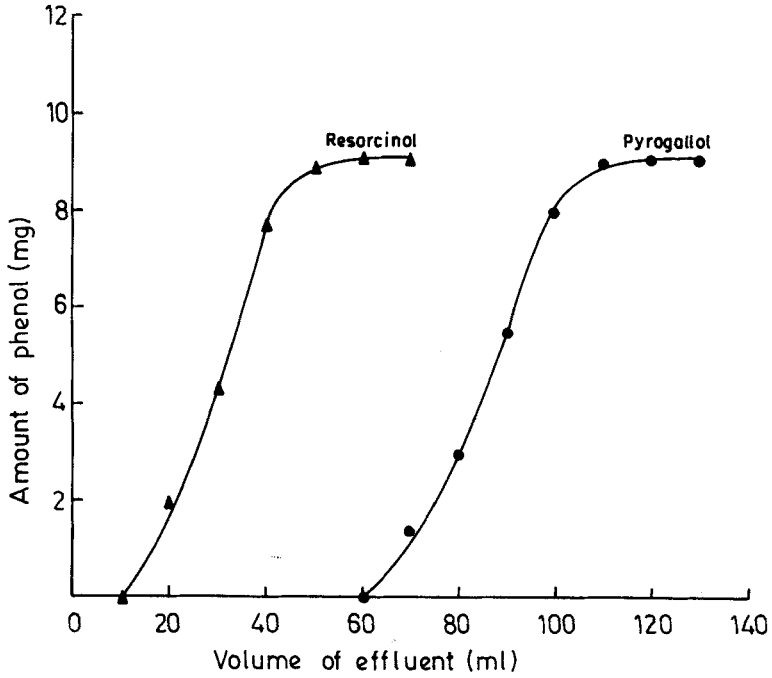

Figure 1 Break-through curves of Resorcinol and Pyrogallol

TABLE 2

R_F values of phenols

Phenols	Ethanol	0.01 M NH_4OH	0.1 M NH_4OH	0.5 M NH_4OH	1.0 M NH_4OH
Pyrogallol	0.08	0.09	0.09	0.09	0.10
Catechol	0.09	0.25	0.28	0.29	0.31
2,5-dinitrophenol	0.59	0.62	0.62	0.64	0.70
2,4-dinitrophenol	0.66	0.70	0.72	0.72	0.73
p-tert. amyl phenol	0.84	0.00	0.02	0.06	0.12
2-methyl resorcinol	0.75	0.45	0.50	0.58	0.59
O-nitrophenol	0.13	0.58	0.65	0.73	0.75
m-nitrophenol	0.67	0.47	0.52	0.63	0.72
p-nitrophenol	0.77	0.48	0.60	0.62	0.67
Quinol	0.74	0.26	0.35	0.40	0.42
Hydroxyquinone	0.77	0.33	0.33	0.34	0.36
Phloroglucinol	0.60	0.35	0.42	0.50	0.56
Vanilline	0.57	0.53	0.63	0.74	0.74
2,4-dinitro-1-naphthol	0.88	0.33	0.35	0.40	0.42
Bromocresol green	0.25	0.43	0.60	0.74	0.80
p-cresolgreen	0.64	0.37	0.65	0.70	0.70
Picric acid	0.79	0.67	0.68	0.70	0.78
Phenolphthalein	0.89	0.16	0.30	0.33	0.54
Phenol	0.50	0.02	0.06	0.08	0.10
Resorcinol	0.71	0.45	0.50	0.52	0.55
P-bromophenol	0.25	0.33	0.36	0.39	0.57

TABLE 2 (continued)

α-naphthol	0.76	0.00	0.05	0.07	0.14
β-naphthol	0.82	0.25	0.30	0.35	0.58
Bromothymol blue	0.68	0.61	0.65	0.72	0.89
Tannic acid	0.00	0.00	0.04	0.05	0.13
O-cresol	0.72	0.05	0.10	0.20	0.32
m-cresol	0.81	0.34	0.40	0.43	0.56
3,4-Xylen-1-ol	0.68	0.24	0.32	0.44	0.53
Xylenol orange	0.06	0.12	0.22	0.32	0.37
Gallic acid	0.13	0.10	0.12	0.12	0.32
Salicyclic acid	0.51	0.56	0.62	0.68	0.74

ammonia otherwise all the phenols gave coloured spots and no separate detector was required. The spots obtained on these impregnated papers were compact and discernible. The results show that increased concentration of ammonia causes increase in R_F values. This behaviour can be attributed to the high solubility of phenols in higher concentration of ammonia.

Impregnated paper chromatography separations. Separations were tried for phenols having appreciable difference in R_F values. Spots of the mixtures were placed on the impregnated strips and developed with the desired developer. Those practically achieved are summerized in Table 3. Separations of O-nitrophenol from m-nitrophenol and α-naphthol from β-naphthol can be easily achieved. Some ternary separations have also been possible on these papers.

TABLE 3

Separations achieved on impregnated iron(III) diethanolamine papers

Sl. No.	Separations achieved			Solvent
1	Catechol (0.08)	-	Resorcinol (0.70)	Ethanol
2	Catechol (0.08)	-	Quinol (0.74)	,,
3	Catechol (0.08)	-	Phenol (0.50)	,,
4	Catechol (0.08)	-	2-Methyl resorcinol(0.72)	,,
5	Catechol (0.08)	-	Phloroglucinol (0.66)	,,
6	Catechol (0.08)	-	Picric acid (0.78)	,,
7	O-Nitrophenol (0.12)	-	p-Nitrophenol (0.77)	,,
8	O-Nitrophenol (0.12)	-	2,4-Dinitrophenol(0.64)	,,
9	O-Nitrophenol (0.12)	-	2,5-Dinitrophenol(0.60)	,,
10	O-Nitrophenol (0.12)	-	Picric acid (0.80)	,,
11	O-Nitrophenol (0.12)	-	Quinol (0.74)	,,
12	O-Nitrophenol (0.12)	-	m-Nitrophenol (0.66)	,,
13	O-Nitrophenol (0.12)	-	O-Cresol (0.70)	,,
14	Pyrogallol (0.08)	-	Phloroglucinol (0.60)	,,
15	Pyrogallol (0.08)	-	Quinol (0.76)	,,
16	Pyrogallol (0.08)	-	Resorcinol (0.68)	,,
17	Pyrogallol (0.07)	-	2-Methyl resorcinol(0.70)	,,
18	Pyrogallol (0.08)	-	Hydroxyquinone (0.75)	,,
19	Pyrogallol (0.08)	-	Phenol (0.50)	,,
20	Bromocresol green(0.24)	-	Phenolphthalein (0.90)	,,

TABLE 3 (continued)

21	Xylenol orange (0.06)	-	p-Tert.Amyl phenol(0.86)	Ethanol
22	Xylenol orange (0.05)	-	2-Methyl resorcinol(0.72)	,,
23	Xylenol orange (0.06)	-	Phenol (0.50)	,,
24	Xylenol orange (0.06)	-	O-Cresol (0.70)	,,
25	Xylenol orange (0.06)	-	m-Cresol (0.80)	,,
26	p-Tert.Amyl phenol(0.00)	-	Bromothymol blue (0.62)	0.01 M NH_4OH
27	O-Cresol (0.05)	-	2-Methyl resorcinol(0.46)	,,
28	O-Cresol (0.05)	-	m-Cresol (0.35)	,,
29	O-Cresol (0.05)	-	Bromothymol blue (0.60)	,,
30	O-Cresol (0.05)	-	Vanilline (0.52)	,,
31	O-Cresol (0.05)	-	Picric acid (0.68)	,,
32	Tannic acid (0.00)	-	Phloroglucinol (0.35)	,,
33	Tannic acid (0.00)	-	Salicylic acid (0.56)	,,
34	α-Naphthol (0.07)	-	β-Naphthol (0.35)	0.5 M NH_4OH
35	α-Naphthol (0.07)	-	Quinol (0.40)	,,
36	Phenol (0.08)	-	Quinol (0.40)	,,
37	Phenol (0.08)	-	Phloroglucinol (0.50)	,,
38	Phenol (0.08)	-	Resorcinol (0.50)	,,
39	Phenol (0.08)	-	Vanilline (0.72)	,,
40	Phenol (0.08)	-	Picric acid (0.70)	,,
41	p-Tert.Amyl phenol(0.60)	-	2-Methyl resorcinol(0.56)	,,
42	p-Tert.Amyl phenol(0.06)	-	m-Cresol (0.40)	,,
43	Gallic acid (0.10)	-	Salicylic acid (0.66)	,,
44	Gallic acid (0.10)	-	Picric acid (0.70)	,,

(continued)

TABLE 3 (continued)

45	Gallic acid (0.10)	- 2,4-Dinitrophenol (0.74)		0.5 M NH_4OH
46	Pyrogallol (0.08)	- O-Nitrophenol (0.70)		,,
47	Pyrogallol (0.08)	- Vanilline (0.72)		,,
48	α-Naphthol (0.07)	- 2,4-Dinitrophenol (0.74)		,,
49	α-Naphthol (0.07)	- O-Nitrophenol (0.70)		,,
50	α-Naphthol (0.07)	- Picric acid (0.70)		,,
51	Tannic acid (0.04)	- Picric acid (0.70)		,,
52.	Pyrogallol (0.10)	- 2,4-Dinitrophenol (0.70)		1 M NH_4OH
53	Pyrogallol (0.10)	- m-Nitrophenol (0.69)		,,
54	p-Tert. Amyl Phenol (0.10)	- m-Nitrophenol (0.69)		,,
55	p-Tert. Amyl Phenol (0.10)	- Bromocresol green (0.75)		,,
56	Phenol (0.08)	- O-Nitrophenol (0.73)		,,
57	Phenol (0.08)	- m-Nitrophenol (0.70)		,,
58	α-Naphthol (0.14)	- 2,4-Dinitrophenol (0.70)		,,
59	α-Naphthol (0.14)	- 2,5-Dinitrophenol (0.68)		,,
60	α-Naphthol (0.14)	- m-Nitrophenol (0.69)		,,
61	Catechol (0.08)	- Phenol (0.50)	- p-Tert. Amyl Phenol (0.80)	Ethanol
62	Phenol (0.08)	- Quinol (0.38)	- O-Nitrophenol (0.70)	0.5 M NH_4OH
63	α-Naphthol (0.06)	- m-Cresol (0.40)	- O-Nitrophenol (0.72)	,,
64	Pyrogallol (0.09)	- Quinol (0.40)	- Picric acid (0.75)	1 M NH_4OH
65	α-Naphthol (0.14)	- 2,4-Dinitro-1-naphthol (0.40)	- 2,4-Dinitrophenol (0.72)	,,

Column separations. A glass column 30x0.39 cm^2 cross-sectional area was packed with one gram of IDA. The column was washed with about 50 ml of distilled water. The sample solutions containing the desired phenols having the largest differences in R_F values were tried and those whose quantitative separation was achieved are listed in Table 4. The order of elution and eluents for various separations are presented in figures 2. The flow rate in all the separations was about 0.5 ml min^{-1}. The results of this study indicate that R_F values from impregnated papers can be utilized to predict the chromatographic separation on the packed columns. The results in figures 2(a-i) reveal that most of the separations achieved on impregnated papers are achieved quantitatively on the columns of iron(III) diethanolamine. The positional isomers such as catechol and resorcinol, quinol and catechol, O- and p-nitrophenol, α- and β-naphthol and O- and m-cresol have been easily separated on the columns of IDA. Other binary separations are resorcinol from pyrogallol and tannic acid from salicylic acid. Some ternary separations achieved are 2,4-dinitrophenol - O-nitrophenol - pyrogallol and 2,4-dinitro-1-naphthol - catechol - tannic acid. The separations are sharp and the recoveries quantitative. Tailing is practically non-existent and small volumes of eluents are required to give compact chromatograms. This is demonstrated by the elution curves (figure 2).

The method described provides an excellent means for the quantitative separations of phenols (in microgram amounts)

TABLE 4

Separations achieved on iron(III) diethanolamine columns

Sl. No.	Mixture	Eluent	Eluate (ml)	Amount loaded (μg)	Amount found (μg)	% Error
1	Resorcinol	Ethanol	30	400	399.0	0.3
	Catechol	2 M NH_4OH	40	500	490.0	2.0
2	Quinol	Ethanol	30	400	394.0	1.5
	Catechol	2 M NH_4OH	40	500	490.0	2.0
3	p-Nitrophenol	Ethanol	30	350	344.1	1.7
	O-Nitrophenol	2 M NH_4OH	50	400	404.0	1.0
4	Resorcinol	Ethanol	30	400	398.0	0.5
	Pyrogallol	2 M NH_4OH	50	450	440.0	2.2
5	m-Cresol	0.01 M NH_4OH	40	350	353.5	1.0
	O-Cresol	Ethanol	30	425	420.0	1.2
6	β-Naphthol	0.01 M NH_4OH	40	300	296.0	2.0
	α-Naphthol	Ethanol	30	400	404.8	1.2
7	Salicylic acid	Ethanol	30	400	398.0	0.5
	Tannic acid	2 M NH_4OH	40	500	496.0	0.8
8	2,4-Dinitrophenol	Ethanol	20	300	306.0	2.0
	O-Nitrophenol	0.01 M NH_4OH	30	400	404.0	1.0
	Pyrogallol	2 M NH_4OH	50	400	391.2	2.2
9	2,4-Dintro-1-naphthol	Ethanol	20	300	304.0	1.3
	Catechol	0.01 M NH_4OH	30	450	440.0	2.2
	Tannic acid	2 M NH_4OH	40	500	496.0	0.8

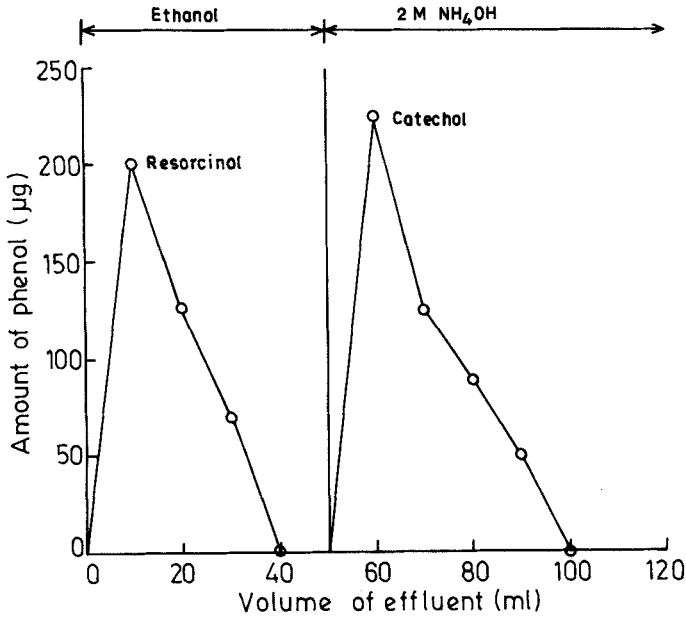

Figure 2a Separation of Resorcinol-Catechol

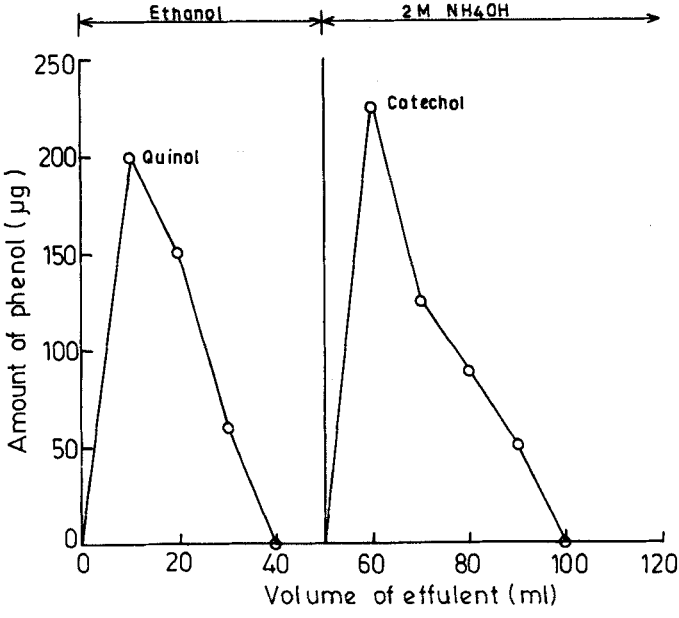

Figure 2b Separation of Quinol-Catechol

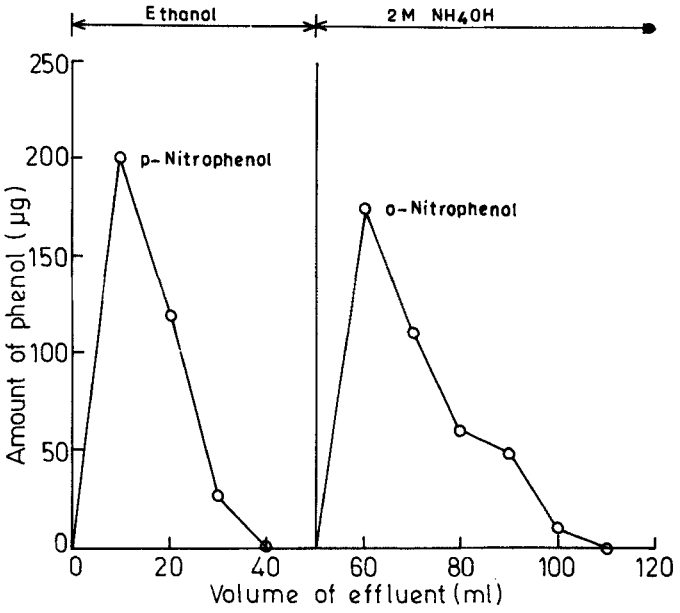

Figure 2c Separation of p- Nitrophenol-o-Nitrophenol

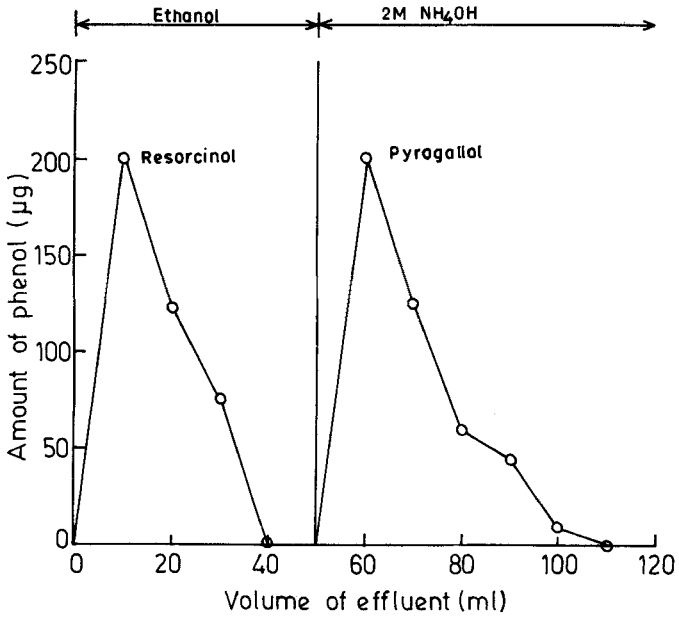

Figure 2d Separation of Resorcinol-Pyrogallol

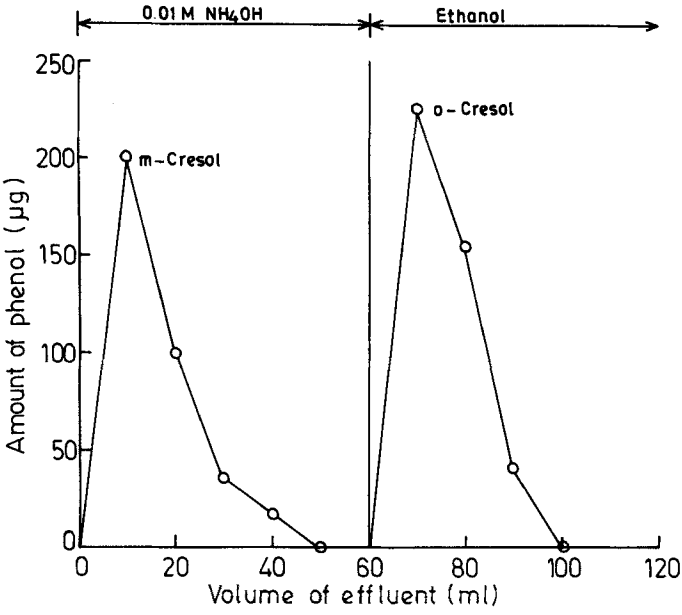

Figure 2e Separation of m-Cresol-o-Cresol

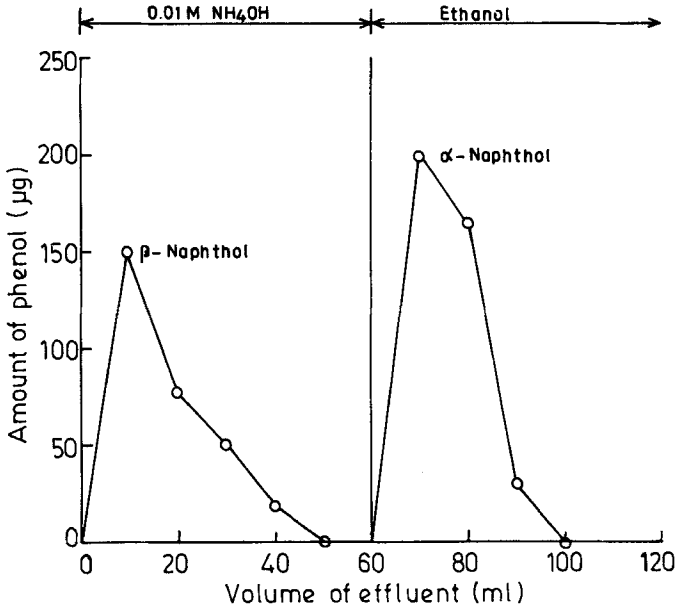

Figure 2f Separation of β-Naphthol-α-Naphthol

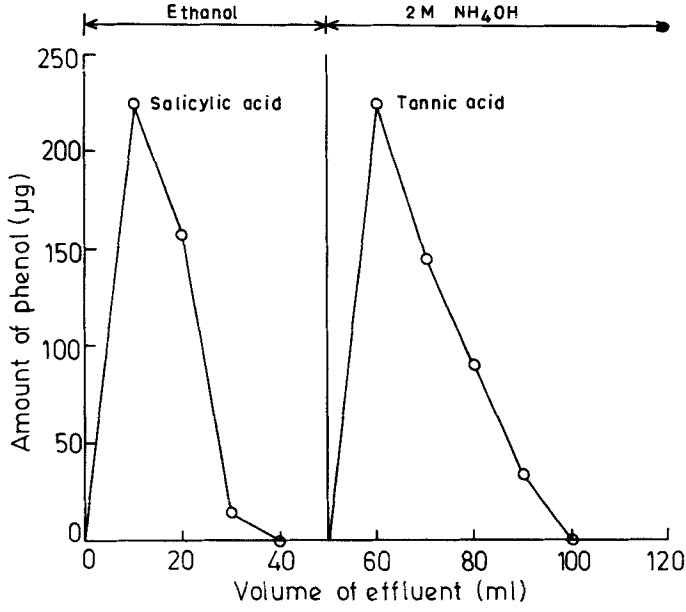

Figure 2g Separation of Salicylic acid-Tannic Acid

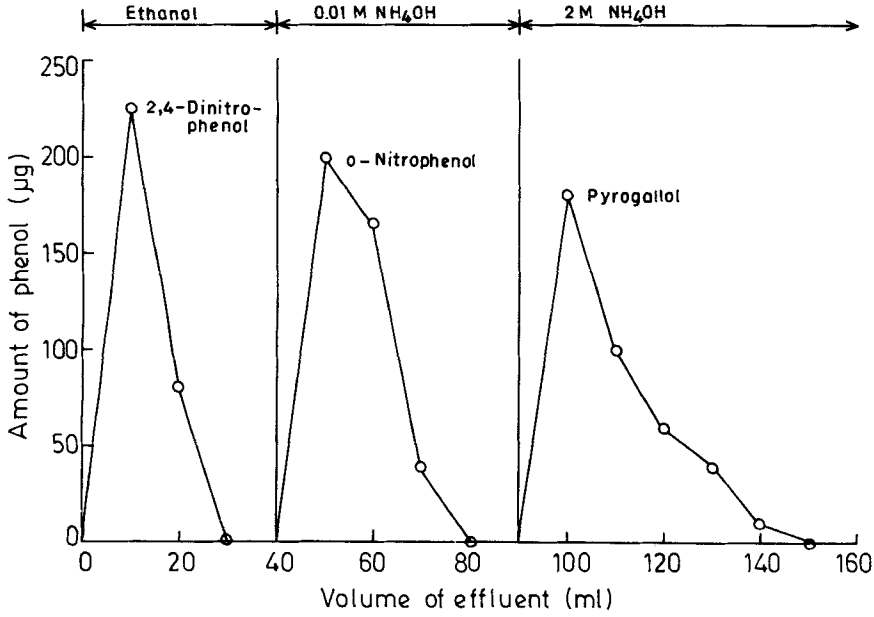

Figure 2h Separation of 2,4-Dinitrophenol-o-Nitrophenol-Pyrogallol

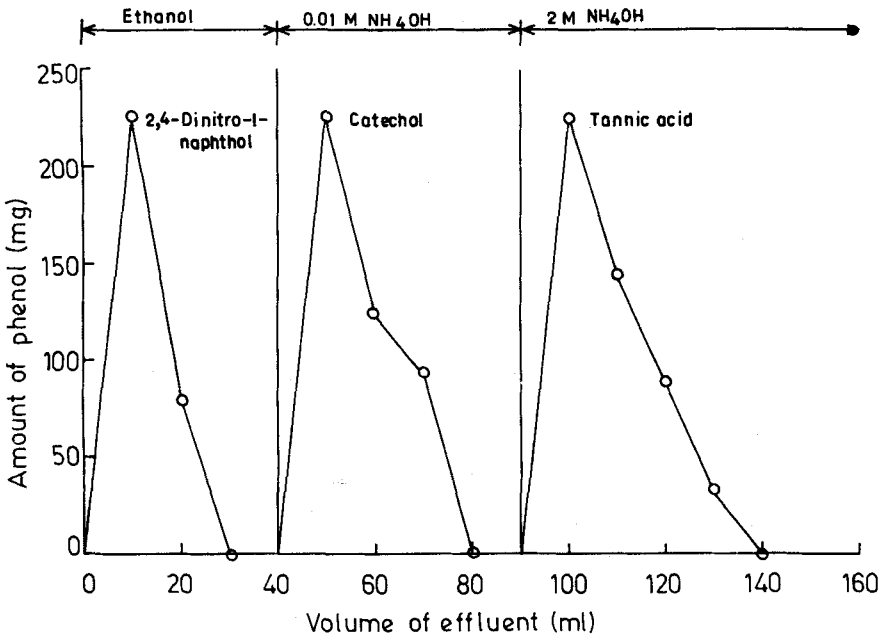

Figure 2i Separation of 2,4-Dinitro-1-naphthol-Catechol-Tannic Acid

in a single column run. After each experiment the adsorbent can be reactivated. However, the amount of adsorbent (IDA) used for each experiment (1 g) is so small so that the cost is minimal even if no recovery is attempted. Iron(III) diethanolamine columns can also be used successfully for the removal of phenols (polluants) from waste effluents.

Acknowledgement. The authors are thankful to Prof. A.K. Vasishtha, Director and Prof. R.S. Tewari, Head, Department of Chemistry, H.B. Technological Institute, Kanpur for providing research facilities.

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